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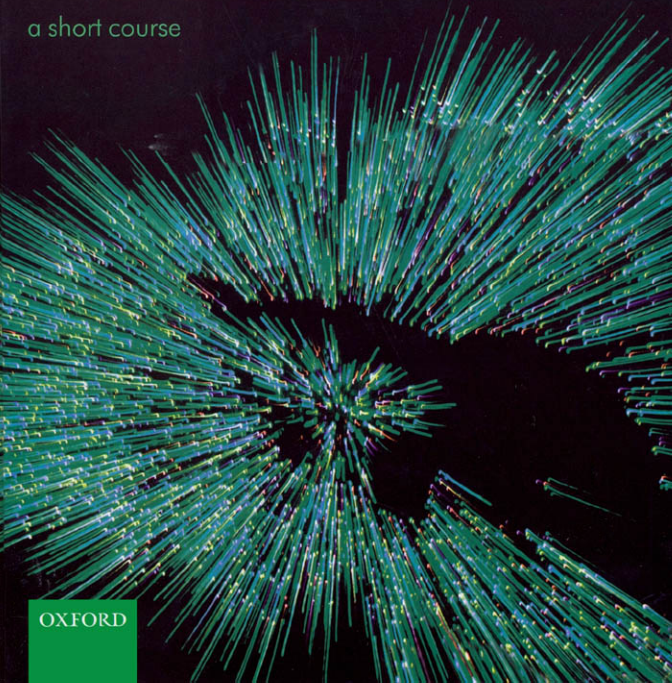
thermodynamics & kinetics in materials science

a short course



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THERMODYNAMICS AND KINETICS IN MATERIALS SCIENCE

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Thermodynamics and Kinetics in Materials Science

A short course

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Preface

This text presents a short, but thorough, introduction to the main concepts and practical application of thermodynamics and kinetics appropriate for materials science. It assumes that the reader is familiar with the concepts typically taught in introductory, university-level courses in physics and chemistry. The book is designed with two types of uses in mind: (1) a one or two semester university course for mid- to upper-level undergraduate or first year graduate students in a materials science oriented discipline and (2) individuals who want to study this material on their own.

This text discusses the following major topical areas: basic laws of classical and irreversible thermodynamics, phase equilibria, theory of solutions, chemical reaction thermodynamics and kinetics, surface phenomena, stressed systems, diffusion, and statistical thermodynamics. The text is accompanied by a large number of example problems with detailed solutions. The pedagogical appeal of the book is enhanced with computer-based self-tests. These include over 400 questions and 2000 answers, including many hints for the student.

While it is difficult to give a student a laboratory experience in either a lecture course or in a self-study learning mode, the book is augmented with computer-based laboratories. A laboratory problem is posed and the experiment is described. The student has the ability to “perform” the experiments and change the laboratory conditions to obtain the data needed to meet the laboratory objective. If the student chooses inappropriate laboratory conditions, the program will give him meaningful, but useless data. The “laboratory” results are stored in a file that can be sent directly to the instructor. Text is provided within the “laboratory” as both background material and as an aid to the student as he or she analyzes the experimental results. “Laboratory experiments” are available in the following areas:

1. Construction of phase diagrams from cooling curves.
2. Determination of carbon activity in austenite.
3. Determination of nitrogen activity in Fe–Mn alloys.
4. Gas adsorption on a solid surface.
5. Determination of the order and activation energy of a chemical reaction.
6. Determination of diffusivity.
7. Chemical reactions.

Note to students

Our ultimate goal was to develop a textbook that can be used as a supplement to a lecture course in thermodynamics and kinetics of materials and also be sufficient for you to learn this material on your own. The book is written in a manner that assumes that you have some background in elementary physics and chemistry and some basic mathematical skills (differentiation, integration, solution of very simple differential equations).

If you are using the book in a self-study mode, you should, of course, first read the text. You should then solidify your understanding by reproducing the main derivations from the chapter yourself, with the book closed. If you have difficulties, go ahead and open the book, find out what you were missing, and repeat. There are some Review questions at the end of most sections. Do not ignore these! Do not panic if you cannot answer all of them. Rather, reread the appropriate section of the text and try again. If you have the opportunity, discuss these questions with other students or instructors.

Once you feel that you understand the theoretical issues, try to solve the Example problems included in the text. We tried to choose problems which illustrate or expand upon the theoretical ideas in the text. Note that not all of these problems are simple. If you have no idea how to solve the problem, look at the solution at the end of the book, then take a few days off and try to solve the problem again (you do not want to mechanically memorize the solution). If you still have trouble, peak in the back again and then return to this problem. Remember, there is only way to learn how to solve problems—just do it!

After you have completed a chapter or two, you should use the computer-based tests supplied with the text. These tests include many multiple choice questions. In some cases, hints are provided. The hints will not tell you which answer is correct, but will give you some additional information that you may find useful in answering the questions. This is a powerful learning tool and we strongly recommend that you use it.

Finally, this text-book contains seven computer-based Laboratory Projects. You will find a complete description of each laboratory including what you are trying to determine in the menu option labeled "Background". In these laboratories, you must determine how to perform the experiments, how to analyze your results, and determine if any additional experimental data must be obtained (and give you the opportunity to do this). Therefore, you must really understand the theoretical material in order to obtain meaningful results; otherwise you will get absurd data.

If you are using this text to supplement a lecture course, the same procedure can be followed. However, in this case, your instructor will guide you. Nonetheless, you will undoubtedly find that following the pedagogical approach outlined above will increase what you get out of your lecture course and improve your performance in the course.

Note to instructors

This textbook is appropriate for use in several different types of courses. This was done because thermodynamics is often combined with other topics in a single course. Such courses include (1) *Thermodynamics*, (2) *Thermodynamics and Statistical Mechanics*, (3) *Thermodynamics and Kinetics*, (4) *Thermodynamics of Materials*, (5) *Chemical Thermodynamics*, and (6) *Physical Chemistry*. Of course, which topics you cover in a course will depend on the breadth of the course and the amount of time available.

In a one-semester course of any type, we recommend that you include the following topics/chapters:

Chapter	Topic	Omit
1	Basic laws of thermodynamics	1.2.3, 1.2.4, 1.3.2
2	Phase equilibria I	
3	Thermodynamic theory of solutions	3.6, 3.7
4	Phase equilibria II	
5	Thermodynamics of chemical reactions	
6	Interfacial phenomena	6.1.3, 6.3
8	Kinetics of homogeneous chemical reactions	8.2.3

Depending on the scope of the course you may want to include the following topics:

Chapter	Topic	Comments
Thermodynamics of materials		
7	Thermodynamics of stressed systems	If the students had an Elasticity course, you can omit 7.1, 7.3, 7.5
10	Diffusion	This entire chapter may be omitted if the students will have a specific course on diffusion
11	Kinetics of heterogeneous processes	
12	Statistical thermodynamics I	This entire chapter may be omitted if students had a Statistical Physics or Physical Chemistry course
13	Statistical thermodynamics II	If students had a Solid State Physics course, you can omit 13.3; you may also choose to omit 13.4.4
Thermodynamics and kinetics		
9	Thermodynamics of irreversible processes	
10	Diffusion	You may omit 10.3–10.5
11	Kinetics of heterogeneous processes	
Thermodynamics and statistical mechanics		
12	Statistical thermodynamics I	
13	Statistical thermodynamics II	

This book can also be used for a classical Mechanical Engineering Thermodynamics course, but in this case, should be supplemented by additional materials on heat engines. Other major omissions from this book for specific applications include galvanic cells, corrosion/oxidation, polymer thermodynamics, catalysis, and phase transformations. If these subjects are necessary for your course, we recommend supplementing this text.

The textbook is accompanied by three types of software: laboratory experiments, self-tests for the students, and exams. The laboratory experiments and self-tests were described above. These are both important pedagogical tools. We suggest that you recommend to your students that they do all of the self-tests. The laboratory experiments can be assigned as homework, however, we recommend that the students do these computer-based laboratory experiments together with a teaching assistant in a room equipped with an appropriate number of personal computers.

The computer-based exams are designed to be a part of a real exam. These can be administered in a classroom (with personal computers) or as a “take home” exam. Each exam has 20–40 questions, drawn either from the entire course or from selected sections. The questions are all multiple choice, with five possible answers. The exams are timed such that the student has, on average, 1 min per question (i.e. a half-hour for 30 questions). When the time expires, the exam will be terminated in its current state. The final results are put into an encrypted file to be e-mailed to the instructor, along with the students score.

Acknowledgment

We are grateful to S. Trushevsky who prepared all of the figures used in this book and to C. Srolovitz for editing the text.

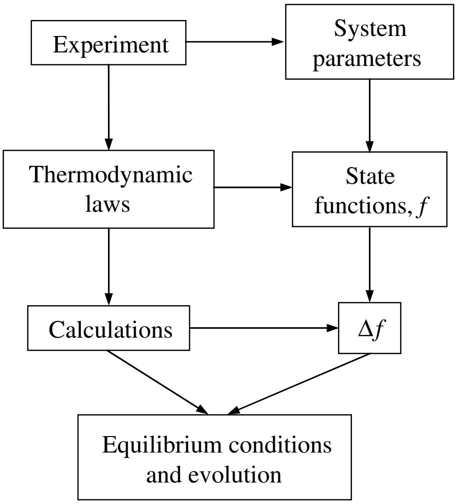
Contents

1

Basic laws of thermodynamics

In this chapter, we first introduce the basic laws of thermodynamics and the most important thermodynamic functions. Even though many of the concepts introduced here will be familiar to many readers with a background in elementary physics, this chapter should not be ignored as it presents these concepts in the language of physical chemistry. Since these concepts form the basis of physical chemistry, this subject will make no sense without a firm footing in these fundamentals.

Thermodynamics focuses on the thermal behavior of macroscopic systems (i.e. systems containing a very large number of particles). Thermal processes include both heat exchange between a system and its surroundings and work. The general scheme of a thermodynamic description of such processes can be described as in the picture:



Thermodynamic descriptions are usually based upon experimental observations. Experiments can characterize the thermodynamic state of the system in terms of a small number of measurable parameters (e.g. temperature T and pressure p). The generalization of these measurements yields thermodynamics laws. Thermodynamic laws identify state functions that describe the system behavior solely in terms of the system parameters and not on how the system came to be in a particular state. Changes in the state functions during some process depend on only the intial and final states of the system but not on the path between them. Therefore, these changes can be determined from calculations based on a very small set of data. Thermodynamics can be used to answer such questions as (1) is a particular process possible? (2) can the system spontaneously evolve in a particular direction?, and (3) what is the final or equilibrium state? all under a given set of conditions. **Equilibrium** can be understood as the state in which the system parameters no longer evolve, there are no fluxes of matter or energy through the system, and for which all small disturbances decay. According to the **zeroeth law of thermodynamics** any isolated system will eventually evolve to an equilibrium state and will never spontaneously leave this state (without a substantial external disturbance). It is important to emphasize that when a state function is properly chosen and how it changes is determined (using very limited thermodynamic data from experiment), we are able to answer all three questions raised above without any consideration of the molecular nature of the system.

The basic laws of thermodynamics are generalizations of experimental observations and are not derived. In this sense, thermodynamics is a first principles theory. Since it is based upon a generalization of experimental results, Einstein said that thermodynamics is "the only physical theory of universal content concerning which I am convinced that within the framework of the applicability of its based concepts, it will never be overthrown."

1.1 First law of thermodynamics

1.1.1 Basic definitions

Since thermodynamics describes the macroscopic behavior of different types of systems, we start with a formal definition of the term "system" and a classification of types of systems. A **system** is an ensemble of bodies that can either be extracted or imagined to be extracted from its surroundings (see Fig. 1.1). A system is referred to as **isolated** if it neither exchanges energy nor matter with its surroundings and its volume is constant. A system which does not exchange matter with its surroundings is **closed**; otherwise it is **open**. The **state** of a system is determined by a set of system parameters such as the volume V, temperature T, pressure p, and concentration of each of its components c_i. These parameters are not independent but rather are related to each other by the **equations of state**. For a one-component system, this equation takes the form: $f(p,V,T)=0$ where f may, for example, be the ideal gas law $f=pV-nRT=0$ (n is the number of moles and R is the ideal gas constant).

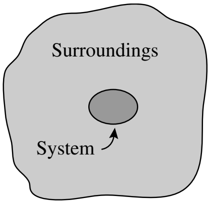


Fig. 1.1
Schematic illustration of a system and its surroundings.

How a system participates in a thermodynamic processes is characterized by two quantities: work W, and heat Q. The following sign convention is standard in thermodynamics: work done by the system is positive (work done on the system is negative) and the heat supplied to the system is positive.[1] The work due to expansion (work against an external pressure) is often separated from other types of work (e.g. the work to establish a potential difference between electrodes in a galvanic cell or the work to separate charges in the presence of an electric field). All types of work with the exception of that associated with expansion are called **non-mechanical work**.

The work of expansion associated with an elementary (infinitesimal) process that changes the volume is

$$\delta W_{\text{expan}} = pdV. \tag{1.1}$$

The work of expansion is positive if the system volume increases and it is in accordance with Eq. (1.1). For a finite change in volume, the work of expansion is

$$W_{\text{expan}} = \int_{V_1}^{V_2} pdV. \tag{1.2}$$

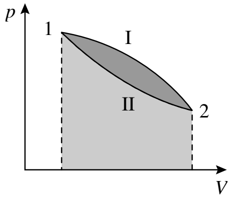


Fig. 1.2
Schematic to illustrate that work (area under curve) depends on path.

Equation (1.2) shows that the work of expansion is simply the area under the curve p(V). Figure 1.2 shows that the work of expansion depends on path. For example, the system evolving along path I does more work than that along path II. Thus, the work does not characterize the state of the system, but rather the path which the system followed to get from one particular state to another. This can be phrased more rigorously by stating that δW is not a full differential (an integral of a full differential is path independent). This is why we use the sign δ instead of d in Eq. (1.1). In general, the work associated with any infinitesimal change in the system can be written as:

$$\delta W = pdV + \delta W_{\text{non-mechanical}} \tag{1.3}$$

The amount of heat transferred to the system also depends on the path. Functions that depend only on the system parameters, and not the path that led to those values of the system parameters, are **state functions**. Neither heat nor work are state functions.

The **first law of thermodynamics** postulates that for any system there is a state function, U, called the **internal energy**, which increases by a quantity equal to the heat added to the system and decreases by the work done by the system. Formally, this implies that the difference between the heat (δQ) added to and the work (δW) done by the system is a full differential of a state function U:

$$\mathrm{d}U = \delta Q - \delta W. \tag{1.4}$$

Since the internal energy is a state function, it does not change when the system undergoes any cycle that returns it to its initial state; that is, $\oint dU = 0$. Equation (1.4) can be rearranged as

$$\delta Q = \delta W + \mathrm{d}U, \tag{1.5}$$

---

[1] Other conventions have been adopted elsewhere in the literature. Changing convention simply leads to changes in signs within some of thermodynamic equations.

which implies that all heat added to the system is either used by the system to perform work or to increase the internal energy of the system. Since Eq. (1.4) is written in terms of differentials, the internal energy itself is only defined to within an additive constant. This constant may be determined once a reference state is chosen (see Section 1.1.4).

Although the internal energy may have contributions from several different terms, thermodynamics requires no information on the magnitude of these individual terms. Recall, however, that molecular theory or statistical mechanics can be used to determine the magnitude of such contributions as the kinetic energy associated with molecular motion (this is related to the temperature of the system), the interaction energy of molecules, and the internal energy of the molecules themselves.

In a closed system, the internal energy depends on the system parameters: p, V, and T.[2] These quantities are related to each other through the equation of state. Therefore, the internal energy can be written in terms of any two of these parameters. For example, if we choose to focus upon the temperature and volume, the full differential of the internal energy is simply:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V. \tag{1.6}$$

Review questions

1. What is the analytical expression for the first law of thermodynamics?
2. Which of the following are state functions: heat, work, internal energy?
3. Which of the following are system parameters: temperature, volume, number of molecules, ideal gas constant, pressure, internal energy?

1.1.2 Implications of the first law of thermodynamics

We now examine some applications of the first law of thermodynamics. In these applications, we consider only cases in which the only type of work is that associated with the expansion of the system, but make no assumptions about the type of system. The next section considers applications to an ideal gas.

1. ***Isochoric processes*** *(i.e. processes that leave V unchanged)*. In such processes, the work done is equal to zero and all heat entering the system is used to change the internal energy; $\delta Q = \mathrm{d}U$.

The **heat capacity** of the system is defined as

$$c = \lim_{\Delta T \to 0} \frac{\delta Q}{\Delta T}, \tag{1.7}$$

where ΔT is the change in the temperature of the system associated with the addition of heat δQ. Frequently, the heat capacity is normalized by

---

[2] If concentrations of the individual components in the system can change, the internal energy also depends on the quantity of each component. We consider this case in Section 1.5.

either mass or moles of the species in the system. The heat capacity per mole is called the **molar heat capacity** and the heat capacity per gram is called the **specific heat capacity**. Under isochoric conditions, the heat capacity is

$$c_V = \left(\frac{\partial U}{\partial T}\right)_V. \tag{1.8}$$

Since the internal energy is a state function, so too is the isochoric heat capacity. We can relate the change in internal energy associated with any isochoric process to the heat capacity as

$$\Delta U = \int_{T_1}^{T_2} c_V \mathrm{d}T. \tag{1.9}$$

2. ***Isobaric processes*** *(i.e. processes that leave p unchanged).* In this case,

$$\delta Q = \mathrm{d}U + p\mathrm{d}V = \mathrm{d}(U + pV) = \mathrm{d}H$$

where

$$H = U + pV, \tag{1.10}$$

is referred to as the **enthalpy** of the system. Since the enthalpy depends only on the internal energy and system parameters, it is a state function. Just as the internal energy is only defined to within an additive constant, the enthalpy too depends on the reference state. In isobaric processes, all heat added to the system increases the enthalpy: $\delta Q = \mathrm{d}H$. The isobaric heat capacity is defined as

$$c_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{1.11}$$

such that the enthalpy change is

$$\Delta H = \int_{T_1}^{T_2} c_p \mathrm{d}T. \tag{1.12}$$

The isochoric and isobaric heat capacities, c_V and c_p, may be related by inserting the definition of the enthalpy (Eq. 1.10) into Eq. (1.11).

$$c_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial(U + pV)}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p. \tag{1.13}$$

This relation can be rewritten in another form by noting that T, V, and p are related by an equation of state and by using standard rules of differentiating a multivariate function:[3]

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p = c_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p.$$

---

[3] Some useful hints on working with partial derivatives are provided in Appendix I.

Inserting this relation into Eq. (1.13) yields the well-known result

$$c_p - c_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p. \tag{1.14}$$

3. ***Adiabatic processes*** *(i.e. processes that occur without exchanging heat between the system and its surroundings, $\delta Q = 0$).* In such processes, all of the work performed by the system leads to a decrement of the internal energy: $\delta W = -\mathrm{d}U$.

Review question

1. What are the dimensions of the molar heat capacity?

Example problem[4]

1. 1 g of ice at T = 0°C and 10 g of water at T = 100°C are mixed in an adiabatic container. What is the temperature within the container when its contents reach equilibrium? Express your answer in K.
   For H_2O, the change in enthalpy on melting $\Delta H_{\text{melt}} = 6.01$ kJ/mole and $c_p = 75.3$ J/K mole.

1.1.3 Ideal gas

A gas is referred to as an "ideal gas"[5] if it can be described by the following equation of state (i.e. the ideal gas law):

$$pV = nRT. \tag{1.15}$$

An important property of an ideal gas follows from this equation: the internal energy does not depend on volume at fixed temperature,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \tag{1.16}$$

Thus, the molar internal energy of an ideal gas is only a function of temperature. While a qualitative explanation of Eq. (1.16) is provided here, a formal derivation may be found in Section 1.4.2. The internal energy of a gas consists of three terms: the kinetic energy of the molecules, the energy of interaction between the molecules and the internal energy of the molecules. Of these, only the interaction energy depends on the volume (density) of the gas because the mean nearest neighbor distance between molecules is proportional to $(V/N)^{1/3}$ and the intermolecular interaction energy is a function of the distance between molecules. However, the definition of an ideal gas is one for which the molecules

---

[4] Solutions to and discussion of Example problems are provided at the back of the book.

[5] In the remainder of this chapter, the only gases considered are ideal gases. Hence, the term "ideal" will be omitted. Note, for pressures up to approximately 10 atm and temperatures above room temperature, nearly all gases behave ideally.

do not interact. Therefore, the internal energy of an ideal gas does not depend on volume.

The differential of the internal energy (Eq. (1.6) of an ideal gas can be expressed in terms of the isochoric molar heat capacity (Eq. (1.8)):

$$\mathrm{d}U = nc_V\mathrm{d}T. \tag{1.17}$$

For an ideal gas, the relationship between the isobaric and isochoric heat capacities can be obtained by inserting the ideal gas equation of state into Eq. (1.14):

$$c_p = c_V + R. \tag{1.18}$$

We now derive several expressions for the work done by an ideal gas under different conditions.

1. ***Isothermal process*** *($T = const$)*. In general, work is defined as: $W = \int_{V_1}^{V_2} p\mathrm{d}V$. For an ideal gas, $W = \int_{V_1}^{V_2} \frac{nRT}{V}\mathrm{d}V$. Performing the integration at constant T yields:

$$W = nRT\ \ln\frac{V_2}{V_1}. \tag{1.19}$$

Since $\mathrm{d}U = 0$ in an isothermal process (see Eq. 1.17), $\delta Q = \delta W$. This implies that all heat added to an isothermal ideal gas is converted into work.

2. *Isobaric process ($p = const$)*. In this case, the expression for work $W = \int_{V_1}^{V_2} p\mathrm{d}V$ is simply

$$W = p\Delta V = nR\Delta T, \tag{1.20}$$

where the second equality is obtained using the ideal gas equation of state.

3. *Adiabatic process ($\delta Q = 0$)*. Combining Eqs (1.17) and (1.5) for an adiabatic process yields: $nc_V\mathrm{d}T + p\mathrm{d}V = 0$. From the ideal gas equation of state it follows that $\mathrm{d}T = (p\mathrm{d}V + V\mathrm{d}p)/(nR)$. We can now rewrite the previous equation as:

$$nc_V\frac{p\mathrm{d}V + V\mathrm{d}p}{nR} + p\mathrm{d}V = 0.$$

By inserting the ideal gas result $c_p - c_V = R$ into this equation and rearranging terms we find $p\mathrm{d}V + V\mathrm{d}p + (\gamma - 1)p\mathrm{d}V = V\mathrm{d}p + \gamma p\mathrm{d}V = 0$, where we have used the definition

$$\gamma = \frac{c_p}{c_V}. \tag{1.21}$$

We can rewrite $V\mathrm{d}p + \gamma p\mathrm{d}V = 0$ as $\mathrm{d}p/p + \gamma\mathrm{d}V/V = 0$ and integrate to obtain $\ln p + \gamma \ln V = \text{constant}$ or, equivalently,

$$pV^\gamma = C, \tag{1.22}$$

where C is a constant. This equation is valid for an adiabatic ideal gas. Combining the first law of thermodynamics with $\delta Q = 0$ and Eq. (1.17) provides an expression for the work done by an ideal gas:

$$W = -\Delta U = -n\int_{T_1}^{T_2} c_V\mathrm{d}T. \tag{1.23}$$

The first equality is valid for any adiabatic system, while the second only applies to an adiabatic ideal gas. Another approach is to directly integrate the function $p(V)$:

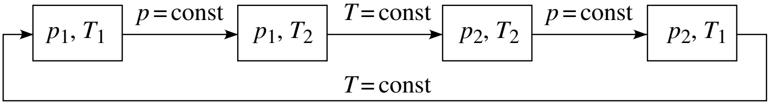
$$\begin{aligned} W &= \int_{V_1}^{V_2} p\,\mathrm{d}V = C\int_{V_1}^{V_2} V^{-\gamma}\,\mathrm{d}V = \frac{C}{1-\gamma} V^{1-\gamma}\Big|_{V_1}^{V_2} \\ &= \frac{p_1 V_1^{\gamma} V_1^{1-\gamma} - p_2 V_2^{\gamma} V_2^{1-\gamma}}{\gamma - 1} \\ &= \frac{p_1 V_1 - p_2 V_2}{\gamma - 1}. \end{aligned} \tag{1.24}$$

Review questions

1. On what system parameters does the internal energy of a mole of an ideal gas depend?
2. On what system parameters does the enthalpy of a mole of an ideal gas depend?
3. Which ideal gas system parameter must be held fixed for $Q = RT \ln(V_2/V_1)$ to be valid?

Example problems

1. 2 g of air was isobarically heated from $T_1 = 0°\mathrm{C}$ to $T_2 = 1°\mathrm{C}$ at a pressure $p = 1$ atm. The density of air at $T = 0°\mathrm{C}$ is $\rho = 0.00129\ \mathrm{g/cm^3}$. What is the work of expansion?
2. 2 l of nitrogen, originally at $T = 0°\mathrm{C}$ and $p_1 = 5$ atm, isothermally expands until the final pressure is $p_2 = 1$ atm. How much heat flows into this system during the expansion?
3. 10 g of nitrogen, originally at $T_1 = 17°\mathrm{C}$, is adiabatically compressed from 8 to 5 l. How much work was done to compress the nitrogen? The isochoric heat capacity of a mole of nitrogen is $2.5R$.
4. 1 mole of an ideal gas undergoes the following cycle:



Derive an expression for the heat added to the gas during this process using only those parameters shown in the figure.

1.1.4 Thermochemistry

The first law of thermodynamics allows us to systematize the data on the heat of chemical reactions. Consider, for example, the burning of hydrogen to produce water:

$$\mathrm{H_2} + \tfrac{1}{2}\mathrm{O_2} = \mathrm{H_2O}.$$

Burning 1 mole of hydrogen changes the internal energy of the system by $\Delta U = U(H_2O) - U(H_2) - 1/2U(O_2)$, where all values are per mole. At constant volume, the change in internal energy of the system is equal to the heat generated during this reaction. If the reaction proceeds at constant pressure, the heat generated is equal to the change in the enthalpy of the system $\Delta H = H(H_2O) - H(H_2) - 1/2H(O_2)$. Since both the internal energy and enthalpy are state functions, changes in these functions are independent of the path along which this process occurred. This is the basis of **Hess's law**: the heat generated in a chemical reaction is determined by only the type and state of the reactants and the products of the reaction, and does not depend on the reaction path or the existence of any intermediate substances formed during the reaction. This law has great practical significance because it allows us to build rather compact thermodynamic databases and to limit the number of experiments that are necessary for the determination of the heats of reaction. To illustrate this, we consider a simple example. The heat of the reaction

$$2\mathrm{Fe} + \tfrac{3}{2}\mathrm{O}_2 = \mathrm{Fe}_2\mathrm{O}_3, \tag{1.25}$$

is equal to $\Delta H^{(1)} = -822$ kJ/mole, and the heat of the reaction

$$2\mathrm{Fe} + \mathrm{O}_2 = 2\mathrm{FeO}_3, \tag{1.26}$$

is equal to $\Delta H^{(2)} = -530$ kJ/mole. Now, consider the following new reaction:

$$2\mathrm{FeO} + \tfrac{1}{2}\mathrm{O}_2 = \mathrm{Fe}_2\mathrm{O}_3. \tag{1.27}$$

We do not need to perform a separate experiment to determine the heat of this reaction. Rather, we note that this reaction can be described by subtracting Eq. (1.26) from Eq. (1.25). Therefore, the heat of reaction associated with Eq. (1.27) is simply $\Delta H^{(3)} = \Delta H^{(1)} - \Delta H^{(2)} = -292$ kJ/mole.[6] We can do this because we know Hess's law.

In creating a thermodynamic database, we should distinguish between two types of substances, namely, elementary and compound substances. The latter can be synthesized from the former (more formal definitions are discussed below). Any chemical reaction that involves compound substances can be represented as one or more reactions involving only elementary substances to produce those compounds. Consider the oxidation of ammonia as an example:

$$4\mathrm{NH}_3 + 5\mathrm{O}_2 = 4\mathrm{NO} + 6\mathrm{H}_2\mathrm{O}. \tag{1.28}$$

In this reaction, NH_3, NO, and H_2O are compound substances. This reaction can be rewritten as the following series of reactions:

$$\begin{aligned} &(a)\ \tfrac{1}{2}\mathrm{N}_2 + \tfrac{3}{2}\mathrm{H}_2 = \mathrm{NH}_3 \\ &(b)\ \tfrac{1}{2}\mathrm{N}_2 + \tfrac{1}{2}\mathrm{O}_2 = \mathrm{NO} \\ &(c)\ \tfrac{1}{2}\mathrm{O}_2 + \mathrm{H}_2 = \mathrm{H}_2\mathrm{O}. \end{aligned}$$

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[6] Note that these heats of reaction are typical for reactions amongst inorganic substances (i.e. 10–1000 kJ/mole).

Formally, we can rewrite the reaction for the oxidation of ammonia (Eq. 1.28) as:[7]

$$\text{Eq.}(1.28) = (4 \times \text{b}) + (6 \times \text{c}) - (4 \times \text{a})$$

Using Hess's law, we can write the heat of reaction associated with Eq. (1.28) as:

$$\Delta H^{(4)} = 4\Delta H^{(\text{b})} + 6\Delta H^{(\text{c})} - 4\Delta H^{(\text{a})}.$$

Thus, to calculate the heat of any chemical reaction, we need only know the heats of formation of all of the compound substances involved in the reaction from elementary substances. It is these heats of formation that are normally tabulated in databases. Since, in practice, we more frequently encounter reactions proceeding at constant pressure rather than constant volume, the enthalpies of formation are commonly tabulated at room temperature and atmospheric pressure, that is, $T = 25°\text{C}$ and $p = 1$ atm. The enthalpy of formation of elementary substances is, by definition, $\Delta H^0_{\text{f}298} = 0$ (the subscript "f 298" implies formation at $T = 298$ K and the superscript "0" implies that $p = 1$ atm.[8]) If an elementary substance can exist in more than one structure (polymorphic) at $T = 25°\text{C}$ and $p = 1$ atm, $\Delta H^0_{\text{f}298} = 0$ for the most stable form. For example, for graphite $\Delta H^0_{\text{f}298}\left(\text{C}_{(\text{gr})}\right) = 0$ and for diamond $\Delta H^0_{\text{f}298}\left(\text{C}_{(\text{diamond})}\right) = 1.83$ kJ/mole. As a rule, inorganic compounds have $\Delta H^0_{\text{f}298} < 0$ (their formation is exothermic). However, there are exceptions, such as NO, which has a positive enthalpy of formation. The heat of any reaction that takes place under standard conditions[9] can be determined in terms of the standard enthalpy of formation of all of the reactants and products:

$$\Delta H^0_{298} = \sum_{\text{products}} \nu_i \Delta H^0_{f298}(i) - \sum_{\text{reactants}} \nu_i \Delta H^0_{f298}(i) \qquad (1.29)$$

where the ν_i are **stoichiometric coefficients** of the participants in the reaction (e.g. in Eq. (1.25), $\nu_{\text{Fe}} = 2,\ \nu_{O_2} = \frac{3}{2},\ \nu_{\text{Fe}_2\text{O}_3} = 1$).

We can calculate the standard heat of reaction at any temperature if we know the heat capacity of all of the participants in the reaction. Since

$$c_p = \left(\frac{\partial H}{\partial T}\right)_p$$

we can define

$$\Delta c_p = \frac{\text{d}\Delta H^0_T}{\text{d}T}, \qquad (1.30)$$

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[7] Check this yourself.

[8] If gases take part in the reaction their partial pressures must be equal to 1 atm.

[9] "Standard conditions" implies that the partial pressures of all gasses are 1 atm. Cases in which the reactants or products are in solutions are discussed in Chapter 5. The enthalpy corresponding to standard conditions is known as the **standard enthalpy of reaction**.

which is calculated from the heat capacities in the same manner as in the determination of the heat of reaction in Eq. (1.29). Integrating Eq. (1.30), we find:

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta c_p \mathrm{d}T. \tag{1.31}$$

We can also use the tabulated data on the standard enthalpies of formation to determine the heats of reaction at constant volume. At constant volume, the heat of reaction is the change in internal energy. Therefore, we need only find the relationship between U and H. For a gas, this is simply

$$H = U + pV = U + nRT.$$

For a condensed phase (solid, liquid, or glass), pV is usually small relative to heats of reaction. Consider, as an example, the case of water at room temperature and atmosphere pressure:

$$\begin{aligned} pV &\sim 10^5\,\mathrm{Pa} \cdot 10^{-3}\ \mathrm{m^3/kg} \cdot 0.018\,\mathrm{kg/mole} = 1.8\,\mathrm{J/mole} \\ &\approx 0.002\,\mathrm{kJ/mole}. \end{aligned}$$

Therefore, we usually neglect the pV contribution to the enthalpy of condensed phases.

The heat of a chemical reaction occurring at constant pressure is related to that at constant volume by

$$\Delta H_T^0 = \Delta U_T^0 + \Delta \nu_{\mathrm{gas}} RT, \tag{1.32}$$

where $\Delta \nu_{\mathrm{gas}}$ is the difference in the stoichiometric coefficients between the gas phase products and reactants. For example, for the reaction

$$\mathrm{C_{gr}} + 2\mathrm{H_2} = \mathrm{CH_4}$$
$$\Delta H_T^0 = \Delta U_T^0 + (1-2)RT = \Delta U_T^0 - RT,$$

that is, $\Delta \nu_{\mathrm{gas}} = -1$.

Review questions

1. What is the typical magnitude of the heat of chemical reactions involving inorganic substances?
2. Define the term $\Delta H_{\mathrm{f}298}^0$.
3. The standard heat of formation of ammonia is $\Delta H_{\mathrm{f}\,298}^0(\mathrm{NH_3}) = -294.1\,\mathrm{kJ/mole}$. Write the chemical reaction corresponding to this heat of formation.

Example problems

1. Calculate the heat of reaction for

$$\mathrm{CH_4} + 2\mathrm{CO} = 3\mathrm{C_{(gr)}} + 2\mathrm{H_2O}$$

at 1100 K. The following thermodynamic data are available from standard thermodynamic databases:

Substance	CH_4	CO	C_{gr}	H_2O
ΔH^0_{f298} kJ/mole	– 74.60	– 110.53	0	– 241.81
S^0_{298}, J/(K mole)	186.26	197.55	5.74	188.72
a	42.06	28.41	16.86	30.00
b	31.50	4.10	4.77	10.71
c	– 17.29	– 0.46	– 8.54	0.33

where the temperature dependence of the heat capacities of the reactants and products are described by

$$c_p = a + b \cdot 10^{-3} T + c \cdot 10^5 T^{-2}$$

(The S^0_{298} data are included for other examples, below.)

2. Find the heat of formation of SiO_2

$$Si + O_2 = SiO_2$$

at constant volume and $T = 700$ K, given the following thermodynamic data:

$$c_p(Si) = 20.0\,\text{J/(K mole)}$$
$$c_p(O_2) = 29.4\,\text{J/(K mole)}$$
$$c_p(SiO_2) = 44.2\,\text{J/(K mole)}$$
$$\Delta H^0_{298} = -908\,\text{kJ/mole}.$$

1.2 The second law of thermodynamics

While the first law of thermodynamics tells us that energy is conserved, it tells us nothing about whether a reaction will proceed and, if so, in which direction. In order to resolve this issue, we must first introduce a new state function which is central to the establishment of the second law of thermodynamics. Unlike the first law, the second law is difficult to succinctly articulate. The next four sections of this chapter describe the establishment of the second law. However, if it is enough that you know what it is, rather than where it comes from, you can skip ahead to Section 1.2.5.

1.2.1 Thomson and Clausius postulates

A thermodynamic system can exchange heat with its surroundings and perform work. Therefore, it can be viewed as if it were part of a heat engine. The theory of heat engines was developed primarily in the eighteenth and nineteenth centuries in connection with answering the following question: is it possible to construct a perpetual motion machine? (Although this question has long been settled, counter proposals still appear in newspapers and investment seminars.) Such a theory is applicable to all thermodynamic systems and not just heat engines. We now briefly state the main ideas of this theory.

We start with a discussion of several features that are common to all types of heat engines. The heat engine consists of a **medium** that performs work (e.g. by expanding) and mechanisms for adding and removing heat, i.e. a **heater** and a **cooler**, respectively. To perform work, the medium must obtain heat, Q_{h}, from the heater. This acquisition of heat brings the system from state 1 to state 2 along some path, a. (We shall label such a transition as 1 → a → 2.) We can represent this process on a p–V diagram, as shown in Fig. 1.3. According to the first law of thermodynamics, the amount of work done by the medium is related to the heat transferred and the change in internal energy of the medium: $W_{1\to\mathrm{a}\to 2} = |Q_{\mathrm{h}}| - (U_2 - U_1)$.[10]

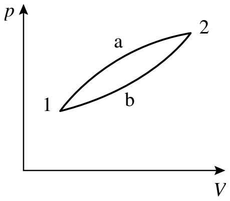

Fig. 1.3
Schematic illustration that shows that the net work done in one heat engine cycle is the area enclosed between the two paths.

If the medium returns to state 1 along the same path, 2 → a → 1, the total work will be zero. However, if the medium returns to state 1 by a different path b, 2 → b → 1, the net work will be non-zero. During this process 2 → b → 1 the medium gives up some heat, Q_{c}, to the cooler and performs (negative) work $W_{2\to\mathrm{b}\to 1} = -|Q_{\mathrm{c}}| - (U_1 - U_2)$. The net work performed by the medium in transversing this circuit is $W = W_{1\to\mathrm{a}\to 2} + W_{2\to\mathrm{b}\to 1} = |Q_{\mathrm{h}}| - |Q_{\mathrm{c}}|$, where $Q = |Q_{\mathrm{h}}| - |Q_{\mathrm{c}}|$ is the total heat absorbed by the medium in this process. This work is simply the area enclosed in going around the circuit in the p–V diagram in Fig. 1.3 (1 → a → 2 → b → 1).

The efficiency of the heat engine η is defined as

$$\eta = \frac{W}{|Q_{\mathrm{h}}|}. \tag{1.33a}$$

Replacing the work with its heat equivalent, as per the first law of thermodynamics, we can rewrite the efficiency as

$$\eta = \frac{|Q_{\mathrm{h}}| - |Q_{\mathrm{c}}|}{|Q_{\mathrm{h}}|}. \tag{1.33b}$$

Thus, the first law of thermodynamics tells us that the efficiency $\eta \leq 1$. Since the efficiency can never be greater than one, it is impossible to construct a device that produces more work than the heat provided. If η were greater than 1, we could produce some work, while returning all of the original heat provided to the heater (e.g. as a result of friction). This would be a perpetual motion machine since we are getting work for nothing. Such a device is known as a perpetual motion machine of the first type and is prohibited by the first law of thermodynamics.

If $Q_{\mathrm{c}} = 0$, then $\eta = 1$. Such a machine is called a perpetual motion machine of the second type. Indeed, if we could create an engine without a cooler, we could simply use the universe as the heater, let it cool by an infinitesimal amount while transferring an infinite amount of heat to our medium, and produce an infinite amount of work. However, this violates all known experience, so we must conclude that it is impossible. This observation is known as **Thomson's postulate**: no *closed* path through p–V

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[10] In Sections 1.2.1–1.2.3, we always use the absolute value of the heat and explicitly indicate the direction of the heat flow.

space is possible in which the *only* result is the production of work and the removal of heat from a heater. This is one statement of the **Second Law of Thermodynamics.**

An alternative statement of the Second Law was given by Clausius. **Clausius's postulate** states: heat cannot flow *spontaneously* from a cooler to a hotter system (without producing some other change in the universe). The Thomson and Clausius postulates are equivalent; one follows from the other. However, we should keep in mind that both the first law of thermodynamics and these two postulates are not the results of thermodynamics, but are, in fact, assertions that thermodynamics uses. Both are consistent with centuries of experience.

Example problem

1. Prove the equivalence of the Thomson and Clausius postulates.

1.2.2 Reversible and irreversible processes

Consider the transformation of a system from state A to state B as the result of some process. If it is possible to return the system from state B back to state A by a path for which the entire circuit A → B → A leaves the universe completely unchanged, the original transformation A → B is **reversible**. On the other hand, if no such return path exists, the original process A → B is **irreversible**. Consider two examples. According to the Clausius postulate, the spontaneous flow of heat from a body at a higher temperature to one at a lower temperature is irreversible. According to the Thomson postulate, the release of heat by friction is an irreversible process.

Let us consider the piston example shown in Fig. 1.4. Point A corresponds to the initial state of the gas on a $p-V$ diagram. If we remove a shovel full of sand from the top of the piston, the pressure in the gas will drop to the value indicated by point B on the $p-V$ diagram and the volume will increase to that indicated by point C. If we continue shoveling away the sand, the system will traverse path 1 to state E, going through D along the way. We can return the system to its original state by adding sand, as indicated by path 2 (i.e. the dotted line in the $p-V$ diagram). Examination

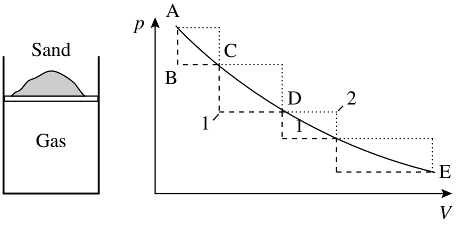

Fig. 1.4
Schematic illustration of the difference between a reversible and an irreversible process.

of Fig. 1.4 shows that the work associated with the compression of the gas in going from E to A along path 2 (i.e. the area under path 2 in Fig. 1.4) is larger than the original work done by the gas in the expansion from A to E along path 1. If instead of removing and adding sand by the shovel full, we use a teaspoon, path 1 will be much closer to path 2 and hence the excess work is drastically reduced. In the limit that we remove one sand particle at a time, path 1 and path 2 will be indistinguishable. In this case, the excess work is (almost exactly) zero and the process corresponding to path A → E is reversible. Provided we change the system sufficiently slowly so that it is always in equilibrium, a reversible process traverses a locus of equilibrium states. If the process is reversible, we could go either way on the solid curve by adding or removing sand particles one at a time. In other words, we can always reverse the direction of a reversible process by infinitesimally changing external conditions.

The piston example suggests that the maximum amount of work a system can perform in going from one state to another is achieved when the system moves along a reversible path. We will prove this statement in Section 1.4.1.

1.2.3 Carnot cycle

One particular thermodynamic circuit is of special significance: this is the Carnot cycle. By definition, the **Carnot cycle** is a reversible process in which the system is alternately in contact with two heat reservoirs (a heater and a cooler) at constant temperatures T_h and T_c ($T_\mathrm{h} > T_\mathrm{c}$). At first, the system is in contact with the heater. According to the Clausius postulate, this process can be reversible only if the system has the same temperature as the heater. Since the heater temperature is constant, this contact must correspond to an isothermal process. During this contact, the system acquires heat, $|Q_\mathrm{h}|$ and performs work, W_{12} (see Fig. 1.5). Now, after the system is removed from the heater and before it is brought into contact with the cooler, it must be cooled to the temperature of the cooler (otherwise the contact with the cooler will not correspond to a reversible process, as per the Clausius postulate). Since there are no other heat reservoirs available, this process must occur adiabatically. During this process, the system performs work, W_{23}. Then, when the system contacts the cooler, it loses heat, $|Q_\mathrm{c}|$ and performs negative work, W_{34}. Point 4 in Fig. 1.5 is chosen such that the system can return to the initial state (i.e. point 1) adiabatically. During this last adiabatic compression, the system performs negative work, W_{41}. Thus, a Carnot circle consists of two isotherms 12 and 34 and two adiabats 23 and 41 (see Fig. 1.5). During the entire Carnot cycle, the internal energy of the system does not change (this is a closed circuit), but the system performs work $W = W_{12} + W_{23} + W_{34} + W_{41} = |Q_\mathrm{h}| - |Q_\mathrm{c}|$. Note that the heat flow from and to the heater and cooler are related by the efficiency η, as per Eq. (1.33 b)

$$|Q_\mathrm{c}| = (1 - \eta)|Q_\mathrm{h}|. \tag{1.34}$$

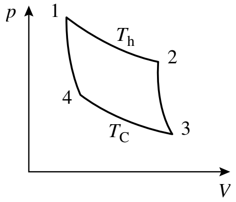

Fig. 1.5
A schematic Carnot cycle.

The **first Carnot theorem** states that the efficiency of a machine operating with the Carnot cycle depends only on the temperatures of the heater and cooler and does not depend on any details of how the machine is constructed or the working medium employed. To proof this theorem, we consider two Carnot machines that share the same common heater and cooler but have efficiencies η_1 and η_2. In order to make this analysis concrete, we shall assume that $\eta_1 > \eta_2$. We will show below that if this inequality holds, then we contradict Thomson's postulate. We begin by allowing machine 1 to perform m_1 forward cycles, acquiring heat $|Q_\mathrm{h}|_1 = m_1 q_1$ from the heater and losing heat $|Q_\mathrm{c}|_1$ to the cooler and in the process, doing work $W_1 = |Q_\mathrm{h}|_1 - |Q_\mathrm{c}|_1$ (e.g. the machine may lift a weight off of the floor). Now, we stop machine 1 and use the potential energy stored by the weight dangling above the floor to start machine 2, which will operate in the reverse direction (this is possible since the Carnot cycle is reversible). When machine 2 performs m_2 cycles, it acquires heat $|Q_\mathrm{c}|_2$ from the cooler and losing heat $|Q_\mathrm{h}|_2 = m_2 q_2$ to the heater (i.e. it works like a refrigerator). During this process machine 2 does negative work $W_2 = |Q_\mathrm{h}|_2 - |Q_\mathrm{c}|_2$. Summarizing the results of the actions of both machines, we find:

- heat $|Q_\mathrm{h}|_1 - |Q_\mathrm{h}|_2$ was transferred from the heater to the system
- heat $|Q_\mathrm{c}|_2 - |Q_\mathrm{c}|_1$ was transferred from the cooler to the system
- work $W = W_1 - W_2 = (|Q_\mathrm{h}|_1 - |Q_\mathrm{c}|_1) - (|Q_\mathrm{h}|_2 - |Q_\mathrm{c}|_2) = \eta_1 |Q_\mathrm{h}|_1 - \eta_2 |Q_\mathrm{h}|_2$ was performed.

Since m_1 and m_2 are, to this point, arbitrary, we can choose them such that $|Q_\mathrm{h}|_1 - |Q_\mathrm{h}|_2 = 0$. In this case, the heater lost no heat, the cooler lost heat $|Q_\mathrm{c}|_2 - |Q_\mathrm{c}|_1 = (1 - \eta_2)|Q_\mathrm{h}|_2 - (1 - \eta_1)|Q_\mathrm{h}|_1 = (\eta_1 - \eta_2)|Q_\mathrm{h}|_1 > 0$ to the system, and the machines produced work $W = (\eta_1 - \eta_2)|Q_\mathrm{h}|_1 > 0$. No other changes were made to the universe. However, such a process is prohibited by Thomson's postulate (i.e. no closed circuit is possible if that produces only work and transfers heat from a thermal reservoir). Alternatively, if $\eta_1 < \eta_2$, we would contradict the second law of thermodynamics if machine 2 does work in the forward direction while machine 1 does work in the backward direction. Thus, η_1 must be equal to η_2. This proves that any Carnot machines sharing the same heater and cooler have the same efficiency.

Since the efficiency of a Carnot machine does not depend on the type of the medium, we can simplify our analysis by choosing an ideal gas as the medium. Because we know how ideal gases behave, we can derive an expression for Carnot efficiency that is valid for all Carnot machines. To this end, we first recall that for any isothermal ideal gas $\Delta U = 0$, $|Q_\mathrm{h}| = RT_\mathrm{h} \ln V_2/V_1$, and $|Q_\mathrm{c}| = RT_\mathrm{c} \ln V_3/V_4$ (see Section 1.1.3). Thus, we find

$$\frac{|Q_\mathrm{h}|}{|Q_\mathrm{c}|} = \frac{T_\mathrm{h} \ln V_2/V_1}{T_\mathrm{c} \ln V_3/V_4} \tag{1.35}$$

For adiabatic processes, $c_V \mathrm{d}T + RT\mathrm{d}V/V = 0$. Since $c_V = \left(\frac{\partial U}{\partial T}\right)_V$, the isochoric heat capacity of an ideal gas depends only on temperature; hence,

$$\int_{p.2}^{p.3} c_V \frac{\mathrm{d}T}{T} = -\int_{p.4}^{p.1} c_V \frac{\mathrm{d}T}{T},$$

where the limits of the integrals denote points in the $p-V$ diagram in Fig. 1.5. Since $c_V\mathrm{d}T/T = R\mathrm{d}V/V$, we find:

$$\int_{p.2}^{p.3} \frac{\mathrm{d}V}{V} = -\int_{p.4}^{p.1} \frac{\mathrm{d}V}{V}; \qquad \ln\frac{V_3}{V_2} = \ln\frac{V_4}{V_1}; \qquad \ln\frac{V_3}{V_4} = \ln\frac{V_2}{V_1}.$$

Combining this result with Eq. (1.35) implies

$$\frac{|Q_\mathrm{h}|}{T_\mathrm{h}} = \frac{|Q_\mathrm{c}|}{T_\mathrm{c}}. \tag{1.36}$$

Now using Eqs (1.34) and (1.36), we obtain an expression for the Carnot efficiency:

$$\eta = \frac{|Q_\mathrm{h}| - |Q_\mathrm{c}|}{|Q_\mathrm{h}|} = 1 - \frac{|Q_\mathrm{c}|}{|Q_\mathrm{h}|} = 1 - \frac{T_\mathrm{c}}{T_\mathrm{h}};$$

$$\eta = \frac{T_\mathrm{h} - T_\mathrm{c}}{T_\mathrm{h}}. \tag{1.37}$$

Recall that although this derivation was for an ideal gas, Eq. (1.37) is equally valid for any Carnot machine.

Finally, we note that we can rewrite Eq. (1.36) without the absolute value signs by being careful about the direction of the heat flow,

$$\frac{Q_\mathrm{h}}{T_\mathrm{h}} + \frac{Q_\mathrm{c}}{T_\mathrm{c}} = 0 \tag{1.38}$$

This expression has the benefit that it looks symmetric with respect to the identification of the different heat reservoirs as the heater and cooler.

1.2.4 The Clausius inequality

We now consider the general case of a circuit process involving an arbitrary thermodynamic medium, M. This medium acquires heat Q_1 from heat reservoir R_1, heat Q_2 from reservoir R_2, etc. in this circuit (see Fig. 1.6(a)). We now isolate the medium M from the reservoirs and connect these reservoirs to Carnot machines that operate between the reservoirs R_i and a common reservoir, R_0, as shown in Fig. 1.6(b). Since we do this after medium M is isolated, the addition of these Carnot machines does not change medium M in any way. Let Carnot machine C_i perform a circuit, taking heat Q_{0i} from reservoir R_0 and heat Q_i' from reservoir R_i. We now combine the circuit involving medium M with the processes associated

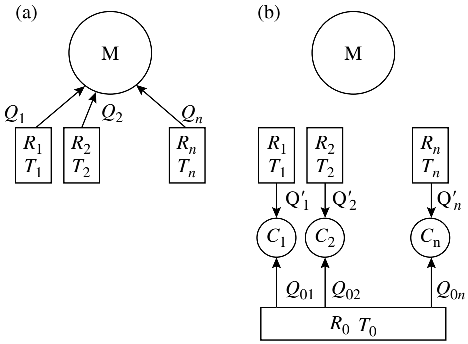

Fig. 1.6

A schematic process involving (a) work performed by medium M and heat flow between n distinct heat reservoirs R_i and the medium and (b) work performed by n Carnot machines C_i and the transfer of heat between these reservoirs and a common reservoir R_0. In step (b), the medium is isolated from all reservoirs.

with all n Carnot machines into a single complex circuit. In the resultant complex circuit,

reservoir R_0 lost heat $Q_0 = \Sigma_i Q_{0i}$,
reservoir R_i lost heat $Q_i + Q'_i$, and
work $W = Q_0 + \Sigma_i(Q_i + Q'_i)$ was performed.

By changing the length of the isotherms in the Carnot cycle (see Fig. 1.5), we can change the quantity of heat transferred to or from the reservoir. Without loss of generality, we choose Carnot cycles for which $Q_i + Q'_i = 0$. In this case, the states of all of the reservoirs R_i do not change as we traverse this complex circuit. We can write Eq. (1.38) for Carnot machine C_i in the following form

$$\frac{Q_{0i}}{T_0} + \frac{Q'_i}{T_i} = 0.$$

Therefore, during the complex circuit of Fig. 1.6, reservoir R_0 transfers heat

$$Q_0 = \sum_i Q_{0i} = -T_0 \sum_i \frac{Q'_i}{T_i} = T_0 \sum_i \frac{Q_i}{T_i},$$

and does work $W = Q_0$. According to the Thomson postulate, this work cannot be positive, since there are no other changes in the universe. Therefore,

$$0 \geq W = Q_0 = T_0 \sum_i \frac{Q_i}{T_i}$$

$$\sum_i \frac{Q_i}{T_i} \leq 0. \tag{1.39}$$

Note that in this derivation, no restrictions were put on medium M. Rather, our only constraint was that the temperature of all of the reservoirs remain constant as the complex circuit is traversed (in practice, this means that the reservoirs are large).

We now consider an arbitrary thermodynamic system which makes a circuit transferring heat to or from its surroundings. In this way, we consider the surroundings as a set of heat reservoirs. We can divide the circuit into infinitesimal parts where the system exchanges heat with a single heat reservoir, the temperature of which remains constant. Inequality Eq. (1.39) can be rewritten for this circuit as

$$\sum_i \frac{\delta Q_i}{T_i} \le 0,$$

where δQ_i is the heat transferred during the infinitesimal part, i, of the circuit. This summation can be replaced by integration; hence,

$$\oint \frac{\delta Q}{T} \le 0, \tag{1.40}$$

where T is the temperature of the surroundings. This result is known as the **Clausius inequality**.

We now examine an important consequence of the Clausius inequality. If the system exchanges heat with only two heat reservoirs, the inequality in Eq. (1.39) can be rewritten as:

$$\frac{|Q_\mathrm{h}|}{T_\mathrm{h}} - \frac{|Q_\mathrm{c}|}{T_\mathrm{c}} \le 0; \qquad \frac{T_\mathrm{c}}{T_\mathrm{h}} \le \frac{|Q_\mathrm{c}|}{|Q_\mathrm{h}|}; \qquad -\frac{T_\mathrm{c}}{T_\mathrm{h}} \ge -\frac{|Q_\mathrm{c}|}{|Q_\mathrm{h}|};$$

$$1 - \frac{T_\mathrm{c}}{T_\mathrm{h}} \ge 1 - \frac{|Q_\mathrm{c}|}{|Q_\mathrm{h}|}; \qquad \frac{T_\mathrm{h} - T_\mathrm{c}}{T_\mathrm{h}} \ge \frac{|Q_\mathrm{h}| - |Q_\mathrm{c}|}{|Q_\mathrm{h}|}.$$

The left side of this expression is the efficiency of a Carnot machine (see Eq. (1.37)), while the right side is the efficiency of an arbitrary machine which exchanges heat with the same heater and cooler as the Carnot machine. This result is known as the **second Carnot Theorem**: the efficiency of any machine cannot be larger than the efficiency of the Carnot machine with the same heater and cooler.

1.2.5 Entropy

Consider the case of an arbitrary reversible circuit, as shown in Fig. 1.7. Since in a reversible process the system is always very close to equilibrium, the temperature of the system must be the same as the temperature of its surroundings. Therefore, in the case of a reversible process, the temperature in the Clausius inequality should be understood as the temperature of the system.

For the process $1 \xrightarrow[\mathrm{a}]{} 2 \xrightarrow[\mathrm{b}]{} 1$ $\oint \delta Q/T \le 0$. Similarly, for the process $1 \xrightarrow[\mathrm{b}]{} 2 \xrightarrow[\mathrm{a}]{} 1$ $\oint \delta Q'/T \le 0$. Since $\delta Q' = -\delta Q$ in a reversible process, we must have:

$$\oint \frac{\delta Q}{T} = 0. \tag{1.41}$$

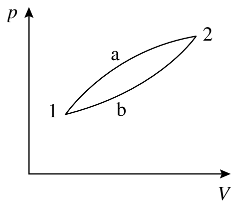

Fig. 1.7
An arbitrary circuit process.

Equation (1.41) is known as the **Clausius equality**. We can rewrite this equality in the following form:

$$\oint \frac{\delta Q}{T} = \int_{1\xrightarrow[\mathrm{a}]{}2} \frac{\delta Q}{T} + \int_{2\xrightarrow[\mathrm{b}]{}1} \frac{\delta Q}{T} = \int_{1\xrightarrow[\mathrm{a}]{}2} \frac{\delta Q}{T} - \int_{1\xrightarrow[\mathrm{b}]{}2} \frac{\delta Q}{T} = 0,$$

where 1 and 2 are arbitrary points on the circuit and a and b are the two paths that connect these two points. Therefore,

$$\int_{1\xrightarrow[\mathrm{a}]{}2} \frac{\delta Q}{T} = \int_{1\xrightarrow[\mathrm{b}]{}2} \frac{\delta Q}{T}.$$

Thus, the integral of $\delta Q/T$ depends only on the endpoints of the integral and not on the path of a reversible process. Therefore, $\delta Q/T$ is a full differential of a state function for a reversible process:

$$\mathrm{d}S = \frac{\delta Q}{T}; \qquad \Delta S = S_2 - S_1 = \int_{1\to 2} \frac{\delta Q}{T}. \tag{1.42}$$

Following Clausius, we name this state function the **entropy**. Note that according to Eq. (1.42), the entropy is defined to within an additive constant. We will return to the question of the value of this additive constant in Section 1.3.1.

Now, consider the case in which the system irreversibly goes from state 1 to state 2 by path a and then returns from 2 to 1 via a reversible path b. Since the complete circuit is still irreversible, we have to use sign $>$ in the Clausius inequality:

$$0 > \oint \frac{\delta Q}{T} = \int_{1\xrightarrow[\mathrm{a}]{}2} \frac{\delta Q}{T} + \int_{2\xrightarrow[\mathrm{b}]{}1} \frac{\delta Q}{T} = \int_{1\xrightarrow[\mathrm{a}]{}2} \frac{\delta Q}{T} - \int_{1\xrightarrow[\mathrm{b}]{}2} \frac{\delta Q}{T} = \int_{1\xrightarrow[\mathrm{a}]{}2} \frac{\delta Q}{T} - \Delta S$$

Thus we find that for any irreversible process

$$\Delta S = S_2 - S_1 > \int_{1\to 2} \frac{\delta Q}{T}; \qquad \mathrm{d}S > \frac{\delta Q}{T}. \tag{1.43}$$

Combining Eqs (1.42) and (1.43), we find

$$\mathrm{d}S \geq \frac{\delta Q}{T}, \tag{1.44}$$

where the equality corresponds to reversible processes and the inequality corresponds to irreversible processes. Note that for adiabatic systems $\delta Q = 0$ and $\mathrm{d}S \geq 0$.

Equation (1.44) is the analytical statement of the second law of thermodynamics, first given by Clausius in 1862. It was on this basis that he first postulated the existence of a new state function—entropy. For adiabatic systems, the entropy remains constant if the process is reversible and always increases if the process is irreversible. The entropy continues to increase until the system reaches equilibrium. This necessarily implies that equilibrium is the state of maximum entropy. Since in an adiabatic system all spontaneous processes increase the entropy, no spontaneous process that decreases the entropy is possible. This is the first hint that thermodynamics provides as to which direction a process will go.

Review question

1. Does the change of the entropy depend on the path by which the system goes from one state to another?

1.2.6 Implications of the second law of thermodynamics

As we discussed at the beginning of this chapter, thermodynamics makes predictions based upon changes in state functions. The first law of thermodynamics provides one state function, the internal energy. In Sections 1.1.2 and 1.1.3, we saw how this function changes during different processes. The second law of thermodynamics provides another state function, the entropy. We now examine how this function changes during different processes. Inserting the first law of thermodynamics (Eq. (1.5)) into the Clausius inequality (Eq. (1.44)) yields:

$$T\mathrm{d}S \geq \mathrm{d}U + \delta W. \tag{1.45}$$

This relationship is called the **combined statement of the first and second laws of thermodynamics**. The equality pertains for reversible processes:

$$T\mathrm{d}S = \mathrm{d}U + \delta W.$$

If the work of expansion is the only work performed during a process, this equation reduces to

$$T\mathrm{d}S = \mathrm{d}U + p\mathrm{d}V. \tag{1.46}$$

While the temperature in Eq. (1.45) refers to the temperature of the surroundings, in Eq. (1.46) it is the temperature of the thermodynamic system itself. Equation (1.46) can be used to find the change of entropy associated with different processes. Although Eq. (1.46) refers specifically to a reversible process, the change of entropy is valid for all processes. This is because the entropy is a state function and its change depends only on the initial and final states but not on the path the process takes (i.e. it applies equally to reversible and irreversible processes).

For isochoric processes, $T\mathrm{d}S = \mathrm{d}U = c_V\mathrm{d}T$, which can be integrated as follows:

$$\Delta S_{\mathrm{V}} = \int_{T_1}^{T_2} \frac{c_V}{T}\mathrm{d}T. \tag{1.47}$$

For isobaric processes, $TdS = d(U + pV) = dH = c_p dT$ and

$$\Delta S_p = \int_{T_1}^{T_2} \frac{c_p}{T} dT. \tag{1.48}$$

These expressions give a definition for the heat capacity in terms of S, rather than in terms of U and H (Section 1.1.2):

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_V; \qquad c_p = T\left(\frac{\partial S}{\partial T}\right)_p. \tag{1.49}$$

For isothermal processes,

$$\Delta S_{\mathrm{T}} = \frac{Q}{T}. \tag{1.50}$$

This expression can be used to describe the change in entropy associated with an isothermal phase transition in terms of the heat of the transition and the temperature,

$$\Delta S_{p.t.} = \frac{\Delta H_{p.t.}}{T_{p.t.}}. \tag{1.51}$$

The relationships derived above are valid for all systems. We can specialize to the case of isothermal processes involving an ideal gas,

$$dU = 0; \qquad TdS = pdV = \frac{nRT}{V} dV;$$

$$\Delta S_{\mathrm{T}} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{p_1}{p_2}. \tag{1.52}$$

We now turn our attention to the important case of the mixing of two ideal gases at constant temperature and pressure. Consider a closed container, divided by a membrane into two sections; the first section has volume V_1 and contains gas 1, and the second has volume V_2 and contains gas 2. Initially, the gases are at the same temperature and pressure. When the membrane separating the two sections is removed at constant temperature, both gases expand into the entire volume of the container. The change of entropy associated with this mixing of the two gasses (i.e. the **entropy of mixing**) is determined through Eq. (1.52)

$$\Delta S_{\mathrm{mix}} = n_1 R \ln \frac{V}{V_1} + n_2 R \ln \frac{V}{V_2}, \tag{1.53}$$

where n_1 and n_2 are the number of moles of gasses 1 and 2, and $V = V_1 + V_2$ is the volume of the container. The total pressure after mixing is the same as before mixing, therefore,

$$pV = nRT; \qquad pV_1 = n_1 RT.$$

Combining these equations, we find:

$$\frac{V}{V_1} = \frac{n}{n_1} = \frac{1}{x_1},$$

where x_1 is the molar fraction of gas 1 in the mixture. Inserting this relationship into Eq. (1.53) implies

$$\Delta S_{\text{mix}} = -R\left[n_1 \ln \frac{n_1}{n_1+n_2} + n_2 \ln \frac{n_2}{n_1+n_2}\right] = -nR[x_1 \ln x_1 + x_2 \ln x_2] \tag{1.54}$$

(Note: gases 1 and 2 must be different; otherwise, of course, $\Delta S_{\text{mix}} = 0$.)

Review questions

1. What are the dimensions of entropy?
2. Does the entropy of the system increase or decrease upon heating a substance at constant volume or at constant pressure?
3. Does the entropy of the system increase or decrease when two ideal gases are mixed?

Example problems

1. Calculate the change of entropy associated with the process described in Example problem 1.1.2.1.
2. 2 moles of nitrogen (N_2) change from a state where $T_1 = 25°\text{C}$ and $p_1 = 1$ atm to one in which $T_2 = 200°\text{C}$ and $V_2 = 10^5\,\text{cm}^3$. The heat capacity of 1 mole of nitrogen at constant pressure is $c_p = 3.5R$. Calculate the change of entropy of this process.
3. At $T = 25°\text{C}$, $1000\,\text{cm}^3$ of nitrogen (N_2) at pressure $p_1 = 1$ atm is mixed with $2000\,\text{cm}^3$ of oxygen (O_2) at pressure $p_2 = 2$ atm. The volume of the mixture is then changed such that the temperature and pressure in the final state are $T = 25°\text{C}$ and $p = 1$ atm, respectively. Calculate the change of entropy associated with this two-step process.
4. Find the change of entropy at $T = 1100$ K associated with the reaction in Example problem 1.1.4.1.

1.3 The third law of thermodynamics

1.3.1 Nernst heat theorem

We begin our discussion of the third law of thermodynamics by reference to the second law which defines the entropy to within an integration (additive) constant. Just as we cannot describe the internal energy without making reference to some standard state, it is necessary to establish a reference point to fully describe the entropy. Another difficulty with the definition of entropy occurs at $T = 0$ K. Indeed, it is not obvious that the integral of the differential of the entropy (Eq. (1.42))

$$S_T = S_{T_0} + \int_{T_0}^{T} \frac{\delta Q}{T} = S_{T_0} + \int_{T_0}^{T} \frac{c}{T}\mathrm{d}T, \tag{1.55}$$

is convergent as $T \to 0$ (the integrand will diverge as $T \to 0$ provided, for example, that the heat capacity is finite at $T = 0$).

We cannot resolve these problems on the basis of the first or second laws of thermodynamics without the introduction of additional postulates. The **Nernst heat theorem** (frequently called the **third law of thermodynamics**), formulated in 1906, provides the requisite new postulates. The first statement of this theorem postulates that the heat capacity of any substance goes to zero as $T \to 0\,\text{K}$. Furthermore, experimental observations (and quantum mechanics) demonstrate that the heat capacity goes to zero as $T \to 0$ in such a way that the ratio c/T does not diverge. Therefore, the entropy is well defined in the $T \to 0\,\text{K}$ limit. The second statement of the Nernst heat theorem says that at $\text{T} = 0\,\text{K}$ all processes that take a system from one equilibrium state to another occur with no change of entropy. Furthermore, the **Planck postulate** states that the second statement of the Nernst heat theorem will always be valid provided that the entropy of any equilibrium system goes to zero as $T \to 0\,\text{K}$. This statement is also frequently called the third law of thermodynamics. The Planck postulate is very useful from a practical point of view since it provides a reference point for the entropy (i.e. $T = 0\,\text{K}$). While these statements of the third law of thermodynamics are simply postulates, they can be understood in physical terms through quantum mechanics and statistical physics.

While the first statement of the Nernst heat theorem is always valid, the second statement is not valid for all substances, for example, amorphous materials. This is not a contradiction to the third law of thermodynamics which applies to equilibrium systems because amorphous materials are not in equilibrium.

Review question

1. Can entropy be negative?

1.3.2 Determination of absolute entropy

The third law of thermodynamics gives us an opportunity to determine the absolute value of entropy at any temperature using calorimetric measurements. In such measurements, a known, small quantity of heat is introduced into an otherwise adiabatic container (i.e. a calorimeter) and the corresponding change in temperature is measured. The ratio of the heat introduced to the temperature change is the heat capacity. The heat capacity can be measured down to very low temperature (point A in Fig. 1.8). Debye theory (see Section 13.3.2), which shows that $c_p \sim T^3$, can be used to estimate c_p down to just a few degrees Kelvin. While we focus on the high temperature behavior of the heat capacity hereafter, a formal discussion of the behavior of the heat capacity at low temperature can be found in Chapters 12 and 13. The heat capacity is a smooth function except at phase transitions. Figure 1.8 demonstrates two such breaks related to melting (point B) and evaporation (point D). Every phase transition

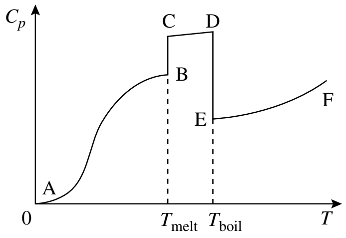

Fig. 1.8
The dependence of the heat capacity on temperature for a substance that exhibits both melting and boiling.

adds $\Delta H_{p.t.}/T_{p.t.}$ to the entropy. If there are no phase transitions in the condensed states, the entropy of the gas (point F) can be calculated as:

$$S_{T_\mathrm{F}} = \int_0^{T_\mathrm{melt}} \frac{c_p}{T}\mathrm{d}T + \frac{\Delta H_\mathrm{melt}}{T_\mathrm{melt}} + \int_{T_\mathrm{melt}}^{T_\mathrm{boil}} \frac{c_p}{T}\mathrm{d}T + \frac{\Delta H_\mathrm{evap}}{T_\mathrm{boil}} + \int_{T_\mathrm{boil}}^{T_\mathrm{F}} \frac{c_p}{T}\mathrm{d}T.$$

If there is a phase (polymorphous) transition in the solid state, the corresponding $\Delta H_{p.t.}/T_{p.t.}$ must be added to the entropy for all $T > T_{p.t.}$.

Databases usually quote the value of the entropy at $T = 298\,\mathrm{K}$ and $p = 1$ atm, S^0_{298}. Note that there is no Δ before S^0_{298} (in contrast with $\Delta H^0_{\mathrm{f}298}$) since this is an absolute value.

Example problem

1. Iron (α–Fe) is ferromagnetic at room temperature, but undergoes a phase transition to the paramagnetic state (β-Fe) at $T_{\alpha\to\beta} = 768°\mathrm{C}$. The heat of this transition is $\Delta H_{\alpha\to\beta} = 1.53\,\mathrm{kJ/mole}$. A database gives the following data for α–Fe: $S^0_{298} = 27.15\,\mathrm{J/(K\ mole)}$; $c_p = 23.9 + 8.7\cdot 10^{-3}\,\mathrm{T\,J/(K\ mole)}$. Find the entropy of 1 mole of β–Fe at $T = 768°\mathrm{C}$.

1.4 Helmholtz and Gibbs free energies

1.4.1 Direction of spontaneous processes at constant temperature

We have already seen that entropy determines the direction of spontaneous processes in adiabatic systems. However, if a system can exchange heat with its surroundings, the entropy alone does not predict the direction of spontaneous processes. In this section, we consider the very important case of isothermal processes. We start from the Clausius inequality (Eq. (1.45)), which can be rewritten as:

$$\delta W \le -(\mathrm{d}U - T\mathrm{d}S).$$

For isothermal processes, $\mathrm{d}U – T\mathrm{d}S = \mathrm{d}(U – TS)$. We can introduce a new state function, called the **Helmholtz free energy**, as

$$A = U - TS. \tag{1.56}$$

Substituting this definition into the inequality, above, we find

$$\delta W \le -\mathrm{d}A. \tag{1.57}$$

Thus, the maximum work that can be done by the system is equal to minus the change of the Helmholtz free energy. Since the equality in Eq. (1.57) corresponds to reversible processes, we find that the maximum work is obtained only in reversible processes.

At constant volume, the work of expansion ($p\mathrm{d}V$) is zero. Therefore, Eq. (1.57) for isochoric-isothermal processes can be rewritten as:

$$\delta W_\text{non-mechanical} \le -\mathrm{d}A. \tag{1.58}$$

At constant pressure, Eq. (1.57) implies:

$$\delta W_{\text{non-mechanical}} \leq -\mathrm{d}A - p\mathrm{d}V = -\mathrm{d}(A + pV).$$

In this case, it is convenient to introduce a new state function, the **Gibbs free energy**, defined as

$$G = A + pV = U - TS + pV = H - TS. \tag{1.59}$$

For isobaric-isothermal processes,

$$\delta W_{\text{non-mechanical}} \leq -\mathrm{d}G. \tag{1.60}$$

In order to prevent a spontaneous process from proceeding, we must do some work on the system. Obviously, this work must exceed the non-mechanical work that the system performs during the spontaneous process. Therefore, the non-mechanical work can be used to determine whether a spontaneous process will occur: $W_{\text{non-mechanical}} \geq 0$ implies that such a process will occur. Using Eq. (1.58), we can rewrite this condition for isochoric–isothermal processes as:

$$\mathrm{d}A \leq 0. \tag{1.61}$$

This implies that all spontaneous processes lead to a decrease of the Helmholtz free energy at constant T and V. Similarly, Eq. (1.60) implies that a process will occur spontaneously at constant T and p if the Gibbs free energy satisfies

$$\mathrm{d}G \leq 0. \tag{1.62}$$

The equality in Eqs (1.61) and (1.62) corresponds to equilibrium, that is, the conditions of equilibrium are

$$\mathrm{d}A = 0, \quad \text{at } T = \text{const}, \;\; V = \text{const} \tag{1.63}$$

$$\mathrm{d}G = 0, \quad \text{at } T = \text{const}, \;\; p = \text{const}. \tag{1.64}$$

When the system is in equilibrium, the process no longer spontaneously proceeds in any direction. This implies that if a thermodynamic system is in equilibrium it cannot spontaneously leave this state.

Review questions

1. What are the dimensions of the Helmholtz and Gibbs free energies?
2. Under what conditions is the equation $\Delta G = \Delta H - T\Delta S$ valid?
3. Can the Gibbs free energy of a substance be negative?

1.4.2 Dependence of the Helmholtz and Gibbs free energies on *p*, *T*, and *V*

Since the Helmholtz and Gibbs free energies determine the direction of a spontaneous process at constant temperature, it is important to know how these functions depend on the parameters that describe the system (e.g. p, T, and V). We begin by rewriting Eq. (1.46) as:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V. \tag{1.65}$$

We can make use of the definition of the enthalpy, $H = U + pV$, and the differential identity $\mathrm{d}(pV) = p\mathrm{d}V + V\mathrm{d}p$, to re-express Eq. (1.65) as

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p. \tag{1.66}$$

Analogous relations can be obtained from Eq. (1.65) for the Helmholtz and Gibbs free energies (please confirm these for yourself!)

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V \tag{1.67}$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p. \tag{1.68}$$

Several useful relationships can be obtained directly from Eqs (1.67) and (1.68). For example, Eq. (1.68) implies

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \tag{1.69}$$

$$V = \left(\frac{\partial G}{\partial p}\right)_T. \tag{1.70}$$

These equations show how the Gibbs free energy depends on T and p. The description of the entropy in Eq. (1.69) can be used to obtain another useful relationship between the Gibbs free energy and the enthalpy:

$$G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_p; -\frac{H}{T^2} = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p;$$
$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2}. \tag{1.71}$$

This relationship is known as the **Gibbs–Helmholtz equation**. An analogous equation for the Helmholtz energy takes the following form:

$$\left[\frac{\partial(A/T)}{\partial T}\right]_V = -\frac{U}{T^2}.$$

We now investigate the dependence of the Gibbs free energy on pressure. Integrating Eq. (1.70) for the special case of an ideal gas yields:

$$G_T^{p_2} = G_T^{p_1} + \int_{p_1}^{p_2} V\mathrm{d}p = G_T^{p_1} + nRT\int_{p_1}^{p_2}\frac{\mathrm{d}p}{p} = G_T^{p_1} + nRT\ln\frac{p_2}{p_1}.$$

The pressures p_1 and p_2 in this equation can have arbitrary values (of course, provided that the ideal gas model is applicable at these pressures!). Since in most real applications we obtain the free energy from a database where it is usually tabulated for $p = 1$ atm, it is convenient to set $p_1 = 1$ atm. If we express the pressure in atmospheres, we can rewrite the previous equation as

$$G_T = G_T^0 + nRT\ln p, \tag{1.72}$$

where G_T^0 is the Gibbs free energy of the gas at the same temperature at $p = 1$ atm. The value of G_T^0 depends only on temperature. Equation (1.72) is an explicit description of the dependence of the Gibbs free energy of an ideal gas on pressure.[11]

Inserting Eq. (1.72) for an ideal gas into Eq. (1.71) we find

$$H = -T^2 \frac{\mathrm{d}(G_T^0/T)}{\mathrm{d}T}.$$

The function on the right side depends only on temperature. Therefore, the enthalpy of an ideal gas depends only on temperature. Since $U = H\text{–}nRT$ for an ideal gas, the internal energy must also depend only on the temperature, as we assumed in Section 1.1.3.

We now consider the case of condensed substances. The volume of condensed substances depends only very weakly upon the pressure. Therefore, the pressure dependence of the free energy of a condensed substance can be expressed as

$$G_T^{p_2} = G_T^{p_1} + \int_{p_1}^{p_2} V\mathrm{d}p \approx G_T^{p_1} + V(p_2 - p_1).$$

Since $G = H\text{–}TS$, the Gibbs energy has the same order of magnitude as the enthalpy. Further, since pV is usually small compared with the internal energy (and, hence, the enthalpy), as demonstrated in Section 1.1.4, we can rewrite this expression in the following trivial form:

$$G_T \approx G_T^0. \tag{1.73}$$

Of course, such an expression would be inapplicable to cases where we want to investigate the pressure dependence of phase transitions or if we have been sucked into a black hole, where the pressure is not so small.

From Eqs (1.69) and (1.70), it follows that

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{\partial^2 G}{\partial T \partial p} = -\left(\frac{\partial S}{\partial p}\right)_T. \tag{1.74}$$

Equations such as this are known collectively as **Maxwell's relations** and are useful for deriving many important results in thermodynamics. We show how to mathematically work with such relations in Appendix I. For example, we can use Eq. (1.74) to find the relationship between the heat capacities at constant pressure and volume (see Appendix I, Eq. AI.7):

$$c_p - c_V = \frac{TV\alpha^2}{\chi_T} = \frac{T\alpha^2}{\rho\chi_T}, \tag{1.75}$$

---

[11] Note that since we have assumed that pressures are expressed in atmospheres, p, in Eq. (1.72), is a dimensionless number (i.e. the number of atmospheres). This is necessary since we can only evaluate the logarithm of a number, rather than something with dimensions.

where V is the volume of 1 mole of the substance, $\rho = 1/V$ is the density (expressed in mole/m^3),

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{1.76}$$

is the **coefficient of thermal expansion** and

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \tag{1.77}$$

is the **isothermal compressibility**. Since the isothermal compressibility is positive for all stable systems (see Section 1.5.2), Eq. (1.75) implies that $c_p > c_V$. Equation (1.75) is a more convenient expression for the difference in the two heat capacities than the one we derived earlier (Eq. 1.14) since it only contains quantities that are readily available from databases (i.e. ρ, α, and χ_T) while $(\partial U/\partial V)_T$ is not. Consider iron at room temperature, as an example, for which we find (in databases) the density is 7.9 g/cm^3 (that gives $\rho = 1.4 \cdot 10^5$ mole/m^3); $\alpha = 3.5 \cdot 10^{-5}\,\mathrm{K}^{-1}$; $\chi_T = 5.9 \cdot 10^{-12}\,\mathrm{Pa}^{-1}$ at $T = 298$ K. Inserting these data into Eq. (1.75), we obtain $c_p - c_V =$ 0.44 J/(mole K). **Dulong and Petit** proposed the empirical rule that the heat capacity of 1 mole of atoms (in the case of molecular species, this is still per mole of atoms) of any condensed substance is approximately $3R =$ 24.9 J/(mole K). This rule can also be obtained from statistical mechanics (the Debye theory for the heat capacity). Thus we see that for iron the difference between the heat capacities at constant pressure and volume is about 2% of the heat capacity. Since this difference is small, it is commonly neglected and, hence, we approximate $c_p \approx c_V$ for condensed substances.

Review questions

1. Does the Gibbs free energy increase or decrease when a substance is heated at constant pressure?
2. Does the Helmholtz free energy increase or decrease when a substance expands at constant temperature?
3. If you know the Gibbs free energy of a substance at some temperature and pressure and you know its enthalpy as function of temperature and pressure, how would you calculate the Gibbs free energy at a different temperature and the same pressure?
4. For what type of material is the equation $c_p - c_V = T\alpha^2/\rho\chi_T$ invalid?

Example problems

1. You are given a substance for which the Gibbs free energy can be expressed as:

$$G = -3.5nRT\ln T + nRT\ln p - 12.73nRT + nbp - \frac{nap}{RT},$$

where p is in Pa, $a = 0.138\,\mathrm{J\cdot m^3/mole^2}$, $b = 3.258 \cdot 10^{-5}\,\mathrm{m^3/mole}$. The volume of one mole of this substance at $T = 298$ K is $V = 1000$ cm^3.

Under these conditions, what is (1) the pressure, (2) the entropy, (3) the heat capacity at constant pressure, (4) the isothermal compressibility, (5) the coefficient of thermal expansion, and (6) the heat capacity at constant volume?

2. At $T=25°\mathrm{C}$, the molar volume of water varies with pressure as

$$V = 18.066 - 7.15 \cdot 10^{-4} p + 4.6 \cdot 10^{-8} p^2 \ \mathrm{cm}^3/\mathrm{mole},$$

and the coefficient of thermal expansion is

$$\alpha_T = \frac{1}{V}\left(4.5 \cdot 10^{-3} + 1.4 \cdot 10^{-6} p\right) \ \mathrm{cm}^3/\mathrm{K\ mole},$$

(the pressure is in atm in both expressions). Find the change in the internal energy upon isothermal compression from $p_1 = 1$ atm to $p_2 = 1000$ atm at $T = 25°\mathrm{C}$.

1.5 Thermodynamics of open systems

1.5.1 Chemical Potential

Until this point, we focused on systems where the number of moles of each component was fixed. We now turn our attention to the case where the number of moles of each component n_i can vary, either by exchanging atoms with the surroundings or as a result of chemical reaction. Therefore, we must expand our definition of the internal energy to account for variation in n_i (cf. with Eq. (1.65)):

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i, \tag{1.78}$$

where k is the number of components.[12] The function

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}}, \tag{1.79}$$

is called the **chemical potential**. According to this definition, the chemical potential is the work necessary to remove 1 mole of component i from the system (if the system is so large that this operation does not lead to a measurable change in the properties of the system). It is clear from the derivations of Eqs (1.66)–(1.68) that the differentials of H, A, and G also must also be likewise adjusted:

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i \tag{1.80}$$

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i \tag{1.81}$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i. \tag{1.82}$$

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[12] A rigorous definition of the number of components will be given in Section 2.1.

These equations imply

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,\, p,\, n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,\, V,\, n_{j\neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,\, p,\, n_{j\neq i}} \tag{1.83}$$

Consider the case of a one-component system. The internal energy of 1 mole of the substance is a function of only the molar entropy and volume:

$$U_\mathrm{m} = f_U(S_\mathrm{m}, V_\mathrm{m}).$$

The internal energy of n moles, is thus simply

$$U = nU_\mathrm{m} = nf_U\left(\frac{S}{n}, \frac{V}{n}\right).$$

Analogously,

$$H = nf_H\left(\frac{S}{n}, p\right)$$

$$A = nf_A\left(T, \frac{V}{n}\right)$$

$$G = nf_G(T, p).$$

The dependence on the number of moles in the system is explicit only in the expression for the Gibbs free energy. Differentiating of this expression with respect to n at constant T and p implies that $\mu = f_G(T, p)$. Therefore, for pure materials, the chemical potential is the Gibbs free energy per mole:

$$\mu = G/n. \tag{1.84}$$

The extension of this equation to multi-component systems is given in Section 3.1. Using Eq. (1.84) and the expressions for the Gibbs free energy derived above, we can find several important properties of the chemical potential of a one-component system:

$$\mathrm{d}\mu = -S_\mathrm{m}\mathrm{d}T + V_\mathrm{m}\mathrm{d}p; \qquad S_\mathrm{m} = -\left(\frac{\partial \mu}{\partial T}\right)_p; \qquad V_\mathrm{m} = \left(\frac{\partial \mu}{\partial p}\right)_T \tag{1.85}$$

$$\mu_T = \mu_T^0 + RT\ln p \tag{1.86a}$$

$$\mu_T \approx \mu_T^0, \tag{1.86b}$$

where Eq (1.86a) and (1.86b) are valid for ideal gases and condensed phases, respectively.

Finally, we consider two important cases: a mixture of ideal gases and a mixture of mutually insoluble, condensed one-component substances. For the first, we return to the experiment considered at the end of Section 1.2.6. Since there are no intermolecular interactions in ideal gases,[13] they mix

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[13] Of course, we do not consider the case where chemical reactions occur in the mixture. Note that although the assumption that the molecules do not interact in an ideal gas is convenient for our thermodynamic considerations, some form of interactions is necessary to obtain almost all kinetic properties (e.g. diffusivity, thermal conductivity, viscosity).

with no change in enthalpy (i.e. the heat of mixing is zero). Using the expression for the entropy of mixing found above (Eq. (1.54)), we can write the Gibbs free energy of the mixture as

$$G = G_1^{\text{init}} + G_2^{\text{init}} + \Delta G_{\text{mix}} = n_1\left(\mu_1^0 + RT\ln p\right) + n_2\left(\mu_2^0 + RT\ln p\right)$$
$$+ RT(n_1 \ln n_1 - n_1 \ln (n_1 + n_2) + n_2 \ln n_2 - n_2 \ln (n_1 + n_2)).$$

Differentiating with respect to n_1 we obtain the chemical potential of component 1 in this mixture:

$$\begin{aligned}\mu_1 &= \mu_1^0 + RT\ln p + RT\left(\ln n_1 + 1 - \ln (n_1 + n_2) - \frac{n_1}{n_1 + n_2} - \frac{n_2}{n_1 + n_2}\right) \\ &= \mu_1^0 + RT\ln p + RT\ln\frac{n_1}{n_1 + n_2} = \mu_1^0 + RT\ln\,(px_1) = \mu_1^0 + RT\ln p_1\end{aligned}$$

where p_1 is the partial pressure of component 1 in this gas mixture. Thus, the chemical potential of component i in an ideal gas mixture is:

$$\mu_i = \mu_i^0 + RT\ln p_i \tag{1.87}$$

where μ_i^0 is the chemical potential of pure i at the same temperature at 1 atm.

The Gibbs free energy of a system of condensed, mutually insoluble, one-component substances is the sum of Gibbs energies of these substances:

$$G = \sum_i G_i = \sum_i n_i\mu_i \approx \sum_i n_i\mu_i^0.$$

Differentiating with respect to n_i, we find

$$\mu_i \approx \mu_i^0. \tag{1.88}$$

This means that if condensed, one-component substances are mutually insoluble, their chemical potentials do not change upon mixing.

Review question

1. What are the dimensions of the chemical potential?

1.5.2 Conditions for equilibrium

We now identify the conditions under which two sub-systems are in thermodynamic equilibrium. Two such conditions are obvious. Mechanical equilibrium requires that, in the absence of an applied field (stress, magnetic, electric, etc.), the pressures in two sub-systems in contact must be the same.[14] Analogously, thermal equilibrium requires that the temperatures in these two sub-systems must be the same. If the temperatures of the

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[14] Here, we are discussing systems that cannot support shear stresses, such as liquids or gases. We return to the important case of mechanical equilibrium in solids in Chapter 7.

sub-systems are different, heat will spontaneously and irreversibly flow from the warmer to cooler sub-system. These two conditions, while necessary for equilibrium, are not sufficient. In fact, the two sub-systems can exchange atoms or molecules (just like they exchange heat). Such exchanges can occur by way of diffusion or through chemical reactions. When such processes go to completion, the sub-systems are in chemical equilibrium.

How can we quantitatively express the conditions of chemical equilibrium? We can do so through the combined statement of the first and second law of thermodynamics (see Eq. (1.78)):

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V + \sum_{i=1}^{k}\frac{\mu_i}{T}\mathrm{d}n_i. \tag{1.89}$$

Consider equilibrium between the two sub-systems (I and II) that compose an isolated system. Equation (1.89) can be applied to the individual sub-systems:

$$\begin{aligned}\mathrm{d}S^{\mathrm{I}} &= \frac{1}{T^{I}}\mathrm{d}U^{\mathrm{I}} + \frac{p^{\mathrm{I}}}{T^{\mathrm{I}}}\mathrm{d}V^{\mathrm{I}} + \sum_{i=1}^{k}\frac{\mu_i^{\mathrm{I}}}{T^{\mathrm{I}}}\mathrm{d}n_i^{\mathrm{I}}\\ \mathrm{d}S^{\mathrm{II}} &= \frac{1}{T^{\mathrm{II}}}\mathrm{d}U^{\mathrm{II}} + \frac{p^{\mathrm{II}}}{T^{\mathrm{II}}}\mathrm{d}V^{\mathrm{II}} + \sum_{i=1}^{k}\frac{\mu_i^{\mathrm{II}}}{T^{\mathrm{II}}}\mathrm{d}n_i^{\mathrm{II}}.\end{aligned}$$

Since the entire system is isolated, $\mathrm{d}U = \delta Q - p\mathrm{d}V = 0$ or, alternatively, $U = U^{\mathrm{I}} + U^{\mathrm{II}} = \text{constant}$. Furthermore, in an isolated system $V = V^{\mathrm{I}} + V^{\mathrm{II}} = \text{constant}$ and $n_i^{\mathrm{I}} + n_i^{\mathrm{II}} = \text{constant}$. These can be expressed in differential form as

$$\begin{aligned}\mathrm{d}U^{\mathrm{I}} + \mathrm{d}U^{\mathrm{II}} &= 0\\ \mathrm{d}V^{\mathrm{I}} + \mathrm{d}V^{\mathrm{II}} &= 0\\ \mathrm{d}n_i^{\mathrm{I}} + \mathrm{d}n_i^{\mathrm{II}} &= 0.\end{aligned}$$

Using these relationships between the properties of the two sub-systems, the differential form of the entropy of the entire system becomes

$$\mathrm{d}S = \mathrm{d}S^{\mathrm{I}} + \mathrm{d}S^{\mathrm{II}} = \left(\frac{1}{T^{\mathrm{II}}} - \frac{1}{T^{\mathrm{I}}}\right)\mathrm{d}U^{\mathrm{II}} + \left(\frac{p^{\mathrm{II}}}{T^{\mathrm{II}}} - \frac{p^{\mathrm{I}}}{T^{\mathrm{I}}}\right)\mathrm{d}V^{\mathrm{II}} + \sum_{i=1}^{k}\left(\frac{\mu_i^{\mathrm{II}}}{T^{\mathrm{II}}} - \frac{\mu_i^{\mathrm{I}}}{T^{\mathrm{I}}}\right)\mathrm{d}n_i^{\mathrm{II}}. \tag{1.90}$$

Since the entropy is a maximum in equilibrium, the derivatives with respect to any variable must be zero. Therefore, each of the bracketed terms in Eq. (1.90) must individually be zero. The first bracketed term gives

$$T^{\mathrm{I}} = T^{\mathrm{II}}, \tag{1.91}$$

that is, the condition for thermal equilibrium. The second bracket gives the condition for mechanical equilibrium:

$$p^{\mathrm{I}} = p^{\mathrm{II}}. \tag{1.92}$$

The last bracketed term in Eq. (1.90) yields

$$\mu_i^{\mathrm{I}} = \mu_i^{\mathrm{II}}. \tag{1.93}$$

which is the condition for chemical equilibrium.

The derivation presented above can be easily extended to the case of three or more sub-systems. Equations (1.91)–(1.93) represent the thermodynamically necessary conditions for equilibrium but do not address how long it takes to achieve equilibrium. In practice, mechanical equilibrium is usually achieved very quickly, while it may take a very long time (even years or centuries) to achieve chemical equilibrium.

Although Eqs. (1.91)–(1.93) are necessary conditions for equilibrium, even these are not sufficient. While the entropy must be a maximum in equilibrium, the equilibrium conditions that we obtained only show that the entropy is an extremum (i.e. the first derivatives with respect to all variables are zero). The missing equilibrium conditions can be obtained by analyzing the behavior of the second derivates where the first derivates are zero. Such an analysis demonstrates that equilibrium requires that the heat capacity at constant volume and the isothermal compressibility must be positive. Indeed, if the heat capacity of a body was negative, it could never achieve thermal equilibrium with its initially higher temperature surroundings (according to the Clausius postulate, heat would flow from the warmer surroundings to the body, but since $c_V < 0$ $\mathrm{d}T = \delta Q / c_V < 0$, the temperature of the body would decrease). If the compressibility was negative, it could never achieve mechanical equilibrium with its surroundings (i.e. if the surroundings exerted a positive pressure on the body, the body would expand).

Phase equilibria I

2

This chapter addresses the general features of phase equilibria and applies them to single component systems. Before extending our study of phase equilibria to the interesting case of multiphase, multicomponent systems, we examine the special case of single phase, two-component systems (Chapter 3). Phase equilibria in multiphase, multicomponent systems is deferred until Chapter 4.

2.1 Gibbs phase rule

A single substance may exist in different states. For example, H_2O can exist as water vapor, liquid water, or any one of several solid phases (ices). Different states can co-exist indefinitely under certain sets of conditions. Under such conditions, the co-existence of these states suggests that they are in equilibrium with respect to one another, that is, phase equilibrium has been established. It is convenient to graphically represent phase equilibria in the form of phase diagrams. An example of such a diagram for a one-component system (with no solid state allotropes) is shown in Fig. 2.1. The AO, OB, and OC lines represent conditions for which two phases are in equilibrium. Since each set of two-phase equilibrium is represented by a one-dimensional surface (i.e. a line), we see that we can vary one parameter (either T or p) without entering a one-phase region of the diagram. For example, if we set the temperature to T_1 we can find a saturated vapor pressure p_1 such that the liquid and gas co-exist.[1]

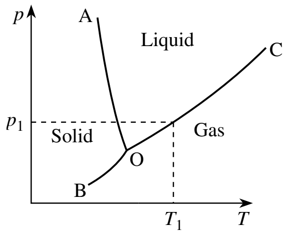

Fig. 2.1
A typical p–T diagram for a one-component system.

Three phases simultaneously co-exist at point O, which is called the **triple point**. Since the three-phase co-existence surface is zero dimensional (i.e. a point), three-phase equilibrium only exists at a specific temperature and pressure, that is, no conditions can be varied. On the other hand, every single-phase region of the diagram is a two-dimensional area and, hence, we can simultaneously, vary two parameters (i.e. both the temperature and pressure) and still remain in the same single-phase region of the diagram. Equations describing the lines of phase equilibria will be derived in Section 2.2, below.

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[1] Recall that a saturated vapor is, by definition, a vapor which is in equilibrium with a corresponding condensed phase.

Unlike the lines describing the solid–liquid or solid–vapor co-existence, the liquid–vapor co-existence line terminates in a single-phase region of the diagram. This terminus, labeled as Point C on the phase diagram (Fig. 2.1), is called the **critical point**. The vapor and liquid have exactly the same structure and properties at $T > T_c$ or $p > p_c$; hence, these are single-phase regions.

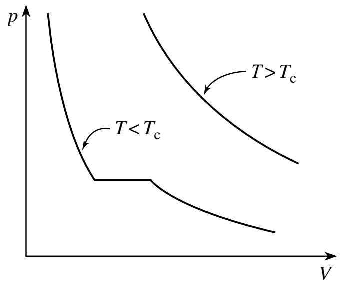

Fig. 2.2
A schematic illustration of the p–V diagram for CO_2.

The existence of a critical point was first found for CO_2 by observation that increasing the pressure at $T > 31°C$ led to a smooth increase in the density ($1/V$), while for $T < 31°C$ the smooth increase in density was interrupted by a jump in the density, as represented by the horizontal line in the p–V diagram (Fig. 2.2). This horizontal line describes the condensation (to form liquid CO_2) of the gas at constant pressure. This figure shows that the gas can be transformed into a liquid by compression only at temperatures lower than a critical value, T_c.

We now define some of the terms used above. A **phase** is a system or part of a heterogeneous system that is uniform throughout, not only in chemical composition, but also in physical state. Each phase has a unique equation of state. Two phases are separated from one another by one or more abrupt interfaces. In principle, a phase can be extracted from a heterogeneous system by some macroscopic mechanical method (e.g. by a process of cutting on a scale that is coarse compared to atomic dimensions). A system can be described by a set of parameters such as the temperature, pressure, and concentration of each component in each phase of the system. The number of **degrees of freedom**, F, is the number of independent parameters that must be set in order to fully determine the state of a system that is in equilibrium.

The **number of components**, C, is the number of substances combined to form the system *minus* the number of independent equations describing the chemical reactions relating these substances. For example, in a system formed by combining CO, CO_2, O_2, Fe, and FeO, the number of individual substances is 5. These can be related to each other through:

$$2\mathrm{Fe} + \mathrm{O}_2 \rightarrow 2\mathrm{FeO}$$
$$\mathrm{FeO} + \mathrm{CO} \rightarrow \mathrm{Fe} + \mathrm{CO}_2$$
$$2\mathrm{CO} + \mathrm{O}_2 \rightarrow 2\mathrm{CO}_2.$$

These equations are not independent since the third equation can be obtained by adding the first equation to two times the second. Thus the number of independent equations describing chemical reactions between these substances is 2, such that the the number of components in the system $C = 5 - 2 = 3$.

Gibbs showed that the number of components (C), the number of phases (P), and the number of degrees of freedom (F) are related when the system is in equilibrium. To find this relation, we must also consider the number of conditions that the system must satisfy in equilibrium; for example, the equality of pressure, temperature, and chemical potentials of each component in each phase. We shall explicitly assume that the pressure and temperature in all phases in equilibrium are the same and that the chemical potentials within each phase are functions of p, T, and concentrations of all components. Therefore, the total number of parameters that must be used to fully describe the system is $2+CP$, where the first term corresponds to the number of external parameters (pressure and temperature here) and the second term gives the total number of concentrations of each component in each phase. (If the system is subjected to external fields, such as an electrical or magnetic field, the number of parameters describing these external fields must also be added.) These $2+CP$ parameters are not independent, since they are interrelated via equations describing the equality of chemical potentials between the phases:

$$\mu_i^{\mathrm{I}}(p, T, c_1^{\mathrm{I}}, \ldots, c_C^{\mathrm{I}}) = \mu_i^{\mathrm{II}}(p, T, c_1^{\mathrm{II}}, \ldots, c_C^{\mathrm{II}}) = \ldots = \mu_i^{P}(p, T, c_1^{P}, \ldots, c_C^{P}).$$

We can write down $P-1$ such equations for each of the C components. There are $C(P-1)$ such equations for the entire system. Additionally, there is one equation of state for each phase in the system:

$$f^{\alpha}(p, T, c_1^{\alpha}, \ldots, c_C^{\alpha}) = 0.$$

There are P such equations. Therefore, the number of degrees of freedom is $F=2+CP-C(P-1)-P$

$$F = C + 2 - P. \tag{2.1}$$

Equation (2.1) is the **Gibbs phase rule**. Since a negative number of degrees of freedom has no physical meaning, $F \geq 0$ and Eq. (2.1) gives

$$P \leq C + 2. \tag{2.2}$$

Hence, the number of phases in equilibrium cannot exceed $C+2$. For example, the maximum number of phases in equilibrium with one another in a one-component system is 3 (i.e. the triple point—see Fig. 2.1).

We frequently work with systems composed solely of condensed phases. The thermodynamic properties of condensed phases are usually only weakly dependent on the pressure (at least for the pressures typically see in the laboratory). Therefore, if we can ignore the dependence of the properties on pressure, we can treat the system as if the pressure was fixed. In this case, the degree of freedom associated with pressure is removed and the Gibbs phase rule takes the following form for condensed systems

$$F = C + 1 - P. \tag{2.3}$$

Equation (2.3) implies, for example, the number of degrees of freedom associated with an equilibrium solid–liquid mixture is $F=1+1-2=0$. In other words, this equilibrium only occurs at a unique temperature—the melting temperature. This is consistent with our common experience—ice and water are only in equilibrium at 0°C at $p=1$ atm.

A system for which $F=0$ is called **invariant**, if $F=1$ it is **monovariant**, if $F=2$ it is **bivariant**, etc.

2.2 Clausius–Clapeyron equation

We now consider phase equilibrium in a one-component system. In such a system, only two phases can co-exist (with the single exception of the triple point). The phase equilibrium condition in a one-component system can be written in the form

$$\mu^{\mathrm{I}}(p, T) = \mu^{\mathrm{II}}(p, T), \tag{2.4}$$

where p and T are not independent, but are related by $p = p(T)$, which describes, for example, the co-existence lines AO, OB, and OC lines in Fig. 2.1. Since along these co-existence lines the chemical potential depends only upon the temperature, we can take the full derivatives of both sides of Eq. (2.1):

$$\left(\frac{\partial \mu^{\mathrm{I}}}{\partial T}\right)_p + \left(\frac{\partial \mu^{\mathrm{I}}}{\partial p}\right)_T \frac{\mathrm{d}p}{\mathrm{d}T} = \left(\frac{\partial \mu^{\mathrm{II}}}{\partial T}\right)_p + \left(\frac{\partial \mu^{\mathrm{II}}}{\partial p}\right)_T \frac{\mathrm{d}p}{\mathrm{d}T}.$$

Using the definitions of the partial derivatives from Eq. (1.85), we can rewrite this equation as $-S_m^{\mathrm{I}} + V_m^{\mathrm{I}}(\mathrm{d}p/\mathrm{d}T) = -S_m^{\mathrm{II}} + V_m^{\mathrm{II}}(\mathrm{d}p/\mathrm{d}T)$ or

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_m^{\mathrm{II}} - S_m^{\mathrm{I}}}{V_m^{\mathrm{II}} - V_m^{\mathrm{I}}} = \frac{\Delta S}{\Delta V}. \tag{2.5}$$

The expression is known as the Clausius–Clapeyron relation. No approximations were used in the derivation of this equation, hence, it is exact. Since phase transitions in a one–component system at constant pressure occur at a single temperature, Eq. (2.5) can be rewritten as

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T\Delta V}, \tag{2.6}$$

where ΔH is the heat generated during the phase transition.

We now consider several particular cases. For the case of the solid–liquid phase transition (i.e. melting), Eq. (2.6) is

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{melt}}}{T(V_{\mathrm{L}} - V_{\mathrm{S}})}. \tag{2.7}$$

Since most solid phases have a larger density than that of their corresponding liquids, $V_{\mathrm{L}} > V_{\mathrm{S}}$. In this case, an increase in the pressure produces an increase in the melting temperature. For water, the situation is opposite, $V_{\mathrm{S}} > V_{\mathrm{L}}$, such that an increase in the pressure decreases the melting temperature.

For the evaporation processes (liquid → vapor),

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{evap}}}{T(V_{\mathrm{V}} - V_{\mathrm{L}})}. \tag{2.8}$$

If the vapor is an ideal gas (i.e., the system is far from the critical point $V_{\mathrm{V}} \gg V_{\mathrm{L}}$), Eq. (2.8) can be rewritten as $(\mathrm{d}p/\mathrm{d}T) = (\Delta H_{\mathrm{evap}} \cdot p)/(T \cdot RT)$ or

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{evap}}}{RT^2}. \tag{2.9}$$

Trouton noted that for most liquids $\Delta H_{\mathrm{evap}}/T_{\mathrm{boil}} \approx 92$, where T_{boil} is the normal boiling temperature (i.e. at a total pressure of 1 atm.). For the case of a solid in contact with its saturated vapor, we find

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{subl}}}{RT^2}, \tag{2.10}$$

where ΔH_{subl} is the heat of sublimation. Unlike Eq. (2.9), which was only valid for $T \ll T_{\mathrm{c}}$ this equation is true at all temperatures because the density of the solid is always much greater than that of its vapor (there is no solid–vapor critical point[2]). Equations (2.9) and (2.10) both suggest that the saturated vapor pressure increases with increasing temperature.

Equations (2.9) and (2.10) were derived for the case in which there is no contribution to the pressure other than from the saturated vapor itself. Other sources of pressure may arise, for example, from the presence of an inert gas or stresses in the condensed phase. If the additional pressure is large, it may alter the state functions of the condensed phase and, therefore, the pressure of the saturated vapor. We now derive an equation to account for this effect. The chemical potential of the vapor remains

$$\mu_{\mathrm{v}} = \mu_{\mathrm{v}}^0 + RT\ln p,$$

and the chemical potential of the condensed phase should include a term associated with the additional pressure. According to Eq. (1.70), this chemical potential takes the following form:

$$\mu_{\mathrm{c}} = \mu_{\mathrm{c}}^0 + p_{\mathrm{a}}V_m.$$

where p_{a} is the additional pressure and V_m is the molar volume of the condensed phase. In equilibrium, the chemical potentials of the vapor and condensed phase must be equal to each other, such that

$$p = \mathrm{e}^{(\mu_{\mathrm{c}}^0 - \mu_{\mathrm{v}}^0)/RT}\mathrm{e}^{p_{\mathrm{a}}V_m/RT}.$$

If $p_{\mathrm{a}} = 0$, the pressure reduces to the saturated vapor pressure $p = p_{\mathrm{s}}$ described by Eqs. (2.9) and (2.10). Therefore, we can write:

$$p = p_{\mathrm{s}}\mathrm{e}^{p_{\mathrm{a}}V_m/RT}. \tag{2.11}$$

For example, in the case of water at $T = 273\,\mathrm{K}$ under an inert gas of pressure 1 atm, the factor $\mathrm{e}^{p_{\mathrm{a}}V_m/RT} = 1.0008$. Clearly, this additional pressure has little effect and we, therefore, ignore it. This demonstrates that at atmospheric pressure we can safely assume that $p = p_{\mathrm{s}}$. If an additional pressure of ~100 MPa is applied (this is not considered a large stress within most solids), $\mathrm{e}^{p_{\mathrm{a}}V_m/RT} \approx 2$. Under such conditions, we cannot neglect this factor.

Example problems

1. Find the change in the melting temperature of tin when the pressure increases by 100 atm. The following data for tin can be found in a

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[2] While the atomic structure of crystalline solids always exhibits higher symmetries than liquids or gasses, liquids and gasses have no difference in symmetry. Therefore there must be a change in symmetry on going from a solid to a liquid or gas and none going from a liquid to a gas.

handbook: $T_{\mathrm{melt}} = 231.9°\mathrm{C}$, $\Delta H_{\mathrm{melt}} = 7.07\,\mathrm{kJ/mole}$, and the densities of liquid and solid tin are $d_{\mathrm{L}} = 6.99\,\mathrm{g/cm^3}$ and $d_{\mathrm{S}} = 7.18\,\mathrm{g/cm^3}$, respectively.

2. Find the saturated vapor pressure over carbon tetrachloride at $T = 60°\mathrm{C}$. The normal boiling temperature of CCl_4 is equal to $75°\mathrm{C}$ and the heat of evaporation is $\Delta H_{\mathrm{evap}} = 45860 - 44.06T$ J/mole.
3. Estimate the saturated vapor pressure over solid argon at $T = 50\,\mathrm{K}$. The following Ar properties were found in a standard handbook: $T_{\mathrm{boil}} = -185.9°\mathrm{C}$, $T_{\mathrm{melt}} = -189.3°\mathrm{C}$, $\Delta H_{\mathrm{evap}} = 6.50\,\mathrm{kJ/mole}$, and $\Delta H_{\mathrm{melt}} = 1.19\,\mathrm{kJ/mole}$.

3

Thermodynamic theory of solutions

A **solution** is a homogeneous mixture consisting of two or more components in which the composition can be continuously varied (within some range) with no change of phase. Solutions can be gases, liquids, or solids. We have already considered the properties of gaseous solutions (when we considered a mixture of ideal gases). In this chapter, we focus on condensed phases (i.e. liquids and solids).

3.1 Thermodynamic description of solutions

The composition of a solution can be described in several ways. Here are the most common:

1. The **molar fraction** of the *i*th component, x_i, is the ratio of the number of moles of component *i*, n_i, to the total number of moles of all species within the solution, n:

$$x_i = \frac{n_i}{n} = \frac{n_i}{\sum_{j=1}^{k} n_j}. \tag{3.1}$$

2. The **weight fraction** of the *i*th component, $[i]$, is the ratio of the mass of component *i*, w_i, to the total mass of all species within the solution, w:

$$[i] = \frac{w_i}{w} = \frac{w_i}{\sum_{j=1}^{k} w_j}, \tag{3.2}$$

the weight fraction is often written as a weight percent $[\text{wt}\%] = 100[i]$.

3. The **molarity** of the *i*th component, c_i, is the number of moles of component *i*, n_i per liter of solution, V:

$$c_i = \frac{n_i}{V}. \tag{3.3}$$

4. The **molality** of *i*th component (used only for dilute solutions), m_i, is the number of moles of component *i*, in 1 kg of solvent.

There are several other definitions used to describe the composition of a solution, but we shall only refer to those described above in this text.

The reason that there are so many definitions of the composition is related to how the term "concentration" is applied. For example, from the physical–chemical point of view, the molar fraction is the most convenient definition of the concentration since it is on an atomic basis. However, from the point of view of someone who has to prepare solutions from separate solutes and solvents, the mass fraction is the most convenient definition since it is directly related to the mass of the components, rather than the number of moles of the component. The former is easily measured, while the latter requires the additional knowledge of the molecular weight (and a trivial calculation).

We are often called upon to convert between one definition of concentration to another. Here is an example of how we can convert from molality to molar fraction in a binary (two-component) solution. We start from a formal definition of that concentration that we wish to obtain:

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{w_1/(M_1/1000) + n_2} = \frac{m_2}{1000/M_1 + m_2},$$

where M_1 is molar weight of the solvent expressed in g/mole. Assuming that the solution is dilute, we can approximate the last expression as

$$x_2 \cong \frac{M_1}{1000} m_2. \tag{3.4}$$

For an infinitesimal concentration of the solute, the molar fraction is proportional to the molality. This conclusion is valid for all multicomponent solutions: in the limit that the fraction of the component is very small, all of the measures of concentration are proportional to one another.

The properties of a solution are characterized by thermodynamic functions such as V, S, U, H, A, and G. These values are extensive and refer to the entire solution. It is convenient to use intensive values (e.g. pressure, temperature, and concentrations) as parameters since these values do not depend on the quantity of the solution. In order to estimate the contribution to the extensive property (F) made by each of the i-components in the solution, Lewis defined the **partial molar values** of a property as

$$\bar{F}_i = \left(\frac{\partial F}{\partial n_i}\right)_{p,\,T,\,n_{j \neq i}}. \tag{3.5}$$

The chemical potential is an example of a partial molar value; it is the partial molar Gibbs free energy.

It is frequently useful to express the properties of a solution relative to those of the pure components at the same temperature and pressure. For this purpose, we define the **excess values** of the thermodynamic function associated with mixing as

$$\Delta F_{\text{mix}} = F - \sum_i n_i F_i^0, \tag{3.6}$$

where F_i^0 is the value of F for one mole of pure component i. ΔF_{mix} is also called the **relative integral molar value** of F. In some texts, ΔF_{mix} is denoted as F^{M} and the corresponding partial values as $\overline{F}_i^M$ (see below). ΔF_{mix} tells us how the extensive property, F, changes when a solution is formed from its pure components.

To illustrate this concept, consider the change in volume that occurs when a solution is formed from its pure components. For a solution that is formed with no change in volume, Eq. (3.6) implies that $V = \sum_i n_i V_i^0$. Differentiating this expression with respect to n_i shows that $\overline{V}_i = V_i^0$. However, if the volume of the system does change upon forming a solution from its individual pure components ($\Delta V_{\mathrm{mix}} \neq 0$), $\overline{V}_i \neq V_i^0$. Unlike a physical volume, the partial volume can be either positive or negative (or zero). $\overline{V}_i < 0$ implies that the solution volume decreases upon addition of component i.

The **relative partial molar value** of property F is defined, through Eqs (3.5) and (3.6), as

$$\overline{F}_i^{\mathrm{M}} = \frac{\partial \Delta F_{\mathrm{mix}}}{\partial n_i} = \overline{F}_i - F_i^0.$$

$\overline{F}_i^{\mathrm{M}}$ characterizes the effect on F of dissolving 1 mole of pure i in a very large quantity of the solution. A solution is considered "very large" if dissolving 1 mole of component i leads to only negligible changes in the properties of the solution. As an example, the heat of solution of 1 mole of pure i is $\overline{H}_i^{\mathrm{M}} = \overline{H}_i - H_i^0$.

If we double the number of moles of a particular material, all of the extensive properties will increase by a factor of two. Analogously, if the numbers of moles of all components increase by a factor of α, all extensive properties increase α-fold:

$$F(\alpha n_1, \alpha n_2, \ldots, \alpha n_k) = \alpha F(n_1, n_2, \ldots, n_k).$$

From a mathematical perspective, this implies that any extensive property is a homogeneous function of the numbers of moles of all of its components. Euler's theorem for homogeneous functions states that

$$F = \sum_{i=1}^{k} \frac{\partial F}{\partial n_i} n_i.$$

Inserting the definition of the partial molar value (Eq. (3.5)) into this expression provides the link between an extensive property and its partial molar values:

$$F = \sum_{i=1}^{k} \overline{F}_i n_i. \tag{3.7}$$

Since F is a homogeneous function of the numbers of moles of the components of the solution, Eq. (3.7) implies that the partial molar values are themselves independent of the numbers of moles of each component and are, therefore, intensive parameters. The partial molar values do, however, depend on the overall composition of the solution.

Equation (3.7) can be re-expressed in another form. To this end, we differentiate Eq. (3.7) with respect to the number of moles of component j, n_j:

$$\frac{\partial F}{\partial n_j} = \sum_{i=1}^{k} \frac{\partial \overline{F}_i}{\partial n_j} n_i + \sum_{i=1}^{k} \overline{F}_i \frac{\partial n_i}{\partial n_j} = \sum_{i=1}^{k} \frac{\partial \overline{F}_i}{\partial n_j} n_i + \overline{F}_j.$$

Since the partial molar value of F is defined as $\overline{F}_j = \frac{\partial F}{\partial n_j}$ (Eq. (3.5)), this implies

$$\sum_{i=1}^{k} \frac{\partial \overline{F}_i}{\partial n_j} n_i = 0. \tag{3.8}$$

Multiplying this equation by $\mathrm{d}n_j$ and summing over j,

$$0 = \sum_{j=1}^{k} \mathrm{d}n_j \sum_{i=1}^{k} \frac{\partial \overline{F}_i}{\partial n_j} n_i = \sum_{i=1}^{k} n_i \sum_{j=1}^{k} \frac{\partial \overline{F}_i}{\partial n_j} \mathrm{d}n_j = \sum_{i=1}^{k} n_i \mathrm{d}\overline{F}_i$$

yields

$$\sum_{i=1}^{k} n_i \mathrm{d}\overline{F}_i = 0. \tag{3.9}$$

Equations (3.7)–(3.9) are all expressions of the so-called **Gibbs–Duhem relation**. Recall that all of these expressions are simple consequences of the fact that any extensive property is a homogeneous function of the numbers of moles of each of the components in a solution.

We now examine the relationship between partial molar values of thermodynamic functions. Equation (3.7) can be immediately applied to the Gibbs free energy

$$G = \sum_{i=1}^{k} n_i \mu_i, \tag{3.10}$$

where the chemical potential μ_i is the partial molar value of the Gibbs free energy. This equation is the generalization of the Gibbs free energy of one-component systems, $G = n\mu$. Differentiating the expression for the Gibbs free energy ($G = H - TS$) with respect to the number of moles of component i at constant temperature, pressure and numbers of moles of the remaining components, shows that

$$\mu_i = \overline{H}_i - T\overline{S}_i. \tag{3.11}$$

Now, inserting the definition of the entropy, $S = -(\partial G/\partial T)_{p,\,n_i}$, into that for its partial molar value, $\overline{S}_i = (\partial S/\partial n_i)_{p,\,T,\,n_{j\neq i}}$, we find

$$\overline{S}_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\,n_j} = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\,x_j}, \tag{3.12}$$

where we are free to replace n_j with x_j because constant numbers of moles implies constant mole fractions. We can use the same approach to derive the Gibbs–Helmholtz equation (Eq. (1.71)) that relates the chemical potential and the partial molar enthalpy

$$\left(\frac{\partial(\mu_i/T)}{\partial T}\right)_{p,x_i} = -\frac{\overline{H}_i}{T^2}, \tag{3.13}$$

and the equation that relates the chemical potential to the partial molar volume:

$$\overline{V}_i = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,x_i} \tag{3.14}$$

Finally, we consider the application of Eq. (3.9) to the special case of binary solutions. Dividing Eq. (3.9) by the total number of moles in the solution, we obtain

$$x_1 \mathrm{d}\overline{F}_1 + x_2 \mathrm{d}\overline{F}_2 = 0. \tag{3.15}$$

In a binary solution, the mole fraction of components 1 and 2 are not independent, rather $x_1 + x_2 = 1$ and $\mathrm{d}x_1 = -\mathrm{d}x_2$. Therefore, Eq. (3.15) can be rewritten in the form

$$x_1 \left(\frac{\partial \overline{F}_1}{\partial x_1}\right)_{p,T} = x_2 \left(\frac{\partial \overline{F}_2}{\partial x_2}\right)_{p,T}. \tag{3.16}$$

This relation enables us to calculate the partial molar value of one component if the dependence of the partial molar value of the other component on composition is known.

Example problem

1. The composition of the ternary alloy Al–Ni–Ti is [Ni] = 70 wt% and [Al] = 25 wt%. Find the atomic fractions of all components. Note wt% implies percentage by weight.
2. The density of a 20 wt% solution of methyl alcohol (CH_3OH) in water is 0.9666 g/cm^3. The partial molar volume of water in this solution is 17.7 cm^3/mole. Find the partial molar volume of methyl alcohol in this solution.
3. Let the partial molar volume of the solute in a binary solution depends on its molality in the following manner:

$$\overline{V}_2 = a + bm_2,$$

where a and b are constants. The molecular weight of the solvent is M_1g/mole, and the volume of 1 mole of the pure solvent is V_1^0. Derive an expression for the dependence of the partial molar volume of the solvent on the solute molality.

3.2 Ideal dilute solutions

The thermodynamic description of solutions developed in the previous section provides general relations that apply to all solutions. It is, however, of limited utility without a supplemental description of the behavior of specific solutions. This supplemental description cannot be derived from thermodynamics. For example, a supplemental description may express the relationship between the saturated vapor pressure and the solute concentration.

While each solution has a unique description, there are general classifications of types of solutions that share certain features and, hence, may be treated as members of a special class. The most widely studied classes represent certain limiting cases. Such classifications are, by nature, simplifications. But it is such simplifications that allow us to make thermodynamics a practical tool.

The general schema for developing any theory of solutions is the following. First, we create an expression for the Gibbs free energy (or, equivalently, the chemical potentials of all components of the solution) as a function of the temperature and concentrations of the solution components. This can be done for a class of solutions that share some fundamental behavior. Next, we employ this free energy function within the general thermodynamic framework for solutions described in the previous section. In this way, we can predict all of the thermodynamic properties of a particular class of solutions.

It is natural to start the study of solutions from the theories for the simplest classes of solutions; namely, ideal solutions and ideal dilute solutions.[1]

3.2.1 Thermodynamic functions

It is simplest to begin our exploration of types of solutions from the theory of ideal dilute solutions. **Ideal dilute solutions**[2] are those for which the molar fraction of the first component (**solvent**) approaches unity, $x_1 \to 1$, while those of the other components (**solutes**) tend to zero, $x_{i \neq 1} \to 0$. In this limiting case, it is a simple matter to write the Gibbs free energy of the solution as an expansion in terms of the molar fractions of the individual solutes. However, such an approach requires some knowledge of statistical physics (see Section 13.4.1). In order to avoid such a digression here, we shall employ a different approach. Rather, we shall start from some experimental observations of dilute solutions that are captured in the form of Henry's law, which is described below. Although it is enough to use an experimentally motivated description to develop the thermodynamics of these solutions, we will provide a qualitative derivation of this law.

Let us consider how the pressure of a saturated vapor of a solute depends on its concentration in the solution. Since we cannot obtain this dependence within the framework of thermodynamics (we still have no

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[1] While this description of solutions is widespread, it is not convenient. Ideal and ideal dilute solutions are not the same, as discussed below. For example, ideal solutions properties are defined in terms of the thermodynamic properties of the pure components only, while ideal dilute solution theory contains parameters which cannot be derived from the properties of the pure components.

[2] We explain the difference between the ideal dilute and dilute solutions in Section 3.4.

thermodynamic description of the solution), we shall use a kinetic approach. The rate of the transfer of solute molecules from the vapor to the solution is proportional to the number of impacts the solute molecules in the vapor make upon the surface of the condensed (solid or liquid) solution per unit area of the surface per unit time. The kinetic theory of gases tells us that this rate of solute molecule impacts is proportional to the vapor pressure (see Section 12.2.9). Thus the rate of the condensation is equal to

$$\omega_{\downarrow} = k_{\downarrow} p_2,$$

where $k_{\downarrow}$ is the proportionality constant. Similarly, the rate of evaporation must be proportional to the solute concentration in the solution, that is

$$\omega_{\uparrow} = k_{\uparrow}(c_2) c_2,$$

where $k_{\uparrow}$ is also a proportionality constant. $k_{\uparrow}$ must depend on how much a solute molecule prefers to be in the solution than in the vapor. Clearly, how much a solute molecule wants to stay in the solutions depends on its surroundings. Since the mean composition of the surroundings of the solute molecule depends on the concentration of solute molecules in the solution, the proportionality constant, $k_{\uparrow}$, must depend on the solute concentration.

In equilibrium the rates of condensation and evaporation must be equal to each other, therefore

$$p_2 = \frac{k_{\uparrow}(c_2)}{k_{\downarrow}} c_2.$$

This demonstrates that the saturated vapor pressure of the solute molecules over the solution depends on the solute concentration in the solution. This, however, should be obvious without any derivation.

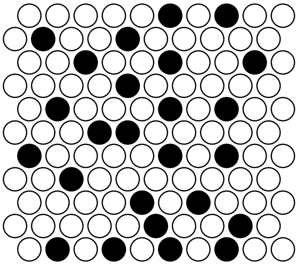
Now, we consider what happens when $c_2 \to 0$. As the illustration in Fig. 3.1 demonstrates, when the solute concentration is low, the probability that two solute molecules are adjacent to each other is negligibly small, such that solute molecules only have solvent molecule neighbors. In this limit ($c_2 \to 0$), the coefficient $k_{\uparrow}$ does not depend on the solute concentration. This implies that the saturated vapor pressure of the solute is proportional to the solute concentration in the solution,

$$p_2 = h c_2, \tag{3.17}$$

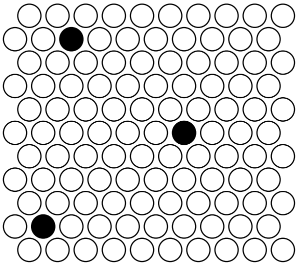
where the constant $h = k_{\uparrow}/k_{\downarrow}$. This law was first stated by Henry and h is known as Henry's constant. Note, that since in dilute solutions all of the measures of the solute concentration are proportional to each other, we can use any type of concentration in Eq. (3.17), but, of course, the numerical value of h depends on the type of concentration used.

In our derivation of **Henry's law**, we implicitly assumed that the gas phase constituent and the solute are the same. Consider the case of nitrogen dissolved in water. Nitrogen is diatomic (N_2) both in the gaseous state as well as when dissolved in water

$$N_{2(\text{gas})} \rightarrow N_{2(\text{water})}.$$



Concentrated solution



Dilute solution

○ —Solvent molecules

● —Solute molecules

Fig. 3.1
An illustration of concentrated and dilute solutions showing that solute atoms have a much higher probability of having solute nearest neighbors in the concentrated solution and such neighbors are rare in the dilute case.

Therefore, according to Henry's law

$$p_{N_2} = h_{N_2} c_{N_2}.$$

Diatomic nitrogen is too large to fit in between the atoms of a metal and, hence, nitrogen dissolves in metals in its atomic form (N rather than N_2). Therefore, before nitrogen dissolves into the metal, it must first dissociate on the metal surface. In this case, the process of dissolving N into metal can be described as

$$N_{2(\mathrm{gas})} \rightarrow 2[N],$$

(note, the square brackets around the N is a common notation indicating that the species is dissolved in a metal). In deriving an expression for the dependence of the partial pressure of N_2 in a saturated vapor above its condensed solution we must account for the fact that evaporation must wait for two N atoms in the solution to find each other. The rate of such events is proportional of the square of the nitrogen atom concentration, that is

$$\omega_{\uparrow} = k_{\uparrow} c_{[N]}^2.$$

As in the Henry's law situation, the rate of condensation of N_2 is simply proportional to its partial pressure within the vapor. Therefore, in equilibrium where the rate of evaporation and condensation are equal, we find

$$p_{N_2} = s c_{[N]}^2. \tag{3.18}$$

This type of equation is valid for solutions of all diatomic gases (O_2, H_2, and others) in metals and is known as **Sieverts's law**, where s is Sieverts's constant.[3]

Consideration of the schematic derivations of Henry's and Sieverts's laws presented above provides a means to understand their limitations. The first limitation is that the solute concentration must be so small that each solute molecule is unaware of the existence of any other solute molecule. In the simple model presented above, this would require that no solute has solute neighbors. This approach would certainly be valid if (and only if) the interactions between solute molecules decrease very quickly with increasing separation. For example, it is widely suitable for organic solutions, metallic alloys, and solutions of gases in metals, where interactions decrease roughly as $1/r^n$ and $n \geq 3$. However, this condition fails for ionic species dissolved in water (e.g. a solution of NaCl in H_2O). In this case, the ions interact through a very long-range $1/r$ Coulomb interaction (see Sections 3.7 and 13.4.4).

Once we know one law (e.g. Henry's or Sieverts's law), we can apply the machinery of thermodynamics to fully describe the ideal dilute solutions. We start by deriving expressions for the chemical potentials of all of the components of a solution. While we now focus on the special case of binary solutions, the final results will be valid for ideal dilute solutions of any number of components. Consider the case in which the partial pressure in a saturated vapor obeys Henry's law. The condition that the vapor is in

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[3] Computer Laboratory #3 examines dissolving nitrogen in Fe–Mn alloys.

equilibrium with the solution is the equality of the chemical potentials of the solute in the solution and in the gas:

$$\mu_2 = \mu_{2\,\mathrm{vapor}}.$$

Replacing the chemical potential of component 2 in the vapor with Eq. (1.87) and p_2 from Henry's law, yields

$$\mu_2 = \mu_{2\,\mathrm{vapor}} = \mu^0_{2\,\mathrm{vapor}} + RT \ln p_2 = \mu^0_{2\,\mathrm{vapor}} + RT \ln h + RT \ln c_2,$$

or

$$\mu_2 = \psi_2 + RT \ln c_2, \tag{3.19}$$

where ψ_2 is a concentration-independent constant. ψ_2 can be thought of as the chemical potential of the solute in a hypothetical solution with solute concentration $c_2 = 1$ which, nonetheless, remains an ideal solution where component 1 is still the solvent. Such a solution is called the **standard state of the solute**. As for Henry's law, we can use any form of the concentration in Eq. (3.19), however, changing the form of the concentration employed implies a change in the numerical value of ψ_2.

We now derive an expression for the chemical potential of the solvent appropriate for an ideal dilute solution. It is convenient to represent the solute concentration in terms of its molar fraction, in which case Eq. (3.19) becomes

$$\mu_2 = \psi_x + RT \ln x_2.$$

Combining this equation with the Gibbs–Duhem equation (Eq. (3.16)) yields:

$$x_1 \frac{\partial \mu_1}{\partial x_1} = x_2 \frac{\partial \mu_2}{\partial x_2} = RT; \qquad \int_{\mu_1^0}^{\mu_1} \mathrm{d}\mu_1 = \int_1^{x_1} \frac{RT}{x_1} \mathrm{d}x_1.$$

We briefly digress to explain the limits of these integrals. First, while the use of the same variables in the integrands and the limits of the integrals is formally improper, we retain this notation because it is unambiguous here and is consistent with the notation used in most other thermodynamics texts. Second, the choice of the limits of the integrals was made to correspond to a state of the system in which the chemical potential of the solvent is known. One such state corresponds to the case of the pure solvent ($x_1 = 1$). The chemical potential of the pure solvent, μ_1^0 is its Gibbs free energy per mole. The upper limits of the integrals are chosen to correspond to the state of interest, that is, one with arbitrary values of the molar fraction and chemical potential. Evaluating these integrals shows that

$$\mu_1 = \mu_1^0 + RT \ln x_1. \tag{3.20}$$

Now that we have derived expressions for the chemical potentials of both components of the solution, we can employ the thermodynamic methods of Section 3.1 to obtain all other properties of the solution without any further approximations.

For completeness, we examine equilibrium between the solvent in the solution and in the saturated vapor. The equilibrium condition is

$$\mu_1 = \mu_{1\,\text{vapor}}.$$

Inserting the chemical potential of the solvent in the solution (Eq. (3.20)) and that for a component of an ideal gas mixture (Eq. (1.87)) yields

$$\mu_1^0 + RT\ln x_1 = \mu^0_{1\,\text{vapor}} + RT\ln p_1; \qquad \frac{p_1}{x_1} = e^{\left(\mu_1^0 - \mu^0_{1\,\text{vapor}}\right)/RT}.$$

If we call the right-hand side of the last expression p_1^0, we can rewrite the relationship between the partial pressure of the solute in the saturated vapor and its concentration in the solution as

$$p_1 = p_1^0 x_1. \tag{3.21}$$

Since $p_1 = p_1^0$ in the pure solvent ($x_1 = 1$), p_1^0 is simply the saturated vapor pressure over the pure solvent. Note that x_1 in Eq. (3.21) is the concentration expressed in molar fraction (only). Equation (3.21) was first proposed by Raoult on the basis of a generalization of a body of experimental data and is widely known as **Raoult's law**. Raoult's law states that the partial pressure of a solvent in the saturated vapor above a solution is proportional to its molar fraction in the solution. Consequently, the partial pressure in the saturated vapor above a solution is always smaller than that for the pure solvent.

We now proceed to derive several of the thermodynamic functions associated with the ideal dilute solution. The partial molar entropy, enthalpy, and volume of the solvent can be obtained from Eq. (3.20) and the definitions in Section 3.1:

from $\overline{S}_1 = -(\partial\mu_1/\partial T)_{p,x_i} = -(d\mu_1^0/dT) - R\ln x_1$ we find

$$\overline{S}_1 = S_1^0 - R\ln x_1, \tag{3.22}$$

from $\overline{H}_1 = \mu_1 + T\overline{S}_1 = \mu_1^0 + TS_1^0$ we find

$$\overline{H}_1 = H_1^0, \tag{3.33}$$

and finally from $\overline{V}_1 = (\partial\mu_1/\partial p)_{T,x_i} = \left(\partial\mu_1^0/\partial p\right)_{T,x_i}$ we find

$$\overline{V}_1 = V_1^0, \tag{3.34}$$

where, of course, S_1^0, H_1^0, and V_1^0 are the entropy, enthalpy, and volume per mole of the pure solvent, respectively.

We can obtain the corresponding expressions for the partial molar functions associated with the solute from Eq. (3.19) and the definitions in Section 3.1:

from $\overline{S}_2 = -(\partial\mu_2/\partial T)_{p,x_i} = -(\mathrm{d}\psi_2/\mathrm{d}T) - R\ln c_2$ we find

$$\overline{S}_2 = \dot{S}_2 - R\ln c_2, \tag{3.35}$$

from $\overline{H}_2 = \mu_2 + T\overline{S}_2 = \psi_2 + T\dot{S}_2$ we find

$$\overline{H}_2 = \dot{H}_2, \tag{3.36}$$

and finally from $\overline{V}_2 = (\partial\mu_2/\partial p)_{T,x_i} = (\partial\psi_2/\partial p)_{T,x_i}$ we find

$$\overline{V}_2 = \dot{V}_2, \tag{3.37}$$

where $\dot{H}_2$, $\dot{S}_2$, and $\dot{V}_2$ are concentration-independent constants. Note that the values of these constants depend upon the nature of *both* the solvent and solute[4] and, in fact, are parameters of the theory (i.e. they cannot be determined from the thermodynamic theory of ideal dilute solutions).

Review questions

1. If the temperature of a solution increases or decreases upon dissolving a small quantity of solute, can this solution be considered an ideal dilute solution?
2. How does p_1^0 in Raoult's law vary with temperature? Which equation describes this?
3. How do the partial molar enthalpy and entropy of the solute in the ideal dilute solution depend on the solute concentration?

Example problem

1. Two glasses were placed in a sealed chamber and monitored using a web-cam. The first glass originally contained 100 ml of pure water and the second contained 100 ml of a solution of urea ($CO(NH_2)_2$) in water. After some time, you observed that the volume of the solution in glass 2 increased and the volume of the pure water in glass 1 decreased. How can you explain this?

3.2.2 Boiling point

We now consider evaporation in an ideal dilute solution. The change of the enthalpy of the system (the solution + the vapor) upon transferring dn_1 molecules of solvent from the solution to the vapor is

$$\mathrm{d}H = H^0_{1\mathrm{vapor}}\mathrm{d}n_1 - \overline{H}_1\mathrm{d}n_1 = \left(H^0_{1\,\mathrm{vapor}} - \overline{H}_1\right)\mathrm{d}n_1.$$

Therefore, the heat of evaporation of 1 mole of solvent from an ideal dilute solution[5] is

$$\Delta H_{\mathrm{evap}} = \frac{\mathrm{d}H}{\mathrm{d}n_1} = H^0_{1\mathrm{vapor}} - \overline{H}_1 = H^0_{1\,\mathrm{vapor}} - H^0_1 = \Delta H^0_{\mathrm{evap}}.$$

Note, this result shows that the heat of evaporation of solvent from an ideal dilute solution is exactly the same as the heat of evaporation from the pure

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[4] These constants are not the equal to H_2^0, S_2^0, and V_2^0, which are properties of the pure solute!

[5] We assume that the volume of the solution is so large that the evaporation of 1 mole of the solvent does not significantly modify the properties of the solution.

solvent. In the case of a non-volatile solute ($p_2 \ll p_1$), the total pressure in the saturated vapor above the solution is $p = p_1 + p_2 \approx p_1$. Since the solute concentration does not depend on temperature (assume that we are not near the saturation limit), the derivation of the Clausius–Clapeyron equation in Section 2.2 for a one-component system is unchanged upon adding solute to form an ideal dilute solution. Therefore, the solvent partial pressure in the saturated vapor satisfies

$$\frac{\mathrm{d}\ln p_1}{\mathrm{d}T} = \frac{\Delta H^0_{\mathrm{evap}}}{RT^2}. \tag{3.38}$$

How does the boiling point change when a small amount of (low-volatility) solute is added to the pure solvent? The liquid boils when its total saturated vapor pressure is equal to the atmospheric pressure. The pressure of the saturated vapor is approximately p_1, which is smaller than that over the pure solvent (see Fig. 3.2). Therefore, the solution must boil at a higher temperature than the pure solvent. To derive an expression for the boiling point of a solution we integrate Eq. (3.38), neglecting the dependence of $\Delta H^0_{\mathrm{evap}}$ on temperature. This is a reasonable assumption if the difference between the boiling points of the solvent and solution is small, as for dilute solutions. We find

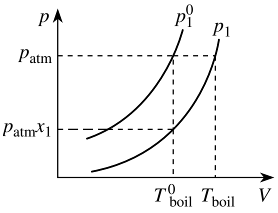

Fig. 3.2
The temperature dependence of the saturated vapor pressure of the solvent over a liquid solution and pure solvent.

$$\int_{p_{\mathrm{atm}}x_1}^{p_{\mathrm{atm}}} \mathrm{d}\ln p_1 = \frac{\Delta H^0_{\mathrm{evap}}}{R}\int_{T^0_{\mathrm{boil}}}^{T_{\mathrm{boil}}} \frac{\mathrm{d}T}{T^2}$$

$$\ln\frac{p_{\mathrm{atm}}}{p_{\mathrm{atm}}x_1} = -\frac{\Delta H^0_{\mathrm{evap}}}{R}\left(\frac{1}{T_{\mathrm{boil}}} - \frac{1}{T^0_{\mathrm{boil}}}\right)$$

$$\ln x_1 = \frac{\Delta H^0_{\mathrm{evap}}}{R}\left(\frac{1}{T_{\mathrm{boil}}} - \frac{1}{T^0_{\mathrm{boil}}}\right). \tag{3.39}$$

For a dilute solution

$$\ln x_1 = \ln(1 - x_2) \approx -x_2.$$

Therefore, we can rewrite Eq. (3.39) as

$$-x_2 = \frac{\Delta H^0_{\mathrm{evap}}}{R}\frac{T^0_{\mathrm{boil}} - T_{\mathrm{boil}}}{T_{\mathrm{boil}}T^0_{\mathrm{boil}}} \approx \frac{\Delta H^0_{\mathrm{boil}}}{R}\frac{T^0_{\mathrm{boil}} - T_{\mathrm{boil}}}{\left(T^0_{\mathrm{boil}}\right)^2}.$$

Introducing the notation $\Delta T_{\mathrm{boil}} = T_{\mathrm{boil}} - T^0_{\mathrm{boil}}$, we obtain

$$\Delta T_{\mathrm{boil}} = \frac{R\left(T^0_{\mathrm{boil}}\right)^2}{\Delta H^0_{\mathrm{evap}}}x_2. \tag{3.40}$$

This expression for the change in the boiling point is written in a slightly different form in many chemistry texts. To rewrite Eq. (3.40) in that form, we replace the molar fraction of the solute by its molality using Eq. (3.4):

$$\Delta T_{\text{boil}} = \frac{R\left(T^0_{\text{boil}}\right)^2}{\Delta H^0_{\text{evap}}} \frac{M_1}{1000} m_2 = \frac{R\left(T^0_{\text{boil}}\right)^2}{1000\lambda^0} m_2,$$

where λ^0 is the specific heat of evaporation (in units of J/g). We can rewrite Eq. (3.40) in the form of

$$\Delta T_{\text{boil}} = K_{\text{b}} m_2 \tag{3.41}$$

where

$$K_{\text{b}} = \frac{R(T^0_{\text{boil}})^2}{1000\lambda^0}, \tag{3.42}$$

is known as the **ebullioscopic constant** and is a function of only the solvent properties. Equation (3.41) was originally proposed by Raoult.

3.2.3 Freezing point

We now consider the freezing of an ideal dilute solution. We define the **freezing point** as the highest temperature for which a crystalline solid solution is in equilibrium with a liquid solution with the same components. In other words, the freezing point is the temperature at which we first see crystals in the liquid as we *very* slowly cool the liquid solution. For a pure solvent, the freezing point and the melting point are identical, T^0_{freeze}. At this temperature, the chemical potentials of the pure solid and pure liquid solvent are equal, hence

$$\Delta\mu^0_1(T^0_{\text{freeze}}) = \mu^0_{1\text{L}}(T^0_{\text{freeze}}) - \mu^0_{1\text{S}}(T^0_{\text{freeze}}) = 0. \tag{3.43}$$

However, for a solution at the freezing point of the pure solvent T^0_{freeze}, we find

$$\Delta\mu_1(T^0_{\text{freeze}}) = \mu_{1\text{L}}(T^0_{\text{freeze}}) - \mu_{1\text{S}}(T^0_{\text{freeze}}) \neq 0.$$

Therefore, the temperature at which the solution freezes differs from that of the pure solvent. In a solution, the equilibrium between solid and liquid occurs at the temperature where the chemical potentials of the solvent in the solid and liquid are identical: that is,

$$\Delta\mu_1(T_{\text{freeze}}) = \mu_{1\text{L}}(T_{\text{freeze}}) - \mu_{1\text{S}}(T_{\text{freeze}}) = 0. \tag{3.44}$$

The Gibbs–Helmholtz equations for the chemical potential of the solvent in ideal dilute liquid and solid solutions take the following form:

$$\left(\frac{\partial(\mu_{1\text{L}}/T)}{\partial T}\right)_{p,x_i} = -\frac{\overline{H}_{1\text{L}}}{T^2} = -\frac{H^0_{1\text{L}}}{T^2}$$

$$\left(\frac{\partial(\mu_{1\text{S}}/T)}{\partial T}\right)_{p,x_i} = -\frac{\overline{H}_{1\text{S}}}{T^2} = -\frac{H^0_{1\text{S}}}{T^2}.$$

Combining these equations, we obtain:

$$\left(\frac{\partial(\Delta\mu_1/T)}{\partial T}\right)_{p,x_i} = -\frac{\Delta H^0_{\text{melt}}}{T^2}.$$

(Note: to be consistent we should write $\Delta H^0_{\text{freeze}}$ instead of ΔH^0_{melt}, however the latter is the more commonly accepted notation and so we adopt it here.) We can integrate this expression from T^0_{freeze} to T_{freeze} to find

$$\int_{\Delta\mu_1(T^0_{\text{freeze}})/T^0_{\text{freeze}}}^{\Delta\mu_1(T_{\text{freeze}})/T_{\text{freeze}}} \mathrm{d}\left(\frac{\Delta\mu_1}{T}\right) = -\Delta H^0_{\text{melt}} \int_{T^0_{\text{freeze}}}^{T_{\text{freeze}}} \frac{\mathrm{d}T}{T^2}$$

$$\frac{\Delta\mu_1(T_{\text{freeze}})}{T_{\text{freeze}}} - \frac{\Delta\mu_1(T^0_{\text{freeze}})}{T^0_{\text{freeze}}} = \Delta H^0_{\text{melt}}\left(\frac{1}{T_{\text{freeze}}} - \frac{1}{T^0_{\text{freeze}}}\right).$$

Employing the equilibrium conditions from Eqs (3.43) and (3.44), we can rewrite the previous equation as

$$0 = \frac{\Delta\mu_1^0(T^0_{\text{freeze}}) + RT^0_{\text{freeze}} \ln x_{1\text{L}}/x_{1\text{S}}}{T^0_{\text{freeze}}} + \Delta H^0_{\text{melt}}\left(\frac{1}{T_{\text{freeze}}} - \frac{1}{T^0_{\text{freeze}}}\right)$$

or

$$\ln\frac{x_{1\text{S}}}{x_{1\text{L}}} = \frac{\Delta H^0_{\text{melt}}}{R}\left(\frac{1}{T_{\text{freeze}}} - \frac{1}{T^0_{\text{freeze}}}\right). \tag{3.45}$$

Interestingly, to this point, this derivation was based only upon expression for the chemical potential of the solvent and we did not explicitly make use of the assertion that the solution is dilute. However, if we assume that the solute molar fractions in both the liquid and solid solutions are much less than unity, we can simplify Eq. (3.45). Small solute concentration implies $\ln x_{1\text{S}}/x_{1\text{L}} = \ln x_{1\text{S}} - \ln x_{1\text{L}} \approx -x_{2\text{S}} + x_{2\text{L}} = x_{2\text{L}}\ (1 - L)$, where

$$L = \frac{x_{2\text{S}}}{x_{2\text{L}}}, \tag{3.46}$$

is called the **partition coefficient** of the solute between the liquid and solid. (We will show in the next section that L is independent of solute concentration.) Introducing the notation $\Delta T_{\text{freeze}} = T^0_{\text{freeze}} - T_{\text{freeze}}$, we obtain

$$\Delta T_{\text{freeze}} = \frac{R(T^0_{\text{freeze}})^2}{\Delta H^0_{\text{melt}}}(1 - L)x_{2\text{L}}. \tag{3.47}$$

This result demonstrates that if the solute dissolves in the liquid solvent better than in the solid solvent ($L < 1$), the freezing temperature of the solution is lower than that of the pure solvent. However, if the solute dissolves better in the solid solvent ($L > 1$), the solution freezes at higher temperature than the pure solvent. In practice, freezing point depression upon adding solute ($L < 1$) is much more common than freezing point elevation.

If we rewrite Eq. (3.47) in terms of molality instead of molar fraction, we find (analogously to the derivation of Eq. (3.41)):

$$\Delta T_{\text{freeze}} = K_{\text{f}}(1 - L)m_{2\text{L}} \tag{3.48}$$

where

$$K_{\text{f}} = \frac{R(T^0_{\text{freeze}})^2}{1000q^0}, \tag{3.49}$$

is called the **cryoscopic constant** and q^0 is the specific heat of melting of the pure solvent (in units of J/g). Like the ebullioscopic constant, the cryoscopic constant is only a function of the properties of the pure solvent.

If the solute does not dissolve in the pure solid solvent ($L = 0$), Eq.(3.48) takes the following form

$$\Delta T_{\text{freeze}} = K_{\text{f}}m_2. \tag{3.50}$$

This law too was originally proposed by Raoult. It is interesting to note that all three of the ideal dilute solution laws ($p_1 = p^0_1 x_1$, $\Delta T_{\text{boil}} = K_{\text{b}}m_2$, and $\Delta T_{\text{freeze}} = K_{\text{f}}m_2$) were discovered independently nearly 80 years after the discovery of Henry's law. This delay had two main causes: (1) the thermodynamic methods used here were not yet developed and (2) Raoult made a fortuitous choice of chemical systems to investigate (e.g. he would have never discovered these laws if he had studied NaCl in H_2O, as we discuss in Section 3.7).

Review question

1. You are given three solutions. The solutions were prepared by dissolving 10 g of (1) sucrose—$C_{12}H_{22}O_{11}$, (2) fructose—$C_6H_{12}O_6$, and (3) urea—$CO(NH_2)_2$ in 1000 cm^3 of water. Compare the freezing temperatures of these three solutions.

Example problem

1. By how much is the freezing temperature of liquid iron lowered by the addition of 1 wt% of sulfur? For simplicity, assume that the sulfur does not dissolve in solid iron. The following data for iron are from a handbook: $q^0 = 262.5$ J/g, $T^0_{\text{freeze}} = 1813$ K.

3.2.4 Solute partitioning

How is the solute distributed, in equilibrium, between two phases that are in contact? This partition of the solute between the two phases is known as solute partitioning. From the condition that the two phases are in equilibrium with one another, we find:

$$\mu^{\text{I}}_2 = \mu^{\text{II}}_2; \qquad \psi^{\text{I}}_2 + RT\ln c^{\text{I}}_2 = \psi^{\text{II}}_2 + RT\ln c^{\text{II}}_2.$$

The ratio of the equilibrium solute concentrations in the two phases is the partition coefficient:

$$L = \frac{c_2^{\mathrm{I}}}{c_2^{\mathrm{II}}} = \mathrm{e}^{\left(\psi_2^{\mathrm{II}} - \psi_2^{\mathrm{I}}\right)/RT}. \tag{3.51}$$

Since the right-hand side of Eq. (3.51) depends only upon temperature and the solvent and solute species, the partition coefficient is independent of the solute concentration. This statement is called the **partition law**. Because the expression we used for the chemical potential is appropriate only for dilute solutions, Eq. (3.51) can only be applied to dilute solutions. To illustrate this point, consider the partition of iodine (I_2) between water and carbon tetrachloride (CCl_4) at room temperature (CCl_4 is nearly immiscible in water) shown in Fig. 3.3. This figure demonstrates that the partition law for I_2 in an H_2O/CCl_4 mixture is indeed valid for small I_2 concentrations.

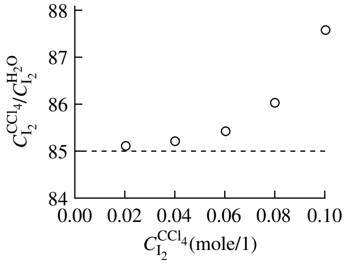

Fig. 3.3
The ratio of the concentrations of iodine in CCl_4 and H_2O as a function of its concentration in H_2O, showing that this ratio approaches a constant for sufficiently small $C_{I_2}^{H_2O}$.

Example problem

1. Calculate how much iodine can be removed from 500 cm^3 of a water solution containing 0.1 g of iodine by the addition of 80 ml of CCl_4 (take the partition coefficient from Fig. 3.3).

3.2.5 Composition of a saturated solution

What is the maximum amount of a pure substance, A, that can be dissolved in a solvent? This is determined by the saturation concentration of A in the solution. The **saturation concentration** is the concentration of A in the solution when the solution is in equilibrium with pure A (we neglect the solubility of the solvent in A). In equilibrium, the chemical potential of A in the solution is equal to that in pure A,

$$\mu_{\mathrm{A}}^0 = \psi_{\mathrm{A}} + RT \ln c_{\mathrm{A}}^{\mathrm{s}},$$

where $c_{\mathrm{A}}^{\mathrm{s}}$ is the concentration of A in the saturated solution. Inserting this equation into the Gibbs–Helmholtz equation we find:

$$-\frac{H_{\mathrm{A}}^0}{T^2} = \frac{\mathrm{d}(\mu_{\mathrm{A}}^0/T)}{\mathrm{d}T} = \frac{\mathrm{d}(\psi_A/T)}{\mathrm{d}T} + R\frac{\mathrm{d}\ \ln c_{\mathrm{A}}^{s}}{\mathrm{d}T} = -\frac{\dot{H}_{\mathrm{A}}}{T^2} + R\frac{\mathrm{d}\ \ln c_{\mathrm{A}}^{\mathrm{s}}}{\mathrm{d}T}$$

or

$$\frac{\mathrm{d}\ \ln c_{\mathrm{A}}^{\mathrm{s}}}{\mathrm{d}T} = \frac{\dot{H}_{\mathrm{A}} - H_{\mathrm{A}}^0}{RT^2}, \tag{3.52}$$

where $\dot{H}_{\mathrm{A}} - H_{\mathrm{A}}^0$ is the **heat of solution** of pure A in the solvent. Equation (3.52) shows that if dissolving pure A in the solute is exothermic (produces heat, $\dot{H}_{\mathrm{A}} - H_{\mathrm{A}}^0 < 0$), the solubility of A must decrease with increasing temperature.

Equation (3.52) can be integrated to show that

$$c_{\mathrm{A}}^{\mathrm{s}}(T) = c_{\mathrm{A}}^{\mathrm{s}}(T_0)\exp\left\{-\frac{\dot{H}_{\mathrm{A}} - H_{\mathrm{A}}^0}{R}\left(\frac{1}{T_0} - \frac{l}{T}\right)\right\}, \tag{3.53}$$

where we have neglected any dependence of the heat of solution on temperature and where T_0 is a reference temperature where we know the saturation concentration.

3.3 Ideal solutions

The theory of ideal dilute solutions is valid only for solutions in which the solute concentration is very small. While ideally we would like to find a theory that is capable of describing the thermodynamic properties of all solutions at all concentrations, no such analytical theory currently exists. Fortunately, several models exist that work for a wide range of concentrations, albeit not for all solutions. The simplest of these is known as the ideal solution model.

Recall that the first step in deriving any theory of solutions is to obtain expressions for the chemical potentials. In the theory of ideal dilute solutions, described above, the chemical potentials of the solvent and solute took the following form:

$$\mu_1 = \mu_1^0 + RT \ln x_1; \qquad \mu_2 = \psi_x + RT \ln x_2.$$

In an **ideal solution** model, we *assume* that such expressions are valid for all solute concentrations. In the pure solute case ($x_2 = 1$), the logarithmic term in the second equation is zero and, hence, $\psi_x = \mu_2^0$. Thus the chemical potential of any component of an ideal solution can be described by:

$$\mu_i = \mu_i^0 + RT \ln x_i. \tag{3.54}$$

In Section 3.2.1, we saw that this equation implies that the pressure of the saturated vapor of component i obeys Raoult's law:

$$p_i = p_i^0 x_i. \tag{3.55}$$

Alternatively, we can state that if all components obey Raoult's law, the solution is ideal. Recall, that in an ideal dilute solution, only the solvent obeys Raoult's law and the solute obeys Henry's law. In an ideal solution model, which describes the entire concentration range, there is no difference between solute and solvent and hence, we will abandon these terms here.

Equation (3.54) implies that

$$\overline{S}_i = S_i^0 - R \ln x_i \tag{3.56}$$

$$\overline{H}_i = H_i^0 \tag{3.57}$$

$$\overline{V}_i = V_i^0. \tag{3.58}$$

Using these results, the extensive thermodynamic properties that describe mixing take the form:

$$\begin{aligned} &\Delta H_{\text{mix}} = 0; \qquad \Delta V_{\text{mix}} = 0; \\ &\Delta S_{\text{mix}} = -nR(x_1 \ln x_1 + x_2 \ln x_2) \end{aligned} \tag{3.59}$$

This set of equations for the extensive thermodynamic properties is frequently used as a definition of the ideal solution. In other words, an ideal solution is one in which the heat of mixing is zero, there is no change in volume upon mixing, and the change of entropy upon mixing takes the same form as for an ideal gas mixture. The equivalence of the expressions for the entropy of mixing of an ideal gas and an ideal solution is not coincidental. Rather, statistical thermodynamics can be used to show that ΔS_{mix} in Eq. (3.59) is a natural consequence of the assumption that the molecules of all types are randomly arranged, as will be discussed in Section 13.4.2.2.

As example of an application of ideal solution theory, consider dissolving a pure solid substance B in the liquid phase of A. By analogy with the derivation of Eq. (3.52), we find

$$\frac{\mathrm{d}\ln x_{\mathrm{B}}^{\mathrm{s}}}{\mathrm{d}T} = \frac{\overline{H}_{\mathrm{B}} - H^0_{\mathrm{B_S}}}{RT^2} = \frac{H^0_{\mathrm{B_L}} - H^0_{\mathrm{B_S}}}{RT^2} = \frac{\Delta H^0_{\mathrm{B,melt}}}{RT^2}, \tag{3.60}$$

where $H^0_{\mathrm{B_L}}$ is the enthalpy of the pure, supercooled liquid at temperature T. In contrast to Eq. (3.52), this expression does not accurately describe any real system, but has the advantage that it can approximately describe many solutions over the entire concentration range. Equation (3.60) can be integrated to predict the saturation concentration at any temperature,

$$\int_0^{\ln x_{\mathrm{B}}^{\mathrm{s}}} \mathrm{d}\ln x_{\mathrm{B}}^{\mathrm{s}} = \frac{\Delta H^0_{\mathrm{B,melt}}}{R} \int_{T^0_{\mathrm{B,freeze}}}^{T} \frac{\mathrm{d}T}{T^2},$$

where we have assumed that B is completely soluble in liquid A. At the melting point of B, $T^0_{\mathrm{B,freeze}}$, solid B is in equilibrium with liquid B. Since liquid B is completely soluble in liquid A, $x_{\mathrm{B}}^{\mathrm{s}} = 1$ at $T^0_{\mathrm{B,freeze}}$. Performing the integration in the previous equation yields:

$$\ln x_{\mathrm{B}}^{\mathrm{s}} = \frac{\Delta H^0_{\mathrm{B,melt}}}{R}\left(\frac{1}{T^0_{\mathrm{B,freeze}}} - \frac{1}{T}\right). \tag{3.61}$$

To obtain the saturation concentration for an ideal dilute solution, Eq. (3.52), we needed to know both the saturation concentration at one temperature and the heat of solution. Theory provides no guidance on how to obtain these quantities. In contrast the saturation concentration for an ideal solution can be calculated using only properties of pure components, the heat of melting and the melting temperature, which are both widely available in handbooks.

As an example, we estimate the solubility of copper in liquid lead at $T = 980°\mathrm{C}$ using Eq. (3.61). We obtained the following data from a standard handbook:

$$T^0_{\mathrm{B,freeze}}(\mathrm{Cu}) = 1356\,\mathrm{K};\ \ \Delta H^0_{\mathrm{melt}}(\mathrm{Cu}) = 12.97\,\mathrm{kJ/mole};$$
$$T^0_{\mathrm{B,freeze}}(\mathrm{Pb}) = 601\,\mathrm{K}.$$

At $T = 980°\text{C}$, lead is a liquid and copper is a solid. Using these data and Eq. (3.61), we find that saturation concentration of Cu in Pb is $x^{s}_{\text{Cu}} = 0.91$, while experimental measurement shows that $x^{s}_{\text{Cu}} = 0.92$. At least for this case, the ideal solution theory works very well. This level of agreement is not common! Nevertheless, we emphasize again that ideal solution theory provides a simple means to estimate the properties of certain solutions at any concentration using only readily available data for pure components.

Review questions

1. Some solutions exist for which the heats of formation are zero. Does this imply that these are all ideal solutions?
2. The saturated vapor pressure of component A in a binary solution obeys Raoult's law for all concentrations. Does it follow from this that Raoult's law is also valid for the saturated vapor pressure of component B?

Example problems

1. At $T = 20°\text{C}$, the pressure of the saturated vapor over pure methyl alcohol (CH_3OH) is 96 mm of mercury and the pressure of the saturated vapor over pure ethyl alcohol (C_2H_5OH) is 44 mm of mercury. Their densities are 0.7915 and 0.7894 g/cm^3, respectively. To prepare a solution, 1 part methyl alcohol is mixed with 2 parts ethyl alcohol by volume. Find the composition of the vapor over the solution.
2. Estimate the boiling temperature of a Hg–Sn alloy in which the Sn concentration is 10 wt%. The following data are known for the two components: $T^{0}_{\text{boil}}(\text{Sn}) = 2620°\text{C}$, $T^{0}_{\text{boil}}(\text{Hg}) = 357°\text{C}$, and $\lambda^{0}(\text{Hg}) = 272$ J/g.

3.4 Non-ideal solutions

3.4.1 Activity

As a rule, real solutions are neither ideal dilute solutions nor ideal solutions. In most cases of interest, the solute concentration is too large for a solution to be considered dilute. Further, an ideal solution is simply a model for a solution that we postulated and may, therefore, not be applicable in any case. So, we are left with the question, "how can we describe the thermodynamic properties of real solutions?" Even today, we have little hope of deriving a theory that is capable of predicting the properties of solutions from "first principles" (i.e. based only upon fundamental laws of physics or chemistry, such as quantum theory). A more practical approach is to describe a real solution in terms of how its properties deviate from that of an ideal or ideal dilute solution. Two schematic examples of such deviations are shown in Fig. 3.4 for

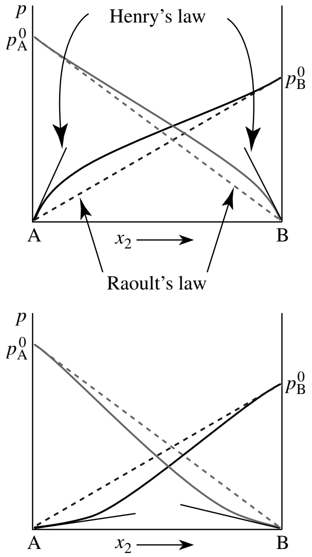

Fig. 3.4
Schematic illustrations of the saturated vapor pressures above two different non-ideal solutions. The continuous solid curves represent the behavior of the real solutions, the dashed lines represent Raoult's law and short solid lines represent Henry's law.

the case of the saturated vapor pressure. The upper figure depicts a solution for which there is a positive deviation from Raoult's law and a negative deviation from Henry's law, while the lower figure shows a negative deviation from Raoult's law and a positive deviation from Henry's law.

Since the vapor pressure of the solute deviates from Henry's law to a smaller extent than from Raoult's law at small solute concentrations (see Fig. 3.4), it is convenient to focus on the deviations from Henry's law. Recall that if Henry's law is valid, the chemical potential of the solute takes the following form:

$$\mu_i = \psi_i + RT \ln c_i.$$

We can describe the chemical potential of the solute in a real dilute solution as that in an ideal solution, plus a correction term which accounts for the deviation from ideality

$$\mu_i = \psi_i + RT \ln c_i + RT \ln f_i, \tag{3.62}$$

where f_i measures that deviation. This definition implies that $f_i > 0$. The **standard state** (**standard solution**) for the solute in this case is the hypothetical solution in which the solute concentration is unity $c_i = 1$ and the thermodynamic properties are described by the same equations as for ideal dilute solution where the first component is the solvent. Below, we will refer to such a hypothetical solution as a solution with unitary concentration. As $c_i \to 0$, Eq. (3.62) must reduce to the expression for the chemical potential of the solute in an ideal dilute solution, therefore,

$$f_i \to 1 \quad \text{as} \quad c_i \to 0. \tag{3.63}$$

We can recover an expression for the chemical potential of the solute in a real solution that looks more similar to that in the ideal dilute solution by making the substitution

$$a_i = f_i c_i \tag{3.64}$$

into Eq. (3.62):

$$\mu_i = \psi_i + RT \ln a_i. \tag{3.65}$$

The thermodynamic functions a_i and f_i are known as the **activity** and **activity coefficient**, respectively.

Figure 3.4 shows that in the case of a solvent in a dilute solution (or any of the components in a concentrated solution), it is more convenient to use Raoult's law as our reference. Raoult's law implies that the chemical potential of component i in the solutions takes the following form:

$$\mu_i = \mu_i^0 + RT \ln x_i.$$

Following the procedure we used above, we express deviations from this for a non-ideal solution, as

$$\mu_i = \mu_i^0 + RT \ln x_i + RT \ln \gamma_i, \tag{3.66}$$

where γ_i is also called the **activity coefficient**. This differs from f_i in that the standard state is now pure component i. From this definition, it follows that $\gamma_i > 0$ and

$$\gamma_i \to 1 \quad \text{as} \quad x_i \to 1. \tag{3.67}$$

Similarly, the **activity** of component i using this standard state is

$$a_i = \gamma_i x_i \tag{3.68}$$

Inserting Eq. (3.68) in Eq. (3.66), we find:

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{3.69}$$

Equations (3.65) and (3.69) were derived on the bases of different standard states. We can rewrite these equations in a more general form as

$$\mu_i = \mu_i^{\text{st}} + RT \ln a_i, \tag{3.70}$$

where μ_i^{st} indicates the chemical potential of component i in whichever standard state we choose. This choice affects the value of the activity.

We can now consider the equilibrium between a non-ideal solution and its saturated vapor. The equilibrium condition takes the following form

$$\mu_i = \mu_{i\,\text{vap}} = \mu_{i\,\text{vap}}^0 + RT \ln p_i.$$

Using this result, we can relate the chemical potential of component i in the standard state to its pressure in its saturated vapor above a standard solution as

$$\mu_i^{\text{st}} = \mu_{i\,\text{vap}}^0 + RT \ln p_i^{\text{st}}.$$

Combining these two equations with Eq. (3.70), we find

$$\mu_{i\,\text{vap}}^0 + RT \ln p_i = \mu_i = \mu_i^{\text{st}} + RT \ln a_i = \mu_{i\,\text{vap}}^0 + RT \ln p_i^{\text{st}} + RT \ln a_i,$$

which implies

$$p_i = p_i^{\text{st}} a_i \tag{3.71}$$

$$a_i = \frac{p_i}{p_i^{\text{st}}}. \tag{3.72}$$

Equation (3.72) is frequently used as the definition of the activity.

If the standard state is taken to be a solution with unitary concentration, we can use Eq. (3.71) and the fact that as $c_i \to 0$, $a_i \to c_i$, and $p_i/c_i = h$, to write

$$p_i = h a_i. \tag{3.73}$$

This is the generalization of Henry's law to non-ideal solutions. If we choose to use the pure component as the standard state, we similarly find

$$p_i = p_i^0 a_i. \tag{3.74}$$

Note, there are other reasonable choices of the standard state which we have not discussed here.

To this point, we have discussed non-ideal solutions in terms of their deviations from ideality, as represented by the value of the activity. However, we are no closer to describing non-ideal solutions then before since we did not specify how to obtain these activities. Thermodynamic theory is of no use for this; therefore, we must resort either to experiment or to some more microscopic theory.

Before we discuss experimental and theoretical approaches to determine the activity, we first relate the activity of one component in a solution to that of the other component and the activity at one temperature to that at another. The first problem can be solved with the help of the Gibbs–Duhem Eq. (3.70). Inserting Eq. (3.16) into Eq. (3.16) yields the relationship between the activities of the components of a binary solution:

$$x_1\left(\frac{\partial \ln a_1}{\partial x_1}\right)_{p,T} = x_2\left(\frac{\partial \ln a_2}{\partial x_2}\right)_{p,T}. \tag{3.75}$$

If the pure components are chosen as the standard states for both components, this equation can be transformed into

$$x_1\frac{\partial \ln x_1}{\partial x_1} + x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{p,T} = x_2\frac{\partial \ln x_2}{\partial x_2} + x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{p,T}$$

or

$$x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{p,T} = x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{p,T}, \tag{3.76}$$

where we have made use of Eq. (3.68). This equation relates the concentration dependence of the activity coefficient of one component to that of the other.

The temperature dependence of the activity can be derived from the expression for the chemical potential and the Gibbs–Helmholtz equation. If the pure component is chosen as the standard state, we obtain:

$$-\frac{\overline{H}_i}{T^2} = \left(\frac{\partial(\mu_i/T)}{\partial T}\right)_{p,x_i} = \frac{\partial(\mu_i^0/T)}{\partial T} + R\frac{\partial \ln a_i}{\partial T} = -\frac{H_i^0}{T^2} + R\frac{\partial \ln \gamma_i}{\partial T}$$

which can be rewritten as

$$\frac{\partial \ln \gamma_i}{\partial T} = -\frac{\overline{H}_i - H_i^0}{RT^2}. \tag{3.77}$$

On the other hand, if we choose the standard state to be the solution with unitary concentration, we find:

$$-\frac{\overline{H}_i}{T^2} = \left(\frac{\partial(\mu_i/T)}{\partial T}\right)_{p,x_i} = \frac{\partial(\psi_i/T)}{\partial T} + R\frac{\partial \ln a_i}{\partial T} = -\frac{\dot{H}_i}{T^2} + R\frac{\partial \ln f_i}{\partial T}$$

or

$$\frac{\partial \ln f_i}{\partial T} = -\frac{\overline{H}_i - \dot{H}_i}{RT^2}. \tag{3.78}$$

Review questions

1. Is the activity always positive?
2. You are told $p_i > p_i^0 x_i$ for component i in a solution. What does this imply about the activity coefficient of this component (assume that the standard state is pure component i)?

Example problems

1. In a liquid Pb–Bi alloy, the activity coefficient of Pb depends on its molar fraction in the following way:

$$\log_{10}(\gamma_{\mathrm{Pb}}) = -0.32(1 - x_{\mathrm{Pb}})^2.$$

   What is the activity coefficient of Bi at $x_{\mathrm{Bi}} = 0.4$?
2. The change in the Gibbs free energy upon forming 500 g of an equimolar[6] solution from $\mathrm{SnCl_4}$ and $\mathrm{CCl_4}$ is $\Delta G_{\mathrm{mix}} = -7.03$ kJ. The activity of $\mathrm{SnCl_4}$ in this solution is 0.52. What is the activity of $\mathrm{CCl_4}$? Assume that the standard states are the pure components.
3. The heat liberated upon dissolving Mg in a Mg–Bi alloy with $x_{\mathrm{Mg}} = 0.9$ at 1000 K is $\overline{H}^{\mathrm{M}}_{\mathrm{Mg}} = -0.84$ kJ/mole and the Mg activity coefficient is found to be $\gamma_{\mathrm{Mg}} = 0.93$ (assuming a pure Mg is the standard state). What is the relative partial molar entropy of Mg in this alloy?
4. At 1693 K, silicon is distributed between iron- and silver-rich phases that are in contact as $x_{\mathrm{Si}}^{\text{Fe-rich}} = 0.326$ and $x_{\mathrm{Si}}^{\text{Ag-rich}} = 0.00847$. Find the activity coefficient of the silicon in the iron-rich phase if $\gamma_{\mathrm{Si}}^{\text{Ag-rich}} = 0.155$ (consider a pure silicon as the standard state in both solutions).

3.4.2 Experimental determination of activity

As we discussed above, the activity of a component in a solution cannot be derived from thermodynamics unless we make some simplifying assumptions. For example, if we assume that the solution is ideal, then the activity is trivially just the concentration (additional simplifying assumptions are suggested later in this chapter). In general, however, these assumptions are of limited utility and the activity must be extracted from either experiment or a microscopic theory. Recall, that once we determine the activity, by whatever means, we can then consistently predict all other thermodynamic properties. We now turn to the question: how can we experimentally determine the activities of the components of a real solution? The most common answers to this question are outlined here.

1. The activity can be determined through measurements of the saturated vapor pressure.

   This method is based on the definition of the activity given in Eq. (3.72). An example of such an approach is the subject of Computer Laboratory #3.
2. The activity can be determined on the basis of the partition law.

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[6] That is, equal molar fraction of each component.

For non-ideal solutions, the partition law, discussed in Section 3.2.4, can be rewritten in terms of the activities as:

$$L = \frac{a_2^{\mathrm{I}}}{a_2^{\mathrm{II}}}, \tag{3.79}$$

where L depends only on the temperature and the properties of the solvents and solute.

In a experiment, one measures the solute concentrations in each of the two phases and plots the ratio as a function of one of the concentrations, as in Fig. 3.5. In the limit that $c_2^{\mathrm{I}} \to 0$, the solutions in each of the two phases behave as ideal dilute solutions. Therefore, the activities are simply equal to the solute concentrations and the partition coefficient is equal to $L = c_2^{\mathrm{I}}/c_2^{\mathrm{II}}$. Thus, extrapolating the dependence of $c_2^{\mathrm{I}}/c_2^{\mathrm{II}}$ on c_2^{I} at $c_2^{\mathrm{I}} = 0$ we obtain the partition coefficient. If we know the activity of the solute in one phase (a fairy told you), we can determine its activity in the other phase. However, we commonly do not know the activities in either phase. This is a problem. If we assume that the solution in which the solute concentration is smallest can be described as an ideal dilute solution (i.e. where the solute activity is equal to its concentration), then $L \approx c_2^{\mathrm{I}}/a_2^{\mathrm{II}}$ and we can use this expression and our measurement of $c_2^{\mathrm{I}}/c_2^{\mathrm{II}}$ to determine a_2^{II}.

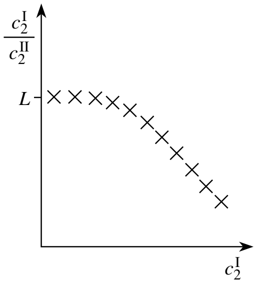

Fig. 3.5
Schematic plot of the ratio of the concentrations in phases I and II versus the solute concentration in phase I. The flat region of this plot indicates the range of concentration over which the solution can be described as an ideal dilute solution.

3. The activity can be determined on the basis of the law of mass action, which is described in Section 5.4, below.

   This method is similar to the previous one and is the subject of Computer Laboratory #2.

4. The activity can be determined from electric voltage measurements.

   This method is widely used for metallic alloys. The experiment is as follows: an electrode made from the alloy is put in contact with an electrode made containing solely the less-noble of the alloy components and the voltage between these electrodes is measured. The difference between the chemical potentials of the less-noble component in the two electrodes is

   $$\Delta G_T = \Delta\mu_T = \mu_1^0 + RT \ln a_1 - \mu_1^0 = RT \ln a_1.$$

   ΔG_T is related to the electrical work done in dissolving the less-noble component in the alloy; that is, $\Delta G_{\mathrm{T}} = -zFE$, where E is the measured voltage, F is Faraday's constant, and z is the number of electrons involved in dissolving one atom of the less-noble component into the alloy. Thus, measuring the voltage in this electric cell can be used to obtain the activity of the less-noble component (from which the activity of the second component can be calculated from the Gibbs–Duhem equation).

5. The activity can be determined from the phase diagram.

   This method will be considered in detail in Chapter 4.

3.5 Regular solutions

We already noted that in the case of concentrated solutions, it is convenient to describe their properties in terms of how they deviate from those of ideal solutions. Recall, that by definition, the heat of mixing of an ideal solution from its components is zero

$$\Delta H_{\text{mix}} = 0$$

and the entropy of mixing takes the same form as for ideal gases:

$$\Delta S_{\text{mix}} = -nR(x_1 \ln x_1 + x_2 \ln x_2). \tag{3.80}$$

Generally speaking, neither of these expressions are valid for non-ideal solutions. However, it would be difficult to develop a theory that simultaneously accounts for deviations of both ΔH_{mix} and ΔS_{mix} from their ideal values. Of these two, it is the deviation of the enthalpy of mixing from its ideal solution value that is most important for many solutions (e.g. metallic alloys). This is known as the **regular solution** case (discussed originally by Hildebrant and generalized by Guggenheim) and will be considered here (i.e. we will continue to treat the entropy of mixing as per Eq. (3.80)). The opposite case, where the deviation of the entropy of mixing is central (e.g. in polymer solutions), will be the subject of the next section.

Since we already have an expression for the entropy of mixing of regular solutions (Eq. (3.80)), we need only propose an expression for the enthalpy of mixing ΔH_{mix} in order to determine the Gibbs free energy. To do this, we make the following assumptions for the regular solution model:

(1) the interatomic interactions are pairwise (i.e. the energy of the system can be described as a summation of interactions between pairs of atoms plus a constant);
(2) the coordination number, z (the number of the nearest neighbors), is the same in the solution and each of the pure components;
(3) the interaction between atoms is limited to its z nearest neighbors;
(4) the interaction energy associated with a pair of atoms only depends on the type of atoms and not their concentration;
(5) the probability that a given atomic site is occupied by an atom of type i only depends on the concentration of i atoms (independent of the occupancies of its neighbor sites).

Additionally, we make the standard approximation $\Delta H_{\text{mix}} \approx \Delta U_{\text{mix}}$ ($p\Delta V \ll \Delta H$ in condensed phases, as discussed in Section 1.1.4) and arbitrarily define the zero of energy as that of the isolated atoms.

We can calculate the interaction energy of atoms in pure component 1 in the pairwise approximation by writing the interaction energy of an atom with its z nearest neighbor is $z\varepsilon_{11}$ and the total energy of the system as the product of the interaction energy of an atom and the number of atoms, N_1. However, if we blindly follow this approach, we will count each "bond" twice. Therefore, we must divide the result by 2; hence,

$$U_1^0 = \frac{1}{2} N_1 z \varepsilon_{11}.$$

We can follow the same procedure to calculate the energy of the solution. First, consider an atom of component 1. On average, it has zx_1 atoms of component 1 and zx_2 atoms of component 2 as nearest neighbors (see assumption 5, above). Therefore, the contribution to the total energy associated with an atom of component 1 is $\varepsilon_{11}zx_1 + \varepsilon_{12}zx_2$. Analogously, the contribution to the total energy associated with an atom of component 2 is $\varepsilon_{21}zx_1 + \varepsilon_{22}zx_2$. (Since the interaction energy is pairwise, $\varepsilon_{21} = \varepsilon_{12}$). Thus the total energy of solution is

$$U_s = \frac{1}{2}N_1(\varepsilon_{11}zx_1 + \varepsilon_{12}zx_2) + \frac{1}{2}N_2(\varepsilon_{12}zx_1 + \varepsilon_{22}zx_2).$$

Using these results, we can finally propose an expression for the enthalpy of mixing within the regular solution model:

$$\Delta H_{\text{mix}} = U_s - U_1^0 - U_2^0 = \frac{1}{2}N_1zx_1\varepsilon_{11} + \frac{1}{2}N_2zx_2\varepsilon_{22} + \frac{1}{2}(N_1zx_2\varepsilon_{12} + N_2zx_1\varepsilon_{12})$$
$$-\frac{1}{2}N_1z\varepsilon_{11} - \frac{1}{2}N_2z\varepsilon_{22} = \frac{N_1N_2}{N_1+N_2}\frac{z}{2}(2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}).$$

Introducing the notation

$$B_{12} = \frac{zN_{\text{A}}}{2}(2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}) \tag{3.81}$$

we find

$$\Delta H_{\text{mix}} = B_{12}\frac{n_1n_2}{n_1+n_2} = B_{12}(n_1+n_2)x_1x_2, \tag{3.82}$$

where N_{A} is Avogadro's number and n_i is the number of moles of component i. The Gibbs free energy of the regular solution is now simply:

$$G = G^{\text{ideal}} + \Delta H_{\text{mix}} = G^{\text{ideal}} + B_{12}\frac{n_1n_2}{n_1+n_2}, \tag{3.83}$$

where G^{ideal} is the Gibbs free energy of the ideal solution. For the chemical potential of component 1, we find:

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{n_2} = \mu_1^{\text{ideal}} + B_{12}\frac{n_2(n_1+n_2) - n_1n_2}{(n_1+n_2)^2}$$

or

$$\mu_1 = \mu_1^0 + RT\ln x_1 + B_{12}x_2^2. \tag{3.84}$$

Comparing this expression with Eq. (3.69), we obtain:

$$\gamma_1 = \mathrm{e}^{B_{12}x_2^2/RT} \tag{3.85}$$

Note, we have taken the pure components as the standard states.

The magnitude of the parameter, B_{12}, depends on the bond energies ε_{ij} used in the model. Since these are usually not known, B_{12} can be viewed as a parameter of the theory that is determined by fitting to experimental data. Note that B_{12} is the only empirical parameter of this theory (recall that even the theory of ideal dilute solutions has several empirical parameters).

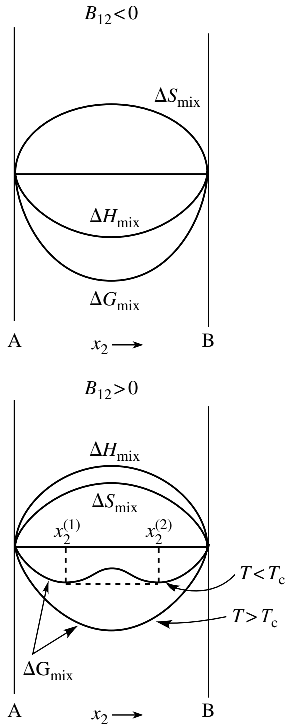

Fig. 3.6
The thermodynamic functions of a regular solution.

Figure 3.6 shows how ΔH_{mix}, ΔS_{mix}, and ΔG_{mix} vary with the molar fraction of the second component. If $B_{12} < 0$ (negative deviation from Raoult's law), the ΔG_{mix} curve appears to be very similar to that for ideal solutions. On the other hand, if $B_{12} > 0$ (positive deviation from Raoult's law), regular solution theory predicts a new feature, which is absent in ideal solution theory. Figure 3.6 shows that at high temperatures ΔG_{mix} has only one minimum (at 0.5), while at low temperatures two minima (at $x_2^{(1)}$ and $x_2^{(2)}$) and one maximum (at 0.5) are present ($x_2^{(1)} \leq 0.5 \leq x_2^{(2)}$). Therefore, if the concentration of the second component lies in the range $x_2^{(1)} \leq x_2 \leq x_2^{(2)}$, the Gibbs free energy of the homogeneous solution is higher than the Gibbs free energy of the heterogeneous system consisting of the two solutions with concentrations of $x_2^{(1)}$ and $x_2^{(2)}$. The free energy of this heterogeneous system does not depend on concentration since the two solutions (of compositions $x_2^{(1)}$ and $x_2^{(2)}$) have the same Gibbs free energy (see the dashed horizontal line in Fig.). A critical temperature T_c exists such that at $T > T_c$, the homogeneous system corresponds to a minimum of the free energy, while at $T < T_c$, the minimum free energy corresponds to a mixture of two solutions with concentrations $x_2^{(1)}$ and $x_2^{(2)}$. In other words, T_c is the temperature below which the system spontaneously separates into a mixture of two solutions. This is known as **phase separation**. How is this critical temperature related to the parameter that defines the regular solution, B_{12}? The existence of phase separation implies that the curvature of the free energy with respect to concentration (i.e. $\partial^2 \Delta G_{\text{mix}}/\partial x^2$) is negative over some composition range (and positive over rest of the composition range). Therefore, we can find the critical temperature by setting $\partial^2 \Delta G_{\text{mix}}/\partial x^2 = 0$:

$$\Delta G_{\text{mix}} = n\{RT[(1-x_2)\ln(1-x_2) + x_2 \ln x_2] + B_{12}(1-x_2)x_2\}$$

$$\frac{\partial \Delta G_{\text{mix}}}{\partial x_2} = n\{RT[-\ln(1-x_2) - 1 + \ln x_2 - 1] + B_{12}(1-2x_2)\}$$

$$\frac{\partial^2 \Delta G_{\text{mix}}}{\partial x_2^2} = n\left\{RT\left[\frac{1}{1-x_2} + \frac{1}{x_2}\right] - 2B_{12}\right\} = 0$$

$$\frac{RTx_2 + RT(1-x_2) - 2B_{12}x_2(1-x_2)}{x_2(1-x_2)} = 0$$

$$2B_{12}x_2^2 - 2B_{12}x_2 + RT = 0.$$

Phase separation can occur provided that this final equation has solutions for physically meaningful values of $0 < x_2 < 1$ Mathematically, we can show that this is satisfied provided that $B_{12} \geq 2RT$ or

$$T_c = \frac{B_{12}}{2R}. \tag{3.86}$$

We shall return to the interesting case of phase separation in Section 4.7.

3.6 Athermal solution model

In this section, we briefly review the athermal solution model. In contrast to the regular solutions, athermal solutions are formed from pure components with no change in energy, that is

$$\Delta H_{\text{mix}} = 0. \tag{3.87}$$

However, the entropy of mixing in an athermal solution is not equal to that in an ideal solution: $\Delta S_{\text{mix}} \neq -nR(x_1 \ln x_1 + x_2 \ln x_2)$. We can define the excess entropy of mixing in an athermal solution as

$$\Delta S_{\text{excess}} = \Delta S_{\text{mix}} + nR(x_1 \ln x_1 + x_2 \ln x_2) \neq 0. \tag{3.88}$$

The corresponding excess Gibbs free energy of mixing (with respect to the ideal mixing case) is

$$\Delta G_{\text{excess}} = -T\Delta S_{\text{excess}}. \tag{3.89}$$

The Gibbs–Helmholtz equation for excess properties takes the following form:

$$\frac{\partial(\Delta G_{\text{excess}}/T)}{\partial T} = -\frac{\Delta H_{\text{excess}}}{T^2}. \tag{3.90}$$

Since Eq. (3.87) asserts that $\Delta H_{\text{excess}} = 0$, Eqs (3.89) and (3.90) imply

$$\frac{\partial \Delta S_{\text{excess}}}{\partial T} = 0, \tag{3.91}$$

for athermal solutions. Differentiating this relation with respect to the number of moles of component i, we find

$$\frac{\partial \Delta \overline{S}_{\text{excess}_i}}{\partial T} = 0. \tag{3.92}$$

Since the activity coefficient is

$$RT \ln \gamma_i = \Delta \overline{G}_{\text{excess}_i},$$

we see that

$$\frac{\partial \ln \gamma_i}{\partial T} = 0. \tag{3.93}$$

Thus, in contrast with regular solutions (see Eq. (3.85)), activities in athermal solutions are temperature independent.

In what circumstances can we expect the entropy of mixing to differ from that of the ideal solution? We need statistical thermodynamics to answer this question. (Statistical thermodynamics is the subject of Chapter 13.) In short, the entropy of mixing is associated with the number of ways the molecules in the system can be arranged. In an ideal solution, the entropy of mixing simply accounts for the replacement of molecule of one type with molecules of another type, with no change in the structure. This is reasonable in situations in which the two types of molecules are of about the same size. On the other hand, if the two types of molecules have very different size, it is not possible to simply switch one molecule with another without changing the structure. This change in structure necessarily implies that there are more ways to arrange the molecules in the solution than in the case where there is no structure change (i.e. the ideal solution). Therefore, the excess entropy of mixing should be positive and the deviation from ideality should be negative. This is indeed observed in experiments for solutions of substances with large molecules in solvents composed of small molecules.

3.7 Ionic solutions

To this point, our discussion focused on solutions of substances for which the molecules are unchanged on going from the pure substance to a solution. This is a broad class of solutions, including such materials as metallic alloys (where the molecules are simply atoms). However, we have already encountered a case where this assumption fails; namely, dissolving a diatomic gas in a metal (where the diatomic molecule frequently dissociates into atoms before going into solution, as discussed in Section 3.2.1). When dissociation occurs, we must use a different form of solution thermodynamics; for example, Sieverts's law rather than Henry's law in the case of a solution of a diatomic gas in metals. In this section, we consider solutions of ions in water, where the situation is even more complicated. First, some molecules can dissociate into multiple (more than two) ions. Second, the interactions between ions are typically long range (electrostatic), implying that such solutions are never ideal. We consider both of these effects below.

We first investigate the effect of the dissociation of the solute on the thermodynamic properties of the solution (we do not yet consider the deviation from ideality related to electrostatic interactions between ions). Consider the following dissociation reaction:

$$\mathrm{B} = \nu_+ B^{z_+} + \nu_- B^{z_-}, \tag{3.94}$$

where z_+q and z_-q are the charges of the positive and negative ions, ν_+ and ν_- are the numbers of these ions formed from the dissociation of one molecule and q is the elementary charge carried by one electron. The values of these parameters are related by the condition that the original molecule is electrically neutral:

$$\nu_+ z_+ + \nu_- z_- = 0. \tag{3.95}$$

If molecules of B exist in the saturated vapor then, by analogy with Sieverts's law, we find

$$p_\mathrm{B} = s(x_{\mathrm{B}^{z_+}})^{\nu_+}(x_{\mathrm{B}^{z_-}})^{\nu_-}. \tag{3.96}$$

In the case of complete dissociation, Eq. (3.94) implies:

$$x_\mathrm{B} = \frac{1}{\nu_+} x_{\mathrm{B}^{z_+}} = \frac{1}{\nu_-} x_{\mathrm{B}^{z_-}} \tag{3.97}$$

where x_B is the molar fraction of B that would be in the solution if no dissociation occurred. The chemical potential of the solute can be found from the condition of equilibrium between the saturated vapor and the solution:

$$\begin{aligned}\mu_\mathrm{B} &= \mu^0_{\mathrm{B}_\mathrm{gas}} + RT \ln p_\mathrm{B} = \mu^0_{\mathrm{B}_\mathrm{gas}} + RT \ln[s(\nu_+ x_\mathrm{B})^{\nu_+}(\nu_- x_\mathrm{B})^{\nu_-}] \\ &= \mu^0_{\mathrm{B}_\mathrm{gas}} + RT \ln[s(\nu_+)^{\nu_+}(\nu_-)^{\nu_-}] + RT(\nu_+ + \nu_-) \ln x_\mathrm{B}.\end{aligned}$$

Using the following notation for the total number of ions arising from the dissociation of a single B molecule

$$\nu = \nu_+ + \nu_-, \tag{3.98}$$

we find

$$\mu_B = \psi_B + \nu RT \ln x_B, \tag{3.99}$$

where ψ_B contains all of the terms in the chemical potential that do not depend on the concentration of B.

In order to derive an expression for the chemical potential of the solvent A, we insert Eq. (3.99) into the Gibbs–Duhem equation (3.16):

$$x_A \frac{\partial \mu_A}{\partial x_A} = x_B \frac{\partial \mu_B}{\partial x_B}$$

$$\int_{\mu_A^0}^{\mu_A} d\mu_A = -\int_0^{x_B} \frac{x_B}{1-x_B} \nu RT \frac{dx_B}{x_B}$$

$$\mu_A = \mu_A^0 + \nu RT \ln(1-x_B)\big|_0^{x_B}$$

$$\mu_A = \mu_A^0 + \nu RT \ln x_A. \tag{3.100}$$

Since the chemical potential of the solvent in the saturated vapor is

$$\mu_A = \mu^0_{A_{\text{gas}}} + RT \ln p_A,$$

the partial pressure of the solvent in the saturated vapor is

$$p_A = p_A^0 (x_A)^\nu. \tag{3.101}$$

Note that this equation implies that Raoult's law never works in ionic solutions (even at very small concentration). However, if we rewrite Eq. (3.101) using the molar fraction of the solvent consistent with the complete dissociation of the solute molecules, x_A^*,[7] we find that Raoult's law is still valid at small concentration. Indeed, at small B concentrations, we can relate x_A^* to x_A as

$$x_A^* = 1 - \sum_i x_{B^i} = 1 - \sum_i \nu_i x_{B^i} = 1 - x_B \sum_i \nu_i = 1 - \nu x_B \approx (1-x_B)^\nu = x_A^\nu$$

and Eq. (3.101) can be rewritten as

$$p_A = p_A^0 x_A^*. \tag{3.102}$$

Equations (3.100) and (3.102) imply that the thermodynamic relations which were derived from the expression for the chemical potential of the solvent in an ideal dilute solution will also be valid in the case of dissociating solutes if we replace R by νR. For example, the change in the freezing

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[7] While $x_A + x_B = 1$ in the solution, when B dissociates into B^{z+} and B^{z-}, we write $x_A^* + x_{B^{z+}} + x_{B^{z-}} = 1$.

temperature induced by the addition of a solute which is soluble in the liquid, but not in the solid solvent, is:

$$\Delta T_{\text{freeze}} = \frac{\nu R\left(T^0_{\text{A,freeze}}\right)^2}{1000q}m = \nu K_f m, \tag{3.103}$$

where K_f is the cryoscopic constant. Unfortunately, experiments show that this equation is not accurate even at very small concentration. The problem is that we derived all of the equations above starting from Eq. (3.96), which is simply the analog of Sieverts's law. But we know that Sievert's law is only valid for non-ionic solutions! Recall that ideal dilute solution theory is based on the fact that at small concentrations, the molecules of the solute do not interact. This cannot be valid in ionic solutions because electrostatic interactions are extremely long ranged. We use the term **ionic solution** to imply a solution in which a solute dissociates into ionic species in a solvent (where the solvent molecules are electrically neutral).

To account for the deviation from ideality arising from electrostatic interaction between the ions in the solution, we must consider the activity. In the case of dissociating molecules, we can consider two types of activity: the activity of the solute molecule and the activities of its ions (formed upon dissociation). Equilibrium between the solute molecules and its component ions implies

$$\Delta G \equiv \nu_+\mu_{\text{B}^{z+}} + \nu_-\mu_{\text{B}^{z-}} - \mu_{\text{B}} = 0$$

$$\mu_{\text{B}} \equiv \psi_{\text{B}} + RT\ \ln\left(a^{\nu_+}_{\text{B}^{z+}}\ a^{\nu_-}_{\text{B}^{z-}}\right) = \psi_{\text{B}} + \nu RT\ \ln\ a_{\pm} \tag{3.104}$$

where the value

$$a_{\pm} = \left(a^{\nu_+}_{\text{B}^{z+}}\ a^{\nu_-}_{\text{B}^{z-}}\right)^{1/\nu}. \tag{3.105}$$

is called the **mean ionic activity**. Analogously we can define the **mean ionic activity coefficient**:

$$f_{\pm} = \frac{a_{\pm}}{x_{\pm}} = \left(f^{\nu_+}_{\text{B}^{z+}}\ f^{\nu_-}_{\text{B}^{z-}}\right)^{1/\nu}, \tag{3.106}$$

where $x_{\pm} = \left(x^{\nu_+}_{\text{B}^{z+}}\ x^{\nu_-}_{\text{B}^{z-}}\right)^{1/\nu}$.

As is always the case, thermodynamics does not itself provide any tools that can be used to determine the activity. Therefore, we must resort to other theories or to experiments. A wide range of experimental data and Debye–Hückel theory (see Section 13.4.4) suggest that the logarithm of the activity coefficient is proportional to the square root of the solute concentration:

$$\ln f_i = L_i\sqrt{x_{\text{B}}}, \tag{3.107}$$

where L_i is independent of the solute concentration, but strongly dependent upon the charge on the ion.[8] Combining this relationship

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[8] Note that $\partial f_i/\partial x_i \rightarrow$ constant in the $x_i \rightarrow 0$ limit for non-ionic solutions considered above. However, Eq. (3.107) shows that $\partial f_i/\partial x_i \rightarrow \infty$ in the $x_i \rightarrow 0$ limit for ionic solutions. Therefore, ionic solutions are never ideal.

with Eq. (3.106), we find

$$\ln f_\pm = L\sqrt{x_\mathrm{B}}. \tag{3.108}$$

Now, we are in a position to derive an expression for the chemical potential of the solvent. Inserting the definition of $x_\pm$ and Eq. (3.97)

$$x_\pm = (\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}\left(x_\mathrm{B}^{\nu_+}\ x_\mathrm{B}^{\nu_-}\right)^{1/\nu} = (\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}x_\mathrm{B},$$

into the expression for the chemical potential (Eq. (3.104)), and making use of Eq. (3.108), we find

$$\mu_\mathrm{B} = \psi'_\mathrm{B} + \nu RT\ \ln x_\mathrm{B} + \nu RT\ \ln f_\pm = \psi'_\mathrm{B} + \nu RT\ \ln x_\mathrm{B} + \nu RTL\cdot\sqrt{x_\mathrm{B}}.$$

The chemical potential of the solvent is easily obtained using the chemical potential of the solute and the Gibbs–Duhem equation

$$x_\mathrm{A}\mathrm{d}\mu_\mathrm{A} + x_\mathrm{B}\left(\frac{\nu RT}{x_\mathrm{B}} + \frac{\nu RTL}{2\sqrt{x_\mathrm{B}}}\right)\mathrm{d}x_\mathrm{B} = 0,$$

which can be integrated to yield

$$\int_{\mu_\mathrm{A}^0}^{\mu_\mathrm{A}} \mathrm{d}\mu_\mathrm{A} = \int_1^{x_\mathrm{A}}\left(\frac{\nu RT}{x_\mathrm{A}} + \frac{\nu RTL}{2}\frac{\sqrt{1-x_\mathrm{A}}}{x_\mathrm{A}}\right)\mathrm{d}x_\mathrm{A}$$

$$\begin{aligned}\mu_\mathrm{A} &= \mu_\mathrm{A}^0 + \nu RT\ln x_\mathrm{A} + \frac{1}{2}\nu RTL\left(2\sqrt{1-x_\mathrm{A}} - \ln\frac{1+\sqrt{1-x_\mathrm{A}}}{1-\sqrt{1-x_\mathrm{A}}}\right)\\ &= \mu_\mathrm{A}^0 + \nu RT\ln x_\mathrm{A} + \frac{1}{2}\nu RTL\left(2\sqrt{x_\mathrm{B}} - \ln\frac{1+\sqrt{x_\mathrm{B}}}{1-\sqrt{x_\mathrm{B}}}\right).\end{aligned}$$

At small solute concentration ($x_\mathrm{B} \ll 1$), this expression reduces to

$$\mu_\mathrm{A} = \mu_\mathrm{A}^0 + \nu RT\left(1 + \frac{1}{3}L\sqrt{x_\mathrm{B}}\right)\ln x_\mathrm{A},$$

which can be rewritten as

$$\mu_\mathrm{A} = \mu_\mathrm{A}^0 + gRT\ \ln\ x_\mathrm{A} \tag{3.109}$$

where

$$g = \nu\left(1 + \frac{1}{3}\ln f_\pm\right). \tag{3.110}$$

Thus, the expression we previously derived for the effects of solute on the freezing temperature (Eq. (3.103)) can be extended to the ionic solution case by replacing ν with g:

$$\Delta T_\mathrm{freeze} = gK_f m \tag{3.111}$$

It is convenient to define a measure of the deviation from ideality as

$$i = 1 - \frac{\Delta T_\mathrm{freeze}}{\nu K_f m}, \tag{3.112}$$

where $i = 0$ implies an ideal solution. Inserting Eqs (3.110) and (3.111) into Eq. (3.112), we find:

$$\nu K_f m(1 - i) = \nu\left(1 + \frac{1}{3}\ln f_{\pm}\right)K_f m$$

or

$$i = -\frac{1}{3}\ln f_{\pm}. \tag{3.113}$$

Equations (3.112) and (3.113) provide a rather simple method to determine the mean ionic activity of a salt dissolved in water. All you have to do is measure the freezing temperature of the solution, find the value of i by using Eq. (3.112), and then apply Eq. (3.113).

Finally we consider the partial pressure of solvent in the saturated vapor over an ionic solution. Repeating the derivation of Raoult's law (see Section 3.2.1) for an ionic solution, we find

$$p_A = p_A^0 (x_A)^g. \tag{3.114}$$

We see that the solvent vapor pressure over an ionic solution differs from that in the non-ionic case in that $g \neq 1$. Even if the solution was not ionic, but resulted from the dissociation of the solute and was ideal, we would find that the exponent g in Eq. (3.114) depends on the type of solute. In this case $g = \nu$, where ν is the number of ions created by the dissociation of the solute (e.g. for NaCl $\nu = 2$ and for Na_2SO_4 $\nu = 3$). However, ionic solutions are never ideal and g also depends on the solute concentration (see Eqs (3.108) and (3.110)). Therefore, the equivalent of Raoult's law for an ionic solution is more complex than a simple power law: $p_A = p_A^0 (x_A)^{g(x_A)}$.

4

Phase equilibria II

4.1 Phase diagrams of two-component systems

In Chapter 2, we considered phase equilibria in a single component system. In the previous chapter, we considered the thermodynamics of multi-component solutions. We are now prepared to discuss phase equilibria in multi-component systems. We consider the case of phase equilibria in a two-component systems in which all phases are condensed (i.e. solids or liquids). Under normal laboratory conditions experience suggests that the free energy of condensed phases is only very weakly dependent on the pressure and, hence, pressure is usually assumed to be constant. At constant pressure, the Gibbs phase rule (Eq. 2.3) for a two-component system takes the following form:

$$F = 3 - P, \tag{4.1}$$

where F is the number of degrees of freedom (i.e. the number of independent parameters that must be set in order to fully determine the state of a system) and P is the number of phases present in equilibrium. This equation implies that the maximum number of independent parameters is 2; corresponding to the single-phase case. The most commonly used parameters are the temperature and the composition of the alloy. $F = 2$ implies that these two parameters can be varied over a finite range while the system remains the same, single phase. If two phases are in equilibrium with each other ($P = 2$), $F = 1$. This implies that the same two phases will be in equilibrium as we vary one parameter (the other parameter is not free). More specifically, we can retain the same two phase equilibrium while varying the alloy concentration over some range, if the temperature is described by some function, $T(x_2)$. $T(x_2)$ describes the curve (locus of points) along which this two-phase equilibrium occurs. Therefore, it is convenient to represent the phase equilibria in two-component condensed systems in T-x_2 coordinates (as done below). Equation (4.1) implies that the maximum number of phases which can be in equilibrium with each other is three. This corresponds to $F = 0$—any change of temperature and/or alloy composition will lead to the disappearance of at least one of the phases.

A phase diagram of a two-component, condensed system is simply the trace of all possible two phase equilibrium curves in temperature–alloy composition space (T-x_2). The ordinate (vertical axis) of the phase diagram is usually chosen to represent the temperature and the abscissa (horizontal axis) represents the alloy composition. The phase diagram provides two main types of information. First, it shows us how many phases are present in equilibrium at any temperature and alloy and, second, it tells us the composition of each phase. If we know the overall alloy composition and the composition of each phase, it is a simple matter to determine the relative amounts of each phase present. This information is not of purely academic interest. In fact, knowledge of the phase composition and the relative amounts of the phases present is central to any description of the structure and properties of an alloy. The phase diagram can also be used to predict how an alloy changes during heating or cooling.

The phase diagrams of real two-component systems can be rather complicated (e.g. see Fig. 4.13). Fortunately, even complicated phase diagrams can be described as a combination of only six fundamental phase diagram types. Each of these fundamental phase diagram types is described separately in the following six sections of this chapter. With this knowledge, we will be prepared to analyze phase diagrams of arbitrary complexity, as done in Section 4.8.

4.2 Type I phase diagrams

The first type of phase diagram we shall consider is the ideal case in which a binary alloy has infinite solubility in the liquid state and zero solubility in the solid state.[1] We shall refer to this as a **Type I phase diagram**. We will start by modeling the liquid as an ideal solution. The chemical potential of component A, therefore, takes the following form:

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^0 + RT \ln x_{\mathrm{A}}.$$

In Section 3.2.3, we demonstrated that a consequence of this assumption is that the freezing temperature (i.e. the temperature at which the first crystals appear upon cooling the liquid solution) satisfies

$$\ln \frac{x_{\mathrm{A_S}}}{x_{\mathrm{A_L}}} = \frac{\Delta H^0_{\mathrm{A,melt}}}{R}\left(\frac{1}{T_{\mathrm{A,freeze}}} - \frac{1}{T^0_{\mathrm{A,freeze}}}\right), \tag{4.2}$$

where we recall that $x_{\mathrm{A_L}}$ and $x_{\mathrm{A_S}}$ are the mole fraction of component A in the liquid and solid, respectively, $T^0_{\mathrm{A,freeze}}$ and $T_{\mathrm{A,freeze}}$ are the freezing temperature in pure A and in the alloy, respectively, and of course $\Delta H^0_{\mathrm{A,melt}}$ is the change in enthalpy upon melting pure A. In contrast with the final formula of Section 3.2.3 ($\Delta T_{\mathrm{freeze}} = K_{\mathrm{f}}(1 - L)m$—valid for an ideal dilute solution), this expression is also valid for an ideal solution. Moreover, since the chemical potentials of all components in an ideal

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[1] Actually, the solubility can never be exactly zero (except at zero temperature). The more realistic case of finite solubility is described in Section 4.4.

solution have the same general form, we can write the same type of relation as in Eq. (4.2) for component B

$$\ln \frac{x_{B_S}}{x_{B_L}} = \frac{\Delta H^0_{B,\text{melt}}}{R}\left(\frac{1}{T_{B,\text{freeze}}} - \frac{1}{T^0_{B,\text{freeze}}}\right). \tag{4.3}$$

Equations (4.2) and (4.3) can also be interpreted in a different light; they indicate the compositions of the solids and liquids which are in equilibrium at any temperature.

If there is no solubility in the solid state ($x_{A_s} = x_{B_s} = 1$), Eqs (4.2) and (4.3) can be rewritten as

$$\begin{aligned} \ln x_{A_L} &= \frac{\Delta H^0_{A,\text{melt}}}{R}\left(\frac{1}{T^0_{A,\text{freeze}}} - \frac{1}{T_{A,\text{freeze}}}\right) \\ \ln x_{B_L} &= \frac{\Delta H^0_{B,\text{melt}}}{R}\left(\frac{1}{T^0_{B,\text{freeze}}} - \frac{1}{T_{B,\text{freeze}}}\right). \end{aligned} \tag{4.4}$$

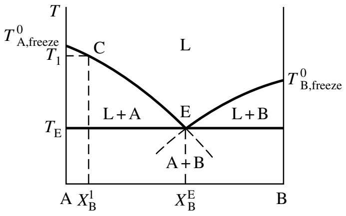

Fig. 4.1
A Type I phase diagram.

From these equations, we obtain two lines $T_{A,\text{freeze}}(x_A)$ and $T_{B,\text{freeze}}(x_B)$. $T_{A,\text{freeze}}(x_A)$ represents the equilibrium between the liquid alloy and solid A and $T_{B,\text{freeze}}(x_B)$ represents the equilibrium between the liquid alloy and solid B (see Fig. 4.1). When $T_{A,\text{freeze}}(x_A) = T_{B,\text{freeze}}(x_B)$, both solids and the liquid alloy are in equilibrium. This special point is labeled E in Fig. 4.1. Such an equilibrium is invariant in the sense that any variation in temperature (or alloy composition) will result in the disappearance of at least one of the phases. Since the solids of the pure components are stable at low temperature, the liquid phase does not exist for $T < T_E$.

Consider the changes in the equilibrium phases present as we cool an alloy of composition 1 from a temperature sufficiently high that the alloy is completely liquid, $T > T_1$ (see Fig. 4.1). As the alloy is cooled through $T = T_1$ (point C in Fig. 4.1), crystals of pure A form within liquid. Recall that Eq. (4.4) implies that T_1 is the temperature at which crystals of A are in equilibrium with the liquid alloy of composition 1. However, when crystals of A appear, the mole fraction of A in the liquid must decrease and, correspondingly, the mole fraction of B in the liquid must increase. An examination of Fig. 4.1 or Eq. (4.4) shows that the freezing temperature decreases with increasing B fraction in the liquid alloy. This implies that freezing of an alloy occurs over a range of temperatures. The alloy described by the phase diagram freezes over a temperature range from T_1 to T_E. In addition, the composition of the liquid varies during freezing from x^1_B to x^E_B, as described by the curve CE. At the temperature T_E, all of the liquid which has not yet solidified does so at the composition x^E_B. The resulting solid consists of a mixture (not a solution) of crystals of pure A and pure B. The horizontal in the phase diagram corresponding to $T = T_E$ separates the two phase A/B solid mixture from the two-phase regions consisting of the liquid phase (L) and crystals of either A or B.

The solidification of the liquid solution at $T = T_E$ can be thought of as a reaction of the form

$$L \rightarrow A + B.$$

This is known as a **eutectic reaction** which occurs at the **eutectic temperature** T_E when the liquid is at the **eutectic composition** x_B^E (see Fig. 4.1). The spatial distribution of the two solid phases (A and B) is described as a **eutectic microstructure**. The curve in the phase diagram above which the alloy is completely liquid is known as the **liquidus** (i.e. this is the curve from the ($x_B = 0$, $T^0_{A,\text{freeze}}$) to (x_B^E, T_E) to ($x_B = 1$, $T^0_{B,\text{freeze}}$)).

All that is necessary to construct a phase diagram of Type I within the framework of ideal solution theory is the melting temperatures and the heats of melting of the pure components. However, ideal solution theory usually does a poor job describing real solutions. We can also use a phase diagram determined from experiment to calculate the activities of the components along the liquidus. Using pure A as the standard state for A, we can write the chemical potential of A as

$$\mu_A = \mu_A^0 + RT \ln a_A.$$

Following the approach used to derive Eq. (4.4), the activity of A in the liquid in the composition range $0 \le x_B \le x_B^E$ can be written as

$$\ln a_{A_L} = \frac{\Delta H^0_{A,\text{melt}}}{R}\left(\frac{1}{T^0_{A,\text{freeze}}} - \frac{1}{T_{A,\text{freeze}}}\right). \tag{4.5}$$

The activity of B in the same composition range can now be determined using this result and the Gibbs–Duhem equation. The activity of B in the composition range $x_B^E \le x_B \le 1$ is (following the same procedure that led to Eq. (4.5))

$$\ln a_{B_L} = \frac{\Delta H^0_{B,\text{melt}}}{R}\left(\frac{1}{T^0_{B,\text{freeze}}} - \frac{1}{T_{B,\text{freeze}}}\right), \tag{4.6}$$

and the activity of A in the same range is given by the Gibbs–Duhem equation. Provided that the partial molar heats of solution are known, the activities of the individual components at any other temperature can be found from Eq. (3.77).

Unfortunately, determination of activities from phase diagrams is seldom reliable because of the experimental uncertainties inherent in determining the location of the curves in most diagrams. However, the same approach can be followed in reverse; that is, the phase diagram is created (or perfected) based upon other measurements of the activities of the components.

There are several experimental approaches that can be used to construct a phase diagram. Kurnakov employed a method based upon measurements of cooling curves (i.e. measurement of the temperature versus time profile within an alloy as it cools from the liquid within a cold, isothermal chamber). You will have the opportunity to determine phase diagrams from cooling curves in Computer Laboratory #1. Consider the reverse problem—predicting the cooling curves from the phase diagram. The most important feature of the cooling curves, for our purposes, is the existence of discontinuities in the slope of the cooling curves which is associated with phase transformations (we shall ignore all other features of the cooling curve). Since we focus only on discontinuities in the slope of the cooling curves, we shall model the shape of these curves as a series of straight segments (see Fig. 4.2). Even more importantly, however, is our assumption that the alloy is in equilibrium at all times during the cooling process (if we cool too quickly the system will not have sufficient time to achieve equilibrium).

We start from the cooling curve for the pure component A (see Fig. 4.2). The segment of the cooling curve labeled I corresponds to cooling liquid A. At the freezing temperature, the number of degrees of freedom is zero; this is the only temperature where the solid and liquid co-exist in a single component system. Although it is difficult to see on the phase diagram, the pure component is a single solid phase below T^0_{freeze}. Therefore, the temperature of the system cannot decrease any further until liquid disappears. The solidification of all of the liquid does not happen instantaneously, but rather requires a finite time—this corresponds to the horizontal segment of the cooling curve, labeled II. This is bizarre! If heat continues to leave the alloy through the walls of the container, you should expect that the alloy will get colder. However, there is a logical explanation. The heat that leaves the alloy through the walls of the container is exactly compensated by the heat generated in the freezing process (recall that the heat of melting is always positive). If we extract heat faster through the walls, the rate of freezing increases and *vice versa*. After the solidification process is complete, the temperature in the alloy resumes falling as we cool the solid A. Such a cooling curve is characteristic of the solidification of all pure components (providing that there are no solid–solid phase transformations). This type of cooling curve also describes the eutectic alloy, where the number of degrees of freedom is also zero at T_E.

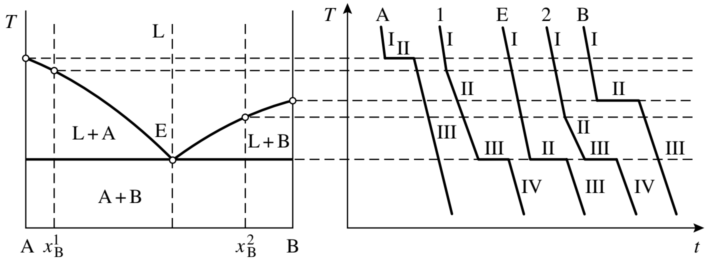

Fig. 4.2
A Type I phase diagram with corresponding cooling curves.

Now, consider the cooling of alloy 1 in Fig. 4.2. Segment I of the cooling curve for this alloy corresponds to the cooling of the liquid (i.e. no phase transformations occur). Segment II reflects the transformation of the liquid to crystals of pure A. While all of a pure A liquid solidifies at one temperature (T^0_{freeze}), the alloy solidifies over a range of temperatures because the liquid composition changes as solidification proceeds. Since the heat extraction through the walls of the container is partially compensated by the generation of heat associated with the liquid–solid transformation, the cooling rate decreases (i.e. the slope of the cooling curve changes, as seen in Fig. 4.2). At the eutectic temperature, the number of degrees of freedom is zero and the cooling curve is horizontal (as described above). At $T < T_{\text{E}}$, the alloy is a mixture of solids, A and B, and no other phase transformations occur (see segment IV). Note, however, the slope of the cooling curve is different in I than in IV because the thermal conductivity of the solid and liquid differ. The cooling curve for alloy 2 is qualitatively similar to that for alloy 1. The main difference between the two cases is the type of solids produced (A versus B).

We now return to the original problem of how to create a phase diagram from cooling curves of different compositions that were obtained from experiment. We focus on temperatures on the cooling curves where the slope changes discontinuously (including the horizontal sections of the cooling curves). Every such point on a cooling curve corresponds to a point on the phase diagram (i.e. each cooling curve is for a known composition and the discontinuities correspond to a particular temperature). Given a sufficient number of cooling curves, we can trace out all of the equilibrium lines on the phase diagram. Computer Laboratory #1 provides you with some experience with this approach to determining phase diagrams.

Example problem

1. The Raoult law is known to accurately describe all Bi–Cd alloys, regardless of the composition. The following data on the pure components were found in handbooks:

$$T^0_{\text{Bi,freeze}} = 544.5\ \text{K}; \qquad \Delta H^0_{\text{Bi,melt}} = 10.88\ \text{kJ/mole}$$
$$T^0_{\text{Cd,freeze}} = 594.2\ \text{K}; \qquad \Delta H^0_{\text{Cd,melt}} = 6.40\ \text{kJ/mole}.$$

   Find the coordinates (temperature and composition) of the eutectic point on the phase diagram.

4.3 Type II phase diagrams

The second type of phase diagram we shall consider is the case in which the binary alloy has infinite solubility in both the liquid and solid states. We shall refer to this as a **Type II phase diagram**. We will start by modeling both the liquid and solid phases as ideal solutions. By analogy with the procedure leading to Eqs (4.2) and (4.3), we obtain the following equations for the phase equilibrium lines:

$$\begin{aligned} \ln \frac{x_{\mathrm{A_S}}}{x_{\mathrm{A_L}}} &= \frac{\Delta H^0_{\mathrm{A,melt}}}{R}\left(\frac{1}{T_{\mathrm{A,freeze}}} - \frac{1}{T^0_{\mathrm{A,freeze}}}\right) \\ \ln \frac{x_{\mathrm{B_S}}}{x_{\mathrm{B_L}}} &= \frac{\Delta H^0_{\mathrm{B,melt}}}{R}\left(\frac{1}{T_{\mathrm{B,freeze}}} - \frac{1}{T^0_{\mathrm{B,freeze}}}\right). \end{aligned} \tag{4.7}$$

Including the condition that the mole fractions of A and B must add to unity in both solid and liquid,

$$x_{\mathrm{A_S}} + x_{\mathrm{B_S}} = 1; \qquad x_{\mathrm{A_L}} + x_{\mathrm{B_L}} = 1, \tag{4.8}$$

we obtain a set of four equations with four unknowns. Solving this set of equations yields two functions, $x_{\mathrm{B_L}}(T)$ and $x_{\mathrm{B_S}}(T)$. The two functions represent the liquidus and **solidus** (i.e. the line below which the entire system is solid) lines, respectively. A prototypical Type II phase diagram and a corresponding cooling curve are shown in Fig. 4.3.

For non-ideal solutions, Eq. (4.7) can be rewritten in the following form:

$$\begin{aligned} \ln \frac{a_{\mathrm{A_S}}}{a_{\mathrm{A_L}}} &= \frac{\Delta H^0_{\mathrm{A,melt}}}{R}\left(\frac{1}{T_{\mathrm{A,freeze}}} - \frac{1}{T^0_{\mathrm{A,freeze}}}\right) \\ \ln \frac{a_{\mathrm{B_S}}}{a_{\mathrm{B_L}}} &= \frac{\Delta H^0_{\mathrm{B,melt}}}{R}\left(\frac{1}{T_{\mathrm{B,freeze}}} - \frac{1}{T^0_{\mathrm{B,freeze}}}\right). \end{aligned} \tag{4.9}$$

However, unlike in the ideal case, there is no condition like Eq. (4.8) in which the mole fractions (or activities) of A and B sum to unity. Instead, we rely on the Gibbs–Duhem relation to provide the two additional equations needed:

$$\begin{aligned} x_{\mathrm{A_S}}\left(\frac{\partial \ln a_{\mathrm{A_S}}}{\partial x_{\mathrm{A_S}}}\right)_{p,T} &= x_{\mathrm{B_S}}\left(\frac{\partial \ln a_{\mathrm{B_S}}}{\partial x_{\mathrm{B_S}}}\right)_{p,T} \\ x_{\mathrm{A_L}}\left(\frac{\partial \ln a_{\mathrm{A_L}}}{\partial x_{\mathrm{A_L}}}\right)_{p,T} &= x_{\mathrm{B_L}}\left(\frac{\partial \ln a_{\mathrm{B_L}}}{\partial x_{\mathrm{B_L}}}\right)_{p,T}. \end{aligned} \tag{4.10}$$

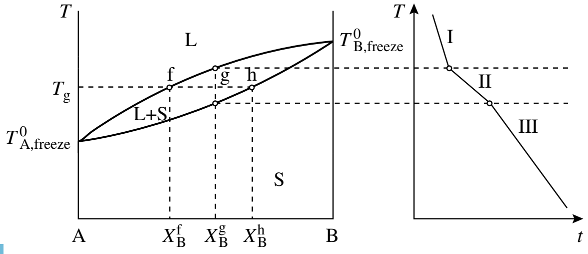

Fig. 4.3
A Type II phase diagram with a corresponding cooling curve.

If the phase diagram is known, Eqs (4.9) and (4.10) can be used to determine the activities along the liquidus and solidus lines.

Figure 4.3 shows the cooling curve for an alloy described by a Type II phase diagram. Segment I of the cooling curve simply corresponds to the cooling of the liquid alloy. Segment II indicates the solid–liquid co-existence region, where heat is extracted from the liquid as it solidifies. This leads to a change in slope, even if there is no change in thermal conductivity. Finally, segment III corresponds to the cooling of the solid solution (no solid–solid phase transformations occur upon cooling below the solidus).

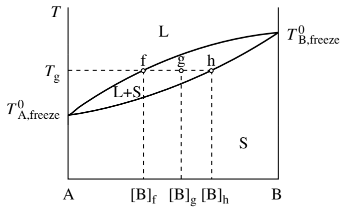

Fig. 4.4
A Type II phase diagram with concentrations expressed in weight fractions.

At the temperature labeled T_g in Fig. 4.4, the alloy consists of two phases: solid and liquid solutions. To find the equilibrium composition of each phase, we draw a horizontal line through point g that terminates on the solidus and liquidus. This line ($\overline{\mathrm{fh}}$) is commonly called a **tie line**. The compositions of the liquid and solid phases are determined by point f (x_B^f) and h (x_B^h), respectively. Frequently, phase diagrams are presented in a form where the horizontal axis is weight fraction (or weight percent) rather than atomic fraction (sometimes both weight and atomic fractions axes are presented).

In this case, we can use the phase diagram to determine the weight fraction of the phases in the alloy and the weight fraction of the components in each phase. The weight fraction of B in the solid and liquid are simply $[\mathrm{B}]_h$ and $[\mathrm{B}]_f$, respectively. The weight fraction of B in the entire alloy can be read off of the axis as $[\mathrm{B}]_g$ or written in terms of the weights of the solid and liquid phases, W_S and W_L:

$$[\mathrm{B}]_g = \frac{[\mathrm{B}]_f W_L + [\mathrm{B}]_h W_s}{W_L + W_S} = \frac{[\mathrm{B}]_f W_L / W_S + [\mathrm{B}]_h}{W_L / W_S + 1}.$$

We can rearrange terms in this equation to determine the weight fraction of the alloy that is liquid as

$$\frac{W_L}{W_{\mathrm{alloy}}} = \frac{[\mathrm{B}]_h - [\mathrm{B}]_g}{[\mathrm{B}]_h - [\mathrm{B}]_f}, \tag{4.11}$$

or in the solid as

$$\frac{W_S}{W_{\mathrm{alloy}}} = \frac{[\mathrm{B}]_g - [\mathrm{B}]_f}{[\mathrm{B}]_h - [\mathrm{B}]_f}, \tag{4.12}$$

where $W_{\mathrm{alloy}} = W_L + W_S$ is the total weight of the alloy. Equations (4.11) and (4.12) are referred to as the **lever rule**. This is an analog of a mechanical lever of length $\overline{\mathrm{fh}}$ with a fulcrum at g which is balanced when the weights at positions f and g are W_S and W_L, respectively.

4.4 Type III phase diagrams

The next type of binary phase diagram we shall consider is the case in which the solubility in the liquid is infinite but is limited in the solids. We shall refer to this as a **Type III phase diagram**. Clearly, this type of phase diagram

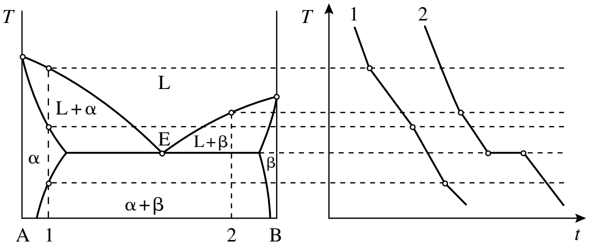

Fig. 4.5
A eutectic Type III phase diagram[2] with corresponding cooling curves.

has features in common with both Type I and Type II phase diagrams. We can distinguish two cases:

(1) the invariant point is below the melting point of both pure components (this is a eutectic diagram);
(2) the invariant point lies between the melting temperatures of the two pure components (this is a peritectic diagram).

Figure 4.5 shows a eutectic phase diagram and two cooling curves corresponding to different alloy compositions. This phase diagram contains three different phases: liquid, solid α and solid β. In solid α, A can be viewed as the solvent and B as the solute and *vice versa* in solid β. The cooling curves exhibit no new features as compared with those for Type I or II diagrams (Figs 4.2 or 4.3). The cooling curve for alloy 1 exhibits no invariant points (i.e. horizontal sections). On the other hand, cooling alloy 2 brings the alloy across the invariant (eutectic) line and, hence, the cooling curve exhibits a horizontal (constant temperature) section at this temperature. The corresponding eutectic reaction is

$$L \rightarrow \alpha + \beta. \tag{4.13}$$

The liquid at the eutectic temperature has composition E (see Fig. 4.5) and the solid solutions (α and β) have compositions corresponding to the left and right ends of the eutectic line, respectively. The lever rule does not apply at the eutectic temperature since the liquid and solid fractions change as the reaction proceeds.[3]

In the case in which the invariant point lies between the melting points of the two pure components (shown in Fig. 4.6), the situation is more complicated. Consider the cooling curve corresponding to an alloy of composition 1. As the alloy is cooled, it goes from a homogenous liquid (I), to a mixture of liquid and solid α (II), to a mixture of liquid and solid β (IV), then to single phase solid β (V), and finally to a mixture of solid α and solid β (VI). Segment III of the cooling curve corresponds to the **peritectic reaction**:

$$L + \alpha \rightarrow \beta. \tag{4.14}$$

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[2] The bottom of this phase diagram corresponds to a finite temperature. The solubility must go to zero at 0 K.

[3] Of course, the phase diagram describes equilibrium and not the kinetics of phase transformation (which is outside the scope of this book).

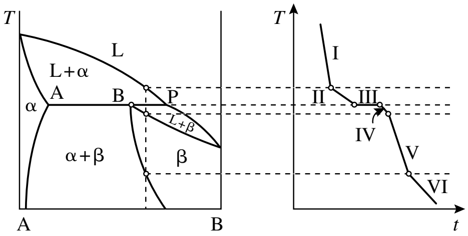

Fig. 4.6
A peritectic Type III phase diagram with a corresponding cooling curve.

During this reaction, the liquid composition is described by point P and the compositions of the α and β solid solutions by points A and B, respectively. Since three phases are in equilibrium, this transition is invariant and is, therefore, represented on the cooling curve by a horizontal line segment. The crystals of α that form first upon cooling the liquid (segment II in the cooling curve) are collectively referred to as primary α, while that which forms upon cooling solid β (segment VI) is referred to as secondary α.

4.5 Type IV phase diagrams

The next type of binary phase diagram we shall consider corresponds to the case in which a compound is present but decomposes at a temperature below the melting point. Such compounds are called **unstable compounds**. We shall refer to this as a **Type IV phase diagram**. Compounds which have a single, distinct composition such as A_2B are known as **stoichiometric** or **daltonide** (Dalton assumed that all chemical compounds have well-defined composition) compounds. Compounds also exist where the composition is variable over a finite range and are known as **non-stoichiometric** or **berthollide** (Berthollet assumed that chemical compounds have variable composition). Usually non-stoichiometric compounds are denoted by Greek letters on phase diagrams, while stoichiometric compounds are commonly represented by their chemical formula. The left diagram in Fig. 4.7 contains a stoichiometric compound A_2B and the one on the right shows a non-stoichiometric compound γ.

Consider the cooling curve corresponding to an alloy in the phase diagram on the right. Upon cooling, the alloy goes from the homogeneous liquid (I) to a liquid/α two-phase system (II), then to two-phase mixtures of liquid and γ (IV), and γ and β (VI). Segment III of the cooling curve corresponds to the peritectic reaction

$$L + \alpha \rightarrow \gamma. \tag{4.15}$$

Segment V represents the eutectic reaction:

$$L \rightarrow \gamma + \beta. \tag{4.16}$$

Finally, we note that cases exist for which the compound is unstable at both high and low temperatures. Figure 4.8 shows such a case for the compound γ.

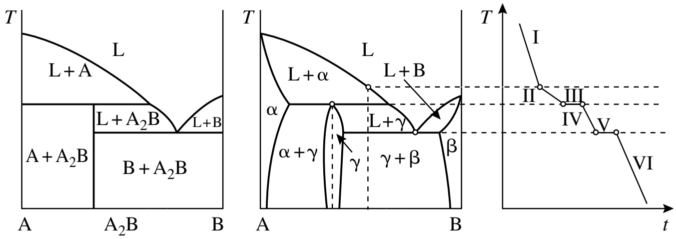

Fig. 4.7
Two Type IV phase diagrams. The left and right phase diagrams show stoichiometric and non-stoichiometric compounds, respectively. A cooling curve is shown corresponding to the phase diagram on the right.

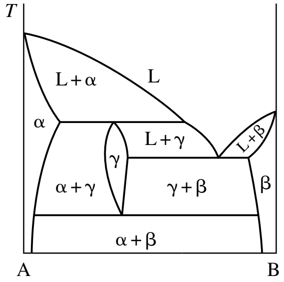

Fig. 4.8
A Type IV phase diagram showing a compound which is unstable at both high and low temperatures.

4.6 Type V phase diagrams

Type V phase diagram describes the case in which a compound is present up to the melting point. Such compounds are called **stable compounds**. The stable compound divides the phase diagram into two parts, each of which can be described as one of the diagrams discussed above (Types I–IV). Two examples of Type V phase diagrams are shown in Fig. 4.9. The left diagram contains two chemical compounds: stable A_2B and unstable AB. This diagram can be represented as one of Type I and one of Type IV. The right diagram, is a combination of two Type III diagrams.

Since Type V phase diagrams can be divided into simpler diagrams, the cooling curves for which were discussed above, we now only discuss the cooling curve for an alloy with the composition of the compound (or for a non-stoichiometric compound, the composition corresponding to the highest temperature for which the compound is a solid). Such a cooling curve is exactly the same as that for a one-component system. The only feature of interest on this cooling curve is the presence of a horizontal segment at the melting point of the compound (see Fig. 4.9).

Before leaving the discussion of phase diagrams which contain a compound which is stable up to the melting point, we point out the existence of an interesting special case, shown in Fig. 4.10. In this diagram, the compound is stable up to the melting point, but unstable at low temperature where it decomposes upon cooling into a two-phase mixture.

4.7 Type VI phase diagrams

The final type of binary (**Type VI**) phase diagram describes binary alloys in which phase separation occurs in either the liquid or solid states. We have already considered phase separation within the framework of the regular solution model (see Section 3.5). Phase separation occurs when it is thermodynamically favorable for the alloy to break into two phases with the same structure but different chemical composition. For example, there exists a critical temperature below which any regular solution with a positive deviation from ideality ($B_{12} > 0$) will separate into two phases. Schematically, such a diagram looks like that shown in Fig. 4.11.

A specific example (the Al–Zn phase diagram) is shown in Fig. 4.12. This diagram shows a case in which solid α separates into two solid solutions of different compositions, α_1 and α_2.

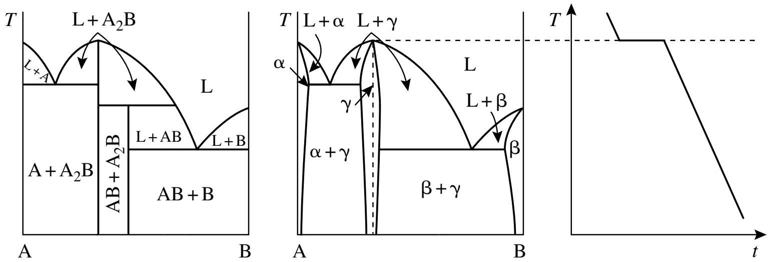

Fig. 4.9
Two Type V phase diagrams. The left diagram shows stoichiometric stable (A_2B) and unstable (AB) compounds and the phase diagram on the right shows a non-stoichiometric stable compound. The cooling curve corresponds to the phase diagram on the right.

4.8 Labeling of one- and two-component regions of a phase diagram

Phase diagrams for most binary alloys can be found in handbooks. Typically, such diagrams only show the phase equilibrium lines and only (some of) the single phase regions are labeled. As a reader, you are expected to know the identity of all of the remaining regions of the diagram. Fortunately, this is not difficult, and with a little practice you can become expert in this. The procedure for labeling binary phase diagrams is outlined below, by reference to the example of the Ce–Ge phase diagram (Fig. 4.13).

The first step is to identify all of the single-phase regions of the diagram by decomposing it into the six fundamental types of diagrams described above. In the Ce–Ge system, we find:

1. A diagram of Type I at small Ge concentration (nearly zero Ge solubility in Ce), as shown in Fig. 4.2.
2. A diagram of Type III at small Ce concentration (finite Ce solubility in Ge), as shown in Fig. 4.5.
3. A diagram of Type IV (unstable, stoichiometric compound) near Ce_4Ge_3, as shown in Fig. 4.7.
4. A diagram of Type IV (unstable, non-stoichiometric compound) near CeGe, as shown in Fig. 4.7.
5. A diagram of Type V (stable, non-stoichiometric compound) near Ce_3Ge_5, as shown in Fig. 4.9.
6. A diagram of Type V (stable, stoichiometric compound) near Ce_5Ge_3, as shown in Fig. 4.9.

The remaining sections of the diagram can be identified with the six basic diagram types described above in an analogous manner. Based upon the coincidence of segments of the Ce–Ge diagram with the basic diagram types, we can deduce all of the single-phase regions of the diagram: liquid (L), Ce (there is negligible Ge solubility so the composition of this phase is nearly pure Ce), the unstable, stoichiometric compounds Ce_3Ge, Ce_4Ge_3, and Ce_5Ge_4, the unstable, non-stoichiometric compound ε (with composition near CeGe), the stable, non-stoichiometric compound δ (with composition near Ce_3Ge_5), and the stable, stoichiometric compound Ce_5Ge_3.

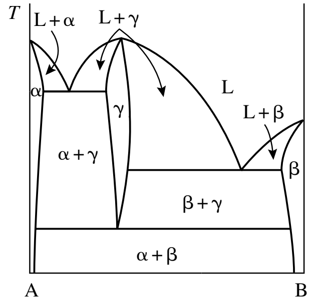

Fig. 4.10
A Type V phase diagram showing a compound which is stable up to melting point but unstable at low temperature.

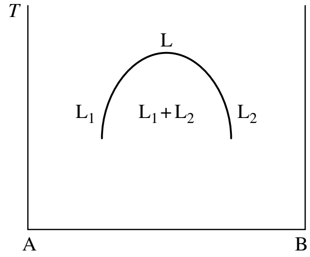

Fig. 4.11
A Type VI phase diagram.

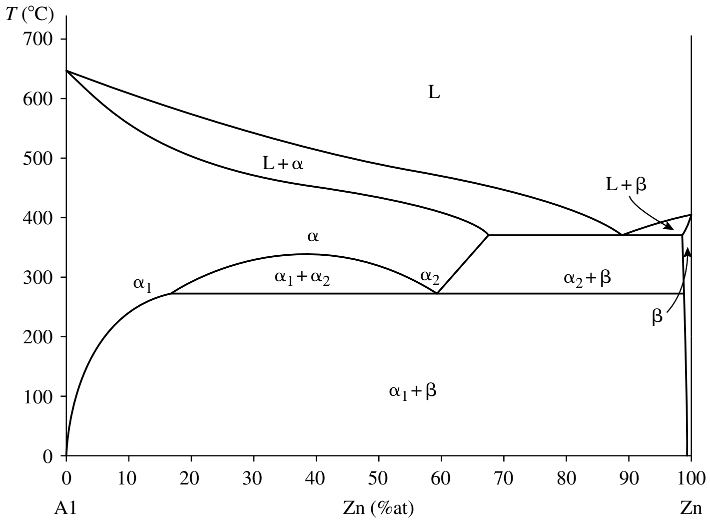

Fig. 4.12
The Al–Zn phase diagram.

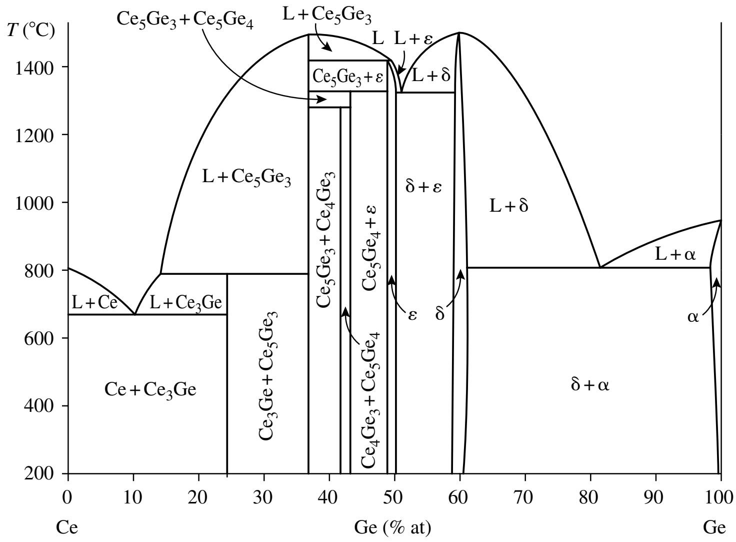

Fig. 4.13
The Ce–Ge phase diagram.

Non-stoichiometric compounds and solid solutions are usually denoted by Greek letters, although solid solutions are, on occasion, denoted as (A) where A is the solvent (e.g. we could write (Ge) instead of α). Stoichiometric compounds are indicated by chemical formulas. However, if the composition of the compound corresponds to an obvious stoichiometry (you need to look at the atomic percent, rather than weight percent scale), a label is often omitted. The table below lists the compositions of the most common stoichiometric compounds:

Compound	Atomic fraction of B (%)	Compound	Atomic fraction of B (%)	Compound	Atomic fraction of B (%)
A_6B	14.3	A_5B_2	28.6	A_4B_3	42.9
A_5B	16.7	A_2B	33.3	A_5B_4	44.4
A_4B	20.0	A_5B_3	37.5	A_6B_5	45.5
A_3B	25.0	A_3B_2	40.0	AB	50.0

After you have identified all of the single-phase regions, it is a simple matter to label all of the two-phase regions. To label the two-phase regions, you must simply remember that single-phase regions are always separated from one another by two-phase regions of the diagram. Each two-phase region is a mixture of the same two phases that make up the neighboring single-phase regions. Therefore, any horizontal line through a phase diagram will go alternately from one phase to two-phase regions. A word of caution: if the one-phase region corresponds to a stoichiometric compound (or a pure component with zero solubility of the other component), it is simply a vertical line in the binary phase diagram.

Before closing this chapter, it is useful to note a simple visual method to distinguish between eutectic and peritectic transformation. Corresponding to each eutectic transformation in the binary-phase diagram is a three-phase stability point where a horizontal line meets a pair of upward directed lines (see Fig. 4.14). On the other hand, a peritectic transformation is characterized by a three-phase stability point where a horizontal line meets a pair of downward-directed lines or one in which the two downward-directed lines are replaced with a single downward-pointing vertical line (e.g. see Fig. 4.7).[4] Finally, we note that if the liquid in the eutectic or peritectic reaction is replaced with a solid, these transformations are called **eutectoid** or **peritectoid** transformations, respectively.

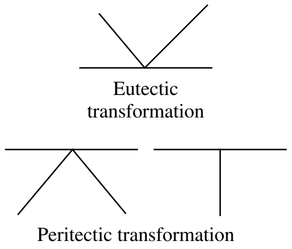

Fig. 4.14
Schematic illustrations of the invariant points corresponding to eutectic and peritectic transformations in a binary phase diagram.

Example problem

1. Label each phase and the constituents of the two-phase regions on the Mn–Si phase diagram (Fig. 4.15). Simply label each phase with a Greek letter (you can choose whichever letters are your personal favorites) or the composition of the compound, respectively.
2. How many phases are in equilibrium at (1) $T = 1000°C$ and 10% Si and (2) $T = 1200°C$ and 35% Si in Mn–Si? What are the compositions of each of the phases you identified?

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[4] You should demonstrate that this is true by inspection of the phase diagrams in Sections 4.2, 4.4–4.6.

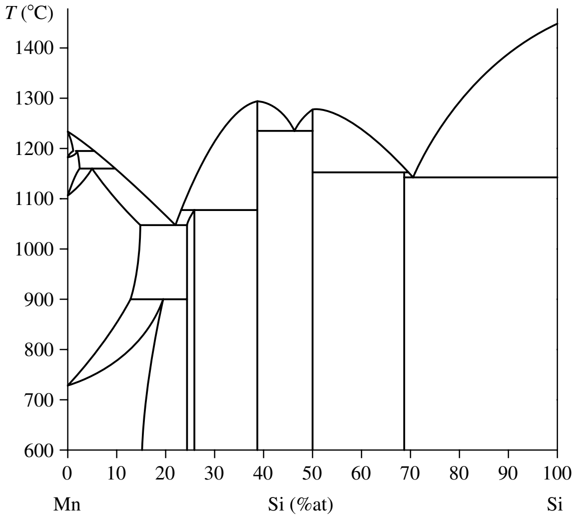

Fig. 4.15
The Mn–Si phase diagram.

3. Draw the cooling curves for Mn–Si alloys with 17% and 80% Si. Describe all of the phase transformations occurring in each segment of the cooling curve.
4. Find the masses of each of the phases and components in each phases at (1) $T = 1000°\mathrm{C}$ and 10% Si and (2) $T = 950°\mathrm{C}$ and 20% Si in 200 g samples of these Mn–Si alloys.
5. What is the minimum amount (mass) of Mn that you must add to a 300 g sample of a Si–Mn alloy containing 60% at $T = 1000°\mathrm{C}$ to make it a single phase alloy (2) same as (1) but add Si instead of Mn.

5

Thermodynamics of chemical reactions

This chapter is devoted to chemical equilibrium. We will use thermodynamics to answer two main questions: (1) “In which direction will a chemical reaction proceed?” and (2) “What is the composition of the system at equilibrium?” These are the oldest and most important questions in all of chemical thermodynamics for obvious reasons. The answers to these questions represent the foundation upon which all modern chemical technologies rest.

5.1 Thermodynamic considerations for chemical reactions

Consider the following chemical reaction:

$$aA + bB \overset{\longleftarrow}{\longrightarrow} cC + dD. \tag{5.1}$$

A, B, C, and D represent the chemical **species** participating in the reaction and *a, b, c*, and *d* are the **stoichiometric coefficients** of these species. We refer to the species on the left side of this chemical equation as **reactants** and those on the right as **products**. The reaction in Eq. (5.1) can either go **forward**, from left to right (reactants to products), or **backward**, from right to left (products to reactants). Therefore, we see that the definition of which we call reactants and which products is arbitrary.

Assume that Eq. (5.1) occurs at constant temperature and pressure. Under these conditions, the direction of the reaction is determined by the sign of the change of the Gibbs free energy. Following Eq. (1.82), we can write the change in free energy as

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B + \mu_C \mathrm{d}n_C + \mu_D \mathrm{d}n_D. \tag{5.2}$$

In a chemical reaction, the variations of the number of moles of each species are not independent since they are related by the stoichiometry of the chemical reaction, namely:

$$-\frac{\mathrm{d}n_A}{a} = -\frac{\mathrm{d}n_B}{b} = \frac{\mathrm{d}n_C}{c} = \frac{\mathrm{d}n_D}{d}.$$

Using these relations, we can rewrite Eq. (5.1) as

$$\mathrm{d}G = (-a\mu_A - b\mu_B + c\mu_C + d\mu_D)\mathrm{d}\chi = \Delta\mu \mathrm{d}\chi, \tag{5.3}$$

at constant temperature and pressure. We shall refer to $\Delta\mu$, defined within Eq. (5.3), as the stoichiometric difference of the chemical potentials of the species in the reaction. The **progress variable** of the chemical reaction χ is related to the number of moles of the species in the reaction as

$$\mathrm{d}\chi = -\frac{\mathrm{d}n_{\mathrm{A}}}{a} = -\frac{\mathrm{d}n_{\mathrm{B}}}{b} = \frac{\mathrm{d}n_{\mathrm{C}}}{c} = \frac{\mathrm{d}n_{\mathrm{D}}}{d}. \tag{5.4}$$

If the reaction proceeds in the forward direction, the progress variable increases ($\mathrm{d}\chi > 0$). We have already seen that the direction in which a reaction (or any other process) spontaneously proceeds at constant temperature and pressure is the same as the direction in which the Gibbs free energy decreases. Therefore, the reaction proceeds in the forward direction provided that

$$\Delta\mu \equiv \left(\frac{\partial G}{\partial \chi}\right)_{T,p} < 0. \tag{5.5}$$

On the other hand, if

$$\Delta\mu \equiv \left(\frac{\partial G}{\partial \chi}\right)_{T,p} > 0, \tag{5.6}$$

the reaction spontaneously proceeds in the backward direction. Finally, in equilibrium, the stoichiometric difference of chemical potentials satisfies

$$\Delta\mu \equiv \left(\frac{\partial G}{\partial \chi}\right)_{T,p} = 0. \tag{5.7}$$

The value $(\partial G/\partial\chi)_{T,p}$ is called the **change of the Gibbs free energy of the chemical reaction**. $(\partial G/\partial\chi)_{T,p}$ is commonly written as ΔG_{T} for the following reason. Consider a case in which the numbers of moles of the species participating in the reaction are so large that their variations by a few moles has practically no effect on their concentration (or partial pressures in the case of gases). In this case, the chemical potentials will not change as the reaction proceeds. This means that $\Delta\mu$ will not change during the reaction and, hence, we can easily integrate $\Delta\mu$ to obtain the change in the free energy as a result of the reaction:

$$\Delta G_T = \int \Delta\mu \mathrm{d}\chi = \Delta\mu \int \mathrm{d}\chi = \Delta\mu\Delta\chi \equiv \left(\frac{\partial G}{\partial \chi}\right)_{T,p} \Delta\chi.$$

For the special case in which $\Delta\chi = 1$, a moles of A and b moles of B have reacted to form c moles of C and d moles of D, and

$$\Delta G_T = \left(\frac{\partial G}{\partial \chi}\right)_{T,p} \equiv \Delta\mu. \tag{5.8}$$

This is why we call $(\partial G/\partial\chi)_{T,p}$ the change of the Gibbs free energy of the chemical reaction, ΔG_T. Analogously, if the reaction occurs at constant temperature and volume, we find:

$$\Delta A_T = \left(\frac{\partial A}{\partial \chi}\right)_{T,V} \equiv \Delta\mu. \tag{5.9}$$

Thus we see that the direction of a reaction and the condition for chemical equilibrium are determined from stoichiometric difference of the chemical potentials.

5.2 Thermodynamics of reactions of gases

We again consider the reaction

$$aA + bB = cC + dD, \tag{5.10}$$

but now we assume that all species are gases. According to Eq. (1.87) the stochiometric difference of the chemical potentials takes the following form

$$\Delta\mu_T = \Delta\mu_T^0 + RT\Delta \ln p_i.$$

Again assuming that the system is large enough that the reactions do not change the partial pressures of the different species (see the discussion leading up to Eq. (5.8) and operating at constant temperature and pressure, we see that the left side of this equation is equal to the change of the Gibbs free energy, ΔG_T. As shown in Eq. (1.84), the chemical potential of the pure component μ_T^0 is equal to the Gibbs free energy per 1 mole, so that we can rewrite Eq. (5.10) as

$$\Delta G_T = \Delta G_T^0 + RT\Delta \ln p_i. \tag{5.11}$$

This expression is called the **van't Hoff isotherm** and is used to determine the direction of a reaction (if $\Delta G_T < 0$ then the reaction proceeds forward, while if $\Delta G_T > 0$ it proceeds backward). Note that the form of Eq. (5.11) is valid if the partial pressure is expressed in atm. ΔG_T^0 is called the **standard change of the Gibbs free energy**; if the reaction occurs at standard conditions (all species are at 1 atm) $\Delta G_T = \Delta G_T^0$. We emphasize again that the direction of the reaction is determined, in general, solely by the sign of ΔG_T (not ΔG_T^0).

Equilibrium is achieved when $\Delta G_T = 0$. Equation (5.11) implies that the partial pressures of the gas phase species satisfy

$$RT \ln \frac{p_C^c p_D^d}{p_A^a p_B^b} = -\Delta G_T^0, \tag{5.12}$$

where we recall that ΔG_T^0 is only a function of temperature. Therefore, the following ratio of the equilibrium partial pressures also depends only on temperature:

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}, \tag{5.13}$$

where K_p is called the **equilibrium constant** which obviously is also a function of temperature alone. Equation (5.13) is called the **law of mass action**. In order to avoid confusion, we remind the reader that while the *instantaneous* partial pressures are used in the van't Hoff isotherm, the *equilibrium* partial pressures should be used in the law of mass action.

Since the van't Hoff isotherm actually uses the dimensionless form of the pressure (i.e. number of atmospheres), the equilibrium constant is always dimensionless. Inserting Eq. (5.13) into Eq. (5.12), we find

$$RT \ln K_p = -\Delta G_T^0. \tag{5.14}$$

Using this relation, we can re-express the van't Hoff isotherm as

$$\Delta G_T = -RT \ln K_p + RT\Delta \ln p_i.$$

The equilibrium constant can be also written in terms of the molar fractions of the species in the reaction or their number of moles:

$$K_p = p^{\Delta\nu} \frac{x_\mathrm{C}^c x_\mathrm{D}^d}{x_\mathrm{A}^a x_\mathrm{B}^b} = \left(\frac{p}{\sum\limits_i n_i} \right)^{\Delta\nu} \frac{n_\mathrm{C}^c n_\mathrm{D}^d}{n_\mathrm{A}^a n_\mathrm{B}^b}, \tag{5.15}$$

where $\Delta\nu$ is the difference of the stochiometric coefficients $(c+d)-(a+b)$ for Eq. (5.10). Since the equilibrium constant does not depend on the total pressure, Eq. (5.15) shows that if $\Delta\nu < 0$, increasing the pressure will produce more products in equilibrium and *vice versa*.

We now examine the temperature dependence of the equilibrium constant. Since the Gibbs–Helmholtz equation takes the form of

$$\left[\frac{\partial (G/T)}{\partial T} \right]_p = -\frac{H}{T^2},$$

we can write the change of the Gibbs free energy for a reaction at standard conditions as

$$\frac{\mathrm{d}(\Delta G_T^0/T)}{\mathrm{d}T} = -\frac{\Delta H_T^0}{T^2}.$$

Combining this equation with Eq. (5.14), yields

$$\frac{\mathrm{d} \ln K_p}{\mathrm{d}T} = \frac{\Delta H_T^0}{RT^2}. \tag{5.16}$$

This equation is called the **van't Hoff isobar** and is useful for solving two types of problems: (1) if we know how the equilibrium constant varies with temperature the van't Hoff isobar tells us the heat of reaction or (2) if we know the heat of reaction and the equilibrium constant at some temperature we can use the van't Hoff isobar to determine the equilibrium constant at any other temperature. Equation (5.16) implies that if the reaction is exothermic (i.e. $\Delta H_T^0 < 0$), increasing the temperature reduces the quantity of products in equilibrium (i.e., the equilibrium shifts toward the reactants).

We can also express the equilibrium constant through the concentrations c_i (usually mole/l in chemical thermodynamics) of the species participating in the reaction. To do this, we use the equation of state for an ideal gas, $p_i V = n_i RT$, which implies $p_i = c_i RT$. Inserting this into Eq. (5.13) gives

$$K_p = \frac{p_\mathrm{C}^c p_\mathrm{D}^d}{p_\mathrm{A}^a p_\mathrm{B}^b} = (RT)^{\Delta\nu} \frac{c_\mathrm{C}^c c_\mathrm{D}^d}{c_\mathrm{A}^a c_\mathrm{B}^b}$$

or

$$K_p = (RT)^{\Delta\nu} K_c \tag{5.17}$$

where

$$K_c = \frac{c_{\mathrm{C}}^{c} c_{\mathrm{D}}^{d}}{c_{\mathrm{A}}^{a} c_{\mathrm{B}}^{b}}, \tag{5.18}$$

is also called the equilibrium constant and depends only upon the temperature. To determine the temperature dependence of K_c, we insert Eq. (5.18) into Eq. (5.16):

$$\frac{\mathrm{d}\ \ln\ K_c}{\mathrm{d}T} = \frac{\mathrm{d}\ \ln\ K_p}{\mathrm{d}T} - \Delta\nu \frac{\mathrm{d}\ \ln\ RT}{\mathrm{d}T} = \frac{\Delta H_T^0}{RT^2} - \frac{\Delta\nu}{T} = \frac{\Delta H_T^0 - \Delta\nu RT}{RT^2}.$$

Using the definition of the heat of reaction at constant volume (Eq. 1.32), we obtain the **van't Hoff isochor**:

$$\frac{\mathrm{d}\ \ln\ K_c}{\mathrm{d}T} = \frac{\Delta U_T^0}{RT^2}. \tag{5.19}$$

Review questions

1. What are the dimensions of the equilibrium constant?
2. Does K_p increase or decrease with increasing temperature if $\Delta H_T^0 > 0$?
3. Can a chemical reaction proceed in the forward direction if $\Delta G_T^0 > 0$?
4. Under what conditions is the equilibrium composition independent of the total pressure?
5. Does the heat of a reaction, in which all of the species are ideal gases, depend on the total pressure?
6. Does $\Delta_S T$, for a reaction in which all species are ideal gases, depend on the total pressure?

Example problems

1. $K_p = 1.00$ at $T = 510$ K for the reaction

   $$PCl_5 \rightarrow PCl_3 + Cl_2.$$

   What fraction of the initial PCl_5 dissociates (degree of dissociation) at a total pressure $p = 9$ atm?
2. $K_p = 1.78$ at $T = 525$ K for the reaction

   $$PCl_5 \rightarrow PCl_3 + Cl_2.$$

   The reaction proceeds at constant volume. Find the total pressure p_0 of an initial equimolar mixture[1] of PCl_3 and Cl_2 if the partial pressure of PCl_5 in equilibrium is $p_{PCl_5} = 0.89$ atm.
3. $K_c = 3.24 \cdot 10^{11}$ at $T = 900$ K for the reaction

   $$H_2 + Cl_2 \rightarrow 2HCl.$$

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[1] That is, a mixture where the numbers of molecules of PCl_3 and Cl_2 are the same.

The degree of dissociation, α, of water at this temperature and $p=1$ atm is $\alpha=2.66\cdot10^{-8}$. Find the equilibrium constant K_p for the reaction at 900 K:

$$4\text{HCl}+\text{O}_2\rightarrow 2\text{H}_2\text{O}+2\text{Cl}_2.$$

4. $K_p=4.2\cdot10^{-5}$ at $T=723$ K for the reaction

$$3\text{H}_2+\text{N}_2\rightarrow 2\text{NH}_3.$$

Find the direction in which this reaction proceeds if $p_{\text{NH}_3}=120$ atm, $p_{\text{H}_2}=80$ atm, and $p_{\text{N}_2}=100$ atm.

5. $K_p=50$ at T = 445°C for the reaction

$$\text{H}_2+\text{I}_2\rightarrow 2\text{HI}.$$

The initial mixture contained 1 mole of iodine and 1 mole of hydrogen. Find the partial pressures of all species in the equilibrium mixture if its volume is 2000 cm^3.

5.3 Thermodynamics of reactions of pure condensed substances

If all species participating in a reaction are in the same phase, the reaction is called **homogeneous**. Such reactions include reactions between species in a gas phase (considered in the previous section) and reactions between species in a solution (considered in the next section). If the species are in different phases, the reaction is called **heterogeneous**.

We begin by considering heterogeneous reactions in which the species in a gas react with a pure liquid or pure solid. As an example, we investigate the decomposition of calcium cyanamide in the presence of water vapor:

$$\text{CaCN}_2+3\text{H}_2\text{O}_{(g)}\rightarrow \text{CaCO}_3+2\text{NH}_{3(g)}.$$

Recall that the chemical potentials of gases and pure condensed substances take the following forms respectively

$$\mu_i=\mu_i^0+RT\ln p_i=G_{Ti}^0+RT\ln\,p_i\quad\text{and}\quad \mu_i\approx\mu_i^0=G_{Ti}^0.$$

Repeating the derivation of the van't Hoff isotherm from the previous section, we find

$$\Delta G_T=\Delta G_T^0+RT\,\ln\frac{p_{\text{NH}_3}^2}{p_{\text{H}_2\text{O}}^3},$$

where $\Delta G_T^0=2G_T^0(\text{NH}_3)+G_T^0(\text{CaCO}_3)-3G_T^0(\text{H}_2\text{O})-G_T^0(\text{CaCN}_2)$ and

$$K_p=\frac{p_{\text{NH}_3}^2}{p_{\text{H}_2\text{O}}^3}.$$

Note that the standard change of the Gibbs free energy, ΔG_T^0, includes all of the species in the reaction (i.e. in gas and condensed phases), while the equilibrium constant only contains terms associated with the gas phase species. The van't Hoff isobar looks exactly the same as it would if all of the species were in the gas phase.

If there are no species in a gas phase in a heterogeneous reaction, the equilibrium conditions cannot be described by the law of mass action. While the direction of a reaction containing species in a gas phase can be changed by a change in the partial pressure, if no gases are present, the direction of the reaction is determined solely by the sign of ΔG_T^0 (recall that we have assumed that pressure has a negligible effect on the free energies of condensed phases). In the latter case, the reactions will proceed to completion. The simplest condensed phase heterogeneous reaction is melting, which can be presented as

$$A_S = A_L.$$

At temperatures below the melting point, this reaction proceeds backward until the system is entirely solid and, at temperature higher than the melting point, it proceeds forward until all of the solid transforms into liquid.

Review question

1. In which direction will a reaction proceed if the quantity of one of the reactants increases in a system that was in equilibrium?

Example problems

1. In which direction does the reaction in Problem 1.1.4.1 proceed at $T = 1100$ K and $p = 5$ atm, if the gaseous mixture has the following composition: 60% CH_4, 30% CO, and 10% H_2O?
2. At $T = 60$°C, the equilibrium constant for the reaction

$$H_2S + I_{2(s)} = 2HI + S_{(s)},$$

   is $K_p = 1.33 \cdot 10^{-5}$. What is the molar fraction of HI in the equilibrium gas mixture at a total pressure $p = 0.1$ atm?

5.4 Thermodynamics of reactions with solutions

We can describe reaction thermodynamics in systems containing solutions by analogy with our discussion of gas phase reactions in Section 5.2. Depending on the type of solution, the chemical potential takes one of the following forms (see Chapter 3):

$$\mu_i = \psi_i + RT \ln c_i$$
$$\mu_i = \mu_i^0 + RT \ln x_i$$
$$\mu_i = \mu_i^{st} + RT \ln a_i.$$

Therefore, either the concentrations or activities of all of the species in a solution that participate in a reaction must be present in the expressions for the van't Hoff isotherm and the equilibrium constant. For example, if all of the species in the reaction

$$aA + bB = cC,$$

are in a non-ideal solution, then the equilibrium constant, the van't Hoff isotherm and isobar take the following forms:

$$K = \frac{a_C^c}{a_A^a a_B^b} \tag{5.20}$$

$$\Delta\mu_i = \Delta\mu_i^{st} + RT\Delta \ln a_i \tag{5.21}$$

$$\frac{d \ln K}{dT} = \frac{\Delta H_i^{st}}{RT^2}. \tag{5.22}$$

Consider the formation of cementite (Fe_3C) from austenite (high temperature Fe–C solid solution):

$$[C] + 3Fe \rightarrow Fe_3C.$$

The van't Hoff isotherm for this reaction takes the following form:

$$\Delta G_T = \Delta G_T^{st} - RT \ln\left[a_{[C]} a_{Fe}^3\right].$$

The standard state for Fe in austenite is usually taken to be pure Fe and that for C is either graphite or the standard solution with unit concentration (this was defined in Section 3.2.1). Depending on the choice of standard state for C, the standard change of the Gibbs free energy takes one of the following forms:

$$\Delta G_T^{st} = G_T^0(Fe_3C) - \psi_{[C]} - 3G_T^0(Fe)$$

$$\Delta G_T^{st} = G_T^0(Fe_3C) - G_T^0(C_{graphite}) - 3G_T^0(Fe).$$

Note that in the last case, the standard change of the Gibbs free energy looks exactly like that for the reaction

$$C_{graphite} + 3Fe \rightarrow Fe_3C.$$

Computer Laboratory #2 provides an opportunity for you to investigate the thermodynamics of this reaction in an Fe–C solution.

Another example of a reaction involving a species in solution is the dissolving of one component of a gas into a condensed solvent. This process can be represented as

$$A_{vapor} \rightarrow [A].$$

The equilibrium constant and the van't Hoff isobar for this reaction take the following form:

$$K = \frac{c_A}{p_A}; \qquad \frac{d \ln K}{dT} = \frac{\dot{H}_{[A]} - H^0_{A_{vapor}}}{RT^2} = \frac{\Delta\bar{H}_A}{RT^2},$$

where $\Delta\overline{H}_A$ is the partial enthalpy of solution of A in the condensed solvent. Comparing the first expression with the Henry law, we see that K is simply the inverse of the Henry constant h. This implies that the temperature dependence of the Henry constant has the following form:

$$\frac{\mathrm{d}\ln h}{\mathrm{d}T} = -\frac{\Delta\bar{H}_A}{RT^2}. \tag{5.23}$$

Review question:

1. Describe the standard conditions for the following reaction: $MnO + H_2 \rightarrow [Mn] + H_2O$.

Example problems

1. At $T = 873$ K and a nitrogen (N_2) partial pressure of $p_1 = 0.01$ atm, the solubility of nitrogen in Co is 0.06%. Will nitrogen dissolve in or evaporate from Co at this temperature if the nitrogen partial pressure is $p_2 = 0.5$ atm and its concentration in Co is 0.5%?
2. A solid Au–Ni alloy with 10% at Ni is exposed to an atmosphere of water vapor at T = 1000 K until equilibrium is achieved. As result, NiO is formed in/on the alloy and the equilibrium mixture contains 0.35% H_2. The following data pertains:

   $$Ni + \tfrac{1}{2}O_2 \rightarrow NiO; \qquad \Delta G^0_{1000} = -149.12\,\mathrm{kJ/mole}$$

   $$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O; \qquad \Delta G^0_{1000} = -192.77\,\mathrm{kJ/mole}.$$

   Find the activity coefficient of nickel in this alloy using pure nickel as the standard state.
3. The temperature dependence of the Henry constant ($p_{Ag} = hx_{Ag}$) for a solution of silver in liquid gold is described by

   $$\ln h = -\frac{40090}{T} + 19.05.$$

   The temperature dependence of the saturated vapor over pure liquid silver takes the following form:

   $$\ln p^0_{Ag} = -\frac{38640}{T} + 18.79.$$

   Find the partial molar enthalpy of solution of pure liquid silver in liquid gold.
4. At $T = 1273$ K, the molar fraction of carbon in austenite in equilibrium with a gaseous mixture of H_2 and CH_4 ($p_{CH_4}/p^2_{H_2} = 0.227 \cdot 10^{-3}$) is $x_{[C]} = 0.233 \cdot 10^{-2}$ and if $p_{CH_4}/p^2_{H_2} = 5.31 \cdot 10^{-3}$, then $x_{[C]} = 4.10 \cdot 10^{-2}$. Find the activity coefficient of carbon in the second alloy, assuming that the first alloy is an ideal dilute solution (use the solution with $x_{[C]} = 1$ as the standard state for carbon).

6

Interfacial phenomena

An interface is a surface across which the phase changes. Interfaces must be present in all heterogeneous systems, such as those discussed above. Interfacial properties necessarily differ from those of the bulk phases since the atomic bonding/structure of an interface represents a compromise between those of the phases on either side of the interface. For example, an atom at a free surface, which is an interface between a condensed phase and a gas (or a vacuum), generally has fewer neighbors with which to bond than it would have if it were in the bulk, condensed phase. In an equilibrium multi-component system, the chemical potential of each species must be the same in all phases, as well as at the interface. Not surprisingly, the chemical composition of the interface will, in general, differ from that of the bulk. For example, molecules in a gas (or solute in a condensed phase) can **adsorb** (**segregate**) onto the surface (interface) of a condensed phase. Interfacial processes play important roles in all areas of materials science and in many (most) areas of modern technology. As the trend toward miniaturization in microelectronics continues and interest in nanoscale structures grows, interfacial phenomena will become even more important. Clearly, the ratio of the number of atoms at surfaces and interfaces to those in the bulk grows as system size decreases (70% of the atoms in a nanometer diameter particle are on a surface!). Therefore, the thermodynamic properties of a system become increasingly dominated by interfacial properties as the dimensions of the system shrink.

We can distinguish several types of interfaces: solid–liquid, liquid–gas, solid–gas, solid phase α–solid phase β, and **grain boundaries**. The meaning of the first four types of interface is self-explanatory. Grain boundaries represent a special class of interfaces; interfaces across which the phase does not change. What does change abruptly across this interface is the spatial orientation of the crystallographic axes. Most crystalline materials are polycrystalline, which means that they are composed of a large number of grains, each with a unique crystallographic orientation with respect to some laboratory frame of reference. We can understand why most solids consist of a large number of distinct grains by considering how a liquid freezes. As the temperature decreases, individual crystalline nuclei form at different places in the liquid. Since one nucleus knows nothing about the other nuclei, it chooses its orientation at random. As more heat is extracted from the system, these nuclei grow to impingement, leaving a solid composed of many differently oriented grains separated by sharp grain boundaries.

6.1 Adsorption of gases

Adsorption is the process in which atoms from a gas (**adsorbate**) impinge upon the surface of a condensed phase (**adsorbent**) and stick there, such that their concentration on the surface is larger than in the gas. In **physical adsorption (physisorption)**, the adsorbate molecules are bonded to the surface by relatively weak (van der Waals) forces and do not form compounds. In **chemical adsorption** (**chemisorption**), the adsorbate molecules form chemical bonds to surface atoms.

We can quantify the degree to which adsorption has occurred as the number of moles of adsorbate per unit area of the adsorbent surface, Γ (moles/cm^2). Other definitions exist in the literature. For example, Γ can be written as the number of moles of adsorbed gas per unit mass of the adsorbent (mole/g) or the volume the adsorbate would occupy if it were in a gas under normal conditions ($T = 0°\mathrm{C}$, $p = 1$ atm) per unit area of the adsorbent (cm^3/cm^2). We will always express Γ in units of moles/cm^2 below.

The main focus of our description of adsorption will be the dependence of Γ on gas pressure at constant temperature—this is known as the **adsorption isotherm**. The adsorption isotherm can be used to determine the surface area of the adsorbent from experiment. Next, we will consider how Γ varies with temperature.

6.1.1 Langmuir isotherm

The **Langmuir isotherm** can be derived on the basis of three postulates:

1. The adsorbent surface has a finite number of independent adsorption sites per unit area, Z, each of which can adsorb only one molecule. In fact, there are three statements in this postulate. First (and obviously), this statement says that the number of sites is limited (i.e. the adsorbent has a finite surface area). Second, independence implies that the probability a site is occupied does not depend on the occupancy of any other site. Third is that each site can be occupied by only a single molecule, such that it is not possible to adsorb one molecule on top of another one. This implies that multi-layer adsorption is not possible.
2. All adsorption sites are equivalent.
3. The adsorbed molecules interact with the surface of the adsorbent (otherwise adsorption will not occur) but not with each other.

We derive the Langmuir adsorption isotherm using the same kinetic approach we used to derive the Henry law (see Section 3.2.1). The main idea underlying this approach is that in equilibrium, the rate of adsorption $\omega_\downarrow$ of molecules onto the surface must be equal to the rate of desorption $\omega_\uparrow$.

We begin by considering the rate of adsorption. In order for a molecule to adsorb onto the surface, it must encounter an unoccupied surface site. The kinetic theory of gases tells us that the number of collisions that gas molecules make with a surface is proportional to the gas pressure (see Section 12.2.9). The probability that a particular collision occurs at an empty adsorption site is proportional to the fraction of unoccupied adsorption sites. If the fraction of occupied sites is θ, the fraction of unoccupied sites is equal to $1-\theta$. Thus, the rate of adsorption can be written as

$$\omega_\downarrow = k_\downarrow p(1-\theta), \tag{6.1}$$

where $\mathrm{k}_\downarrow$ is a constant. The rate of desorption is simply proportional to the number of adsorbed molecules and, therefore, to the fraction of occupied adsorption sites

$$\omega_\uparrow = k_\uparrow \theta, \tag{6.2}$$

where $k_\uparrow$ is also a constant. In equilibrium,

$$\omega_\downarrow = \omega_\uparrow; \qquad k_\downarrow p(1-\theta) = k_\uparrow \theta.$$

We can solve this equation for θ

$$\theta = \frac{bp}{1+bp} \tag{6.3}$$

where

$$b = k_\downarrow / k_\uparrow. \tag{6.4}$$

Since Γ is the number of adsorbates per unit area of the surface, we can express it as the product of the number of sites per unit area, Z and the fraction of sites that are occupied, $\Gamma = Z\theta$. Using this relationship and Eq. (6.3), we find

$$\Gamma = \frac{Zbp}{1+bp}. \tag{6.5}$$

This is the Langmuir adsorption isotherm. In the $p \to 0$ limit, this isotherm reduces to $\Gamma = Zbp$. If we denote $h = Zb$, we see that this isotherm (in the $p \to 0$ limit) is the gas adsorption analogue of the Henry law

$$\Gamma = hp, \tag{6.6}$$

and is called the **Henry adsorption isotherm**.

We now examine the temperature dependence of adsorption within the Langmuir model. We can write the adsorption process as a chemical reaction between molecules in the gas and molecules adsorbed onto the surface:

$$\mathrm{A_{(gas)}} = \mathrm{A_{(ads)}}.$$

At low pressure, the equilibrium between the molecules on the surface and in the gas can be expressed in terms of the equilibrium constant

$$K = \frac{\Gamma}{p} = Zb,$$

where, of course, Z does not depend on temperature. Therefore, inserting this equilibrium constant in the van't Hoff isobar, we find:

$$\frac{\mathrm{d}\ln b}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{ads}}}{RT^2}, \tag{6.7}$$

where ΔH_{ads} is the heat of adsorption. Experiments show that at a given pressure, adsorption decreases with increasing temperature. This can be understood simply: since the van der Waals interactions do not depend on temperature and the kinetic energy of the molecules is proportional to temperature, increasing the temperature provides additional kinetic energy that help molecules escape from the surface (desorb). This experimental observation, when combined with Eq. (6.7), implies that the heat of adsorption ΔH_{ads} is always negative.

Equation (6.5) implies that when $p \to \infty$, $\Gamma \to Z$. This actually follows directly from the first postulate. Since only one gas molecule can adsorb at each site, the maximum value for the adsorption, Γ, must be equal to the total number of sites per unit area, Z. Figure 6.1 shows a typical Langmuir isotherm. The adsorption isotherm is linear at small pressure (this is the Henry law) and saturates at $\Gamma = \mathrm{Z}$ at high pressure. The magnitude of the adsorption depends strongly on temperature at small pressure and it is almost temperature independent at large pressure.

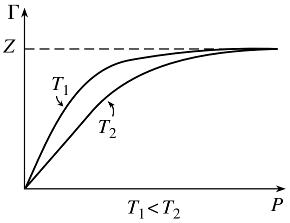

Fig. 6.1
A schematic illustration of the Langmuir adsorption isotherm.

Note that the Langmuir isotherm can be rewritten as

$$\frac{p}{\Gamma} = \frac{1}{Z}p + \frac{1}{Zb}.$$

This equation implies that if the adsorption is described by the Langmuir theory, p/Γ is proportional to the pressure, that is a plot of p/Γ versus p is a straight line.

In practice, pure gases are rare. This suggests that most surfaces are covered with several types of adsorbates. We can describe this situation via Langmuir theory as well. Let θ_i be the fraction of sites occupied by molecules from the gas of type i. By analogy with Eqs (6.1) and (6.2), we can write the rates of adsorption and desorption as

$$\omega_{\downarrow i} = k_{\downarrow i} p_i \left(1 - \sum_j \theta_j\right) \tag{6.8}$$

$$\omega_{\uparrow i} = k_{\uparrow i} \theta_i. \tag{6.9}$$

Introducing $b_i = k_{\downarrow i}/k_{\uparrow i}$ we find:

$$\theta_i = b_i p_i \left(1 - \sum_j \theta_j\right). \tag{6.10}$$

We can determine θ_i from this equation, as follows. We first sum the left and right sides of this equation over i:

$$\sum_i \theta_i = \sum_i b_i p_i \left(1 - \sum_j \theta_j\right) = \sum_i b_i p_i - \sum_i b_i p_i \sum_j \theta_j.$$

Next, we replace the summation index i with j on the left hand side of this expression and rearrange to find:

$$\sum_j \theta_j = \sum_i b_i p_i - \sum_i b_i p_i \sum_j \theta_j; \qquad \sum_j \theta_j = \frac{\sum_i b_i p_i}{1 + \sum_i b_i p_i} = \frac{\sum_j b_j p_j}{1 + \sum_j b_j p_j}.$$

Inserting this result into Eq. (6.10) leads to the final result:

$$\Gamma_i = Z\theta_i = \frac{Z b_i p_i}{1 + \sum_j b_j p_j}. \tag{6.11}$$

This equation shows an interesting effect: increasing the partial pressure of one gas phase species or the introduction of a new species necessarily decreases the concentrations of all other gases on the surface (even if the new species does not interact with the other species!).

Review question

Can the value of Γ be larger than Z in the Langmuir theory?

Example problem

1. Consider the case where diatomic molecules adsorb onto the surface and dissociate into two distinct atoms. Derive the adsorption isotherm using the Langmuir theory postulates. (Hint: it is analogous to the derivation of Sieverts's law in Section 3.2.1).

6.1.2 BET theory for multilayer adsorption

The Langmuir theory provides satisfactory agreement with experimental adsorption data at small and moderate partial pressures of the adsorbate in the gas. However, for the case where the pressure is large, Brunauer demonstrated that this theory is often in poor agreement with experiment. Not surprisingly, the discrepancy occurs where the gas pressure is close to the pressure of the saturated vapor, p_s (i.e. the pressure at which the adsorbate will condense on the adsorbent surface). In other words, in the $p \rightarrow p_s$ limit, $\Gamma \rightarrow \infty$ (i.e. the quantity of condensate on the surface is much larger than that of a completely filled monolayer). The Langmuir theory fails in this case because the first postulate upon which it rests is invalid (i.e. there is more than one adsorbate molecule per surface site). Clearly, a theory capable of describing adsorption at high pressure must allow for multi-layer adsorption. Such a theory was developed by Emmet and extended by Teller (the Brunauer–Emmet–Teller or **BET isotherm**). In multi-layer adsorption, some adsorbate molecules must adsorb upon other adsorbate molecules. This implies that adsorbate molecules must interact with each other (otherwise adsorption of more than a monolayer would not be possible). The description of such molecular interactions is, in general, a very complex problem. The BET theory considers a very limited (and artificial) type of molecular interactions: adsorbed molecules interact with each other along the vertical direction (i.e. normal to the surface—see Fig. 6.2) but not along the horizontal direction (i.e. within the same layer). This type of interaction is motivated solely by mathematical simplicity, rather than by physical insight. The BET theory further assumes that the interactions between molecules in the first and second layer are exactly the same as between those in any other pair of neighboring layers.

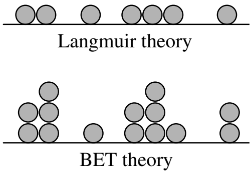

Fig. 6.2
Illustration of monolayer and multilayer adsorption.

We now derive the BET isotherm. Let θ_i be the fraction of the surface adsorption sites above which there are i molecules. Obviously,

$$\sum_{i=0}^{\infty} \theta_i = 1 \tag{6.12}$$

$$\Gamma = Z \sum_{i=0}^{\infty} i\theta_i. \tag{6.13}$$

For the sake of concreteness, we first focus on surface sites that contain only one molecule. There are four distinct processes that affect the value of θ_1: (1) adsorption of a molecule onto an empty adsorbent site, (2) desorption of a molecule from an adsorption site, (3) desorption from the second layer, and (4) adsorption onto the first layer. The principle of detailed balance (see Section 9.5) tells us that processes (1) and (2) must be in equilibrium with each other and process (3) must be in equilibrium with process (4). Both equilibria must yield the same occupancy of layer 1. Therefore, we need only focus on one of these. We consider equilibrium between processes (1) and (2). By analogue with the derivation of the Langmuir isotherm presented in the previous section, we can immediately write

$$\omega_{\downarrow 1} = k_{\downarrow} p \theta_0; \qquad \omega_{\uparrow 1} = k_{\uparrow} \theta_1,$$

where $\omega_{1\downarrow}$ ($\omega_{1\uparrow}$) is the rate of adsorption of molecules from the gas onto empty surface sites (desorption of molecules from sites containing one molecule). Equating the adsorption and desorption rates yields

$$\theta_1 = bp\theta_0, \tag{6.14}$$

where $b = k_{\downarrow} / k_{\uparrow}$. Similarly, for sites containing two molecules, we have:

$$\omega_{\downarrow 2} = k'_{\downarrow} p \theta_1; \qquad \omega_{\uparrow 2} = k'_{\uparrow} \theta_2$$

$$\theta_2 = b' p \theta_1,$$

where the constant $b' = k'_{\downarrow}/k'_{\uparrow}$ is, in general, not equal to b. This inequality results from the fact that adsorption onto an empty surface site depends on the interaction of the adsorbate molecules with the adsorbent surface, while adsorption into a site in the second layer depends on the interactions between adsorbate molecules. Since we assume that the interaction between the adsorbed molecules does not depend on the layer number, we can write

$$\theta_i = b' p \theta_{i-1},$$

for all remaining layers. Inserting expressions for $\theta_{i-1}, \theta_{i-2}, \ldots \theta_1$ in this recursion relation, we find:

$$\theta_i = bp(b'p)^{i-1}\theta_0, \quad \text{for } i \geq 1. \tag{6.15}$$

Using this relation, we can rewrite Eq. (6.12) as

$$1=\sum_{i=0}^{\infty}\theta_i=\theta_0+\sum_{i=1}^{\infty}bp(b'p)^{i-1}\theta_0=\theta_0\left\{1+bp\sum_{i=1}^{\infty}(b'p)^{i-1}\right\}$$
$$=\theta_0\left\{1+bp\frac{1}{1-b'p}\right\}$$

$$\theta_0=\frac{1-b'p}{1+bp-b'p}. \tag{6.16}$$

This is the BET prediction for the fraction of adsorption sites that are empty. The number of moles of adsorbate per unit area of adsorbent, Γ, can then be found by inserting Eqs (6.15) and (6.16) into Eq. (6.13):

$$\Gamma=Z\sum_{i=0}^{\infty}i\theta_i=Z\sum_{i=1}^{\infty}ibp(b'p)^{i-1}\theta_0=Zbp\theta_0\sum_{i=1}^{\infty}i(b'p)^{i-1}$$
$$=Zbp\theta_0\frac{\mathrm{d}}{\mathrm{d}(b'p)}\sum_{i=1}^{\infty}(b'p)^i=Zbp\theta_0\frac{\mathrm{d}}{\mathrm{d}(b'p)}\frac{b'p}{1-b'p}$$
$$=Zbp\frac{1-b'p}{1+bp-b'p}\,\frac{1-b'p+b'p}{(1-b'p)^2}$$

$$\Gamma=\frac{Zbp}{(1+bp-b'p)(1-b'p)}. \tag{6.17}$$

Examination of Eq. (6.17) shows that as $p\to 1/b'$, $\Gamma\to\infty$. Therefore, $b'=1/p_s$ by definition of the saturated vapor pressure (we return to this point in the next Section). Using this identification, we can rewrite Eq. (6.17) as

$$\Gamma=\frac{Zbp}{(1+bp-p/p_s)(1-p/p_s)}. \tag{6.18}$$

This is the BET isotherm. In the $p\to 0$ limit, this isotherm reduces to the Henry isotherm and as $p\to p_s$ it describes condensation. Therefore, this isotherm provides at least a qualitatively correct description of adsorption at any pressure.

If there is no difference between the interactions of the adsorbate molecules with other adsorbate molecules or with the adsorbent surface, $b=b'$. This limit yields the **Emmet isotherm**

$$\Gamma=\frac{Zp/p_s}{1-p/p_s}. \tag{6.19}$$

This isotherm also provides a qualitatively correct description of adsorption at all pressures, but yields somewhat worse quantitative agreement with experimental data than does the BET isotherm.

The BET isotherm can be also rewritten in the following form:

$$\Gamma=\frac{Zgp/p_s}{(1+gp/p_s-p/p_s)(1-p/p_s)} \tag{6.20}$$

where $g = bp_s = b/b'$. If $g > 2$, the BET isotherm has an inflection point, as seen in Fig. 6.3. Both $g > 2$ and $g < 2$ behavior have been seen in experiments. If the number of adsorbate molecules on the surface is approximately equal to the number of available adsorption sites $\Gamma \approx Z$, two types of adsorption are possible, as shown in the two illustrations in Fig. 6.3. If $g > 2$ case and $p \ll p_s$, most of the adsorption sites are occupied by a single molecule and hence the Langmuir isotherm is a good description of the system. If $g < 2$, relatively few adsorbent sites are occupied, but those that are, are occupied by several molecules. The difference between these two is, of course, dictated by whether adsorbate molecules prefer bonding to the adsorbent surface ($g > 2$) or to other adsorbate molecules ($g < 2$).

Finally, we note that Eq. (6.18) can be rewritten in the following form:

$$\frac{p}{\Gamma(1 - p/p_s)} = \frac{1}{Zb}(b - 1/p_s)p + \frac{1}{Zb}. \tag{6.21}$$

If a plot of $p/\Gamma(1 - p/p_s)$ versus p is a straight line, the BET theory provides a good description of the experimental data.

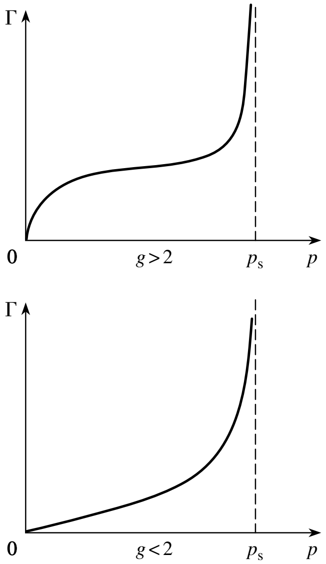

Fig. 6.3
A schematic illustration of the BET adsorption isotherm.

Review questions

1. What is the difference between the physical models of adsorption described by the Langmuir and BET isotherms?
2. Which parameters in the BET isotherm depend on temperature?
3. Can Γ be larger than Z in the BET theory?

Example problems

1. Find the fraction of the free surface sites according to the BET theory if $\Gamma = Z$ and (1) $g = 1$ and (2) $g = 100$.
2. You perform a series of adsorption experiments in which you put a solid adsorbent in a chamber and pass an adsorbate gas through it at fixed temperature and pressure. During the experiment, you measure the change of mass of the sample until it no longer changes in time. Since the change of mass of the sample is simply equal to the mass of the adsorbed gas, you can easily calculate the volume that adsorbed gas would occupy under normal conditions. You obtained the following data:

$T = 250$ K					
p (atm)	0.016	0.032	0.049	0.065	0.081
V (cm^3/g)	80	162	252	352	519
$T = 350$ K					
p (atm)	0.416	0.832	1.248	1.664	2.080
V (cm^3/g)	81	152	231	311	434

The following values for the given adsorbate were found in a standard handbook:

- the area which is occupied by one molecule of the adsorbate on the adsorbent surface is 19.4 Å^2
- $\Delta H_{\mathrm{evap}} = 24.5\,\mathrm{kJ/mole}$
- $T_{\mathrm{boil}} = 300\,\mathrm{K}$.

Show that these results can be described in the framework of the BET theory and find the surface area of the 12 g of the adsorbent and the heat of adsorption.

6.1.3 Capillary condensation

While the BET theory can at least qualitatively account for condensation, it implicitly considers only the case of a flat adsorbent surface (this follows from the assumption that all adsorption sites are equivalent). If the adsorbent surface is not flat, the surface curvature can result in an additional pressure, which can change the saturated vapor pressure (see Section 2.2). Clearly, this change in the saturated vapor pressure will lead to a more complicated adsorption isotherm than that predicted by the BET theory. We now investigate the origin of this effect.

We begin by deriving the additional pressure induced by the surface curvature. For simplicity, we consider an isotropic condensed phase (e.g. glass). Consider the system as composed of a condensed phase and a gas under constant volume and temperature conditions. The differential form of the Helmholtz free energy of the system is (see Eq. (1.67))

$$\mathrm{d}A = -P_{\mathrm{c}}\mathrm{d}V_{\mathrm{c}} - P_{\mathrm{g}}\mathrm{d}V_{\mathrm{g}} - S_{\mathrm{c}}\mathrm{d}T - S_{\mathrm{g}}\mathrm{d}T + \sigma \mathrm{d}a, \tag{6.22}$$

where σ is the surface tension and da is an element of surface area. The last term in this equation gives the increase of the free energy associated with increasing the area of the condensed phase–gas interface (see the next Section for more details). We use P to represent the pressure, rather than the saturated vapor pressure. At equilibrium $\mathrm{d}A = 0$. Since T and V are fixed, $\mathrm{d}T = 0$ and $\mathrm{d}V_{\mathrm{c}} = -\mathrm{d}V_{\mathrm{g}}$. Therefore, we obtain the following equation for the additional pressure:

$$P = P_{\mathrm{c}} - P_{\mathrm{g}} = \sigma \frac{\mathrm{d}a}{\mathrm{d}V_{\mathrm{c}}}. \tag{6.23}$$

In the case of a spherical pore in a solid $\mathrm{d}a/\mathrm{d}V = -(\mathrm{d}a/\mathrm{d}r)/(\mathrm{d}V/\mathrm{d}r) = -\mathrm{d}(4\pi r^2)/\mathrm{d}(4\pi r^3/3)$, where r is the sphere radius. Hence,

$$P_{\mathrm{sphere}} = -\frac{2\sigma}{r}. \tag{6.24}$$

In the case of a cylindrical pore in a solid $\mathrm{d}a/\mathrm{d}V = -(\mathrm{d}a/\mathrm{d}r)/(\mathrm{d}V/\mathrm{d}r) = -\mathrm{d}(4\pi rL)/\mathrm{d}(\pi r^2 L)$, where L is the cylinder length, such that

$$P_{\mathrm{cylinder}} = -\frac{\sigma}{r}. \tag{6.25}$$

Inserting Eqs (6.24) and (6.25) into Eq. (2.11), we obtain the following expression for the saturated vapor pressure inside spherical and cylindrical pores

$$p_{\text{sphere}} = p_{\text{s}} \mathrm{e}^{-2\sigma V_m/rRT} \tag{6.26}$$

$$p_{\text{cylinder}} = p_{\text{s}} \mathrm{e}^{-\sigma V_m/rRT}. \tag{6.27}$$

A flat surface corresponds to $r \to \infty$ and $p_{\text{sphere}} = p_{\text{cylinder}} = p_{\text{s}}$. Note that (1) the saturated vapor pressure in a spherical pore is smaller than that in a cylindrical pore of the same radius and (2) the saturated vapor pressures inside spherical and cylindrical pores are identical for $r_{\text{sphere}} = 2r_{\text{cylinder}}$. (Physically, this is because a sphere is curved in two directions and a cylinder only in one.) In what follows, we rely on only these two facts.

Consider the case of adsorption onto the surface of a conical pit, as shown in Fig. 6.4. Multi-layer adsorption first leads to the formation of a thin film on the entire solid surface. Then, a (spherical) meniscus forms, as shown in Fig. 6.4. This occurs for any pressure $p > p_{\text{s}} \mathrm{e}^{-2\sigma V_m/rRT}$ (r is the meniscus radius). The conical pit will continue to fill with condensate until a meniscus radius is obtained for which $p = p_{\text{s}} \mathrm{e}^{-2\sigma V_m/rRT}$. Condensation begins at the bottom of the pit at a vapor pressure that is nearly zero. As the pressure increases, the pit fills to a greater height. This will continue until the condensate fills the entire pit. When the meniscus goes around the corner, its radius of curvature must necessarily increase. Therefore, the saturated vapor pressure increases and we must raise the pressure of the gas in order to continue the condensation process. The adsorption isotherm, Γ versus p, for the conical pore is shown in Fig. 6.4. The steeply sloped section is associated with filling the conical pore over a range of pressures. The following section with a smaller slope corresponds to increasing the pressure as the meniscus goes around the corner. If we reduce the pressure, we simply traverse the adsorption isotherm in the reverse direction (i.e. the desorption isotherm).

We now consider a cylindrical pore that is closed at the bottom, as shown in Fig. 6.5. Once the gas starts condensing at the bottom of this pore, a hemispherical meniscus forms (for simplicity, focus on the perfect wetting case). The meniscus has a radius of curvature equal to that of the radius of the cylinder (see Fig. 6.5). The saturated vapor pressure adjacent to the wall of the cylindrical pore exceeds that adjacent to the hemispherical meniscus, $p_{\text{cylinder}} > p_{\text{sphere}}$. Once the meniscus forms and extends into the cylindrical section of the pore, condensation will continue—raising the meniscus at fixed $p = p_{\text{sphere}}$. Since the radius of curvature of the cylinder (and hence the meniscus) does not change as the condensate level rises, the pore will continue filling at $p = p_{\text{sphere}}$ until it reaches the edge of the pore (i.e. the surface). The adsorption isotherm for the closed cylindrical pore is shown in Fig. 6.5. The vertical section at $p = p_{\text{sphere}}$ is associated with filling the cylinder at fixed pressure and the remainder of the isotherm is as described above for the conical pore.

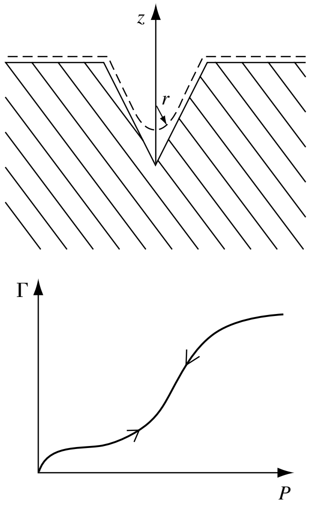

Fig. 6.4
A partially filled conical pore and the corresponding adsorption isotherm. Note that the meniscus radius is a function of the height of the meniscus above the bottom of the pore.

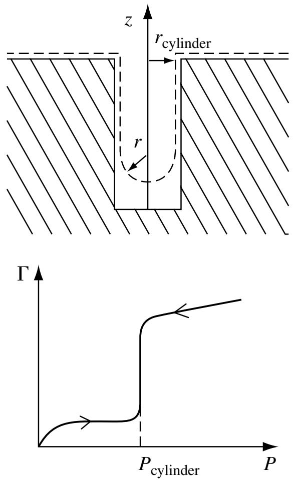

Fig. 6.5
A partially filled cylindrical pore (closed at one end) and the corresponding adsorption isotherm. Note that in this case the meniscus radius $r = r_{\text{cylinder}}$ does not depend on the meniscus height.

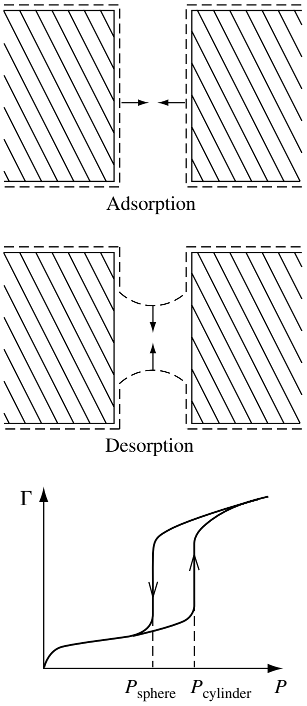

Fig. 6.6
A cylindrical pore that is open at both ends and the corresponding adsorption isotherm.

We now consider the interesting case of a cylindrical hole, open at both ends, as shown in Fig. 6.6. At low pressure, the cylindrical hole interior is not filled, but rather has an adsorbate layer covering its walls (Fig. 6.6). As the pressure increases, the thickness of the adsorbate layer slowly increases until the critical pressure, p_{cylinder}, is achieved and the cylindrical hole fills (Fig. 6.6). This occurs because as we decrease the cylinder radius, we decrease the saturated vapor pressure in accordance with Eq. (6.27) and, hence, increase the tendency for condensation. After filling the pore (Fig. 6.6), two spherical menisci form on its end with the radius $r = r_{\text{sphere}} = 2r_{\text{cylinder}}$ (in order to keep equilibrium with the adsorbate in the gas phase). Increasing pressure will lead to the decreasing of the curvature of the menisci and some additional adsorption. When the pressure is reduced, desorption begins by reversibly decreasing the radius of the menisci. However, as $p = p_{\text{sphere}}$, the menisci move towards the center of the cylindrical hole (Fig. 6.6). This continues until the two menisci meet and we once again have an adsorbate geometry as in Fig. 6.6. The adsorption–desorption isotherm is shown in Fig. 6.6. The vertical jump observed in the isotherm upon adsorption occurs at $p = p_{\text{cylinder}}$ and that observed upon desorption occurs at $p = p_{\text{sphere}}$. Therefore, the isotherm is multi-valued (hysteretic) and the observed branch differs according to whether adsorption or desorption is occurring.

Since no surface of any real material is perfectly flat, adsorptions isotherms that show features similar to those in Figs 6.4–6.6 are the rule, rather than the exception. The geometries of Figs 6.4 and 6.5 are associated with pores, pits, or damage. Geometries such as seen in Fig. 6.6 can be associated with the presence of thin channels between interior pores. Surface profiles other than those considered here explicitly are routinely observed. Therefore, the adsorption–desorption isotherms of real surfaces are complex and often hysteretic. Isotherms such as that shown in Fig. 6.7 are common.

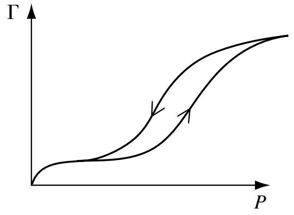

Fig. 6.7
An adsorption isotherm for an adsorbent on a surface containing all of the features of those shown in Figs 6.4–6.6.

6.2 Gibbs interfacial thermodynamics

In this section, we consider the thermodynamic description of interfaces developed by Gibbs. First, we will give a precise definition of an interface. While this may seem to be a trivial issue, it is not. Indeed, consider some extensive property X, with bulk density x (for homogeneous regions of the system, $x = X/V$). Figure 6.8 shows a possible dependence of x on z, where z is the coordinate in the direction normal to the interface. In this plot, the property x varies over some distance as we go through the interface from phase α to phase β. Interestingly, the value of x need not be constrained to the range from x^{α} to x^{β}, where these values represent the bulk values of x. Where is the interface in this figure? Is it at a single location or does it extend over a finite range? The answers to these questions are not obvious and depend on the definition of the interface employed.

Gibbs proposed to answer these questions by arbitrarily assuming that the interface is located at $z = z_0$ and then introduced the following definitions:

1. Both phases are homogeneous, right up to the interface.
2. The interface is perfectly sharp (i.e. of infinitesimal thickness). This implies that the volume of the entire system is simply the sum of the volumes of the two phases

$$V = V^{\alpha} + V^{\beta}. \tag{6.28}$$

3. The interface is homogeneous in all directions perpendicular to z.

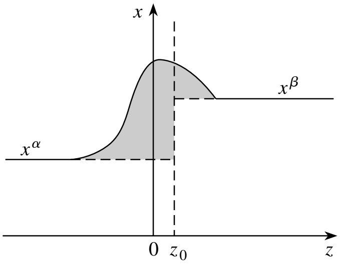

Fig. 6.8
The variation of the density of an extensive property X with distance across an interface.

Examination of Fig. 6.8 shows that condition 1 is violated (i.e. there is a variation in property x within phases α and β near the interface). Therefore, an extensive property of the system, X, cannot be represented by an expression of the form $x^{\alpha}V^{\alpha} + x^{\beta}V^{\beta}$. In order to rectify this deficiency, Gibbs proposed the existence of an **interfacial excess** X^{I}, such that

$$X = x^{\alpha}V^{\alpha} + x^{\beta}V^{\beta} + X^{\mathrm{I}}. \tag{6.29}$$

Since the interface is homogeneous, it is convenient to normalize the interfacial excess by the interface area

$$x^{\mathrm{I}} = \frac{X^{\mathrm{I}}}{a}, \tag{6.30}$$

where x^{I} is the **interfacial excess density**.

For any extensive property, we can always write

$$X = \int_V x\,\mathrm{d}V = \int_{V^{\alpha}} x\,\mathrm{d}V + \int_{V^{\beta}} x\,\mathrm{d}V.$$

Inserting this expression into Eq. (6.29), we find

$$X^{\mathrm{I}} = X - x^{\alpha}V^{\alpha} - x^{\beta}V^{\beta} = \int_{V^{\alpha}} x\,\mathrm{d}V + \int_{V^{\beta}} x\,\mathrm{d}V - x^{\alpha}\int_{V^{\alpha}} \mathrm{d}V - x^{\beta}\int_{V^{\beta}} \mathrm{d}V.$$

$$= \int_{V^{\alpha}} (x - x^{\alpha})\mathrm{d}V + \int_{V^{\beta}} (x - x^{\beta})\mathrm{d}V$$

The integrands in the final expression are non-zero only near the interface. Near the interface, we can use the following expression for the differential volume $\mathrm{d}V = \mathrm{d}a\mathrm{d}z$, where a is the interface area. Using this expression, the last equation can be written as

$$x^{\mathrm{I}}a = X^{\mathrm{I}} = \int_{-\infty}^{z_0} (x - x^{\alpha})\mathrm{d}z \int \mathrm{d}a + \int_{z_0}^{\infty} (x - x^{\beta})\mathrm{d}z \int \mathrm{d}a.$$

Since the interface is homogeneous, the integral over da can be replaced by the interface area a. Thus,

$$x^{I} = \int_{-\infty}^{z_0} (x - x^{\alpha})\mathrm{d}z + \int_{z_0}^{\infty} (x - x^{\beta})\mathrm{d}z \tag{6.31}$$

Equation (6.31) implies that the shaded area in the x-z plot of Fig. 6.8 is equal to the interfacial excess density, x^{I}.

We can use the definition of the interfacial excess density (Eq. (6.31)) to derive several important relationships. Consider two extensive properties, X and Y. Equation (6.31) implies that:

(1) if $X = Y$ then $x^{\mathrm{I}} = y^{\mathrm{I}}$;
(2) $(ax + by)^{\mathrm{I}} = ax^{\mathrm{I}} + by^{\mathrm{I}}$, where a and b are constants;
(3) if $X = \partial Y/\partial T$, then $X^{I} = \partial Y^{I}/\partial T$.

We now consider the interfacial excess of several specific extensive thermodynamic properties. First, consider the number of moles of component i. Equation (6.29) implies that

$$n_i = c_i^{\alpha} V^{\alpha} + c_i^{\beta} V^{\beta} + n_i^{I}. \tag{6.32}$$

Γ_i is the interfacial excess density of the number of moles of component i, defined as $\Gamma_i = n_i^{I}/a$, or

$$n_i = c_i^{\alpha} V^{\alpha} + c_i^{\beta} V^{\beta} + \Gamma_i a. \tag{6.33}$$

Note that this definition of Γ_i differs from that given in Section 6.1, where we defined Γ_i as number of moles of adsorbate on the adsorbent interface. Here, Γ_i is defined as the number of moles of component i in the system minus that which would be present if the bulk phases were each homogeneous up to the interface.

The interfacial excess of the thermodynamic function, U, H, A, and G, can be derived from their differentials with an added term to account for the presence of the interface. Consider the differential of the internal energy of a system with no interfaces (Eq. 1.78)

$$\mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i. \tag{6.34}$$

When interfaces are present, we must add an additional term that corresponds to the reversible work of increasing the interface area:

$$\delta W_{\text{int}} = -\sigma\,\mathrm{d}a. \tag{6.35}$$

The minus sign is chosen in order to keep σ positive for the physical case in which increasing the interface area increases the energy of the system (negative σ in this context implies that the system would be unstable—will create an infinite amount of interface). σ is known as the **interface tension**. Since the work appears on the right-hand side of Eq. (6.34) with a minus sign, we obtain:

$$\mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i + \sigma\,\mathrm{d}a. \tag{6.36}$$

Consider the formation of an interface at constant temperature, volume, and composition (this implies that the chemical potentials are also constant). In this case, Eq. (6.36) can be rewritten as:

$$\mathrm{d}\left(U - TS - \sum_{i=1}^{k} \mu_i n_i\right) = -S\,\mathrm{d}T - p\,\mathrm{d}V - \sum_{i=1}^{k} n_i \mathrm{d}\mu_i + \sigma \mathrm{d}a.$$

We can define a new thermodynamic function from this as

$$\Omega = U - TS - \sum_{i=1}^{k} \mu_i n_i = A - \sum_{i=1}^{k} \mu_i n_i, \tag{6.37}$$

which is called the **Gibbs grand potential**. The differential form of this function is:

$$\mathrm{d}\Omega = -S\,\mathrm{d}T - p\,\mathrm{d}V - \sum_{i=1}^{k} n_i\,\mathrm{d}\mu_i + \sigma\,\mathrm{d}a. \tag{6.38}$$

The interfacial excess of the Gibbs grand potential is the term that is proportional to da in Eq. (6.38):

$$\left(\mathrm{d}\Omega^{\mathrm{I}}\right)_{T,V,\mu_i} = \sigma\,\mathrm{d}a.$$

Integrating both sides of this equation and taking into account the homogeneity of the interface we obtain

$$\int_0^{\Omega^{\mathrm{I}}} \mathrm{d}\Omega^{\mathrm{I}} = \int_0^{a} \sigma \mathrm{d}a$$

or

$$\Omega^{\mathrm{I}} = \sigma a. \tag{6.39}$$

Hence, the interface tension is the interfacial excess of the Gibbs grand potential. In the bulk, the interfacial potential can be written as (using Eqs (3.10) and (6.37))

$$\Omega^{V} = U - TS - \sum_{i=1}^{k} \mu_i n_i = A - G = A - (A + pV).$$

This implies that

$$\Omega^{V} = -pV. \tag{6.40}$$

Now we can express the excess of all other extensive properties through the interface tension and the interfacial excess density of the number of moles of the alloy components. For the Helmholtz free energy we obtain:

$$A^{\mathrm{I}} = \left(\Omega + \sum_{i=1}^{k} \mu_i n_i\right)^{\mathrm{I}} = \Omega^{\mathrm{I}} + \sum_{i=1}^{k} \mu_i n_i^{\mathrm{I}}$$

$$A^{\mathrm{I}} = a\left(\sigma + \sum_{i=1}^{k} \mu_i \Gamma_i\right). \tag{6.41}$$

Since $G = A + pV$ and $V^{\mathrm{I}} = 0$ (see Eq. (6.28)), we find

$$G^{\mathrm{I}} = A^{\mathrm{I}}. \tag{6.42}$$

Equations (6.38) and (6.39) imply

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu_i,a} \quad \text{and} \quad S^{\mathrm{I}} = -\left(\frac{\partial \Omega^{\mathrm{I}}}{\partial T}\right)_{V,\mu_i,a}$$

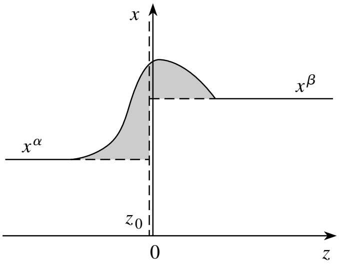

Fig. 6.9
The interface position can be chosen such that the interface excess density of a given extensive property X is zero.

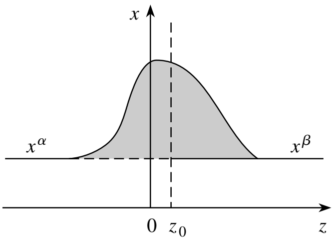

Fig. 6.10
The density of an extensive property X as function of distance across a grain boundary.

such that

$$S^{\mathrm{I}} = -a\frac{\partial \sigma}{\partial T}. \tag{6.43}$$

Inserting Eqs (6.41) and (6.43) into the standard expression for the internal energy $U = A + TS$ yields

$$U^{\mathrm{I}} = a\left(\sigma + \sum_{i=1}^{k}\mu_i\Gamma_i - T\frac{\partial \sigma}{\partial T}\right). \tag{6.44}$$

Finally, since $H = U + pV$ we find

$$H^{\mathrm{I}} = U^{\mathrm{I}}. \tag{6.45}$$

Although the interfacial excesses depend upon the choice of the interface position z_0, the relationships between them do not depend on z_0 (recall we made no assumptions about the interface position in deriving Eqs (6.41–6.45). We can unambiguously locate the position of the interface by fixing the value of the excess of one of the properties (provided, of course, that its value depends on the choice of the interface location). For example, the interface position would be fixed by asserting that $\Gamma_i = 0$ as shown in Fig. 6.9, or $\sum_{i=1}^{k}\Gamma_i = 0$.

In the special case of $x^\alpha = x^\beta$, the value of the interfacial excess does not depend on interface position (see Fig. 6.10). For example, at equilibrium, $p^\alpha = p^\beta$. Equation (6.40) shows that p is minus the bulk density of the Gibbs grand potential. Therefore, the interfacial excess density of the Gibbs grand potential (surface tension—see Eq. 6.39) does not depend on the choice of the interface location. Of course, the condition $x^\alpha = x^\beta$ is always satisfied in the case of a grain boundary such that the excesses of all extensive properties do not depend on the choice of the grain boundary location.

Since the interfacial excesses of all extensive properties can be expressed through σ and Γ_i, it is useful to inquire whether σ and Γ_i can be related. We can divide the Gibbs grand potential into bulk and interface parts such that $d\Omega = d\Omega^V + d\Omega^{\mathrm{I}}$. Making this division using Eq. (6.38) we have

$$\mathrm{d}\Omega^V = -S^V\mathrm{d}T - p\mathrm{d}V - \sum_{i=1}^{k} n_i^V\mathrm{d}\mu_i$$

$$\mathrm{d}\Omega^{\mathrm{I}} = -S^{\mathrm{I}}\mathrm{d}T - \sum_{i=1}^{k} n_i^{\mathrm{I}}\mathrm{d}\mu_i + \sigma\,\mathrm{d}a.$$

Inserting the expression for the excess Gibbs grand potential, Eq. (6.39), into the previous equation, we find

$$\sigma\,\mathrm{d}a + a\,\mathrm{d}\sigma = -S^{\mathrm{I}}\mathrm{d}T - \sum_{i=1}^{k} n_i^{\mathrm{I}}\mathrm{d}\mu_i + \sigma\,\mathrm{d}a$$

$$\mathrm{d}\sigma = -s^{\mathrm{I}}\mathrm{d}T - \sum_{i=1}^{k}\Gamma_i\mathrm{d}\mu_i, \tag{6.46}$$

where s^{I} is the interfacial excess density of the entropy. This relation is called the **Gibbs adsorption equation**. In the case of an isothermal process, this reduces to

$$\mathrm{d}\sigma = -\sum_{i=1}^{k} \Gamma_i \, \mathrm{d}\mu_i. \tag{6.47}$$

We now consider the case of a binary solution at constant temperature. We choose the interface position such that the interfacial adsorption of the first component is zero, that is, $\Gamma_1 = 0$. Then Eq. (6.47) reduces to

$$\mathrm{d}\sigma = -\Gamma_2 \mathrm{d}\mu_2.$$

If the solution is ideal dilute, we obtain

$$\mathrm{d}\sigma = -\Gamma_2 \mathrm{d}\mu_2 = -\Gamma_2 \mathrm{d}(\psi_2 + RT \ln c_2) = -RT\Gamma_2 \mathrm{d}\ln c_2 = -RT\Gamma_2 \frac{\mathrm{d}c_2}{c_2}$$

$$\Gamma_2 = -\frac{c_2}{RT}\frac{\partial\sigma}{\partial c_2}. \tag{6.48}$$

This equation is routinely used to experimentally determine the degree of adsorption from the dependence of the surface tension on concentration. Equation (6.48) implies that if $\Gamma_2 > 0$ (i.e. the solute is attracted to the interface), the surface tension decreases when the bulk solute concentration increases. While Eq. (6.48) is the most commonly used form of the Gibbs adsorption equation, it is important to remember that it is only valid for ideal dilute solutions. For non-ideal solutions, Eq. (6.48) must be rewritten as

$$\Gamma_2 = -\frac{a_2}{RT}\frac{\partial\sigma}{\partial a_2}. \tag{6.49}$$

Review questions

1. Does the value of the interfacial excess of the number of moles of component *i* depend on the exact location of the interface?
2. Does the value of the interface tension depend on the exact location of the interface?
3. Does the value of the interfacial excess of the Gibbs grand potential depend on the exact location of the interface?
4. Under what conditions is the Gibbs equation, $\Gamma_2 = -(c_2/RT)(\mathrm{d}\sigma/\mathrm{d}c_2)$, valid?

Example problem

1. Estimate the concentration of the solute at the surface of a 0.1M water solution, assuming that the solute forms a homogenous surface layer of thickness $\delta = 1\,\mathrm{nm}$. (Note: the surface tension of water is $\sigma_{\mathrm{H_2O}} = 72.2 \cdot 10^{-3}\,\mathrm{J/m^2}$ and that of a 0.1M solution is $\sigma = 62.0 \cdot 10^{-3}\,\mathrm{J/m^2}$ at $T = 22°\mathrm{C}$.)

6.3 Guggenheim and Zhuhovitsky models

The interface theory developed by Gibbs provides a relationship between the adsorption and the interface tension, but it does not provide a means to calculate either of these values. This is not surprising, since thermodynamics can never answer such questions without making explicit assumptions (e.g. the saturated vapor of the solute above the solution obeys Henry's law). Another approach is to provide a reasonable, microscopic model of the system. Although such models are usually oversimplified, they provide the only approach to make a concrete prediction. We now consider the model proposed by Guggenheim and apply it to the simple case of a free surface of a condensed phase (the generalization to an arbitrary type of interface is straightforward). In this model, we assume that the surface layer is homogeneous, and is of thickness δ and volume $\delta \cdot a$. In this section, we will indicate the properties of this surface solution by the superscript Σ. We start by deriving an expression for the excess of the Gibbs grand potential. Recall that this value is equal to the difference between the true value of the Gibbs grand potential and its value assuming that the bulk phase is homogeneous right up to the surface:

$$\Omega^{\mathrm{I}} = \Omega - \Omega^{V} = \left\lfloor -p^{\Sigma}\delta a - p(V - \delta a) \right\rfloor - (-pV) = \delta a(p - p^{\Sigma}).$$

Comparison of this expression with Eq. (6.39) yields

$$\sigma = (p - p^{\Sigma})\delta. \tag{6.50}$$

Since $\sigma > 0$ we find that $p > p^{\Sigma}$. Therefore, the surface layer is stretched more than the bulk. Because this additional stress is tensile, we refer to it as the surface tension (i.e. its sign is such that the surface tries to contract). Note that this analysis applies directly to the case of a liquid or an amorphous solid, but in a crystalline solid we must distinguish between the surface free energy (i.e. the surface tension) and the surface stress tensor, as we discuss in Section 7.6. Since the surface tension is a function of the composition of the solution, Eq. (6.50) implies that $p^{\Sigma} = p^{\Sigma}(x_{\mathrm{i}})$.

The conditions of equilibrium between a bulk solution and its surface were first considered by Zhuhovitsky. The general conditions of equilibrium require that the bulk solution and the surface solution have the same temperature and chemical potentials. The chemical potentials for the bulk and surface solutions take the following form:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

$$\mu_i^{\Sigma} = \mu_i^{\mathrm{st}}\left(p^{\Sigma}\right) + RT \ln a_i^{\Sigma},$$

where μ_i^0 is the chemical potential of the pure component i and $\mu_i^{\mathrm{st}}\left(p^{\Sigma}\right)$ is the chemical potential of component i in the standard surface solution at pressure p^{Σ}. Recall that the chemical potential (as well as the Gibbs energy) of a pure component is a function of pressure. Equation (3.14) implies that

$$\overline{V}_i^{\Sigma} = \left(\frac{\partial \mu_i^{\Sigma}}{\partial p}\right)_{T,x_i^{\Sigma}},$$

where $\overline{V}_i^{\Sigma}$ is the partial molar volume of component i in the surface solution. Since $\overline{V}_i^{\Sigma}$ depends only weakly on the pressure, we can integrate this equation

$$\mu_i^{\mathrm{st}}(p^{\Sigma}) = \mu_i^{\mathrm{st}}(p) + (p^{\Sigma} - p)\overline{V}_i^{\Sigma} = \mu_i^{\mathrm{st}}(p) - \frac{\sigma}{\delta}\overline{V}_i^{\Sigma}$$

and finally

$$\mu_i^{\Sigma} = \mu_i^{\mathrm{st}}(p) - \frac{\sigma}{\delta}\overline{V}_i^{\Sigma} + RT \ln a_i^{\Sigma}.$$

In equilibrium, the chemical potential of species i on the surface and in the bulk are the same

$$\mu_i^0 + RT \ln a_i = \mu_i^{\mathrm{st}}(p) - \frac{\sigma}{Z} + RT \ln a_i^{\Sigma},$$

where $1/Z$ is the area per mole of molecules $Z = \delta/\overline{V}$ and we have assumed, for simplicity, that the partial molar volumes of both components are the same, that is, $\overline{V}_1^{\Sigma} = \overline{V}_2^{\Sigma} = \overline{V}$. Solving this equation for the surface free energy yields

$$\sigma = Z\left(\mu_i^{\mathrm{st}}(p) - \mu_i^0\right) + RTZ \ln \frac{a_i^{\Sigma}}{a_i}.$$

The first term in this expression is independent of concentration. In pure i, the activities on the surface and in the bulk are unity and $\sigma = \sigma_i$. Therefore, we can write

$$\sigma = \sigma_i + ZRT \ln \frac{a_i^{\Sigma}}{a_i}. \tag{6.51}$$

In the case of a binary solution, we have one equation for each component, but only one surface energy. Therefore,

$$\sigma_1 + ZRT \ln \frac{a_1^{\Sigma}}{a_1} = \sigma_2 + ZRT \ln \frac{a_2^{\Sigma}}{a_2}$$

or

$$\frac{a_2^{\Sigma}}{a_2} = B\frac{a_1^{\Sigma}}{a_1}, \tag{6.52}$$

where

$$B = \exp\left\{\frac{\sigma_1 - \sigma_2}{ZRT}\right\}. \tag{6.53}$$

This is the Zhuhovitsky segregation isotherm, which is valid for any type of solution thermodynamics.

As a concrete example, consider the case in which both the surface and bulk solutions are ideal. Then Eq. (6.52) can be rewritten as:

$$\frac{x_2^{\Sigma}}{x_2} = B\frac{x_1^{\Sigma}}{x_1} = \frac{1 - x_2^{\Sigma}}{1 - x_2}$$

or

$$x_2^{\Sigma} = \frac{Bx_2}{1 - x_2 + Bx_2}. \tag{6.54}$$

Inserting this expression into Eq. (6.51), we find

$$\begin{aligned}\sigma &= \sigma_2 + ZRT \ln \frac{x_2^{\Sigma}}{x_2} = \sigma_2 + ZRT \ln \frac{B}{1 - x_2 + Bx_2}\\ &= \sigma_2 + ZRT \frac{\sigma_1 - \sigma_2}{ZRT} - ZRT \ln(1 - x_2 + Bx_2)\end{aligned}$$

$$\sigma = \sigma_1 - ZRT \ln(1 - x_2 + Bx_2). \tag{6.55}$$

This expression is known as the surface tension isotherm. Figure 6.11 shows a typical surface tension versus concentration profile in this model. Since the model does not provide a method to determine Z and B, these quantities should be viewed as parameters.

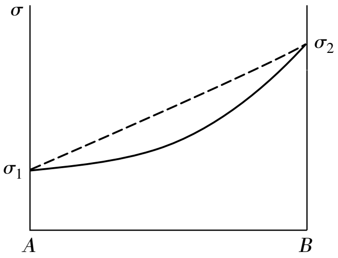

Fig. 6.11
The surface tension as function of concentration in the Zhuhovitsky theory.

If the concentration of the second component is small, all measures of the concentration are proportional to one another, such that Eq. (6.55) can be rewritten as:

$$\sigma = \sigma_1 - ZRT \ln(1 + bc_2), \tag{6.56}$$

where b is the product of $B - 1$ and the constant that relates the molar fraction of component 2 to its concentration. This is the Shishkovsky equation (it can be shown to be valid for all dilute, non-electrolyte solutions). Using the Gibbs equation (Eq. 6.48), it is easy to find the corresponding adsorption isotherm:

$$\Gamma_2 = -\frac{c_2}{RT}\frac{\partial \sigma}{\partial c_2} = \frac{c_2}{RT} ZRT \frac{b}{1 + bc_2}$$

$$\Gamma_2 = \frac{Zbc_2}{1 + bc_2}. \tag{6.57}$$

This equation is identical to the Langmuir isotherm, except that now b can be either positive or negative.

Review question

1. Does the surface tension of an ideal solution obey the Shishkovsky isotherm?

Thermodynamics of stressed systems

7

As every school child knows, the difference between a solid and a liquid is that a liquid takes the shape of the container in which it is placed while the shape of a solid is independent of the shape of the container (providing the container is big enough). In other words, we must apply a force in order to change the shape of a solid. However, the thermodynamic functions described heretofore have no terms that depend on shape. In this chapter, we extend the thermodynamics discussed above to include such effects and therefore make it applicable to solids. However, since this is a thermodynamics, rather than a mechanics text, we focus more on the relationship between stress and thermodynamics rather than on a general description of the mechanical properties of solids.

7.1 Small deformations of solids

7.1.1 Strain tensor

We start out discussion of mechanical deformation by describing the change of shape of a solid. We define the **displacement vector** at any point in the solid $\mathbf{u}(x, y, z)$ as the change in location of the material point (x, y, z) upon deformation: that is, $u_x(x, y, z) = x' - x$, where the prime indicates the coordinates of the material that was at the unprimed position prior to the deformation. In linear elasticity, we explicitly assume that the displacement vector varies slowly from point to point within the solid

$$\frac{\partial u_i}{\partial x_j} \ll 1, \tag{7.1}$$

where i and j denote the directions along the three axes, x, y, and z.

Consider the small parallel-piped section of a solid with perpendicular edges shown in Fig. 7.1. We label the first corner as O, located at position (x_O, y_O, z_O) and subsequent corners as A, B, ... located at positions (x_A, y_A, z_A), (x_B, y_B, z_B), ... The edge lengths are Δx, Δy, and Δz such that, for example, $x_A = x_O + \Delta x$. As a result of the deformation, the material originally at point O is displaced to point O′ with coordinates (x'_O, y'_O, z'_O).

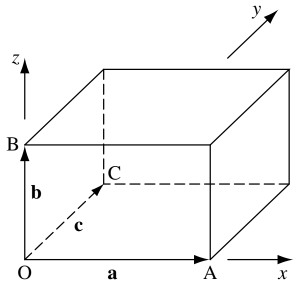

Fig. 7.1
A representative volume element of a solid, prior to deformation.

Using the definition of the displacement vector $\mathbf{u}(x,y,z)$, we find

$$\begin{aligned} x'_{\mathrm{O}} &= x_{\mathrm{O}} + u_x(x_{\mathrm{O}}, y_{\mathrm{O}}, z_{\mathrm{O}}) \\ y'_{\mathrm{O}} &= y_{\mathrm{O}} + u_y(x_{\mathrm{O}}, y_{\mathrm{O}}, z_{\mathrm{O}}) \\ z'_{\mathrm{O}} &= z_{\mathrm{O}} + u_z(\mathrm{x}_{\mathrm{O}}, \mathrm{y}_{\mathrm{O}}, \mathrm{z}_{\mathrm{O}}). \end{aligned} \tag{7.2}$$

Analogous relations can be obtained for the positions of the other corners; for example, upon deformation point A goes to A′:

$$\begin{aligned} x'_{\mathrm{A}} &= x_{\mathrm{O}} + \Delta x + u_x(x_{\mathrm{O}} + \Delta x, y_{\mathrm{O}}, z_{\mathrm{O}}) \\ y'_{\mathrm{A}} &= y_{\mathrm{O}} + u_y(x_{\mathrm{O}} + \Delta x, y_{\mathrm{O}}, z_{\mathrm{O}}) \\ z'_{\mathrm{A}} &= z_{\mathrm{O}} + u_z(x_{\mathrm{O}} + \Delta x, y_{\mathrm{O}}, z_{\mathrm{O}}). \end{aligned} \tag{7.3}$$

Since **u** varies slowly in space, we can expand the displacement vector about point O (e.g. $u_x(x_{\mathrm{O}} + \Delta x, y_{\mathrm{O}}, z_{\mathrm{O}}) = u_x(x_{\mathrm{O}}, y_{\mathrm{O}}, z_{\mathrm{O}}) + (\partial u_x/\partial x)|_{x_{\mathrm{O}}, y_{\mathrm{O}}, z_{\mathrm{O}}}\Delta x$) such that Eq. (7.3) can be rewritten as

$$\begin{aligned} x'_{\mathrm{A}} &= x_{\mathrm{O}} + \Delta x + u_x + \frac{\partial u_x}{\partial x}\Delta x \\ y'_{\mathrm{A}} &= y_{\mathrm{O}} + u_y + \frac{\partial u_y}{\partial x}\Delta x \\ z'_{\mathrm{A}} &= z_{\mathrm{O}} + u_z + \frac{\partial u_z}{\partial x}\Delta x, \end{aligned} \tag{7.4}$$

where u_α and its derivatives are evaluated at $(x_{\mathrm{O}}, y_{\mathrm{O}}, z_{\mathrm{O}})$. Before deformation, the components of vector **a**, connecting points O and A, are $(\Delta x, 0, 0)$. Using Eqs (7.3) and (7.4), we see that deformation changes this vector to

$$\begin{aligned} a'_x &= \Delta x + \frac{\partial u_x}{\partial x}\Delta x \\ a'_y &= \frac{\partial u_y}{\partial x}\Delta x \\ a'_z &= \frac{\partial u_z}{\partial x}\Delta x. \end{aligned} \tag{7.5}$$

This relation suggests that a general deformation changes both the length and direction of **a**. This implies that deformation can modify both volume and shape. However, it is convenient to discuss two limiting cases of deformation. In the first, only the volume changes but the directions of all vectors remain unchanged upon deformation (this implies that the shape does not change). Such a deformation is **pure dilatation**. In the second, the volume does not change with deformation, but the shape does. This deformation is **pure shear**. An arbitrary deformation can be represented as a combination of these two types of deformation.

We focus first on pure dilatation. Assume that $\partial u_y/\partial x = 0$ and $\partial u_z/\partial x = 0$. Then Eq. (7.5) can be rewritten as

$$\begin{aligned} a'_x &= \Delta x + \frac{\partial u_x}{\partial x}\Delta x \\ a'_y &= 0 \\ a'_z &= 0. \end{aligned} \tag{7.6}$$

This shows that this type of deformation does not change the direction of **a**, only its length. Clearly, this conclusion is valid for any vector if all derivatives of the individual components of the displacement vector are zero except for $\partial u_x/\partial x$, $\partial u_y/\partial y$, and $\partial u_z/\partial z$. This is shown in Fig. 7.2. The **elongation** along the x-axis is the change in vector **a** normalized by its original magnitude (see Eq. (7.6)):

$$\frac{a'_x - a_x}{a_x} = \frac{\partial u_x}{\partial x} = \varepsilon_{xx}.$$

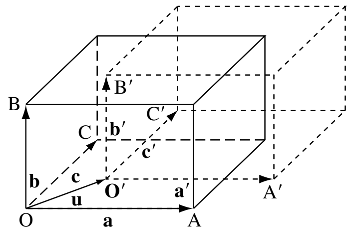

Fig. 7.2
The representative volume element from Fig. 7.1 before (solid lines) and following (dotted lines) the application of normal strains.

$\varepsilon_{\alpha\alpha}$ is called a **normal strain**.[1] If the normal strain is positive, the deformation is **tensile** and if it is negative, the deformation is **compressive**. The scaled change in volume of the section of the solid shown in Fig. 7.1 upon deformation is

$$\frac{V' - V}{V} = \frac{(\Delta x + \varepsilon_{xx}\Delta x)(\Delta y + \varepsilon_{yy}\Delta y)(\Delta z + \varepsilon_{zz}\Delta z) - \Delta x \Delta y \Delta z}{\Delta x \Delta y \Delta z}.$$

Since ε_{xx}, ε_{yy}, and ε_{zz} are small (see Eq. (7.1)), we need only keep the terms that are linear in $\varepsilon_{\alpha\alpha}$, hence

$$\frac{\Delta V}{V} \approx \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} = \varepsilon_{ii}. \tag{7.7}$$

In the last expression, we use the Einstein summation convention and sum over the three values of the repeated index i ($i = x,y,z$), as described in Appendix II.

We now consider pure shear and focus upon the angles between vectors. For example, consider the angle θ between the vectors **a** and **b** connecting point O with points A and B (see Fig. 7.3). The vector **a** in the deformed state was given in Eq. (7.5), above. Analogously, vector **b** in the deformed state is

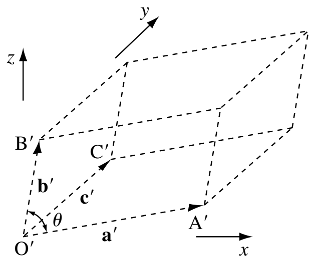

Fig. 7.3
The representative volume element from Fig. 7.1 following the application of a shear strain.

$$\begin{aligned}
b'_x &= \frac{\partial u_x}{\partial y}\Delta y \\
b'_y &= \Delta y + \frac{\partial u_y}{\partial y}\Delta y \\
b'_z &= \frac{\partial u_z}{\partial y}\Delta y.
\end{aligned} \tag{7.8}$$

Since there is no change in volume, $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = 0$, we need only consider derivatives of the form $\partial u_\alpha/\partial x_\beta$, where $\alpha \neq \beta$. Before deformation, the angle between vectors **a** and **b** was $\pi/2$. The new angle is determines from the following equation:

$$\cos\theta = \frac{\mathbf{a}'\mathbf{b}'}{|\mathbf{a}'||\mathbf{b}'|}.$$

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[1] Note, we use two indices to indicate that this is the derivative of the α component of the displacement in the α-direction.

From Eqs (7.5) and (7.8) we find

$$|\mathbf{a}'| = \left[(\Delta x)^2 + \left(\frac{\partial u_y}{\partial x}\Delta x\right)^2 + \left(\frac{\partial u_z}{\partial x}\Delta x\right)^2\right]^{1/2} \approx \Delta x$$

$$|\mathbf{b}| \approx \Delta y$$

$$\mathbf{a}'\mathbf{b}' \approx \frac{\partial u_x}{\partial y}\Delta x \Delta y + \frac{\partial u_y}{\partial x}\Delta x \Delta y,$$

where again we kept only the leading order terms. Since the deformation is small, we can expand θ about its undeformed value ($\pi/2$), such that

$$\cos\theta \approx \frac{\pi}{2} - \theta \approx \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}.$$

Therefore, the change in angle between vectors which were parallel to x_α and x_β axes before deformation, is equal to twice $\varepsilon_{\alpha\beta}$, where

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right), \quad i \neq j. \tag{7.9}$$

$\varepsilon_{\alpha\beta}$ is called the **shear strain**.

We now provide a general definition of the strain

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right). \tag{7.10}$$

This definition implies that the strain is a second rank tensor. The trace of this tensor (i.e. the sum of the components on the diagonal) is the scaled change in volume; the non-diagonal elements represent the shear strains. According to Eq. (7.10), the strain is dimensionless and the strain tensor is symmetric tensor,

$$\varepsilon_{ij} = \varepsilon_{ji}. \tag{7.11}$$

The last equation suggests that in three dimensions the strain tensor only has six independent components.

7.1.2 Stress tensor

Consider a cubic representative volume element in a solid subjected to a small deformation. What is the total force acting on this cube? We can consider this cube as made up of small sub-cubes. The force on sub-cube *i* from a neighboring sub-cube *j* is equal and opposite the force that sub-cube *i* exerts on sub-cube *j* (Newton's third law). Therefore, the net force on the cube is simply the sum of all external forces, that is, those on the external surface of the cube (we do not consider body forces, such as gravity, in this discussion). If the cube is sufficiently small, it is reasonable to assume that the force on any of the cube surfaces does not vary over that surface. We further assume that the forces acting on each pair of parallel faces of the cube are equal in magnitude but opposite in sign. Consider the right face of the cube, which is normal to the x-axis in Fig. 7.4(a). The projection of the force on this face onto the coordinate directions and normalized by the face area is denoted as σ_{xx}, σ_{xy}, and σ_{xz}, where the first index denotes the axis which is normal to the face and the second index denotes the axis along which we project the force (see Fig. 7.4(a)). The same procedure applies to the left face with normal parallel to the x-axis, except we must now account for the fact that the surface normal is $-x$ rather than x (we actually project along the surface normal and surface tangents parallel to the coordinate axes). Since the force acting on the left surface is equal and opposite to that on the right surface, the values of σ_{xx}, σ_{xy}, and σ_{xz} are the same on opposite sides of the cube. By consideration of the other four surfaces, we can introduce σ_{yx}, σ_{yy}, σ_{yz}, σ_{zx}, σ_{zy}, and σ_{zz}. These force projections per unit area are called **stresses**. The stresses σ_{xx}, σ_{yy}, and σ_{zz} act in the directions normal to the cube faces and are called **normal stresses**, which can be either **compressive** (if the force is directed into the face) or **tensile** (if it is directed outward from the face). The stresses $\sigma_{\alpha\beta}$ (where $\alpha \neq \beta$) act in directions, which are parallel to the faces, and are called **shear** stresses. It is a simple matter to show there are only three independent shear stresses. Indeed, consider again the faces normal to the x-axis, shown in Fig. 7.4(b). Examination of this figure shows that if $\sigma_{xy} \neq \sigma_{yx}$ there is a net torque and the cube will rotate. This implies that the stress is a symmetric second rank tensor:

$$\sigma_{ij} = \sigma_{ji}. \tag{7.12}$$

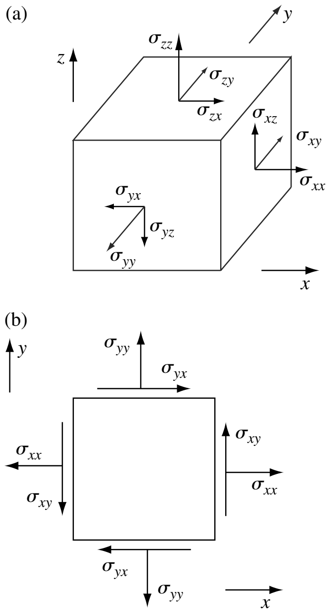

Fig. 7.4
(a) A representative volume element of a solid, indicating the stress components on three orthogonal surfaces, (b) a view of the volume element from the $+x$-direction.

In the discussion above, we implicitly assumed that stress is constant throughout the volume element. However, this is not the general case. We now consider the general case, in which the stress can vary spatially (i.e. the stress is a function of position). The total force in the x-direction F_x acting on a small representative volume element with rectangular faces (edge lengths δx, δy, and δz) has contributions from all of the stresses where the first index is x and from all six faces:

$$\begin{aligned} F_x &= [\sigma_{xx}(x+\delta x, y, z) - \sigma_{xx}(x, y, z)]\delta y \delta z \\ &\quad + \left[\sigma_{xy}(x, y+\delta y, z) - \sigma_{xy}(x, y, z)\right]\delta x \delta z \\ &\quad + [\sigma_{xz}(x, y, z+\delta z) - \sigma_{xz}(x, y, z)]\delta x \delta y \\ &\approx \left(\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} + \frac{\partial \sigma_{xz}}{\partial z}\right)\delta x \delta y \delta z, \end{aligned}$$

where we have replaced the finite differences with derivatives. Therefore the force acting on the unit volume of the deformed solid is

$$f_i = \frac{\partial \sigma_{ij}}{\partial x_j}, \tag{7.13}$$

where we have used the lower case symbol for force to indicate that this is force per unit volume.

Consider now a representative element of a solid of volume V. The ith component of the total force acting on this volume element is

$$\int_V f_i \, \mathrm{d}V = \int_V \frac{\partial \sigma_{ij}}{\partial x_j} \mathrm{d}V = \oint_A \sigma_{ij} n_j \mathrm{d}a, \tag{7.14}$$

where the last integral is evaluated over the entire surface of area A (using the Gauss theorem) and $\mathbf{n}$ is the unit vector normal to the surface. Equation (7.14) demonstrates that $\sigma_{ij}n_j\,\mathrm{d}a$ is the ith component of the force acting on a section of the surface, $\mathrm{d}a$ (with normal $\mathbf{n}$).

Let $\mathbf{t}$ be a force per unit area applied on the external surface of a solid body. In equilibrium, this force has to be compensated by the force acting on the same surface from inside the solid (i.e. an internal stress). Therefore,

$$t_i\mathrm{d}a = \sigma_{ij}n_j\mathrm{d}a$$

or

$$t_i = \sigma_{ij}n_j. \tag{7.15}$$

$\mathbf{t}$ is also known as the **surface traction**.

We now consider the special case of pure hydrostatic stress, that is, no shear stress. This is the stress state in any fluid (liquid or gas). If a solid body is immersed in a fluid, the tractions on all surfaces will be the same and will be directed parallel to the local surface normal vectors. This traction on the surface is balanced by the pressure such that

$$t_i = -pn_i = -pn_j\delta_{ij}.$$

Inserting the definition of the traction from Eq. (7.15), we find that the stress and pressure are related by

$$\sigma_{ij} = -p\delta_{ij} \tag{7.16}$$

or

$$p = -\sigma_{ij}/3, \tag{7.17}$$

where we recall that we sum over repeated indices such that σ_{ii} is the trace of the stress tensor and, hence, the value of the pressure does not depend upon which coordinate system we choose.

7.2 Free energy of strained solids

In Chapter 1, we found that the differential of the free energy of a system contains a term equal to the work of expansion, $p\mathrm{d}V$ (Eq. (1.67)). Above, we found that in addition to strains associated with volume change, there are strains associated with shape change (i.e. shear strains). Therefore, it is reasonable to expect that the free energy of a solid will be a function of all of the strain components, not just those associated with volume change. In order to identify this contribution to the free energy, we first consider the work associated with an arbitrary deformation.

Consider an initially strained solid that is further deformed by the application of an additional displacement $\delta u_{\mathrm{i}}(\mathbf{r})$. The work required to produce this displacement is equal but opposite to the work performed by the system through the internal stresses, that is,

$$\int_V \delta w \mathrm{d}V = \int_V f_i \delta u_i \mathrm{d}V,$$

where δw is the work performed by the element of the strained solid and f_i is the force acting on this volume element. Using Eq. (7.13) we find

$$\int_V f_i \delta u_i \mathrm{d}V = \int_V \frac{\partial \sigma_{ij}}{\partial x_j} \delta u_i \mathrm{d}V = \int_V \frac{\partial(\sigma_{ij}\delta u_i)}{\partial x_j} \mathrm{d}V - \int_V \sigma_{ij} \frac{\partial \delta u_i}{\partial x_j} \mathrm{d}V,$$

where the last result was obtained by integration by parts. We can rewrite one of the integrals over the volume in the above expression as an integral over the surface, A, bounding the volume (using the Gauss theorem)

$$\int_V \frac{\partial(\sigma_{ij}\delta u_i)}{\partial x_j} \mathrm{d}V = \oint_A \sigma_{ij} \delta u_i n_j \mathrm{d}a.$$

If the tractions on the surface are zero ($\sigma_{ij} n_j = 0$), this integral is zero and we obtain

$$\delta w = -\sigma_{ij} \frac{\partial \delta u_i}{\partial x_j}.$$

This expression can be rewritten as

$$\delta w = -\sigma_{ij} \frac{\partial \delta u_i}{\partial x_j} = -\frac{1}{2}\left(\sigma_{ij} \frac{\partial \delta u_i}{\partial x_j} + \sigma_{ij} \frac{\partial \delta u_i}{\partial x_j}\right) = -\frac{1}{2}\left(\sigma_{ij} \frac{\partial \delta u_i}{\partial x_j} + \sigma_{ji} \frac{\partial \delta u_j}{\partial x_i}\right),$$

where the last expression in the second term follows by simple interchange of indices. Using the fact that the stress tensor is symmetric, we obtain

$$\delta w = -\frac{1}{2}\sigma_{ij}\left(\frac{\partial \delta u_i}{\partial x_j} + \frac{\partial \delta u_j}{\partial x_i}\right) = -\frac{1}{2}\sigma_{ij}\delta\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) = -\frac{1}{2}\sigma_{ij}\delta(2\varepsilon_{ij})$$

or

$$\delta w = -\sigma_{ij} \mathrm{d}\varepsilon_{ij}. \tag{7.18}$$

Consider the special case of hydrostatic compression: $\sigma_{ij} = -p\delta_{ij}$ and $d\varepsilon_{ii}$ is the additional scaled change in volume, $\mathrm{d}(V - V_0)/V_0 = \mathrm{d}V/V$. Therefore, the work performed by the entire solid is

$$\delta W = Vp\delta_{ij} \mathrm{d}\varepsilon_{ij} = pV \mathrm{d}\varepsilon_{ii} = p\mathrm{d}V.$$

This is exactly the expression for the work of expansion which we used in Chapter 1 (Eq. (1.1)). This suggests that Eq. (7.18) is the extension of the expression for work to the case of solids.

From this point forward, we focus exclusively on **elastic deformation**; that is, deformations for which the system returns to its original state following removal of the external forces (these are reversible deformations). As per the discussion in the previous chapter, we denote all extensive properties per unit volume by lower case letters and obtain the total extensive properties by integrating these over the entire volume.[2] We start our discussion of thermodynamic functions by considering the differential of the internal energy. Equation (1.45), for the special case of reversible

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[2] Although strain changes the shape and/or volume of a solid, this integration is always performed over the volume of the solid assuming it was unstrained. This is because the integration is actually over a certain set of atoms rather than over the instantaneous volume.

deformation, reads

$$du = Tds - \delta w.$$

Substituting Eq. (7.18) for the work into this expression we find,

$$du = Tds + \sigma_{ij} d\varepsilon_{ij}. \tag{7.19}$$

We can then write the differential of the Helmhotz free energy (cf. Eq. (1.67)), as

$$da = -s dT + \sigma_{ij} d\varepsilon_{ij}. \tag{7.20}$$

This provides a thermodynamic definition of the stress

$$\sigma_{ij} = \left(\frac{\partial a}{\partial \varepsilon_{ij}} \right)_T. \tag{7.21}$$

7.3 Hooke's law

7.3.1 Hooke's law for anisotropic solids

To find the stress from Eq. (7.21) we must determine the free energy as a function of the strain. We can find such an expression for the free energy by expanding it in powers of strain about the unstrained state. We define the unstrained state as the stress-free state in the absence of any applied force. We start from the case in which the temperature is uniform throughout the solid. The expansion of the free energy has the following general form:

$$a = a_0 + A_{ij}\varepsilon_{ij} + \frac{1}{2} C_{ijkl}\varepsilon_{ij}\varepsilon_{kl} + \cdots.$$

Since the strains are small, we truncate this expansion after the first two strain-dependent terms. Since all stresses are zero in the unstrained state (when all strains are zero), Eq. (7.21) implies that $A_{ij} = 0$. Therefore, the free energy takes the following relatively simple form:

$$a = a_0 + \frac{1}{2} C_{ijkl}\varepsilon_{ij}\varepsilon_{kl}. \tag{7.22}$$

The coefficient of the leading order term, C_{ijkl}, is a property of the material and is a fourth-rank tensor. While, in general case, a fourth-rank tensor has 81 components, the number of independent components of C_{ijkl} is much smaller. First, we note that

$$\varepsilon_{ij}\varepsilon_{kl} = \varepsilon_{ji}\varepsilon_{kl} = \varepsilon_{ij}\varepsilon_{lk} = \varepsilon_{kl}\varepsilon_{ij}.$$

Since these terms are all equal, they must all enter the expression for the free energy with the same coefficients; hence,

$$C_{ijkl} = C_{jikl} = C_{ijlk} = C_{klij}. \tag{7.23}$$

These relations reduce the number of independent components from 81 to 21. Because the free energy must be invariant upon the rotation of the coordinate systems, we remove three more degrees of freedom—thereby reducing the number of constants to 18. Further reduction in the number of independent components of C_{ijkl} is possible if the solid has other symmetries. For example, many crystalline solids have rotational or mirror symmetries. In the special, but common, case of cubic crystals, C_{ijkl} has only three independent components.

Equation (7.23) implies that the number of independent combinations of the first pair of indices of C_{ijkl} is 6. A convenient and widely used simplification of the notation is to write

$$\begin{aligned} xx &\rightarrow 1 \\ yy &\rightarrow 2 \\ zz &\rightarrow 3 \\ yz &\rightarrow 4 \\ xz &\rightarrow 5 \\ xy &\rightarrow 6. \end{aligned}$$

In this way, C_{xxxx} and C_{xxyy} are written as C_{11} and C_{12}, respectively. This makes the fourth-rank tensor C_{jhil} appear to be a second rank tensor C_{ij}, where i and j now go from 1 to 6. The student should keep in mind that this is just a short hand for the full fourth-rank tensor.

In order to find an expression for the stress we need only insert Eq. (7.22) into Eq. (7.21)

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}, \tag{7.24}$$

where we have used the identity

$$\frac{\partial \varepsilon_{kl}}{\partial \varepsilon_{ij}} = \delta_{ik}\delta_{jl}.$$

Equation (7.24) is known as **Hooke's law**. It shows that all stresses are linear functions of strain. Note that for crystals with cubic symmetry Hooke's law reduces to the following form:

$$\begin{aligned} \sigma_{xx} &= C_{11}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{12}\varepsilon_{zz} \\ \sigma_{yy} &= C_{12}\varepsilon_{xx} + C_{11}\varepsilon_{yy} + C_{12}\varepsilon_{zz} \\ \sigma_{zz} &= C_{12}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{11}\varepsilon_{zz} \\ \sigma_{yz} &= 2C_{44}\varepsilon_{yz} \\ \sigma_{xz} &= 2C_{44}\varepsilon_{xz} \\ \sigma_{xy} &= 2C_{44}\varepsilon_{xy}, \end{aligned}$$

if x-, y-, and z-axes coincide with the [100], [010], and [001] crystallographic axes. Components C_{11}, C_{12}, and C_{44} are the three **elastic constants** for a cubic crystal. All other crystals have more than three elastic constants.

7.3.2 Hooke's law for isotropic solids

All single crystals are, in general, elastically **anisotropic**—their elastic properties depend upon direction. A consequence of this fact is that the elastic constants form the tensor C_{ijkl}. In contrast with anisotropic solids, the properties of **isotropic** solids do not depend on direction. Examples of isotropic solids include amorphous and polycrystalline (provided that we average over a large number of grains) solids. Therefore, the expansion of the free energy of an isotropic solid in powers of strains contains only scalar material parameters and any function of strain in this expression must be a scalar. We can construct only one scalar of the first order from ε_{ij}: ε_{ii}. Similarly, two scalars of the second order can be formed: $\varepsilon_{ii}^2 \equiv \varepsilon_{ii}\varepsilon_{jj}$ and $\varepsilon_{ij}^2 \equiv \varepsilon_{ij}\varepsilon_{ij}$. Therefore, the expression for the free energy per unit volume takes the following form:

$$a = a_0 + a_1\varepsilon_{ii} + \frac{\lambda}{2}\varepsilon_{ii}^2 + \mu\varepsilon_{ij}^2, \tag{7.25}$$

where a_1, μ, and λ are scalar material properties (the factor of 2 in the term ε_{ii} was included for convenience). Since there is no stress in the unstrained state, we conclude that $a_1 = 0$ (see Eq. (7.21)). The first scalar of the second order in Eq. (7.25), ε_{ii}^2, has a clear physical interpretation: it is associated with changes in the scaled volume ε_{ii} as we discussed in Section 7.1.1. However, the interpretation of the second scalar, ε_{ij}^2, is less obvious. It can be seen more clearly if we rewrite Eq. (7.25) as the sum of a term describing the change in volume and a term describing the change in shape. To this end, we rewrite the strain tensor as

$$\varepsilon_{ij} = \frac{1}{3}\delta_{ij}\varepsilon_{kk} + \left(\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{kk}\right).$$

The first term represents the volume change and is zero in the case of pure shear, while the second term represents shape change and is zero in the case of pure **dilatation** (i.e. all three normal strains are equal and all shear strains are zero). We can now write the free energy as

$$a = a_0 + \frac{B}{2}\varepsilon_{kk}^2 + \mu\left(\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{kk}\right)^2, \tag{7.26}$$

where μ and B are the **shear modulus** and **bulk modulus**, respectively. Since an elastic system spontaneously returns to its unstrained state when the external forces are removed, the unstrained state corresponds to a minimum in the free energy. This implies that

$$\mu > 0, \qquad B > 0. \tag{7.27}$$

In order to obtain an expression for the stress, we can make use of the thermodynamic definition of stress (Eq. (7.21)), the free energy from Eq. (7.26) and the simple identity

$$\frac{\partial\varepsilon_{kk}}{\partial\varepsilon_{ij}} = \delta_{kl}\frac{\partial\varepsilon_{kl}}{\partial\varepsilon_{ij}} = \delta_{kl}\delta_{ik}\delta_{jl} = \delta_{il}\delta_{jl} = \delta_{ij}.$$

Following this procedure, we find

$$\begin{aligned}
\sigma_{ij} &= 2\mu\left(\varepsilon_{lm} - \frac{1}{3}\delta_{lm}\varepsilon_{kk}\right)\left(\delta_{il}\delta_{jm} - \frac{1}{3}\delta_{lm}\delta_{ij}\right) + B\varepsilon_{kk}\delta_{ij} \\
&= 2\mu\left(\varepsilon_{lm}\delta_{il}\delta_{jm} - \frac{1}{3}\varepsilon_{lm}\delta_{lm}\delta_{ij} - \frac{1}{3}\delta_{lm}\varepsilon_{kk}\delta_{il}\delta_{jm} + \frac{1}{9}\delta_{lm}\varepsilon_{kk}\delta_{lm}\delta_{ij}\right) + B\varepsilon_{kk}\delta_{ij} \\
&= 2\mu\left(\varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij} + \frac{1}{3}\varepsilon_{kk}\delta_{ij}\right) + B\varepsilon_{kk}\delta_{ij}
\end{aligned}$$

or

$$\sigma_{ij} = 2\mu\left(\varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij}\right) + B\varepsilon_{kk}\delta_{ij}. \tag{7.28}$$

This is **Hooke's law** for isotropic solids. If the deformation is purely dilatational, the first term is zero and the off-diagonal elements of the stress tensor are zero. In this case, the bulk modulus is the only material parameter that we need to relate stress to strain. If the deformation is pure shear, the second term is zero. In this case, the shear modulus is the only material parameter that we need to relate the stress to the strain.

While Eq. (7.28) provides an expression for the stress in terms of the strain, the inverse relation is also useful. It can be derived as follows. We start by solving Eq. (7.28) for the strain ε_{ij}.

$$\varepsilon_{ij} = \frac{1}{2\mu}\left(\sigma_{ij} - B\varepsilon_{kk}\delta_{ij}\right) + \frac{1}{3}\varepsilon_{kk}\delta_{ij}. \tag{7.29}$$

The relation between the trace of the strain tensor ε_{kk} and the trace of the stress tensor σ_{ii} can also be found from Eq. (7.28)

$$\sigma_{ii} = 2\mu(\varepsilon_{ii} - \varepsilon_{kk}) + 3B\varepsilon_{kk}$$

or

$$\varepsilon_{ii} = \frac{\sigma_{ii}}{3B}. \tag{7.30}$$

Inserting this expression into Eq. (7.29) yields Hooke's law for the strain in terms of the stress

$$\varepsilon_{ij} = \frac{1}{9B}\sigma_{kk}\delta_{ij} + \frac{1}{2\mu}\left(\sigma_{ij} - \frac{1}{3}B\sigma_{kk}\delta_{ij}\right). \tag{7.31}$$

Recall that in the case of hydrostatic stress, $\sigma_{ii} = -3p$ (see Eq. (7.17)) and the scaled change in volume $\varepsilon_{ii} = \Delta V/V$. In this case, Eq. (7.30) reduces to

$$B = -V\frac{\partial p}{\partial V}.$$

Comparing this result with Eq. (1.77) demonstrates that the bulk modulus is the inverse of the isothermal compressibility

$$B = \frac{1}{\chi_T}. \tag{7.32}$$

At this point, it is interesting to inquire as to what is the difference between a solid and liquid from the point of view of elasticity. Both phases are characterized by a positive bulk modulus. However, unlike a solid, a liquid is incapable of supporting a shear. This simply follows from one of the conditions for equilibrium in an isothermal liquid—that is, the pressure is uniform everywhere. This implies that the shear stress is zero everywhere in a liquid. Since we can always impose an arbitrary strain, including a shear strain, the shear stress can only be zero if the shear modulus is zero.[3]

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[3] This discussion assumes that we wait long enough for the molecules in the fluid to flow to relax the strain. How long we have to wait depends on the viscosity of the liquid. Clearly, if we measure the stress in a liquid immediately after imposition of a shear strain we would find a non-zero shear stress. This suggests that the shear modulus is frequency dependent. A more detailed discussion of this point is beyond the scope of this book.

Example problem

1. Write all of the components of the tensor C_{ij} for the case of an isotropic solid in terms of the two constants μ and B.
2. Hooke's law is also commonly written in the following form:

$$\sigma_{ij} = \frac{E}{1+\nu}\left(\varepsilon_{ij} + \frac{\nu}{1-2\nu}\varepsilon_{kk}\delta_{ij}\right),$$

   where E is known as the Young's modulus and ν is the Poisson ratio. How are E and ν related to B and μ?

7.4 Relationship between deformation and change of temperature

In the derivations of Eqs (7.22) and (7.26), we assumed that the temperature is constant throughout the system. We now relax this assumption. For simplicity, we will consider only case of isotropic solids. Note that the temperature can change as the result of deformation, by being in contact with a thermal reservoir, etc. Since, the equilibrium density is, in general, a function of temperature; we must define an unstrained reference state. We will define this state as the equilibrium state at a temperature T_0 in the absence of external forces. The free energy of the system at $T = T_0$ is described by Eq. (7.26). If the temperature is different from T_0, an additional term will appear in the expansion of the free energy

$$a(T) = a_0(T) + a_1(T)\varepsilon_{ii} + \mu\left(\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{kk}\right)^2 + \frac{B}{2}\varepsilon_{kk}^2,$$

where $a_0(T)$ is the free energy per unit volume of the system at temperature T at the density appropriate for T_0 and $a_1\varepsilon_{ii}$ is the additional term associated with the change in equilibrium density when the temperature is changed. Clearly, $a_1\varepsilon_{ii} = 0$ at $T = T_0$. If $|T - T_0| \ll T_0$ this term should be proportional to $T - T_0$. Hence, we can write down the following expression for the free energy

$$a(T) = a_0(T) - B\alpha(T - T_0)\varepsilon_{kk} + \mu\left(\varepsilon_{ij} - \frac{1}{3}\delta_{ij}\varepsilon_{kk}\right)^2 + \frac{B}{2}\varepsilon_{kk}^2, \qquad (7.33)$$

where α is independent of strain and temperature (to lowest order). Inserting this equation into the thermodynamic definition of stress (Eq. (7.21)), we find

$$\sigma_{ij} = 2\mu\left(\varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij}\right) + B\varepsilon_{kk}\delta_{ij} - B\alpha(T - T_0)\delta_{ij}. \qquad (7.34)$$

In the absence of external forces, there are no internal stresses (i.e. $\sigma_{ij} = 0$). Using this condition in Eq. (7.34), we find

$$\varepsilon_{ij} = \frac{1}{3}\varepsilon_{kk}\delta_{ij} + \frac{B}{2\mu}\left[-\varepsilon_{kk} + \alpha(T - T_0)\right]\delta_{ij}$$

$$\varepsilon_{ii} = \varepsilon_{kk} + \frac{3B}{2\mu}\left[-\varepsilon_{kk} + \alpha(T - T_0)\right]$$

or

$$\varepsilon_{ii} = \alpha(T - T_0).$$

Since ε_{ii} is the scaled change in volume and $T - T_0$ is small, we can rewrite this expression as

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}.$$

Therefore, α is the coefficient of thermal expansion (cf. Eq. (1.76)). Note that we can also define a linear coefficient of thermal expansion as the change in length of the sample scaled by its length. In an anisotropic system, this coefficient can have different values in different directions, while in an isotropic system α is simply three times the single linear coefficient of thermal expansion.

As mentioned above, an elastic deformation can lead to a temperature change. For the sake of simplicity, we focus on the case of an adiabatic deformation (this alleviates the need to discuss heat transfer). You can perform a simple experiment to show a temperature change accompanying adiabatic deformation by rapidly stretching a thick rubber band. If you touch the rubber band to your lip before you stretch it and in its highly stretched state, you will feel a distinct temperature change.

We now derive an equation for the change of temperature as a result of an adiabatic deformation. We start from the fact that the entropy remains constant during an adiabatic deformation. To obtain an expression for the entropy, we differentiate Eq. (7.33) and retain only the first-order terms with respect to ε_{ij}.

$$s(T) = s_0(T) + B\alpha\varepsilon_{ii}. \tag{7.35}$$

Since the entropy is constant, this implies

$$\mathrm{d}s_0 = -B\alpha\mathrm{d}\varepsilon_{ii}$$

or

$$\int_{T_0}^{T} \mathrm{d}s_0 = -B\alpha \int_0^{\varepsilon_{ii}} \mathrm{d}\varepsilon_{ii}.$$

Recall that $s_0(T)$ is the entropy of the solid at temperature T provided that its volume is the same as that of the solid at temperature T_0. Therefore, $\mathrm{d}s_0 = c_V \mathrm{d}T/T$. Inserting this expression into the integral on the left-hand side of the previous equation and evaluating the integrals, we obtain

$$c_V \ln(T/T_0) = -B\alpha\varepsilon_{ii}.$$

If $|T - T_0|/T_0 \ll 1$, $\ln(T/T_0) \approx (T - T_0)/T_0$ and

$$\frac{T - T_0}{T_0} = -\frac{B\alpha}{c_V}\varepsilon_{ii}. \tag{7.36}$$

The sign of the temperature change depends on the sign of the coefficient of thermal expansion α. For most solids $\alpha > 0$, however there are cases for which $\alpha < 0$ (such as rubber).

7.5 Equilibrium of stressed solids

We now consider the mechanical equilibrium of stresses in solids. Mechanical equilibrium requires that the total force on each volume element of the solid will be zero. In the absence of an external field (e.g. electrical, magnetic, gravitational), the forces inside the solid body are exerted only through internal stresses. Equation (7.13) relating the force to the stresses implies

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0. \tag{7.37}$$

While this equation is valid in general, we now make the assumption that the solid is isotropic such that we can use Hooke's law for isotropic solids

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 2\mu\left(\frac{\partial \varepsilon_{ij}}{\partial x_j} - \frac{1}{3}\frac{\partial \varepsilon_{kk}}{\partial x_j}\delta_{ij}\right) + B\frac{\partial \varepsilon_{kk}}{\partial x_j}\delta_{ij} = 0. \tag{7.38}$$

Using the definition of the strain (Eq. (7.10)), we find

$$\frac{\partial \varepsilon_{ij}}{\partial x_j} = \frac{1}{2}\left(\frac{\partial^2 u_i}{\partial x_j^2} + \frac{\partial^2 u_j}{\partial x_i \partial x_j}\right)$$

$$\frac{\partial \varepsilon_{kk}}{\partial x_j} = \frac{\partial \varepsilon_{kl}}{\partial x_j}\delta_{lk} = \frac{1}{2}\left(\frac{\partial^2 u_k}{\partial x_l \partial x_j} + \frac{\partial^2 u_l}{\partial x_k \partial x_j}\right)\delta_{lk} = \frac{\partial^2 u_k}{\partial x_k \partial x_j}.$$

Inserting these results into Eq. (7.38), we obtain

$$2\mu\left(\frac{1}{2}\frac{\partial^2 u_i}{\partial x_j^2} + \frac{1}{2}\frac{\partial^2 u_j}{\partial x_i \partial x_j} - \frac{1}{3}\frac{\partial^2 u_k}{\partial x_k \partial x_j}\delta_{ij}\right) + B\frac{\partial^2 u_k}{\partial x_k \partial x_j}\delta_{ij} = 0$$

or

$$\mu\frac{\partial^2 u_i}{\partial x_j^2} + \left(\frac{\mu}{3} + B\right)\frac{\partial^2 u_j}{\partial x_i \partial x_j} = 0. \tag{7.39}$$

This equation can be rewritten as

$$\Delta \mathbf{u} + \left(\frac{B}{\mu} + \frac{1}{3}\right)\nabla(\nabla \mathbf{u}) = 0, \tag{7.40}$$

where ∇ and Δ are the gradient and Laplacian operators, respectively (see Appendix II). This is the equilibrium condition for a strained isotropic solid. It implies that the components of the displacement vector in equilibrium are not independent but rather must satisfy this condition. Note, that this condition does not explicitly show any dependence on externally applied forces (i.e. surface tractions). Such tractions only enter through boundary conditions.

Applying the operator ∇ to Eq. (7.40), we obtain (see Appendix II)

$$\nabla(\Delta \mathbf{u}) + \left(\frac{B}{\mu} + \frac{1}{3}\right)\Delta(\nabla \mathbf{u}) = \left(\frac{B}{\mu} + \frac{4}{3}\right)\Delta(\nabla \mathbf{u}) = 0$$

or

$$\Delta(\nabla\mathbf{u}) = 0. \tag{7.41}$$

Applying the operator Δ to Eq. (7.40), we obtain (See Appendix II):

$$\Delta\Delta\mathbf{u} + \left(\frac{B}{\mu}+\frac{1}{3}\right)\Delta(\nabla(\nabla\mathbf{u})) = \Delta\Delta\mathbf{u} + \left(\frac{B}{\mu}+\frac{1}{3}\right)\nabla(\Delta(\nabla\mathbf{u})) = 0.$$

Equation (7.41) shows that the last term in this expression is identically zero; hence,

$$\Delta\Delta\mathbf{u} = 0. \tag{7.42}$$

Therefore, the equilibrium displacement field must satisfy a biharmonic equation (Eq. (7.42)).

If the temperature varies through the solid, we must include the modification to Hooke's law for thermal expansion (see Eq. (7.34)). Using this expression in the derivation of $\partial\sigma_{ij}/\partial x_j$ (as per Eq. (7.38)) and following the same procedure as above for the isothermal case yields

$$\Delta\mathbf{u} + \left(\frac{B}{\mu}+\frac{1}{3}\right)\nabla(\nabla\mathbf{u}) = \frac{B\alpha}{\mu}\nabla T \tag{7.43}$$

instead of Eq. (7.40).

7.6 Surface stress

As we discussed in Section 6.3, we can think of the surface layer as being stretched to match the bulk material. This creates a surface stress. In this section, we establish the relationship between the surface stress and the free energy of the surface.

Consider a slab with dimensions $L\times L\times d$, where the thickness of the slab $d \ll L$, as shown in Fig. 7.5(a). Since there are no forces applied to the free surface, the stresses σ_{iz} are all zero on the surface and through the entire (thin) slab. However, there can be non-zero stresses with components parallel to the surface, σ_{xx}, σ_{xy}, and σ_{yy}, as shown in Fig. 7.5(b). We can always rotate the coordinate system such that $\sigma_{xy}=0$. Since the total force acting on the slab is zero, we can write:

$$F_x = \int_0^L \mathrm{d}y \int_0^d \sigma_{xx}(z)\,\mathrm{d}z = 0. \tag{7.44}$$

If $d \ll L$, the stress does not depend on y and this integral can be transformed as follows

$$\begin{aligned}\int_0^L \mathrm{d}y \int_0^d \sigma_{xx}(z)\,\mathrm{d}z &= L\int_0^d \sigma_{xx}(z)\,\mathrm{d}z \\ &= L\left(\int_0^\delta \sigma_{xx}\,\mathrm{d}z + \int_\delta^{d-\delta} \sigma_{xx}\mathrm{d}z + \int_{d-\delta}^d \sigma_{xx}\,\mathrm{d}z\right),\end{aligned}$$

where δ is the thickness of the surface layer. As can be seen from Fig. 7.5(b), the stress in the bulk (i.e. in the second integral) only weakly depends on the

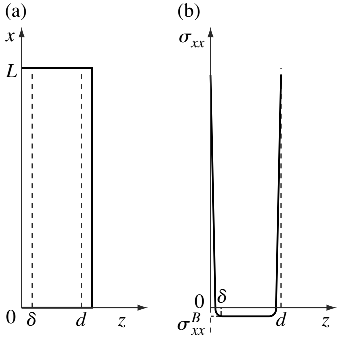


Fig.7.5
(a) A thin slab with two free surfaces and (b) the stress distribution $\sigma_{xx}(z)$ through this slab.

distance from the surface and can be approximated as a constant, σ_{xx}^{B}. The first and third integrals can be combined into one term:

$$L\left(\int_0^{\delta}\sigma_{xx}\mathrm{d}z+\int_{d-\delta}^{d}\sigma_{xx}\mathrm{d}z\right)=2Lf_{xx}^{\Sigma},$$

where f_{xx}^{Σ} is the force acting on each of the two surface layers in x-direction, per unit length in the y-direction. Using this notation and the constancy of the stress in the bulk, Eq. (7.44) can be rewritten as

$$F_x=2Lf_{xx}^{\Sigma}+L\sigma_{xx}^{B}(d-2\delta)=0. \tag{7.45}$$

Since the thickness of the surface layer is limited to a times the spacing between neighboring atoms, $\delta \ll d$ and we can rewrite Eq. (7.45) as

$$f_{xx}^{\Sigma}=-\sigma_{xx}^{B}d/2.$$

Of course, an analogous relation can be obtained for f_{yy}^{Σ}. Rotating the coordinate system with respect to the material, we find that, in general, f_{ij}^{Σ} is a second rank tensor in two-dimensions (i.e. the dimensions that contain the surface)

$$f_{ij}^{\Sigma}=-\sigma_{ij}^{B}d/2, \tag{7.46}$$

where i and j are equal to either x or y. The tensor f_{ij}^{Σ} is called the **surface stress**. However, while the stress has dimensions J/m^3, the surface stress has dimensions J/m^2.

The surface stress and the surface free energy, γ, have the same origin—the fact that the atomic structure and bonding in the surface is different than in the bulk. Therefore, these values should be related. We now derive this relation. Consider a small homogeneous strain, $\mathrm{d}\varepsilon_{ij}$. The change of the free energy of this slab consists of two contributions: elastic contribution described by Eq. (7.20) and the contribution associated with the change of the in the area of the surface

$$\mathrm{d}A=d\cdot S\sigma_{ij}^{B}\mathrm{d}\varepsilon_{ij}+\frac{\partial(2\gamma S)}{\partial\varepsilon_{ij}}\mathrm{d}\varepsilon_{ij}=d\cdot S\sigma_{ij}^{B}\mathrm{d}\varepsilon_{ij}+2\gamma\frac{\partial S}{\partial\varepsilon_{ij}}\mathrm{d}\varepsilon_{ij}+2S\frac{\partial\gamma}{\partial\varepsilon_{ij}}\mathrm{d}\varepsilon_{ij},$$

where S is the surface area ($S=L\times L$). Inserting Eq. (7.46) into the previous relation and setting $\mathrm{d}A=0$ (equilibrium condition), we find

$$f_{ij}^{\Sigma}S=\gamma\frac{\partial S}{\partial\varepsilon_{ij}}+S\frac{\partial\gamma}{\partial\varepsilon_{ij}}.$$

The change of the surface area can be expressed through the strain as

$$\Delta S=S(\varepsilon_{xx}+\varepsilon_{yy}).$$

Therefore $\partial S/\partial\varepsilon_{ij}=S\delta_{ij}$ (recall that i and j can be either x or y) and we finally obtain

$$f_{ij}^{\Sigma}=\gamma\delta_{ij}+\frac{\partial\gamma}{\partial\varepsilon_{ij}}. \tag{7.47}$$

Note, that in a liquid $\partial\gamma/\partial\varepsilon_{ij} = 0$, since it is not possible to elastically strain the surface of a liquid. This is because any strain in the plane of the surface is accommodated by liquid flow. Therefore, the surface stress in a liquid is simply equal to the product of the surface tension and the identity tensor, $f_{ij}^{\Sigma} = \gamma\delta_{ij}$. This is in stark contrast to a solid, where all terms in the surface stress can be non-zero.

8

Kinetics of homogeneous chemical reactions

Kinetics considers the rates of different processes. Chemical kinetics refers to the rates and mechanisms of chemical reactions and mass transfer (diffusion). Recall that since thermodynamic equilibrium implies that the rates of all processes are zero, time is not a thermodynamic variable. Rather, time is the new parameter introduced by the consideration of kinetic processes.

The rate of a kinetic process and how it depends on time is determined, in part, by the degree of the deviation from equilibrium. If the deviation from equilibrium is small, the rate decreases (without changing sign) as the system approaches equilibrium. If the deviation from equilibrium is large, the situation is more complicated. For example, non-monotonic (including oscillatory) processes are possible. The sign of the rate can change during such processes; that is, the reaction can proceed in one direction and then the other. Additionally, if the deviation from equilibrium is large, small changes to the system can produce very large changes in the rate of the kinetic process (i.e. chaos). Non-equilibrium, yet nearly stationary states of the system can arise (i.e. states that exist for a very long time). Finally, if the deviation from equilibrium is very large, the system can explode (i.e. the process continues to accelerate with time).

In this chapter, we develop a formal description of the kinetics of rather simple chemical reactions. Consecutive and parallel reactions will also be considered here. A more general approach (irreversible thermodynamics) will be considered in Chapter 9. In Chapter 10, we examine diffusive processes. Then, in Chapter 11, we consider the kinetics of heterogeneous processes.

8.1 Formal kinetics of homogeneous reactions

8.1.1 Chemical reaction rate

In order to start the study of chemical reaction kinetics, we must first define what we mean by the rate of reaction. Consider the following homogeneous reaction:

$$Cl_2 + 2NO \rightarrow 2NOCl. \tag{8.1}$$

The changes of the concentrations of the reactants are related to each other by the stoichiometric coefficients

$$-\mathrm{d}c_{\mathrm{Cl}_2} = -\frac{1}{2}\mathrm{d}c_{\mathrm{NO}} = \frac{1}{2}\mathrm{d}c_{\mathrm{NOCl}}.$$

By definition, the corresponding **rate of reaction**, or simply the **rate**, is

$$\omega = -\frac{\mathrm{d}c_{\mathrm{Cl}_2}}{\mathrm{d}t} = -\frac{1}{2}\frac{\mathrm{d}c_{\mathrm{NO}}}{\mathrm{d}t} = \frac{1}{2}\frac{\mathrm{d}c_{\mathrm{NOCl}}}{\mathrm{d}t}, \tag{8.2}$$

where t is time.

We now consider the mechanism by which reaction (8.1) proceeds. The simplest assumption is that the elementary step in this reaction is the collision of two NO molecules with one $\mathrm{Cl_2}$ molecule. From the molecular-kinetic theory of gases, we know that the number of such collisions per unit time is proportional to the $\mathrm{Cl_2}$ concentration and the square of the NO concentration. Therefore, the rate of this reaction can be written as

$$\omega = k c_{\mathrm{NO}}^2 c_{\mathrm{Cl}_2}, \tag{8.3}$$

where k is a constant which is independent of concentration and time. k is referred to as the **rate constant** of the chemical reaction.

Expressions like that in Eq. (8.3) are known as **kinetic equations**. The power with which the concentration of a given species enters the kinetic equation, is referred to as the **order of the reaction in that species**. The sum of these orders for all of the reacting species is called the **overall order of the reaction**. According to Eq. (8.3), reaction (8.1) is a third-order reaction; it is second order with respect to NO and first order with respect to $\mathrm{Cl_2}$. In reality, third-order reactions are rare and higher order reactions never happen (except if you are a mathematical purist). The reason for this observation is that although the form of the reaction equation may suggest that a reaction is of high order, in practice the reaction proceeds through a sequence of **elementary reactions** of lower order. The total reaction is referred to as **complex**. It is only for elementary reactions that the order of reaction can be determined directly from the equation of reaction. The elementary reactions can be characterized by **molecularity**, which is the number of reacting molecules: **unimolecular reactions, bimolecular reactions**, etc. In contrast with the reaction order, the molecularity is a theoretical term reflecting the actual mechanism of a chemical reaction. Most reactions occurring in the real world are complex and their reaction equation only shows conservation of elemental species and not molecularity. Although the order of the reaction has no physical meaning, it can be extracted from experiments (as described in Section 8.1.2) and used to characterize a reaction.

In order to illustrate these ideas, consider the following reaction occurring in an aqueous solution

$$2\mathrm{NO}_2^- + \mathrm{O}_2 \rightarrow 2\mathrm{NO}_3^-.$$

If this equation reflects the actual reaction mechanism, the reaction would have the overall order three. However, experiments do not support this conclusion. The actual reaction mechanism was found to be

$$NO_2^- + O_2 \xrightarrow{k_1} NO_3^- + O$$

$$NO_2^- + O \xrightarrow{k_2} NO_3^-$$

$$2O \xrightarrow{k_3} O_2,$$

where each of these reactions is elementary and proceeds toward the right-hand side with the rate constant that is written above the arrow. We now construct kinetic equations corresponding to this mechanism. The ions NO_3^- are formed in the first and second reactions, and their rate of formation can be written as

$$\frac{d[NO_3^-]}{dt} = k_1[NO_2^-][O_2] + k_2[NO_2^-][O],$$

where the square brackets mean the concentration in the water solution. The intermediate product, atomic oxygen, participates in all three reactions: it is formed in the first reaction and is consumed in the second and third reactions. The net rate of formation of atomic oxygen is

$$\frac{d[O]}{dt} = k_1[NO_2^-][O_2] - k_2[NO_2^-][O] - 2k_3[O]^2,$$

(the factor 2 in front of the last term is associated with the fact that for the third reaction, the rate includes a factor of a half—$\omega = -(1/2)d[O]/dt$). Experiments have shown that $d[O]/dt$ is small such that we can assume that $d[O]/dt = 0$ (this is a **steady-state approximation**—see Section 8.2.1). With this assumption, we can solve the previous equation to obtain the steady-state oxygen concentration

$$[O] = \frac{k_1[NO_2^-][O_2]}{k_2[NO_2^-] + 2k_3[O]}.$$

Inserting this expression into equation for the rate of formation of NO_3^-, we obtain

$$\frac{d[NO_3^-]}{dt} = k_1[NO_2^-][O_2]\left(1 + \frac{k_2[NO_2^-]}{k_2[NO_2^-] + 2k_3[O]}\right).$$

Clearly, the kinetic equation for this reaction is more complicated than it would be if we were to base it solely on the order of the reaction we would assume from the reaction equation. However, if the atomic oxygen concentration is small (this implies that $k_2[NO_2^-] \gg 2k_3[O]$), the previous equation reduces to

$$\frac{d[NO_3^-]}{dt} = 2k_1[NO_2^-][O_2].$$

In this limit, the reaction rate is given by the product of powers of the reactant concentrations (i.e. this is consistent with a formal kinetics description). However, the reaction is first order with respect to both the NO_2^- and O_2 concentrations and has an overall reaction order of 2 (not 3, as we would expect based upon the reaction equation).

8.1.2 Determination of the reaction order and the rate constant

Consider the following reaction:

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}. \tag{8.4}$$

The kinetic equation for this reaction takes the form

$$\omega = kc_{\text{A}}^{n_{\text{A}}} c_{\text{B}}^{n_{\text{B}}}, \tag{8.5}$$

where n_i is the reaction order in the ith reactant. If at the beginning of the experiment, there were only reactants and no products and the reactants concentrations were in stoichiometric proportions

$$\frac{c_{\text{A}}^0}{a} = \frac{c_{\text{B}}^0}{b}, \tag{8.6}$$

this ratio of the concentrations will not change during the reaction, that is,

$$\frac{c_{\text{A}}}{a} = \frac{c_{\text{B}}}{b}.$$

Inserting this relation into the right side of Eq. (8.5), and expressing the reaction rate ω in terms of the concentration of A, we obtain

$$-\frac{1}{a}\frac{\mathrm{d}c_{\text{A}}}{\mathrm{d}t} = kc_{\text{A}}^{n_{\text{A}}}\left(c_{\text{A}}\frac{b}{a}\right)^{n_{\text{B}}}.$$

Introducing a new constant

$$k_1 = ka^{1-n_{\text{B}}} b^{n_{\text{B}}}, \tag{8.7}$$

we finally find

$$-\frac{\mathrm{d}c_{\text{A}}}{\mathrm{d}t} = k_1 c_{\text{A}}^n, \tag{8.8}$$

where n is the overall reaction order ($n = n_{\text{A}} + n_{\text{B}}$).

We now consider experimental methods for the determination of the reaction order and the constant k_1 (the rate constant k can be calculated from k_1 through Eq. (8.7) if we know n_{B}).

1. The van't Hoff method. In this method, the time dependence of the A concentration $c_{\text{A}}(t)$, shown in Fig. 8.1, is found from experiment. The derivative $\mathrm{d}c_{\text{A}}/\mathrm{d}t$ as a function of time is found from these data. Equation (8.8) implies

$$\ln\left[-\frac{\mathrm{d}c_{\text{A}}}{\mathrm{d}t}\right] = \ln\, k_1 + n\,\ln\, c_{\text{A}}.$$

Therefore, the slope obtained from a plot of $\ln[\mathrm{d}c_{\text{A}}/\mathrm{d}t]$ versus $\ln(c_{\text{A}})$, as shown in Fig. 8.2, is the overall reaction order n, and the intersection of this curve with the ordinate (vertical) axis is the constant, $\ln(k_1)$.

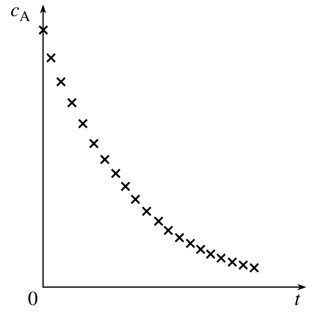


Fig. 8.1
The time dependence of the concentration of a reactant.

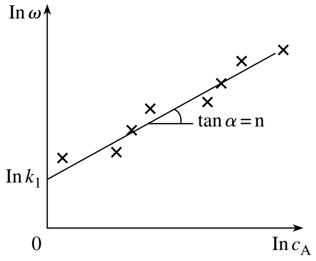


Fig. 8.2
A schematic illustration of the van't Hoff method for determining the overall reaction order and constant k_1 from experimental data.

While this method is simple, it yields the worst accuracy of all of the methods discussed in this section. This is because the uncertainty in the derivative is usually much larger than in the initial data.

2. Determination of the overall reaction order and the constant k_1 from the form of the concentration time curve. The time dependence of the concentration of A can most easily be seen by directly integrating the differential equation (Eq.(8.8)). If $n \neq 1$, we find

$$\int_{c_A^0}^{c_A} \frac{dc_A}{c_A^n} = -k_1 \int_0^t dt$$

or

$$\frac{1}{(c_A)^{n-1}} = \frac{1}{(c_A^0)^{n-1}} + (n-1)k_1 t \quad \text{for } n \neq 1. \tag{8.9}$$

In particular, we obtain

$$c_A = c_A^0 - k_1 t \quad \text{for } n = 0 \tag{8.10}$$

$$\frac{1}{c_A} = \frac{1}{c_A^0} + k_1 \mathrm{t} \quad \text{for } n = 2. \tag{8.11}$$

For $n = 1$, we find

$$\ln c_A = \ln c_A^0 - k_1 t \quad \text{for } n = 1. \tag{8.12}$$

The main idea of this method is to plot the experimentally determined concentration versus time in coordinates corresponding to Eqs (8.9)–(8.12) and see in which the data fall upon a straight line. For example, if the data lie on a straight line in a plot of $\ln c_A$ versus t, the overall reaction order is one (see Eq. (8.12)). The disadvantage of this method is that it is relatively laborious; several different sets of axis coordinates should be tried. If the overall order of reaction is a fraction, it may be difficult to identify the order. Fortunately, this can be done efficiently on a computer. You will have the opportunity to use this method in Computer Laboratory #5.

3. The half-life method. The **half-life** is defined as the time required for one half of the reactants to be consumed. We can obtain the half-life of species A from Eq. (8.9) by setting the concentration of A equal to one half of its initial concentration and solving for the time:

$$\frac{2^{n-1}}{(c_A^0)^{n-1}} = \frac{1}{(c_A^0)^{n-1}} + (n-1)k_1 t_{1/2}$$

or

$$t_{1/2} = \frac{2^{n-1} - 1}{k_1(n-1)(c_A^0)^{n-1}} \quad \text{for } n \neq 1. \tag{8.13}$$

Analogously, we can obtain the half-life for first order reactions from Eq. (8.12)

$$t_{1/2} = \frac{\ln 2}{k_1} \quad \text{for } n = 1. \tag{8.14}$$

These two equations can be represented in a single form as

$$\ln t_{1/2} = \text{const} + (1 - n) \ln c_A^0.$$

Therefore, the overall order can be determined from the slope of the dependence of $\ln t_{1/2}$ from $\ln c_A^0$ (see Fig. 8.3). Note that in the case of a first order reaction, the half-life does not depend on the initial concentration.

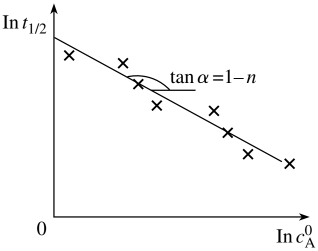


Fig. 8.3
The determination of the overall reaction order and the constant k_1 using the half-life method.

4. *The isolation method.* To this point, we have focused on how to determine the overall order of reaction. However, in order to understand reaction mechanisms, it is necessary to find the order of reaction with respect to each of the reactants. The simplest approach to do this is to combine all of the reactants in large excess except for the one under investigation. For example, for the reaction described by Eq. (8.4), this implies that

$$c_A^0 \ll c_B^0. \tag{8.15}$$

In this limit, any relative changes in the B concentration $\left(c_B(t) - c_B^0\right)/c_B^0$ will be very small such that we can assume that $c_B(t)$ is constant. Using this observation, we can rewrite Eq. (8.5) as

$$-\frac{dc_A}{dt} = k'(c_A)^{n_A}, \tag{8.16}$$

where

$$k' = ka(c_B)^{n_B}. \tag{8.17}$$

Equation (8.16) has the same form as Eq. (8.8); therefore we can use one of the three methods described above to determine the order of the reaction with respect to A.

Review questions

1. The reaction $aA + bB \rightarrow cC$ is first order with respect to both A and B. When is the equation $1/c_A = 1/c_A^0 + kt$ valid?
2. The reaction $aA + bB \rightarrow cC$ is first order with respect to both A and B. When is the equation $\ln c_A = \ln c_A^0 - kt$ valid?
3. What is the dimensionality of the rate constant for a reaction that has an overall order $n = 0.5$?

Example problems

1. A first-order reaction proceeds until 75% of reactant A is consumed within 10 min. Determine the rate constant.
2. Consider the second-order reaction

$$A + B \xrightarrow{k} D \quad k = 5.41/(\text{mole s}).$$

The initial concentration of the reactants was $c_A^0 = c_B^0 = 0.02$ mole/l. Determine the fraction of A which will be consumed during the first minute.

3. The kinetics of the reaction

$$A + B \rightarrow C,$$

proceeding at constant volume and $T = 300\,\mathrm{K}$ was studied by measuring the total pressure as a function of time. The initial mixture of the reactants in the vessel was equimolar. The following data were obtained

t (min)	0	5	10	15	21	30
p (atm)	0.953	0.888	0.818	0.769	0.726	0.663

Determine the overall order of this reaction.

8.1.3 Kinetics of chemical reactions near equilibrium

We have considered only forward reactions to this point. This is reasonable at the beginning of the reaction, provided that the initial concentrations of the products are zero. If this is not the case, we should also consider the backward reaction. For example, consider the synthesis reaction of hydrogen iodide

$$H_2 + I_2 \rightarrow 2HI.$$

We will assume that this equation corresponds to the actual mechanism of this reaction (i.e. this is an elementary reaction). Then the rate of the forward reaction is

$$\omega_1 = k_1 c_{H_2} c_{I_2},$$

and the rate of the backward reaction is

$$\omega_2 = k_2 c_{HI}^2.$$

The experimentally observed reaction rate is

$$\omega = \omega_1 - \omega_2 = k_1 c_{H_2} c_{I_2} - k_2 c_{HI}^2.$$

From this equation, we see that we can neglect the backward reaction only if the second term on the right side is small. Certainly it is not the case of equilibrium, where $\omega = 0$. In equilibrium,

$$\frac{c_{HI}^2}{c_{H_2} c_{I_2}} = \frac{k_1}{k_2} = \text{const.}$$

This is not a new result; we just derived the law of mass action,[1] which we previously discussed from the thermodynamic point of view. Indeed, the equilibrium constant K_c for the reaction under consideration takes the following form:

$$K_c = \frac{c_{HI}^2}{c_{H_2} c_{I_2}}.$$

---

[1] It was actually first obtained based upon kinetic ideas.

Therefore, for elementary reactions, the equilibrium constant is the ratio of the forward and backward rate constants

$$K_c = \frac{k_1}{k_2}. \tag{8.18}$$

8.1.4 Dependence of the rate constant on temperature

There is ample experimental data that demonstrate that the rate constant increases with increasing temperature. Without loss of generality, we can represent the temperature dependence of the rate constant as

$$\frac{\mathrm{d}\ \ln k}{\mathrm{d}T} = \frac{E}{RT^2}, \tag{8.19}$$

where E is an energy and is called the **activation energy**. Since $\mathrm{d}\ \ln k/\mathrm{d}T > 0$, we must conclude that $E > 0$. Equation (8.18) is known as the **Arrhenius law**. The forward and backward reaction rate constants can be expressed as

$$\frac{\mathrm{d}\ \ln k_1}{\mathrm{d}T} = \frac{E_1}{RT^2}; \qquad \frac{\mathrm{d}\ \ln k_2}{\mathrm{d}T} = \frac{E_2}{RT^2}.$$

If both of these reactions are elementary, we can use the expression for the equilibrium constant in Eq. (8.18) together with the van't Hoff isochore (5.19) to show

$$\frac{\Delta U_T^0}{RT^2} = \frac{\mathrm{d}\ \ln K_c}{\mathrm{d}T} = \frac{\mathrm{d}\ \ln k_1}{\mathrm{d}T} - \frac{\mathrm{d}\ \ln k_2}{\mathrm{d}T} = \frac{E_1}{RT^2} - \frac{E_2}{RT^2}$$

or

$$\Delta U_T^0 = E_1 - E_2. \tag{8.20}$$

Equation (8.19) is simply one of many possible forms we could have used to express the temperature dependence of the rate constant. Its utility comes from a key experimental observation: for most reactions, the activation energy, E, is found to be temperature independent. In this case, the Arrhenius equation can be easily integrated to find

$$k = \mathrm{A}\mathrm{e}^{-E/RT}, \tag{8.21}$$

where A is an integration constant and, hence, must be independent of temperature. A is known as the **pre-exponential factor**. The pre-exponential factor can be thought of as the rate constant in the $T \to \infty$ limit.

The observation that the activation energy is independent of temperature is not trivial. The remainder of this section presents a simple, but not very rigorous, interpretation of the Arrhenius equation on the basis of a theory known as the **theory of the activated complex** (see also Section 12.3.3).

Consider the elementary reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{AB} \tag{8.22}$$

the rate of which can be written as

$$\omega = k c_{\mathrm{A}} c_{\mathrm{B}}. \tag{8.23}$$

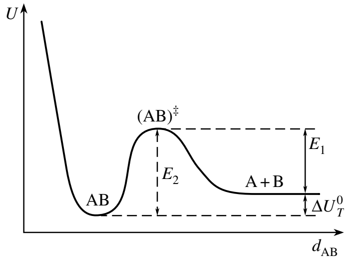


Fig. 8.4
Variation of the energy of the system with the separation between A and B atoms.

We can describe this reaction as a collision of molecules A and B which leads to the formation of the new molecule AB. We can monitor this process in terms of the distance between molecules A and B, d_{AB}. If we start with well-separated A and B molecules, the energy of the system will increase as we bring them close together (d_{AB} decreases), as follows from quantum mechanics. Alternatively, if we start with the AB molecule and increase the A–B spacing (d_{AB}), the energy must also increase (since the AB molecule is stable). If the energy increases as we decrease d_{AB} from large separations and increases when we increase d_{AB} from small separations, there must be a maximum in the energy at intermediate d_{AB}. Figure 8.4 shows this type of variation of the energy of the system with the separation between A and B atoms. We can consider this variation as a **reaction path** or reaction coordinate. The state corresponding to the maximum energy ($(AB)^{\ddagger}$ in Fig. 8.4) is called the **activated complex**.

According to the activated complex theory, the reaction in Eq. (8.22) can be represented as[2]

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AB)^{\ddagger} \xrightarrow{k^*} AB \tag{8.24}$$

and its rate as

$$\omega = k^* c_{(AB)^{\ddagger}}. \tag{8.25}$$

The reaction described by Eq. (8.24) consists of two stages. The first stage of this reaction is reversible and the second stage is not (of course, the reaction $AB \rightarrow (AB)^{\ddagger}$ is also possible, but this is part of the backward reaction of Eq. (8.22) and is treated separately).

The first stage of the reaction can be thought of as a regular reaction, the equilibrium of which is described by the following constant:

$$K_c^{\ddagger} = \frac{c_{(AB)^{\ddagger}}}{c_A c_B}. \tag{8.26}$$

The van't Hoff isochore for this reaction is

$$\frac{d \ln K_c^{\ddagger}}{dT} = \frac{E_1}{RT^2}, \tag{8.27}$$

where E_1 is the heat of formation of the activated complex. Inserting Eq. (8.26) into Eq. (8.25), we find

$$\omega = k^* K_c^{\ddagger} c_A c_B. \tag{8.28}$$

Comparison with the kinetic equation (Eq. (8.23)) for the reaction $A + B \rightarrow AB$ shows that

$$k = k^* K_c^{\ddagger}. \tag{8.29}$$

---

[2] Note that the rate constants k_1 and k_{-1} used in the activated complex theory are not the same as the rate constants k_1 and k_2 for the forward and backward reactions used in Section 8.1.3. The rate constants k_1 and k_{-1} in Eq. (8.24) describe the reaction $A + B \rightarrow (AB)^{\ddagger}$, rather than $A + B \rightarrow AB$.

The rate of the second stage of the reaction described in Eq. (8.24) is determined by the motion of the A–B system along the reaction path. From the molecular-kinetic theory of gases, we know that this velocity is proportional to the square root of the temperature (recall that the kinetic energy of molecules is proportional to temperature). Therefore, we can assume that the rate constant k^* has the same temperature dependence. The temperature dependence of the equilibrium constant, $K_c^\ddagger$ is Arrhenius (i.e. as in Eq. (8.27)); this is a much stronger temperature dependence than that of k^*.

Rewriting Eq. (8.29) as

$$\ln k = \ln k^* + \ln K_c^\ddagger,$$

assuming that k^* is temperature independent and taking the derivative with respect to temperature, we find

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{\mathrm{d}\ln K_c^\ddagger}{\mathrm{d}T}.$$

Inserting this relation into Eq. (8.27), we recover the Arrhenius law

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E_1}{RT^2}.$$

Now we see that the activation energy of the forward reaction is no more than the heat of reaction of the activated complex formation from the reactants. Analogously, the activation energy of the backward reaction is the heat of reaction of the activated complex formation from the products. Examination of Fig. 8.4 clarifies why the heat of reaction is simply the difference between these two activation energies, as per Eq. (8.20).

We can re-express the equilibrium constant for the first stage of the reaction in Eq. (8.24) through $K_p^\ddagger$ using $K_c^\ddagger = K_p^\ddagger RT$. The change of enthalpy associated with this reaction is $\Delta H^\ddagger = \Delta U^\ddagger - RT = E_1 - RT$. Finally, recall that $K_p^\ddagger = e^{-\Delta G^\ddagger/RT}$. Inserting these relations into Eq. (8.29), we find

$$k = k^* K_p^\ddagger RT = k^* RT\mathrm{e}^{-\Delta G^\ddagger/RT} = ek^* RT\mathrm{e}^{\Delta S^\ddagger/R}\mathrm{e}^{-E_1/RT} = A\mathrm{e}^{-E_1/RT}, \quad (8.30)$$

where, of course, $e = \mathrm{e}^1$. The pre-exponential factor, A, is a product of constants and only weak functions of temperature, it is clear that the variation of A from reaction to reaction is dominated by the entropy of the activated complex formation.

Example problem

1. The half-life for a first-order reaction at $T_1 = 260\,\mathrm{K}$ is 693 min. The activation energy for this reaction is $E = 54.3\,\mathrm{kJ/mole}$. Find the time required to consume 2/3 of the reactants at $T_2 = 350\,\mathrm{K}$.

8.2 Kinetics of complex reactions

A complex reaction is composed of several elementary reactions. These reactions can proceed consecutively or in parallel, independently from each other or not. A full discussion of complex reaction is itself complex and beyond the scope of this text. In this section we only consider three simple examples.

8.2.1 Kinetics of consecutive reactions

A **consecutive reaction** is a reaction consisting of several consecutive stages. For example, consider the simplest possible consecutive reaction proceeding at constant volume and consisting of two first-order elementary reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}. \tag{8.31}$$

We assume that initially the concentration of reactant A is c_A^0 and the concentrations of the **intermediate** B and the product C are zero. We can write kinetic equations for the two stages of the reaction in Eq. (8.31):

$$-\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} = k_1 c_\mathrm{A} \tag{8.32}$$

$$\frac{\mathrm{d}c_\mathrm{C}}{\mathrm{d}t} = k_2 c_\mathrm{B} = k_2\left(c_\mathrm{A}^0 - c_\mathrm{A} - c_\mathrm{C}\right), \tag{8.33}$$

where we have used the conservation law, $c_\mathrm{A} + c_\mathrm{B} + c_\mathrm{C} = c_\mathrm{A}^0$, in the right-hand side of Eq. (8.33). Integrating Eq. (8.32), we obtain

$$\int_{c_\mathrm{A}^0}^{c_\mathrm{A}} \frac{\mathrm{d}c_\mathrm{A}}{c_\mathrm{A}} = -k_1 \int_0^t \mathrm{d}t; \qquad \ln c_\mathrm{A} = \ln c_\mathrm{A}^0 - k_1 t$$

$$c_\mathrm{A} = c_\mathrm{A}^0 \mathrm{e}^{-\mathrm{k}_1 \mathrm{t}}. \tag{8.34}$$

As expected, the first reaction, A → B, is indeed first order. Inserting this expression into Eq. (8.33), we find

$$\frac{\mathrm{d}c_\mathrm{C}}{\mathrm{d}t} = k_2\left(c_\mathrm{A}^0 - c_\mathrm{A}^0 \mathrm{e}^{-k_1 t} - c_\mathrm{C}\right)$$

or

$$\frac{\mathrm{d}c_\mathrm{C}}{\mathrm{d}t} + k_2 c_\mathrm{C} = k_2 c_\mathrm{A}^0\left(1 - \mathrm{e}^{-k_1 t}\right).$$

This differential equation has a solution of the following form

$$c_\mathrm{C} = \mathrm{A}\mathrm{e}^{-k_2 t}.$$

Inserting this expression into the previous equation, we can solve for A:

$$A = c_\mathrm{A}^0\left(\mathrm{e}^{k_2 t} - \frac{k_2}{k_2 - k_1}\mathrm{e}^{(k_2 - k_1)t}\right) + B$$

to obtain

$$c_{\mathrm{C}} = c_{\mathrm{A}}^0 \left(1 - \frac{k_2}{k_2 - k_1} \mathrm{e}^{-k_1 t}\right) + B\mathrm{e}^{-k_2 t}.$$

The constant B can be determined from the initial condition $c_{\mathrm{C}}\,(t = 0) = c_{\mathrm{C}}^0 = 0$:

$$B = -c_{\mathrm{A}}^0 \left(1 - \frac{k_2}{k_2 - k_1}\right) = c_{\mathrm{A}}^0 \frac{k_1}{k_2 - k_1}.$$

Inserting this back into the expression for c_{C}, we obtain

$$c_{\mathrm{C}} = c_{\mathrm{A}}^0 \left(1 - \frac{k_2}{k_2 - k_1} \mathrm{e}^{-k_1 t}\right) + c_{\mathrm{A}}^0 \left(\frac{k_1}{k_2 - k_1} \mathrm{e}^{-k_2 t}\right)$$

or

$$c_{\mathrm{C}} = c_{\mathrm{A}}^0 \left(1 - \frac{k_2}{k_2 - k_1} \mathrm{e}^{-k_1 t} + \frac{k_1}{k_2 - k_1} \mathrm{e}^{-k_2 t}\right). \tag{8.35}$$

Using the conservation law, we also obtain expression for the concentration of B:

$$\begin{aligned} c_{\mathrm{B}} &= c_{\mathrm{A}}^0 - c_{\mathrm{A}} - c_{\mathrm{C}} \\ &= c_{\mathrm{A}}^0 - c_{\mathrm{A}}^0 \mathrm{e}^{-k_1 t} - c_{\mathrm{A}}^0 \left(1 - \frac{k_2}{k_2 - k_1} \mathrm{e}^{-k_1 t} + \frac{k_1}{k_2 - k_1} \mathrm{e}^{-k_2 t}\right) \end{aligned}$$

or

$$c_{\mathrm{B}} = c_{\mathrm{A}}^0 \frac{k_1}{k_2 - k_1} (\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}). \tag{8.36}$$

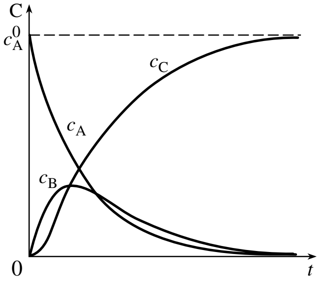


Fig. 8.5
The time dependence of the concentrations of the species in the reaction in Eq. (8.31).

Figure 8.5 shows the time dependence of the concentration of each of the species in the reaction in Eq. (8.31). The concentration of reactant A decreases monotonically during the reaction. The concentration of intermediate B first increases, then reaches a maximum at

$$t_{\max} = \frac{\ln\,(k_2/k_1)}{k_2 - k_1},$$

and finally decreases. Product C initially forms very slowly (Eq. (8.35) implies that $\mathrm{d}c_{\mathrm{C}}/\mathrm{d}t = 0$ at $t = 0$), then the rate of production of C increases until the concentration of B reaches its maximum, and then decreases.

We now consider two limiting cases. In the first case $k_1 \gg k_2$ and Eq. (8.35) reduces to

$$c_{\mathrm{C}} = c_{\mathrm{A}}^0 (1 - \mathrm{e}^{-k_2 t}).$$

This type of kinetic equation is representative of a first-order reaction with rate constant k_2. Therefore the second reaction (which is slower than the first one) is the **rate-determining step** of the entire consecutive reaction.

If $k_2 \gg k_1$, Eq. (8.35) reduces to

$$c_{\mathrm{C}} = c_{\mathrm{A}}^0 (1 - \mathrm{e}^{-k_1 t}).$$

This also represents a first-order reaction, but now with rate constant k_1 instead of k_2. The rate-determining step in this case is the first reaction (which is slower than the second one). Therefore, we can conclude that the rate of a consecutive reaction is determined by the rate of its slowest stage (assuming that the rate constant for the rate-determining step is sufficiently smaller than those of all of the other steps).

If $k_2 \gg k_1$, Eq. (8.36) reduces to

$$c_B = c_A^0 \frac{k_1}{k_2} e^{-k_1 t}.$$

Comparing this result with Eq. (8.34), we find

$$\frac{c_B}{c_A} = \frac{k_1}{k_2} = \text{const.}$$

Therefore, during most of the reaction, the ratio of the concentrations of A and B remains approximately constant and the change of the concentration of the intermediate B can be neglected

$$\frac{dc_B}{dt} = \frac{d\left(c_A^0 - c_A - c_C\right)}{dt} = -\frac{dc_A}{dt} - \frac{dc_C}{dt} = k_1 c_A - k_2 c_B \approx 0.$$

This result is known as the **steady-state approximation**. In fact, we have already used this method in Section 8.1.1.

8.2.2 Kinetics of parallel reactions

In **parallel reactions**, several independent reactions occur simultaneously. For example, consider the kinetics of a parallel reaction consisting of two unimolecular reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$
$$\mathrm{A} \xrightarrow{k_2} \mathrm{C}. \tag{8.37}$$

We assume that initially the concentration of reactant A is c_A^0 and the concentrations of the products B and C are zero. The kinetic equation for the reaction in Eq. (8.37) takes the following form:

$$-\frac{dc_A}{dt} = k_1 c_A + k_2 c_A = (k_1 + k_2) c_A. \tag{8.38}$$

The solution of this differential equation is

$$c_A = c_A^0 e^{-(k_1+k_2)t}. \tag{8.39}$$

This is representative of a first-order reaction with rate constant $k_1 + k_2$. If the rate constant of the first stage is much larger than that of the second stage, than namely the first stage will determine the rate of the entire parallel reaction. Therefore, in contrast with consecutive reactions, the rate-determining step in parallel reaction is the fastest stage.

We now derive expressions for the time dependences of the concentrations of the products. For product B, we find

$$\frac{dc_B}{dt} = k_1 c_A = k_1 c_A^0 e^{-(k_1+k_2)t}$$

or

$$c_B = -\frac{k_1 c_A^0}{k_1 + k_2} e^{-(k_1+k_2)t} + D.$$

The constant D can be determined from the initial condition $c_B(t=0) = c_B^0 = 0$; therefore, $D = k_1 c_A^0 / k_1 c_A^0 (k_1 + k_2)$ and

$$c_B = \frac{k_1 c_A^0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right). \tag{8.40}$$

Analogously for the concentration of C we find

$$c_C = \frac{k_2 c_A^0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right). \tag{8.41}$$

Note that the ratio of the concentrations of B and C at any moment is $c_B/c_C = k_1/k_2$.

Example problems

1. Nitric oxide decomposes through two parallel reactions

$$NO \xrightarrow{k_1} \frac{1}{2}N_2 + \frac{1}{2}O_2 \quad k_1 = 25.7\,s^{-1}$$

$$NO \xrightarrow{k_2} \frac{1}{2}N_2O + \frac{1}{4}O_2 \quad k_2 = 18.2\,s^{-1}.$$

   The reaction proceeds at constant volume. The initial mixture contained only nitric oxide at a concentration of $c_{NO} = 4$ mole/l. Find the concentration of nitrogen and nitrous oxide (N_2O) in 0.05 s after the beginning of the reaction.

2. Consider two possible mechanisms for the synthesis of HI. The first is

$$H_2 + I_2 \xrightarrow{k} 2HI \tag{8.42}$$

   and the second is

$$I_2 \xrightarrow{k_1} 2I$$

$$2I \xrightarrow{k_2} I_2$$

$$2I + H_2 \xrightarrow{k_3} 2HI. \tag{8.43}$$

   Derive expressions for the rate of formation of HI for both mechanisms (in the second case, use the steady-state approximation). Under what conditions will both mechanisms lead to the same type of kinetic equation?

8.2.3 Kinetics of chain reactions

The main feature of a chain reaction is that its elementary steps are not independent as in simple reactions and each one initiates the following. Hence once started, it continues to propagate until all of the reactants are consumed or until a termination event occurs. Consider the synthesis of HCl from H_2 and Cl_2 as an example

$$H_2 + Cl_2 \rightarrow 2HCl.$$

Experiments show that if hydrogen and chlorine are combined in a dark chamber, very little reaction occurs. However, if we shine a light onto the mixture for just a short time, the rate of formation of HCl dramatically increases. Nernst suggested the following mechanism for this process:

$$\begin{aligned}
&Cl_2 + h\nu \rightarrow 2Cl \text{---}\textbf{initiation step}\\
&\left.\begin{aligned} Cl + H_2 &\rightarrow HCl + H\\ H + Cl_2 &\rightarrow HCl + Cl \end{aligned}\right\}\text{---}\textbf{propagation step}\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
&\left.\begin{aligned} 2Cl &\rightarrow Cl_2\\ 2H &\rightarrow H_2 \end{aligned}\right\}\text{---}\textbf{termination step},
\end{aligned}$$

where $h\nu$ represents a photon. The chain reaction proceeds through the formation of thermodynamically unstable intermediates (atomic H and Cl in the case under consideration), known as **radicals**, by the absorption of photons. Note that once radicals are created they take part in the propagation reaction to form HCl. These reactions do not change the number of radicals in the system. Therefore, additional propagation reactions can occur even without the input of any more light. Since each propagation reaction follows from the previous propagation reaction, we can think of this as a **chain reaction**. This process continues until the radicals undergo a reaction that decreases the number of radicals in the system—that is, the termination step. The number of links in the chain or the **chain length** is equal to the average number of propagation reactions that occur from initiation to termination. If β is the probability that a chain will terminate on the next step, the chain length is given by[3]

$$I = \frac{1}{\beta}. \tag{8.44}$$

[3] By definition, the average chain length is

$$I = \sum_{i=1}^{\infty} i w_i$$

where w_i is the probability that a chain has i links. The probability that a chain has more than one link is $1-\beta$. The probability that a chain has exactly two links is simply equal to the probability that it has more than one link minus the probability that it has more than two links $(1-\beta)^2$: $1-\beta-(1-\beta)^2$. Analogously, the probability that a chain has three links is $(1-\beta)^2-(1-\beta)^3$. Inserting these expressions into the definition of the average chain length, we obtain Eq. (8.44)

$$\begin{aligned}
I &= 1\cdot\beta + 2\big((1-\beta)-(1-\beta)^2\big) + 3\big((1-\beta)^2-(1-\beta)^3\big) + \cdots\\
&= \beta + 2(1-\beta) + (1-\beta)^2 + (1-\beta)^3 + \cdots\\
&= 1 + (1-\beta) + (1-\beta)^2 + (1-\beta)^3 + \cdots\\
&= 1/[1-(1-\beta)] = 1/\beta.
\end{aligned}$$

The average chain length can be very large. For example, for the synthesis reaction of HCl the average chain length reaches 10^5.

Termination steps cannot proceed as bimolecular reactions, as written above. For example, consider the reaction

$$H + H \rightarrow H_2.$$

Clearly, if two hydrogen atoms collide and form a molecule H_2, the product has sufficient energy to dissociate. Therefore, to stabilize the H_2 molecule, a third molecule must participate in the reaction in order to remove at least part of the energy. The role of this third molecule can be played by other gas molecules if the pressure is sufficiently high (in this case, the molecule H_2 has no time dissociate since it quickly transfers energy to other gas molecules by collisions) or by collisions of the H_2 molecule with the chamber walls. Substances which lead to a decreasing in the chain length are called **inhibitors**.

Chain reactions are divided into reactions that produce **simple** or **branching** chains. In the first case, each radical participating in a propagation reaction gives rise to one new radical. The synthesis of HCl considered above is an example of a simple chain reaction. Branching chain reactions are those for which several new radicals can be formed during the propagation step. As an example of this, consider the oxidation of hydrogen at low pressure at a temperature of ~500°C. Under these conditions, the reaction proceeds as follows:

$$\begin{gathered} H + O_2 \rightarrow OH + O \\ OH + H_2 \rightarrow H_2O + H \\ O + H_2 \rightarrow OH + H \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots \;. \end{gathered}$$

Note that branching occurs in the first and the third stages but not in the second.

A schematic of an explosive (accelerating) type of chain reaction is shown in Fig. 8.6. If the pressure is small, no explosion occurs at $T = T_1$ because the radicals collide with and are absorbed by the chamber wall (and recombine with other radicals there) prior to any collisions with other gas phase reactants. Therefore, termination occurs prior to propagation. An explosion is possible only when the pressure is larger than a critical value p_1, known as the **first explosion limit**. However, no explosion is possible at pressures larger than pressure p_2, known as the **second explosion limit**. This limit is associated with triple collisions, which were negligible at low pressure. For example, in the case of oxidation of hydrogen a reaction of the form

$$H + O_2 + M \rightarrow HO_2 + M^*,$$

is possible, where M is a third molecule and M^* is a high energy state of the same molecule. In contrast with H, HO_2 is a radical that does not participate in further reactions and simply recombines on the chamber walls. Therefore, as a result of this triple collision, the number of active

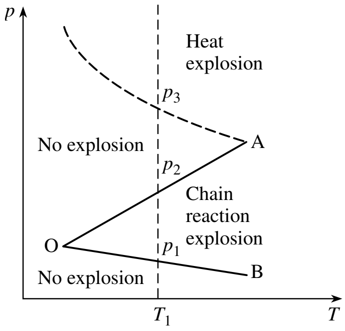


Fig. 8.6
Schematic illustration of the three explosion limits.

radicals in the system decreases, preventing an explosion. Finally, at pressures above the **third explosion limit** p_3, a thermal explosion occurs. This explosion is associated with the fact that if an exothermic reaction proceeds sufficiently quickly, the system heats up, leading to an increased rate of reaction. This produces even more heat and the reaction accelerates (i.e. an explosion occurs).

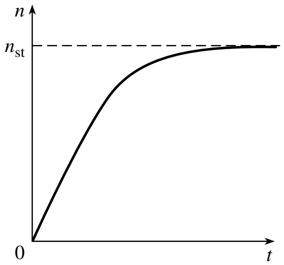


Fig. 8.7
The time dependence of the number of radicals for the case of a reaction with simple chains and constant radical initiation rate.

We now consider a reduced version of the theory of chain reactions with simple chains. We assume that the source of radicals is present and operates at a fixed rate, producing r radicals per unit time. Let τ be the average time required for the system to traverse one link (i.e. the inverse of the number of links traversed per unit time or, equivalently, the average life time of a radical). During the time τ, the chain is either terminated (with probability β) or proceeds along one more link. Therefore, the rate of the change of the number of radicals can be written as

$$\frac{dn}{dt} = r - \frac{n\beta}{\tau}, \tag{8.45}$$

where the second term is number of radicals terminated in unit time. The solution of Eq. (8.45) is (see Fig. 8.7)

$$n = r\frac{\tau}{\beta}\left(1 - e^{-\beta t/\tau}\right). \tag{8.46}$$

The number of radicals in the system tends towards a constant or steady-state value in the long-time limit ($t \to \infty$): $n_{st} = r\tau/\beta = r\tau I$. The reaction rate is

$$\omega = \frac{n}{\tau}(1 - \beta).$$

If $\beta \ll 1$ (the chains are long), then

$$\omega \cong \frac{n}{\tau}, \tag{8.47}$$

and in the steady-state limit

$$\omega_{st} = \frac{n_{st}}{\tau} = \frac{r}{\beta} = rI. \tag{8.48}$$

We now consider a reaction with branching chains. If δ is the probability of the reaction producing two radicals for each radical consumed (the probability of branching), the rate of production of radicals is

$$\frac{dn}{dt} = r - \frac{n\beta}{\tau} + \frac{n}{\tau}(1 - \beta)\delta, \tag{8.49}$$

where the last term on the right accounts for branching. If $\beta \ll 1$ (very long chains—see Eq. (8.44)), Eq. (8.49) reduces to

$$\frac{dn}{dt} = r - \frac{n\beta}{\tau} + \frac{n}{\tau}\delta = r + \frac{n}{\tau}(\delta - \beta). \tag{8.50}$$

The solution of this differential equation has the following form:

$$n = \frac{r\tau}{\beta - \delta}\left(1 - e^{-(\beta-\delta)t/\tau}\right). \tag{8.51}$$

If $\beta > \delta$, then the number of radicals in the system tends to a steady-state value, $n_{st} = r\tau/(\beta - \delta)$ with an average chain length of $I = 1/(\beta - \delta)$. If $\beta < \delta$, the number of radicals in the system grows exponentially in time. In other words, an explosion occurs.

Note that, if $\beta < \delta$, an explosion occurs even if we remove the source of radicals provided that at least n_{init} radicals are present at the beginning. Indeed, in this case, Eq. (8.50) reduces to

$$\frac{dn}{dt} = \frac{n}{\tau}(\delta - \beta).$$

The solution of this equation is

$$n = n_{init}e^{-(\beta-\delta)t/\tau}. \qquad (8.52)$$

This means that the rate of production of radicals diverges in the long time limit (recall that $\beta < \delta$).

The transition from a steady-state reaction to an explosion appears when $\beta = \delta$. The value of β can be varied by changing the reaction conditions. For example, β increases if an inhibitor is added in the reaction chamber. Opposite, if the chamber walls are covered by an inert substance, the adsorption of radicals on the chamber walls is decreased and an explosion is possible.

Example problems

1. Consider the following reaction proceeding in a solution where CCl_4 is the solvent:

   $$C_2Cl_4 + Cl_2 \rightarrow C_2Cl_6.$$

   The chain reaction proceeds through the following steps:

   $$Cl_2 + h\nu \xrightarrow{k_0} 2Cl \text{ — initiation step}$$

   $$\left.\begin{array}{l} Cl + C_2Cl_4 \xrightarrow{k_1} C_2Cl_5 \\ C_2Cl_5 + Cl_2 \xrightarrow{k_2} Cl + C_2Cl_6 \end{array}\right\} \text{— propagation step}$$

   $$C_2Cl_5 + C_2Cl_5 \xrightarrow{k_3} C_2Cl_4 + C_2Cl_6 \text{ — termination step.}$$

   The radicals in this mechanism are atomic Cl and the unstable molecule C_2Cl_5. Derive an expression for the steady-state (late time) rate of formation of C_2Cl_6, assuming that the chains are very long.
2. For a reaction with simple chains, it was found that in 0.1 s after beginning, the reaction rate is $\omega = 0.632\,\omega_{st}$. Find the ratio n_{st}/r for this reaction.

9

Thermodynamics of irreversible processes

The thermodynamics of irreversible processes, formulated by Onsager and Prigogine, considers small deviations from equilibrium in open systems. Despite the fact that the name contains "thermodynamics," this is a type of kinetic theory that describes the rates of irreversible processes.

Since there are no currents of any type in thermodynamic equilibrium, the concept of a current is never used in classical thermodynamics. On the other hand, the thermodynamics of irreversible processes introduces currents as the rates at which processes proceed: the heat or energy current (measured in J/s), matter current (measured in mole/s or kg/s), charge or electrical current (measured in C/s or Amps). Since these currents have a direction and magnitude, they are vectors. The thermodynamics of irreversible processes also considers scalar currents (e.g. rates of chemical reactions) and tensor currents (e.g. momentum currents). In this text, we will focus on current densities or fluxes (that is the current per unit area) rather than currents themselves. The dimensions of the currents described above can be converted to the dimensions of fluxes by dividing through by area or m^2.

Associated with each flux is a driving force. These forces are known as **thermodynamic forces**. How can we determine these driving forces? What is the relation between fluxes and driving forces? The answers to these questions can be found in the thermodynamics of irreversible processes briefly described in this chapter.

9.1 Onsager's first postulate

Onsager's first postulate states that the flux of property i (j_i) is a linear function of *all* thermodynamic forces, X_k, acting in the system

$$j_i = \sum_k L_{ik} X_k, \tag{9.1}$$

where L_{ik} are called **Onsager** (or kinetic) **coefficients**. This postulate was formulated as a generalization of a wide body of experimental observations. In fact, long before Onsager's work it was known that the heat fluxes are proportional to temperature gradients (Fourier's law, 1824), charge fluxes are proportional to electric potential gradients (Ohm's law, 1826), and matter fluxes are proportional to concentration gradients

(Fick's law, 1855). However, Onsager's contribution was the inclusion of the word "all" in his first postulate. Equation (9.1) implies that, for example, the flux of heat depends not only on the temperature gradient but also on the gradients of concentration and electric potential, if they are present in the system. The dependence of the flux of quantity i on "foreign" thermodynamic forces (e.g. k) are known as cross-effects and were also known before Onsager's work. For example, if the two ends of a bimetallic bar (i.e. a bar of one metal joined to a bar of another) are held at different temperatures, an electric potential difference exists between the ends of the bimetallic bar. If these two ends are connected by a wire, an electric current will flow. This is known as the Seebeck effect (thermal electromotive force). Conversely, if an electric potential difference is applied across the bimetallic bar, heat will be produced at the interface where the two bars are joined. This is known as the Peltier effect. Onsager was able to describe both experimental observations with one postulate.

Review questions

1. If the thermodynamic force i is zero, is the flux of quantity i also necessarily zero?
2. If the flux of quantity k is zero, is the thermodynamic force k also necessarily zero?

9.2 Onsager's second postulate

Although we already used the term "thermodynamic force" above, we have not yet fully defined it. It is natural to require that in mechanical cases, the thermodynamic force coincides with the mechanical, or Newtonian, force. For example, consider the motion of particles in a viscous liquid. Let F be a mechanical force acting on each particle. In a vacuum, the mechanical force would cause the particle to accelerate. However, in a viscous liquid, there is a drag force that is proportional to the particle velocity. Therefore, at some velocity v, this drag will compensate the mechanical force F and the particle will move with a constant, steady-state velocity, v. At steady-state, the flux of particles in a system with particle concentration c (number per volume) is

$$j = vc.$$

The work per unit volume associated with the drag force is

$$\delta W = F \cdot cv\,\mathrm{d}t = F \cdot j\,\mathrm{d}t.$$

All of this work is converted into heat such that the entropy of the system irreversibly increases

$$T(\mathrm{d}s)_{\text{irreversible}} = F \cdot j\,\mathrm{d}t$$

or

$$T\left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}} = j \cdot F,$$

where s is the entropy per unit volume.

In the case considered above, there was only a single force. However, we already know that there can be several thermodynamic forces X_i acting upon the same system. In such cases, Onsager postulated that

$$T\left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}} = \sum_i j_i X_i. \tag{9.2}$$

This relation is known as Onsager's second postulate.

9.3 Thermodynamic forces for the transport of heat and matter

We now derive expressions for the thermodynamic forces acting in a system in which concentration and temperature gradients are present. In order to obtain these expressions, it is useful to rewrite Eq. (9.2) in a form in which the right side is a sum of terms which are products of a flux and another quantity. This other quantity will be the thermodynamic force. Since there is a derivative of the entropy in the left side of Eq. (9.2), we start from the combined statement of the first and second laws of thermodynamics (Eq. (1.78)):

$$T\,\mathrm{d}S = \mathrm{d}U + p\,\mathrm{d}V - \sum_{i=1}^{k} \mu_i\,\mathrm{d}n_i. \tag{9.3}$$

In contrast with this equation, Eq. (9.2) contains the entropy per unit volume. Therefore, we rewrite Eq. (9.3) in terms of densities of extensive quantities rather than the extensive quantities themselves. We note that if A is an extensive quantity and a is its density, the following identity is valid:

$$\mathrm{d}\left(\frac{A}{V}\right) = \frac{\mathrm{d}A}{V} - A\frac{\mathrm{d}V}{V^2}$$

or

$$\frac{\mathrm{d}A}{V} = \mathrm{d}a + A\frac{\mathrm{d}V}{V^2}.$$

Taking this identity into account, we can transform Eq. (9.3) as follows:

$$T\frac{\mathrm{d}S}{V} = \frac{\mathrm{d}U}{V} + p\frac{\mathrm{d}V}{V} - \sum_{i=1}^{k} \mu_i \frac{\mathrm{d}n_i}{V}$$

$$T\left(\mathrm{d}s + \frac{S}{V^2}\mathrm{d}V\right) = \left(\mathrm{d}u + \frac{U}{V^2}\mathrm{d}V\right) + p\frac{\mathrm{d}V}{V} - \sum_{i=1}^{k} \mu_i\left(\mathrm{d}c_i + \frac{n_i}{V^2}\mathrm{d}V\right)$$

$$T\,\mathrm{d}s = \mathrm{d}u - \sum_{i=1}^{k} \mu_i\,\mathrm{d}c_i + \frac{\mathrm{d}V}{V^2}\left(U + pV - TS - \sum_{i=1}^{k} \mu_i n_i\right).$$

Since, by definition, $G = U + pV - TS$ and, according to the Gibbs–Duhem equation, $G = \sum_{i=1}^{k} \mu_i n_i$, the expression in the brackets in the last equation is zero and we obtain

$$T\,\mathrm{d}s = \mathrm{d}u - \sum_{i=1}^{k} \mu_i \,\mathrm{d}c_i \tag{9.4}$$

or

$$T\frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \sum_{i=1}^{k} \mu_i \frac{\partial c_i}{\partial t}. \tag{9.5}$$

If the number of particles and the energy of the system do not change, we can write the following continuity equations (see Appendix III)

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \boldsymbol{j_i} = 0 \tag{9.6}$$

$$\frac{\partial u}{\partial t} + \nabla \cdot \boldsymbol{j_E} = 0 \tag{9.7}$$

where $\boldsymbol{j_i}$ is the flux of component i and $\boldsymbol{j_E}$ is the energy flux. Since the entropy does not change in reversible processes, we can also write a continuity equation for such processes

$$\left(\frac{\partial s}{\partial t}\right)_{\text{reversible}} + \nabla \cdot \boldsymbol{j_s} = 0. \tag{9.8}$$

where $\boldsymbol{j_s}$ is the entropy flux. In the general case, the change of entropy per unit volume consists of two contributions: the first is the change in entropy that would occur if the process was reversible and the second accounts for the irreversibility

$$\frac{\partial s}{\partial t} = \left(\frac{\partial s}{\partial t}\right)_{\text{reversible}} + \left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}}.$$

Using the continuity equation for reversible processes (Eq. (9.8)), this can be rewritten as

$$\left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}} = \frac{\partial s}{\partial t} + \nabla \cdot \boldsymbol{j_s}. \tag{9.9}$$

Inserting Eqs (9.6), (9.7) and (9.9) into Eq. (9.5), we obtain

$$T\left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}} - T\nabla \cdot \boldsymbol{j_s} = -\nabla \cdot \boldsymbol{j_E} + \sum_{i=1}^{k} \mu_i \nabla \cdot \boldsymbol{j_i}$$

or

$$T\left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}} = T\nabla \cdot \boldsymbol{j_s} + T\left(-\frac{1}{T}\nabla \cdot \boldsymbol{j_E} + \sum_{i=1}^{k} \frac{\mu_i}{T}\nabla \cdot \boldsymbol{j_i}\right).$$

We can take the fluxes outside of the divergence by using the following identity (see Eq. AII.12):

$$f\nabla \cdot \boldsymbol{a} = \nabla \cdot (f\boldsymbol{a}) - \boldsymbol{a} \cdot \nabla f. \qquad .$$

Using this identity, we can rewrite the previous equation as

$$T\left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}}$$
$$= T\nabla\cdot\boldsymbol{j}_s + T\left(-\nabla\cdot\frac{\boldsymbol{j_E}}{T}+\boldsymbol{j_E}\cdot\nabla\frac{1}{T}+\sum_{i=1}^{k}\nabla\cdot\frac{\mu_i\boldsymbol{j_i}}{T}-\sum_{i=1}^{k}\boldsymbol{j_i}\cdot\nabla\frac{\mu_i}{T}\right).$$

This equation has the same general form as Eq. (9.2), if and only if we adopt the following definitions:

$$\boldsymbol{j}_s = \frac{1}{T}\left(\boldsymbol{j_E}-\sum_{i=1}^{k}\mu_i\boldsymbol{j_i}\right) \tag{9.10}$$

$$\boldsymbol{X_E} = T\nabla\frac{1}{T} = -\frac{1}{T}\nabla T \tag{9.11}$$

$$\boldsymbol{X_i} = -T\nabla\frac{\mu_i}{T}. \tag{9.12}$$

Equations (9.11) and (9.12) provide the definitions of the thermodynamic forces discussed, rather cavalierly, in the previous sections of this chapter.

9.4 Thermodynamic forces for chemical reactions

We now examine isothermal chemical reactions from the point of view of the thermodynamics of irreversible processes. The flux, in this case, is simply the rate of reaction $\mathrm{d}c_i/\mathrm{d}t$. The flux in chemical reactions is a scalar quantity and is not associated with the motion of a chemical species or energy. Rather, this flux is a transition (or transformation) from one set of chemical species to another. As such, the units of this flux are mole/(l s). If all species are ideal gases, then at constant temperature $\mathrm{d}u=0$. Therefore, Eq. (9.4) can be rewritten as

$$T\frac{\partial s}{\partial t} = -\sum_{i=1}^{k}\mu_i\frac{\mathrm{d}c_i}{\mathrm{d}t}.$$

Equation (9.10) implies that if the heat and diffusion fluxes are absent then $\boldsymbol{j}_s=0$. Then from Eq. (9.9) we obtain

$$\frac{\partial s}{\partial t} = \left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}}.$$

Combining these results we find

$$T\left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}} = -\sum_{i=1}^{k}\mu_i\frac{\mathrm{d}c_i}{\mathrm{d}t}. \tag{9.13}$$

Comparing this equation with Eq. (9.2) suggests that the chemical thermodynamic force is simply the chemical potential. However, this would imply that the thermodynamic force is non-zero at equilibrium. We can resolve this contradiction as follows. The variation of the free energy at equilibrium is zero ($dG^e = 0$); therefore,

$$dG^e = \sum_{i=1}^{k} \mu_i^e dn_i = V \sum_{i=1}^{k} \mu_i^e dc_i = 0$$

or

$$\sum_{i=1}^{k} \mu_i^e \frac{dc_i}{dt} = 0.$$

Combining this relation with Eq. (9.13), we find

$$T\left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}} = -\sum_{i=1}^{k} \left(\mu_i - \mu_i^e\right) \frac{dc_i}{dt} \tag{9.14}$$

and, therefore,

$$X_i^{\text{chem}} = -\left(\mu_i - \mu_i^e\right). \tag{9.15}$$

This is the thermodynamic force for chemical reaction. Note that it is exactly zero when the system reaches equilibrium.

We now apply this method to an example chemical reaction

$$H_2 + I_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2HI.$$

The reaction rate can be written as

$$\omega = \omega_1 - \omega_2 = k_1 p_{H_2} p_{I_2} - k_2 p_{HI}^2 = \omega_1 \left(1 - \frac{k_2}{k_1} \frac{p_{HI}^2}{p_{H_2} p_{I_2}}\right)$$
$$= \omega_1 \left(1 - \frac{1}{K_p} \frac{p_{HI}^2}{p_{H_2} p_{I_2}}\right),$$

and the van't Hoff isotherm takes the following form:

$$\Delta G = -RT \ln K_p + RT \ln \frac{p_{HI}^2}{p_{H_2} p_{I_2}} = RT \ln\left(\frac{1}{K_p} \frac{p_{HI}^2}{p_{H_2} p_{I_2}}\right),$$

where we have used the relationship between rates and rate constants from Section 8.1.3. Combining these two equations, we find

$$\omega = \omega_1 \left(1 - e^{\Delta G / RT}\right).$$

Near equilibrium, $\Delta G/RT$ is small and we can expand this expression and retain only the leading order term

$$\omega = -\omega_1 \frac{\Delta G}{RT}. \tag{9.16}$$

The reaction rate can also be expressed through the time derivatives of the concentrations of each species

$$\omega = -\frac{dc_{H_2}}{dt} = -\frac{dc_{I_2}}{dt} = \frac{1}{2} \frac{dc_{HI}}{dt}.$$

Since

$$\Delta G = \Delta G - \Delta G^{e} = 2\left(\mu_{HI} - \mu_{HI}^{e}\right) - \left(\mu_{H_2} - \mu_{H_2}^{e}\right) - \left(\mu_{I_2} - \mu_{I_2}^{e}\right), \quad (9.16)$$

we can write the reaction rate in terms of the individual concentrations as (using Eq. (9.16))

$$\begin{aligned}
\frac{dc_{H_2}}{dt} &= -\frac{\omega_1}{RT}\left(\mu_{H_2} - \mu_{H_2}^{e}\right) - \frac{\omega_1}{RT}\left(\mu_{I_2} - \mu_{I_2}^{e}\right) + \frac{2\omega_1}{RT}\left(\mu_{HI} - \mu_{HI}^{e}\right)\\
\frac{dc_{I_2}}{dt} &= -\frac{\omega_1}{RT}\left(\mu_{H_2} - \mu_{H_2}^{e}\right) - \frac{\omega_1}{RT}\left(\mu_{I_2} - \mu_{I_2}^{e}\right) + \frac{2\omega_1}{RT}\left(\mu_{HI} - \mu_{HI}^{e}\right) \quad (9.17)\\
\frac{dc_{HI}}{dt} &= \frac{2\omega_1}{RT}\left(\mu_{H_2} - \mu_{H_2}^{e}\right) + \frac{2\omega_1}{RT}\left(\mu_{I_2} - \mu_{I_2}^{e}\right) - \frac{4\omega_1}{RT}\left(\mu_{HI} - \mu_{HI}^{e}\right).
\end{aligned}$$

Using the definitions of chemical reaction flux, Eqs (9.1), (9.15), and (9.17), we can write the Onsager coefficients, L_{ik}, as

$$L_{ik} = \begin{pmatrix} \frac{\omega_1}{RT} & \frac{\omega_1}{RT} & -\frac{2\omega_1}{RT} \\ \frac{\omega_1}{RT} & \frac{\omega_1}{RT} & -\frac{2\omega_1}{RT} \\ -\frac{2\omega_1}{RT} & -\frac{2\omega_1}{RT} & \frac{4\omega_1}{RT} \end{pmatrix}. \quad (9.18)$$

Review question

1. When a chemical reaction flux is non-zero, must something be transported?

9.5 Onsager's third postulate—the principle of detailed balance

The thermodynamics of irreversible processes relates fluxes and thermodynamic forces through Onsager coefficients, L_{ik}, but does not provide a method to calculate these coefficients. Rather, the Onsager coefficients are simply parameters that must be determined from experiment or microscopic model. Of course, the problem of the determination of the Onsager coefficients would be simplified if we know a priori some constraints. Two such general constraints are described below.

The first such constraint can be obtained by combining Onsager's first and second postulates

$$T\left(\frac{\partial s}{\partial t}\right)_{\text{irreversible}} = \sum_{i,k} L_{ik} X_i X_k, \quad (9.19)$$

and recognizing that entropy increases for irreversible processes. This implies that

$$\sum_{i,k} L_{ik} X_i X_k > 0. \quad (9.20)$$

A mathematical analysis of this general type of inequality shows that Eq. (9.20) can only be satisfied provided that

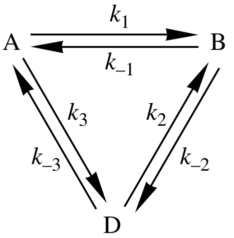
$$L_{ii} > 0. \tag{9.21}$$

The second constraint can be obtained from the results of the previous section, where we found explicit expressions for the Onsager coefficients for the case of isothermal chemical reactions (Eq. (9.18)). Analyzing these expressions shows that

$$L_{ik} = L_{ki}. \tag{9.22}$$

Although this relation was obtained on the basis of a single example reaction, the statement that the matrix of Onsager coefficients is symmetric is general and is known as Onsager's reciprocity theorem. This theorem cannot be derived, in general, within the thermodynamics of irreversible processes framework, but was introduced by Onsager as a postulate (**Onsager's third postulate**). The physical origin of this postulate can be understood within the framework of statistical thermodynamics and is outside of the scope of this text. However, it is useful to note that the third postulate is a consequence of microscopic reversibility, that is, the fact that the equations of classical and quantum mechanics do not change if time is run forward or backward (for example, a particle will move along the same trajectory if time is run forward or backward, albeit in the opposite direction).

We previously referred to the principle of detailed balance in Section 6.1.2. We now demonstrate how this principle works using an example of the reaction of three isomers and show how this principle is related to Onsager's third postulate. Consider a circuit process consisting of six elementary reactions involving the isomers A, B, and D:



The kinetic equations for this process take the following forms:

$$\begin{aligned}
\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} &= -(k_1 + k_{-3})c_\mathrm{A} + k_{-1}c_\mathrm{B} + k_3c_\mathrm{D} \\
\frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} &= k_1c_\mathrm{A} - (k_{-1} + k_2)c_\mathrm{B} + k_{-2}c_\mathrm{D} \\
\frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}t} &= k_{-3}c_\mathrm{A} + k_2c_\mathrm{B} - (k_{-2} + k_3)c_\mathrm{D}.
\end{aligned} \tag{9.23}$$

When the system reaches equilibrium, the concentrations no longer change (i.e. $\mathrm{d}c_i/\mathrm{d}t = 0$) and the kinetic equations reduce to

$$\begin{aligned} 0 &= -(k_1 + k_{-3})c_\mathrm{A}^\mathrm{e} + k_{-1}c_\mathrm{B}^\mathrm{e} + k_3 c_\mathrm{D}^\mathrm{e} \\ 0 &= k_1 c_\mathrm{A}^\mathrm{e} - (k_{-1} + k_2)c_\mathrm{B}^\mathrm{e} + k_{-2}c_\mathrm{D}^\mathrm{e} \\ 0 &= k_{-3}c_\mathrm{A}^\mathrm{e} + k_2 c_\mathrm{B}^\mathrm{e} - (k_{-2} + k_3)c_\mathrm{D}^\mathrm{e}. \end{aligned} \tag{9.24}$$

Solving for c_D^e in the first equation and inserting it into the second equation yields

$$k_1 c_\mathrm{A}^\mathrm{e} - (k_{-1} + k_2)c_\mathrm{B}^\mathrm{e} + \frac{k_{-2}k_{-3}}{k_{-2} + k_3}c_\mathrm{A}^\mathrm{e} + \frac{k_{-2}k_2}{k_{-2} + k_3}c_\mathrm{B}^\mathrm{e} = 0$$

or

$$K_c^{(1)} = \frac{c_\mathrm{B}^\mathrm{e}}{c_\mathrm{A}^\mathrm{e}} = \frac{k_1(k_{-2} + k_3) + k_{-2}k_{-3}}{k_{-1}(k_{-2} + k_3) + k_2 k_3}, \tag{9.25}$$

where $K_c^{(1)}$ is the equilibrium constant for the reaction $\mathrm{A} \rightleftarrows \mathrm{B}$.

We now consider the same set of reactions from the point of view of the thermodynamics of irreversible processes. First, we express the concentrations in Eq. (9.23) through the chemical thermodynamic forces. Equation (9.15) implies that

$$X_i^\mathrm{chem} = -\left(\mu_i - \mu_i^\mathrm{e}\right) = -RT\,\ln\frac{p_i}{p_i^\mathrm{e}} = -RT\,\ln\frac{c_i}{c_i^\mathrm{e}}.$$

Near equilibrium, the ratio c_i/c_i^e is close to unity and hence we may expand the logarithm to obtain

$$X_i^\mathrm{chem} = -RT\left(\frac{c_i}{c_i^\mathrm{e}} - 1\right) = RT\frac{c_i^\mathrm{e} - c_i}{c_i^\mathrm{e}}$$

such that

$$c_i = c_i^\mathrm{e} - \frac{c_i^\mathrm{e}}{RT}X_i^\mathrm{chem}. \tag{9.26}$$

Inserting Eq. (9.26) into Eq. (9.23) and using Eq. (9.24), we find

$$\begin{aligned} \frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} &= (k_1 + k_{-3})\frac{c_\mathrm{A}^\mathrm{e}}{RT}X_\mathrm{A}^\mathrm{chem} - k_{-1}\frac{c_\mathrm{B}^\mathrm{e}}{RT}X_\mathrm{B}^\mathrm{chem} - k_3\frac{c_\mathrm{D}^\mathrm{e}}{RT}X_\mathrm{D}^\mathrm{chem} \\ \frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} &= -k_1\frac{c_\mathrm{A}^\mathrm{e}}{RT}X_\mathrm{A}^\mathrm{chem} + (k_{-1} + k_2)\frac{c_\mathrm{B}^\mathrm{e}}{RT}X_\mathrm{B}^\mathrm{chem} - k_{-2}\frac{c_\mathrm{D}^\mathrm{e}}{RT}X_\mathrm{D}^\mathrm{chem} \\ \frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}t} &= -k_{-3}\frac{c_\mathrm{A}^\mathrm{e}}{RT}X_\mathrm{A}^\mathrm{chem} - k_2\frac{c_\mathrm{B}^\mathrm{e}}{RT}X_\mathrm{B}^\mathrm{chem} + (k_{-2} + k_3)\frac{c_\mathrm{D}^\mathrm{e}}{RT}X_\mathrm{D}^\mathrm{chem}. \end{aligned} \tag{9.27}$$

This set of equations implies that the matrix of Onsager coefficients takes the following form:

$$L_{ik} = \begin{pmatrix} (k_1 + k_{-3})\dfrac{c_\mathrm{A}^\mathrm{e}}{RT} & -k_{-1}\dfrac{c_\mathrm{B}^\mathrm{e}}{RT} & -k_3\dfrac{c_\mathrm{D}^\mathrm{e}}{RT} \\ -k_1\dfrac{c_\mathrm{A}^\mathrm{e}}{RT} & (k_{-1} + k_2)\dfrac{c_\mathrm{B}^\mathrm{e}}{RT} & -k_{-2}\dfrac{c_\mathrm{D}^\mathrm{e}}{RT} \\ -k_{-3}\dfrac{c_\mathrm{A}^\mathrm{e}}{RT} & -k_2\dfrac{c_\mathrm{B}^\mathrm{e}}{RT} & (k_{-2} + k_3)\dfrac{c_\mathrm{D}^\mathrm{e}}{RT} \end{pmatrix}. \tag{9.28}$$

Onsager's third postulate implies $L_{12} = L_{21}$, such that

$$-k_{-1}\frac{c_\mathrm{B}^\mathrm{e}}{RT} = -k_1\frac{c_\mathrm{A}^\mathrm{e}}{RT}$$

or

$$K_c^{(1)} = \frac{c_\mathrm{B}^\mathrm{e}}{c_\mathrm{A}^\mathrm{e}} = \frac{k_1}{k_{-1}}. \tag{9.29}$$

This result is very different from that in Eq. (9.25)! Equation (9.29) is what we would expect to find if we simply considered the reaction

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B},$$

rather than the entire six-reaction circuit. Indeed, the kinetic equation for the $\mathrm{A} \leftrightarrows \mathrm{B}$ reaction takes the following form:

$$\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} = -k_1 c_\mathrm{A} + k_{-1} c_\mathrm{B},$$

and since at equilibrium $\mathrm{d}c_\mathrm{A}/\mathrm{d}t = 0$, we again obtain Eq. (9.29). Obviously, the same discussion can be performed for the other two pairs of reactions in the six-reaction circuit. This suggests that in the case of a complex process, equilibrium must be achieved for each of the component reactions. As a consequence, we see that equilibrium of the reaction $\mathrm{A} \leftrightarrows \mathrm{B}$ is exactly equivalent to equilibrium in the reaction sequence $\mathrm{A} \leftrightarrows \mathrm{D} \leftrightarrows \mathrm{B}$. Therefore, no matter which path in a complex reaction leads to $\mathrm{A} \leftrightarrows \mathrm{B}$, the same A–B equilibrium is achieved. It follows from this conclusion that if we want to describe equilibrium between two states, we only need to consider one transition path rather than all possible transition paths (we used this result in the derivation of the BET isotherm). This conclusion is a statement of the principle of detailed balance. The process that we followed to find this result shows how it is related to Onsager's third postulate.

9.6 Redefinition of the thermodynamic force

Consider a system in which there are two distinct classes of fluxes: the flux of atoms of type *i* and the flux of energy. According to Onsager's first postulate and expressions for the thermodynamic forces (Eqs (9.11) and (9.12)), we can write

$$\boldsymbol{j_i} = -L_{ii}T\nabla\left(\frac{\mu_i}{T}\right) - L_{iE}\frac{\nabla T}{T} \tag{9.30a}$$

$$\boldsymbol{j_E} = -L_{Ei}T\nabla\left(\frac{\mu_i}{T}\right) - L_{EE}\frac{\nabla T}{T}, \tag{9.30b}$$

and $L_{iE} = L_{Ei}$.

These equations are not convenient for application to experiment, since the flux of heat can be directly measured while the flux of energy cannot. This simply follows from the fact that the thermodynamic definition of energy can only be specified to within some arbitrary additive constant. Consider a flux of particles that is not accompanied by a heat flux. Since the moving particles "carry" their own enthalpy, their motion produces an energy flux even though there is no heat flux. Clearly, such an energy flux cannot be measured in experiment. In general case, the energy flux consists of the heat flux and the enthalpy flux

$$\boldsymbol{j_E} = \boldsymbol{j_Q} + \boldsymbol{j_i}\bar{H}_i$$

or

$$\boldsymbol{j_Q} = \boldsymbol{j_E} - \boldsymbol{j_i}\bar{H}_i. \tag{9.31}$$

Inserting the expressions for $\boldsymbol{j_E}$ and $\boldsymbol{j_i}$ from Eq. (9.30) into Eq. (9.31) yields

$$\boldsymbol{j_Q} = -(L_{Ei} - L_{ii}\bar{H}_i)T\nabla\left(\frac{\mu_i}{T}\right) - (L_{EE} - L_{iE}\bar{H}_i)\frac{\nabla T}{T}. \tag{9.32}$$

We have replaced the experimentally impractical flux of energy from Eq. (9.30b) with the flux of heat (Eq. (9.32)). However, comparison of Eqs (9.30a) and (9.32) shows that the resultant matrix of Onsager coefficients do not satisfy Onsager's third postulate (the symmetry of the matrix of Onsager coefficients). This is not surprising, since we changed which fluxes we use but did not modify the corresponding thermodynamic forces. In order to satisfy Onsager's third postulate, the thermodynamic forces $\boldsymbol{X}$ should be defined as

$$\boldsymbol{X_i} = -(\nabla\mu_i)_T \tag{9.33a}$$

$$\boldsymbol{X_Q} = \boldsymbol{X_E} = -\frac{\nabla T}{T}, \tag{9.33b}$$

where the operator $(\nabla f)_T$ is the gradient of a function at constant temperature. We now show that Onsager's third postulate is satisfied using these definitions of the forces. Inserting the Gibbs–Helmholtz equation (Eq. (3.13)) into the mathematical statement

$$\nabla\left(\frac{\mu_i}{T}\right) = \nabla_T\left(\frac{\mu_i}{T}\right) + \frac{\partial}{\partial T}\left(\frac{\mu_i}{T}\right)\nabla T$$

we find

$$T\nabla\left(\frac{\mu_i}{T}\right) = T\left(\nabla\left(\frac{\mu_i}{T}\right)\right)_T - T\frac{\bar{H}_i}{T^2}\nabla T = (\nabla\mu_i)_T - \frac{\bar{H}_i}{T}\nabla T.$$

Combining this result with Eqs (9.30a) and (9.32), we obtain

$$\begin{aligned}
\boldsymbol{j}_i &= -L_{ii}(\nabla\mu_i)_T - (L_{iE} - L_{ii}\bar{H}_i)\frac{\nabla T}{T} = -L_{ii}(\nabla\mu_i)_T - L_{iQ}\frac{\nabla T}{T}\\
\boldsymbol{j}_Q &= -(L_{Ei} - L_{ii}\bar{H}_i)(\nabla\mu_i)_T - \left(L_{EE} - L_{iE}\bar{H}_i - L_{Ei}\bar{H}_i + L_{ii}\bar{H}_i^2\right)\frac{\nabla T}{T}\\
&= -L_{Qi}(\nabla\mu_i)_T - L_{QQ}\frac{\nabla T}{T}.
\end{aligned} \tag{9.34}$$

Since $L_{iE} = L_{Ei}$ (see Eq. (9.30)), we see that Eq. (9.34) satisfies the rule of symmetry of the Onsager coefficients (Onsager's third postulate).

Unlike Eq. (9.30), Eq. (9.34) contains only fluxes which can be measured in experiment. In addition, the new definition of $\boldsymbol{X}_i$ is more convenient than the old definition, since the latter includes both forces associated with the inhomogeneous distribution of matter and with a temperature gradient. However, the thermodynamic force associated with the energy flux also depends on the temperature gradient. Examination of the thermodynamic forces associated with matter and heat fluxes (Eq. (9.33)) shows that the first only depends upon the chemical potential gradient at constant temperature (i.e. the concentration gradient) and the latter only depends upon the temperature gradient. This is clearly much more useful than the forces associated with energy and matter fluxes (Eqs (9.11) and (9.12)) where the former depends on both temperature and chemical potential.

Review question

1. Why is it so difficult (impossible) to experimentally measure the energy flux $\boldsymbol{j}_E$?

9.7 Procedure for the solution of irreversible thermodynamics problems

The procedure for the solution of transport problems in irreversible thermodynamics can be outlined as follows (we will demonstrate this procedure in Section 10.7):

1. Determine which fluxes are present. If there are some fluxes that can be neglected—do so, in order to reduce the number of Onsager coefficients to be included. Determining what to include and what to ignore is the most difficult and important step (you will get better at this with practice).
2. Determine the thermodynamic forces that are associated with these fluxes.
3. Write the thermodynamic equations of motion (Eq. 9.1) and symmetry relations between Onsager coefficients.

4. Determine the conditions under which steady-state can be achieved (we will do this in the problem in Section 10.7). This will give you some important physical relations.
5. Choose a method to determine the Onsager coefficients from experiment or a microscopic model.

10

Diffusion

Diffusion is associated with the random, thermal motion of atoms that produces a change in the macroscopic concentration profile.[1] This process occurs in gases, liquids, amorphous and crystalline solids of metals, ceramics, polymers, semiconductors, etc. The investigation of diffusion provides valuable information about the atomic structure of materials and the defects within them. Perhaps, most importantly, diffusion controls the rates of a wide range of kinetic processes associated with the synthesis of materials, processes by which we modify materials, and processes by which materials fail.

The most common driving force for diffusion in a single-phase systems is associated with the entropy of mixing of its constituents (recall that we showed that the entropy of mixing of gases and the components of an ideal solution are always positive—see Sections 1.2.6 and 3.3). Since diffusional processes occur through the thermal motion of atoms (see below), it will not be surprising to learn that the rate of diffusion increases with increasing temperature. However, note that while the mechanisms of thermal motion in gases (random collision of atoms with each other) and liquids (e.g. Brownian motion) necessarily lead to mixing, the mechanisms of mixing within a solid are not as obvious. In solids, thermal motion corresponds to the vibrations of atoms near their equilibrium positions. Since the amplitude of such vibrations is much smaller than the nearest-neighbor separation, it would seem that such thermal motions cannot lead to mixing. Thus, the question "how do atoms migrate in solids" is not so simple.

10.1 Mathematical description of diffusion

The equations describing diffusion were suggested by the physiologist Fick in 1855 as a generalization of the equations for heat transfer suggested by Fourier in 1824. Fick's equations for diffusion can be obtained by analogy with Fourier's equations for heat transfer by replacing heat with the number of atoms, temperature with concentration, and thermal conductivity with diffusivity.

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[1] Recall that the thermodynamics of irreversible processes shows that atom fluxes can also arise because of other thermodynamic forces. We consider such a problem in Section 10.7.

10.1.1 Fick's first law

Fick's first law provides a relationship between atomic currents and concentration gradients. As discussed above, this relationship can be understood by analogy with thermal conductivity or electrical conductivity. Indeed, it is well known that in the simplest cases, the heat current between two points is proportional to the temperature difference between these points and the electric current is proportional to the difference of electric potentials between these points. Since current is a vector, a more general statement is that these currents are proportional to the gradients of temperature and electric potentials, respectively. Note that these currents lead to the equilibration of temperature or electric potential (i.e. heat or charge flow in the direction to make the system more homogeneous). Similarly, diffusion leads to the homogenization of the concentration within the system.[2] Therefore, by analogy, with heat and electrical currents, we can write the current of species i:

$$\mathbf{I_i} = -D_i S \nabla c_i, \tag{10.1}$$

where S is the area of the surface through which the current passes and D_i is the **diffusivity** of component i. Equation (10.1) is known as **Fick's first law**. Fick's first law is often written in terms of a flux rather than a current

$$\mathbf{j_i} = \frac{\mathbf{I_i}}{S} = -D_i \nabla c_i.$$

In one-dimensional, this equation reduces to

$$j_i = -D_i \frac{\partial c_i}{\partial x}.$$

Note that both $\mathbf{I_i}$ and $\mathbf{j_i}$ are the vectors. Concentration in Eq. (10.1) has dimension of either kg/m^3 or mole/m^3 corresponding to currents measured in kg/s and mole/s, respectively. Therefore, the dimensionality of the diffusivity is m^2/s.

Equation (10.1) can be derived from the thermodynamics of irreversible processes. Consider the case in which the only flux in the system is that of component i, $\mathbf{j_i}$. The corresponding thermodynamic force is $\mathbf{X_i} = -(\nabla \mu_i)_T$ and Onsager's first postulate implies that $j_i = -L_{ii}(\nabla \mu_i)_T$. If the solution is ideal dilute, Eq. (3.19) implies

$$\nabla \mu_i = RT \nabla \ln c_i$$

or

$$\mathbf{j_i} = -L_{ii} RT \nabla \ln c_i.$$

The quantity $M_i = L_{ii}RT$ is the mobility of the particle (the velocity of the particle under the action of a unit force). The flux can then be written as

$$\mathbf{j_i} = -M_i \nabla \ln c_i = -\frac{M_i}{c_i} \nabla c_i = D_i \nabla c_i$$

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[2] This is valid only in the simplest cases where the entropy of mixing is the only contribution to the driving force. Note, however, that cases do exist where diffusion can lead to increasing heterogeneity (see Section 10.7).

and the diffusivity is

$$D_i = \frac{M_i}{c_i} = \frac{L_{ii}RT}{c_i}. \tag{10.2}$$

This brings us back to Eq. (10.1).

Three types of diffusivities can be distinguished, corresponding to three physically different types of diffusion processes. The first is associated with the diffusion of atoms that are labeled. Since atoms are typically indistinguishable, the closest we can come is to monitor the diffusion of a **diffusant** which is a radioactive isotope (e.g. ^{63}Ni) within a material composed of the natural occurring material (e.g. nickel, $^{\mathrm{nat}}$Ni). A typical experiment of this type involves coating the surface of a sample composed of a stable isotope with a film of radioactive isotope, and then monitoring the concentration of the radioactive isotope as it diffuses into the sample. Since the stable and radioactive isotopes have nearly the same physical and chemical properties, we refer to this case as **self-diffusion** and parameterize this type of diffusion using the self-diffusion coefficient. The second type of diffusion refers to the diffusion of one molecular species in another, for example Ni in Cu. This type of diffusion can be observed by coating a large Cu sample with a Ni diffusant film and monitoring the Ni concentration profile in the Cu. This process is called **hetero-diffusion** and the hetero-diffusion coefficient should be used in Fick's first law. Finally, the third type of diffusion describes the diffusion of two species into each other. For example, this type of diffusion can be studied by joining two large Ni and Cu samples together and monitoring the Ni and Cu composition profiles on both sides of the interface. This process is called **mutual diffusion** and it is described by the mutual diffusion coefficient.

Example problems

1. A monoatomic gas (diffusant) is enclosed within a thin metallic spherical shell at constant temperature. During a $t_1 = 100$ h period, some of the gas diffuses through the shell such that the pressure inside drops from $p_0 = 10$ atm to $p_1 = 9.5$ atm. The partial pressure of the diffusant outside the shell is $p_{\mathrm{out}} = 1$ atm. Find the time t_2 necessary for the pressure to drop to $p_2 = 8$ atm.
2. A diatomic gas (diffusant) is enclosed within a thin metallic spherical shell at constant temperature. During a $t_1 = 100$ h period, some of the gas diffuses through the shell such that the pressure inside drops from $p_0 = 10$ atm to $p_1 = 9.5$ atm. The partial pressure of the diffusant outside the shell is $p_{\mathrm{out}} = 1$ atm. Find the time t_2 necessary for the pressure to drop to $p_2 = 8$ atm.

10.1.2 Fick's second law

Fick's second law is the continuity equation (see Appendix III) for the conservation of the quantity of component *i* during diffusion

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{j_i} = 0. \tag{10.3}$$

Inserting Fick's first law into this equation, we obtain

$$\frac{\partial c_i}{\partial t} - \nabla \cdot (D_i \nabla c_i) = 0. \tag{10.4}$$

If the diffusivity does not depend on position within the material, it can be taken outside the differential operator. Using the identity (see Eq. (AII.11))

$$\nabla(\nabla \mathbf{a}) = \nabla^2 \mathbf{a} = \Delta \mathbf{a}$$

we obtain

$$\frac{\partial c}{\partial t} = D \Delta c, \tag{10.5}$$

where we omitted the subscript i. In most applications, we assume D is a constant and hence Eq. (10.5) is the most common form of Fick's second law. In Cartesian coordinates, this equation takes the following form

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \tag{10.6}$$

and in the case of a one-dimensional problem it reduces to

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \tag{10.7}$$

Equations (10.5)–(10.7) are partial differential equations. Their solutions $c(\mathbf{r}, t)$ (or $(c(x, t)$ in the case of one-dimensional problems) depend on the initial condition and two boundary conditions. Some of the most useful solutions of Eq. (10.7) will be given in the next section.

10.1.3 Several useful solutions of the one-dimensional diffusion equation

In this section we consider several solutions to the diffusion equation that are useful in the experimental determination of the diffusivity. Of course, these solutions are useful for a wide range of other applications as well. The forms of the solutions depend on the two boundary conditions and one initial condition, as discussed in Section 10.1.2. For the case of one-dimensional diffusion considered in this section, it is useful to distinguish between the cases of an infinite (or semi-infinite) sample and one that is of finite thickness. In the first case, the diffusion length x_{dif} (the average distance over which the solute diffuses during the course of an experiment) is much smaller the sample length, L. In such a case, the diffusant "does not know that the sample has an end," since the diffusant never gets close to the surfaces. However, when the length of the sample is sufficiently small, some of the diffusant will reach the far end of the sample during the course of the experiment and, hence, the diffusion will be influenced by the presence of the surface.

In order to perform a diffusion experiment, a source of diffusant must be provided. If the quantity of diffusant is large, the concentration of diffusant at the location where it was originally added to the sample will not vary significantly during an experiment—this is an essentially **inexhaustible** (constant concentration) source. On the other hand, if the amount of diffusant provided is small, the concentration of diffusant will change appreciably during the experiment—this is an **exhaustible** source. A common example of an exhaustible source experiment is one in which a very thin coating of a diffusant is initially deposited on the surface of the sample, such that the coating thickness δ is much smaller than the diffusion length ($\delta \ll x_{\mathrm{dif}}$). A common example of an inexhaustible source experiment is one in which the sample is placed within a chamber through which a gas passes such that a chemical reaction of gas phase species with the sample maintains a constant concentration of the reaction product on the surface at all times (see Computer Laboratory #2).

We now discuss the solutions of the diffusion equation for these examples. First, we consider the case where the supply of diffusant is exhaustible and the sample is of infinite extent in both directions. For example, consider the case in which a thin coating of q moles of diffusant is deposited on the end of a bar of pure material and an identical bar is bonded to the outer surface of the coating. The initial condition is

$$c(x,0) = q\delta(x)$$

where $\delta(x)$ is the Dirac function which is equal to zero for $x \neq 0$ and is infinite at $x = 0$, such that

$$\int_{-\infty}^{+\infty} \delta(x)\mathrm{d}x = 1.$$

The appropriate boundary conditions (valid at all times) are

$$\left.\frac{\partial c}{\partial x}\right|_{x=-\infty,t} = 0; \quad \left.\frac{\partial c}{\partial x}\right|_{x=\infty,t} = 0.$$

The diffusion equation with these initial and boundary conditions has the following solution[3]

$$c(x,t) = \frac{q}{2\sqrt{\pi D t}}\mathrm{e}^{-x^2/4Dt}, \tag{10.8}$$

which is valid for all space and all times ($t \geq 0$). This solution is called a Gaussian and it has a bell shape with two inflection points (*at* $\pm\sqrt{2Dt}$), as shown in Fig. 10.1.1. The area under the curve is equal to the amount of diffusant, q, at all times. This is not surprising since diffusant atoms are neither created nor destroyed during the experiment (mass conservation). During the experiment, the maximum of the concentration profile $c(x,t)$ does not move but decreases in amplitude as $1/\sqrt{t} : c_0 = c(0,t) = q/(2\sqrt{\pi D t})$, and the width of the concentration profile (bell) increases. The concentration profile represented by Eq. (10.8) at any fixed time is a straight line in a plot of $\ln c$ versus x^2, the slope of which is $-1/(4Dt)$. If the

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[3] You should confirm for yourself that this concentration satisfies the diffusion equation, the boundary conditions and the initial condition (it is always a good idea to confirm the validity of anything you read in a book yourself!).

Table 10.1 Several common solutions of the diffusion equation

Case	Sample	Boundary conditions	Initial condition	Solution
1	Infinite	$\left.\frac{\partial c}{\partial x}\right\vert_{x=-\infty,t}=0;\ \left.\frac{\partial c}{\partial x}\right\vert_{x=\infty,t}=0$	$c(x,0)=q\delta(x)$	$c(x,t)=\frac{q}{2\sqrt{\pi Dt}}\mathrm{e}^{-x^2/4Dt}$
2	Semi-infinite	$c(0,t)=c_\mathrm{s};\ \left.\frac{\partial c}{\partial x}\right\vert_{x=\infty,t}=0$	$c(x,0)=0$	$c(x,t)=c_\mathrm{s}\mathrm{erf}\,c\left(\frac{x}{2\sqrt{Dt}}\right)$
3	Semi-infinite	$c(0,t)=0;\ \left.\frac{\partial c}{\partial x}\right\vert_{x=\infty,t}=0$	$c(x,0)=c_\mathrm{s}$	$c(x,t)=c_\mathrm{s}\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$
4	Infinite	$\left.\frac{\partial c}{\partial x}\right\vert_{x=-\infty,t}=0;\ \left.\frac{\partial c}{\partial x}\right\vert_{x=\infty,t}=0$	$c(x,0)=\begin{cases}c_\mathrm{s} & \text{at } x\le 0\\ 0 & \text{at } x>0\end{cases}$	$c(x,t)=\frac{c_\mathrm{s}}{2}\mathrm{erf}\,c\left(\frac{x}{2\sqrt{Dt}}\right)$
5	Infinite	$\left.\frac{\partial c}{\partial x}\right\vert_{x=-\infty,t}=0;\ \left.\frac{\partial c}{\partial x}\right\vert_{x=\infty,t}=0$	$c(x,0)=\begin{cases}0 & \text{at } x<0\\ c_\mathrm{s} & \text{at } x\ge 0\end{cases}$	$c(x,t)=\frac{c_\mathrm{s}}{2}\left[1+\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$
6	Infinite	$\left.\frac{\partial c}{\partial x}\right\vert_{x=-\infty,t}=0;\ \left.\frac{\partial c}{\partial x}\right\vert_{x=\infty,t}=0$	$c(x,0)=\begin{cases}0 & \text{at } x<-a\\ c_\mathrm{s} & \text{at } -a\le x\le a\\ 0 & \text{at } x>a\end{cases}$	$c(x,t)=\frac{c_\mathrm{s}}{2}\left[\mathrm{erf}\left(\frac{a+x}{2\sqrt{Dt}}\right)+\mathrm{erf}\left(\frac{a+x}{2\sqrt{Dt}}\right)\right]$
7	Plate	$c(0,t)=c_\mathrm{s}$ $c(L,t)=c_\mathrm{s}$	$c(x,0)=0$	$c(x,t)=c_\mathrm{s}\left\{1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{\mathrm{e}^{-(2n+1)^2\pi^2Dt/L^2}}{2n+1}\sin\frac{(2n+1)\pi x}{L}\right\}$

source does not sit at $x=0$ in the infinite sample but rather at $x=x_0$, the solution in Eq. (10.8) is modified as

$$c(x,t)=\frac{q}{2\sqrt{\pi Dt}}\mathrm{e}^{-(x-x_0)^2/4Dt}. \tag{10.9}$$

The solution of the diffusion equation for the case of a semi-infinite sample (e.g. a sample that extends from $x=0$ to $x=\infty$ with the diffusant coating at $x=0$) is $c(x,t)=(q/\sqrt{\pi Dt})\mathrm{e}^{-x^2/4Dt}$. Inserting this solution into the expression for the flux, Eq. (10.1) shows that the flux out of the free surface at $x=0$ is exactly zero. This is, in fact, a boundary condition for the semi-infinite sample (zero flux at the surface). Note that this solution is exactly twice that for the infinite sample (Eq. (10.8)). The factor of two arises simply because in the present case the diffusant can only diffuse in one direction rather than in two.

We now consider the case of an inexhaustible source. The general solution of the diffusion equation in this case is of the form

$$c(x,t)=A+B\cdot\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right), \tag{10.10}$$

where A and B are constants which can be determined from the boundary conditions. The function, erf(z), is known as the error function[4] and is described in detail in Appendix IV. Table 10.1 and Fig. 10.1(2)–(5) show

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[4] An error function is an integral of a Gaussian function, such as the solution in Eq. (10.8). Since the error function is a superposition of Gaussian solutions to the diffusion equation and because the diffusion equation is linear, the error function must also satisfy the diffusion equation.

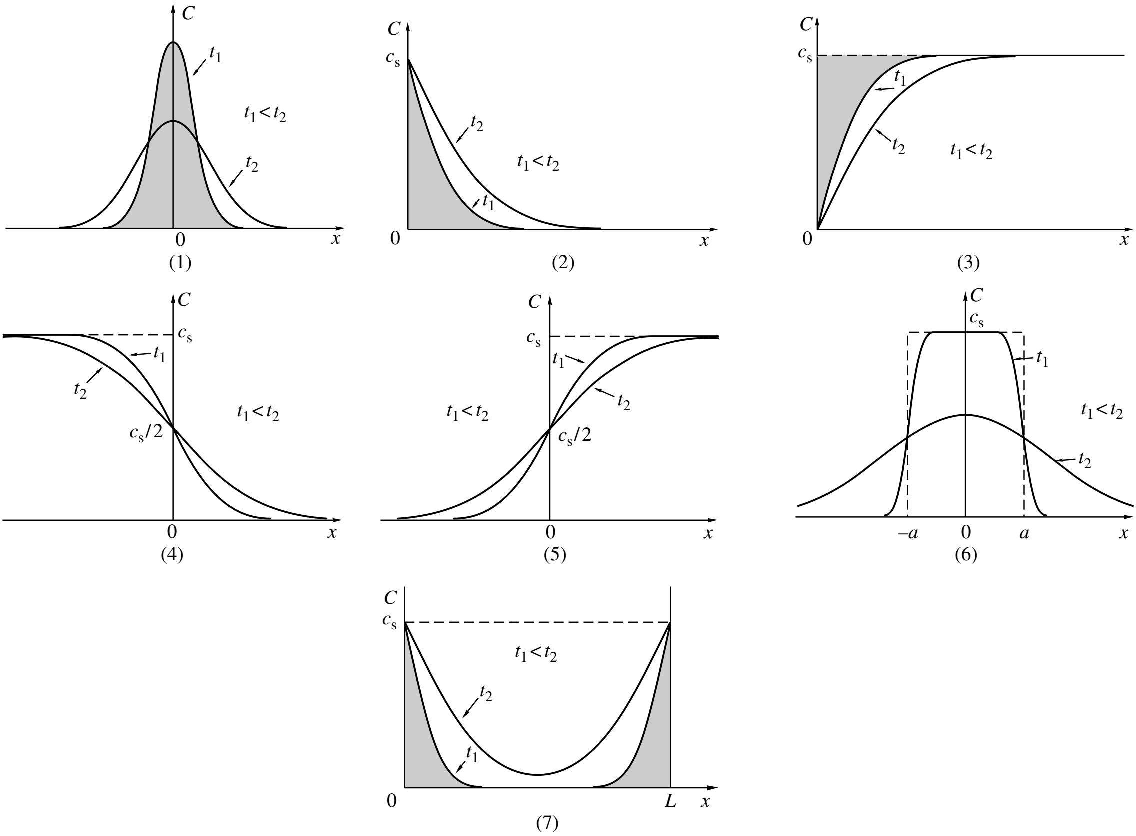

Fig. 10.1
Concentration profiles corresponding to the solutions of the diffusion equation presented in Table 10.1. The shaded area is equal to the amount of diffusant that will enter or leave the sample during time t_1.

several solutions of the form given in Eq. (10.10). You should verify that each satisfies the diffusion equation and the boundary and initial conditions specified in Table 10.1. Note that in cases 2 and 3 in Table 10.1, the amount of diffusant which enters or leaves the sample through a unit area of the surface is $q = 2c_s\sqrt{Dt/\pi}$ (this value is equal to the area shaded in Fig. 10.1, cases 2 and 3), where c_s is the concentration of the diffusant on the end of the bar. Now, consider the case in which a finite source exists in the middle of the bar (case 6). At very short time, the source has not been exhausted and hence the solution should look inexhaustible. However, at very long times, the source becomes depleted and hence the source appears exhaustible. Therefore, the general solution for case 6 should look like a combination of that for an inexhaustible source (for small t) and an exhaustible source (for large t). In examining this solution, it is useful to recall that $\mathrm{erf}(z) \approx (2/\sqrt{\pi})z$ for $z \ll 1$ and $\mathrm{erf}(z) \approx (2/\sqrt{\pi}z)\mathrm{e}^{-z^2}$ for $z \gg 1$ (this is a practical assumption in most cases for $z > 4$).

Finally, we consider the case of an inexhaustible source and a sample of finite thickness (i.e. a plate). The initial and boundary conditions are

$$c(x,0) = 0; \qquad c(0,t) = c(L,t) = c_s.$$

The solution of the diffusion equation for this case (7) takes the following form:

$$c(x,t)/c_s = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\mathrm{e}^{-(2n+1)^2\pi^2Dt/L^2}\sin\frac{(2n+1)\pi x}{L} \qquad (10.11)$$

and is shown in Fig. 10.1(7). The amount of diffusant which will penetrate into the sample during time t is

$$\frac{q(t)}{q_s} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\mathrm{e}^{-(2n+1)^2\pi^2Dt/L^2},$$

where $q_s = c_sLS$ is the maximum amount of diffusant which can be dissolved in the sample and S is the surface area of the plate. The series in Eq. (10.11) converges rapidly to

$$c(x,t)/c_s \approx 1 - \frac{4}{\pi}\mathrm{e}^{-\pi^2Dt/L^2}\sin\frac{\pi x}{L} \qquad \frac{q(t)}{q_s} = 1 - \frac{8}{\pi^2}\mathrm{e}^{-\pi^2Dt/L^2}.$$

For example, if $t > 0.05L^2/D$, the error made in these expressions is smaller than 1%. Note that the last equation implies that the time dependence of the amount of diffusant which entered the sample will lie on a straight line in a plot of $\ln[1-(q/q_s)]$ versus t.

Example problems

1. A thin layer of a diffusant is deposited onto the end of a semi-infinite sample and allowed to diffuse into the sample (one-dimensional problem). At what position in the sample is $\mathrm{d}^2c/\mathrm{d}x^2 = 0$ (i.e. the inflection point)?
2. A thin layer of radioactive copper is deposited onto the end of a long copper bar and the sample is annealed at fixed temperature for 7.2 h. The bar is then cut into 1 μm thick disks perpendicular to the diffusion direction and the quantity of radioactive copper in each is measured using a device similar to a Geiger counter. The detector measured $I_1 = 5000$ counts/(min m^2) and $I_2 = 500$ counts/(min m^2) for disks taken from $x_1 = 100\,\mu$m and $x_2 = 500\,\mu$m from the end of the bar. Calculate the self-diffusivity of copper assuming that the count rate is proportional to the concentration of the radioactive isotope.
3. A steel sample with an initial carbon concentration of 0.1 wt% is carburized at $T = 927$°C such that the carbon concentration is 0.45 wt% at a depth of 0.05 cm. The concentration of carbon on the surface of the steel is constant (fixed by a chemical reaction) and equal to 1 wt%. Calculate the carborization time, assuming that the steel sample is infinitely large. Use the following handbook data: the carbon diffusivity in steel is $D = 0.15\mathrm{e}^{-133{,}900/RT}\,\mathrm{cm}^2/\mathrm{s}$, where $R = 8.314$ J/(mole K).

4. Consider the following one-dimensional diffusion problem: two semi-infinite bars are placed into contact with each other at $x = 0$. The sample at $x < 0$ is a solution of B in A with a concentration $c_B = c_0$ and the sample at $x > 0$ is prepared from pure A ($c_B = 0$). After annealing for 16 h at $T = 800°C$ the B concentration at $x_1 = 0.125$ mm is $c_B = 0.3c_0$. Calculate the diffusivity of B.
5. Find the annealing time necessary to remove 90% of the hydrogen from a plate with a thickness of 0.5 cm which was placed into a chamber that maintains a hydrogen pressure of exactly zero (i.e. a really good vacuum). The hydrogen diffusivity in the plate at the experimental temperature is $D = 10^{-4}\,\text{cm}^2/\text{s}$.
6. A semi-infinite austenitic steel sample with a carbon concentration $c_0 = 0.6$ wt% is annealed for 4 h at $T = 1173$ K in a gas containing hydrogen and methane with $x_{CH_4} = 0.0025$ at a total pressure $p = 1$ atm. Determine the carbon concentration at a depth of 600 μm after annealing. Use the following handbook data: $\Delta G^0_{1173} = 37.2$ kJ/mole for the reaction,

$$C_{(\text{graphite})} + 2H_2 = CH_4.$$

The variation of the carbon activity with carbon concentration is as shown in Fig. 10.2. The carbon diffusivity in austenite at 1173 K is $D = 0.15e^{-133{,}900/RT}\,\text{cm}^2/\text{s}$, where $R = 8.314$ J/(mole K).

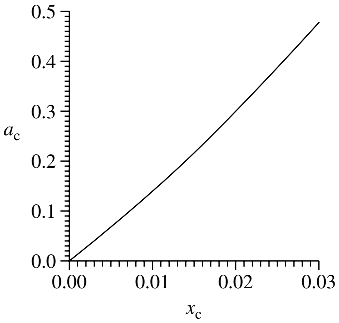

Fig. 10.2
The dependence of the carbon activity on its molar fraction in austenite steel (the standard state for C is graphite).

10.2 Diffusion as a random walk process

An atomic model of diffusion was developed by Einstein in 1905 (a random walk model for the Brownian motion of a particle in a liquid). In 1906, Smoluchowski extended this model to describe the migration of atoms in crystalline metals. According to this model, diffusion is the result of random hops (a sequence of random hops is called a random walk) of atoms. Note that such hops occur even in the absence of a concentration gradient, however, in this case, the net flux is zero. Randomness means that there is no correlation between subsequent hops of the same atom and there is no correlation between hops made by different atoms.

We first consider a simplified version of the Smoluchowski model. In this version, we restrict each atom to move only to the left or right in one-dimension and the motion of each atom is independent of the others, as shown in Fig. 10.3. In this sense, the model is quasi-one-dimensional. Next, we assume that the length of each individual hop, Δ, is always the same. This assumption is natural for atoms moving in a crystal, where Δ is the nearest neighbor separation.

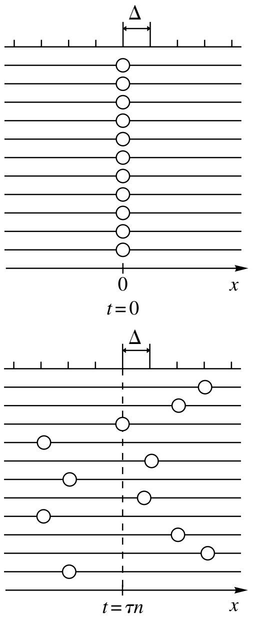

Fig. 10.3
Quasi-one-dimensional random walk.

Let all atoms start migration at the same moment from the same position ($x = 0$), as shown in Fig. 10.3. Consider the migration of one atom, which makes n hops during time $t = \tau n$ and ends up at position x_n, where τ is the average time between subsequent atom hops. Hop $n + 1$ can be either to the left or right, such that

$$x_{n+1} = x_n \pm \Delta.$$

Squaring both sides of this equation and averaging over all atoms, we obtain

$$x_{n+1}^2 = x_n^2 \pm 2\Delta x_n + \Delta^2; \quad \overline{x_{n+1}^2} = \overline{x_n^2} \pm 2\Delta\overline{x_n} + \Delta^2; \quad \overline{x_{n+1}^2} = \overline{x_n^2} + \Delta^2.$$

In obtaining the final expression, we used the fact that if atoms jump to the left or right at random, the average position after any number of hops is exactly zero ($\overline{x_n} = 0$). Since this expression is valid for every n, we find

$$\overline{x_1^2} = \Delta^2,\ \overline{x_2^2} = 2\Delta^2,\ \overline{x_3^2} = 3\Delta^2,\ \cdots$$

or

$$\overline{x_n^2} = n\Delta^2 \tag{10.12}$$

Since $t = \tau n$, we can rewrite Eq. (10.12) as

$$\overline{x_n^2} = \Delta^2 \frac{t}{\tau} = \Delta^2 \Gamma t, \tag{10.13}$$

where $\Gamma = n/t = 1/\tau$ is the hopping frequency. On average, the distance between where an atom starts and where it ends up after n hops (or in time t) is the diffusion length $x_{\text{dif}} = \sqrt{\overline{x_n^2}}$:

$$x_{\text{dif}} = \Delta\sqrt{n} = \Delta\sqrt{\Gamma t} = \Delta\sqrt{\frac{t}{\tau}}. \tag{10.14}$$

The main conclusion of the random walk model is that the diffusion length is proportional to the square root of time. This is consistent with the solutions to Fick's second law, we found in Section 10.1.3 for infinite or semi-infinite samples—that is, that the position where the concentration has a particular value moves in time in proportion to the square root of time. This time dependence is characteristic of the diffusion process. Note that the rate of diffusion decreases with time as

$$\nu_{\text{dif}} = \frac{\mathrm{d}x_{\text{dif}}}{\mathrm{d}t} \sim \frac{1}{\sqrt{t}}. \tag{10.15}$$

We now find the relation between the diffusivity and random walk process. Consider the flux of atoms across the plane $x = x_0$ that lies between two neighboring atomic planes (separated by Δ). The flux of atoms across the plane $x = x_0$ from $x = x_0 - \Delta/2$ is simply the product of the number of atoms per unit are on this plane $N(x_0 - \Delta/2\ )/a$, the rate at which those atoms jump and a factor of $\frac{1}{2}$ to account for the fact that each atom jumps to the left or right with equal probability

$$\frac{1}{2}\frac{N(x_0 - \Delta/2)}{a}\Gamma.$$

Similarly, the flux of atoms across the plane $x = x_0$ from $x = x_0 + \Delta/2$ in the opposite direction is

$$-\frac{1}{2}\frac{N(x_0 + \Delta/2)}{a}\Gamma.$$

These two expressions can be rewritten in terms of concentrations by noting that $c = N/(a\Delta)$. The total flux across the plane $x = x_0$ is now

$$j = \frac{1}{2}c\left(x_0 - \frac{\Delta}{2}\right)\Delta\Gamma - \frac{1}{2}c\left(x_0 + \frac{\Delta}{2}\right)\Delta\Gamma \approx -\frac{1}{2}\Delta^2\Gamma\frac{\partial c}{\partial x}. \tag{10.16}$$

Comparing this equation with Fick's first law demonstrates that

$$D = \frac{1}{2}\Delta^2\Gamma = \frac{1}{2}\frac{\Delta^2}{\tau}. \tag{10.17}$$

Combining this result with Eq. (10.14), we obtain

$$x_{\text{dif}} = \sqrt{2Dt}. \tag{10.18}$$

Equation (10.17) can be written more generally as

$$D = \gamma\Delta^2\Gamma = \gamma\frac{\Delta^2}{\tau}. \tag{10.19}$$

In the case of three dimensions, $\gamma = 1/6$. It can be easily shown that for cubic lattice $D = (1/z)a^2\Gamma$, where a is the traditional cubic lattice parameter and z is the number of nearest neighbors.

In many cases in real crystals, the assumption that the atomic hops are random is not valid. In order to account for the correlations between hops, a correlation factor f is introduced and Eq. (10.17) is rewritten as

$$D = f\gamma\Delta^2\Gamma. \tag{10.20}$$

Usually, the correlation slows down diffusion such that $f \leq 1$. It can be shown that in the case of self-diffusion $f \approx 1 - 2/z$. For face-centered cubic (fcc) metals $z = 12$ and $f \approx 0.83$ (a more careful analysis shows $f = 0.78$) and for body-centered cubic metals $z = 8$ and $f \approx 0.75$ (a more careful analysis shows $f = 0.73$).

Example problems

1. Estimate the temperature at which copper atoms hop, on average, once per second. The following handbook data are available: copper has a fcc lattice with a cubic lattice parameter of 0.36 nm and a self-diffusion coefficient $D = 0.2\mathrm{e}^{-197{,}100/RT}\ \mathrm{cm}^2/\mathrm{s}$, where $R = 8.314\ \mathrm{J/(mole\,K)}$.
2. Estimate the diffusion length for copper self-diffusion in 1 h at (1) $T = 300$ K, (2) $T = 1200$ K, and (3) $T_{\text{melt}} = 1355$ K. Use the handbook data from the previous problem.

10.3 Diffusion in metals

10.3.1 Main experimental results

Most experimental methods for the determination of the diffusivity are based upon either a measurement of the concentration profile, $c(x, t)$, or a measurement of the quantity of diffusant that has penetrated into a sample, $q(t)$. While we will not describe these methods in detail (see Computer Laboratory #6 for a more complete discussion), we discuss some of the key features of these methods here. All methods can be divided into two categories: (1) methods which destroy the sample and (2) methods which are non-destructive. In the first category, the sample is sliced into thin layers oriented perpendicular to the diffusion flux following annealing. Then, the diffusant concentration in each layer is measured. The diffusivity is obtained by comparison of the measured concentration profile with that found from solving the diffusion equation (see Section 10.1.3). In the second category, the concentration profile is measured using non-destructive methods (e.g. X-ray microanalysis, see Computer Laboratory #6) or the quantity of diffusant that has penetrated into the sample is measured non-destructively (see the radioactive absorption method in Computer Laboratory #6).

We now discuss several important experimental observations regarding diffusion in solid metals. In most cases, the temperature dependence of the diffusivity can be described by the Arrhenius law

$$\frac{\mathrm{d}\ln D}{\mathrm{d}T} = \frac{E}{RT^2}$$

or

$$D = D_0 \mathrm{e}^{-E/RT}, \tag{10.21}$$

where E is the activation energy and D_0 is the pre-exponential factor. Both values are nearly temperature independent. Since the diffusivity increases with increasing temperature, we conclude that $E > 0$.

The self-diffusion coefficient near the melting temperature is approximately $D \approx 10^{-12}\,\mathrm{m^2/s}$ for most solid metals. For the sake of comparison, we note that the coefficient of self-diffusion in liquid metals is $D_\mathrm{L} \approx 10^{-9}\,\mathrm{m^2/s}$ and for gases it is approximately $D_\mathrm{g} \approx 10^{-5}\,\mathrm{m^2/s}$. Both of these values depend only weakly on temperature.

The activation energy for self-diffusion in solid metals can be estimated, to within ±20%, as

$$E \approx 18RT_\mathrm{melt} \approx 15.2\Delta H_\mathrm{melt}. \tag{10.22}$$

Applying Eq. (10.22) to estimate the activation energies of Al ($T_\mathrm{melt} = 933\,\mathrm{K}$, $\Delta H_\mathrm{melt} = 10.8\,\mathrm{kJ/mole}$), Cu ($T_\mathrm{melt} = 1356\,\mathrm{K}$, $\Delta H_\mathrm{melt} = 13.0\,\mathrm{kJ/mole}$) and Ni ($T_\mathrm{melt} = 1728\,\mathrm{K}$, $\Delta H_\mathrm{melt} = 17.5\,\mathrm{kJ/mole}$), we find 140, 203, and 259 kJ/mole, respectively. The corresponding experimental values are 142, 197, and 275 kJ/mole, respectively.

In order to estimate D, we can use $D_0 \approx 10^{-5}\,\mathrm{m^2/s}$ for most solid metals. Together with Eqs (10.21) and (10.22), this implies that at $0.4T_\mathrm{melt}$ and $0.7T_\mathrm{melt}$, the coefficient of self-diffusion is $D \approx 10^{-23}\,\mathrm{m^2/s}$ and $D \approx 10^{-16}\,\mathrm{m^2/s}$, respectively.

In the previous section, we found that $x_\mathrm{dif} = \sqrt{2Dt}$. Using the estimates of the diffusivity at $0.4T_\mathrm{melt}$, $0.7T_\mathrm{melt}$, and T_melt from above, we estimate that the diffusion length in a 100-h experiment is 10 nm (just about 30 interatomic separations!), 10 μm, and 1 mm, respectively. The main conclusion is that diffusion is very slow in solids even at high temperatures.

The coefficient of hetero-diffusion of the solvent in substitutional solutions (i.e. a solution where the solvent and solute atoms occupy equivalent sites in the crystalline lattice) is only slightly different from the coefficient of self-diffusion. If the melting temperature of a pure solute is higher than the melting temperature of the solvent, then the solvent diffusivity decreases with increasing solute concentration (1–2 orders of magnitude at $0.7T_{\text{melt}}$) and the activation energy increases. The solute diffusivity in substitutional solutions is usually close to that of the solvent. If the melting temperature of a pure solute is higher than that of the solvent, then the solute diffusivity is smaller than the solvent diffusivity and *vise versa*.

If the atomic radius of the solute atoms is much smaller than that of the solvent atoms, the solute atoms tend to go into interstitial sites (i.e. into the holes between the solvent atoms). In this case, the coefficients of diffusion for the solvent and solute are very different: $D_2 \gg D_1$ and $E_2 < E_1$. For example, the activation energy of self-diffusion in α-Fe (body-centered cubic iron) is $E_{\text{Fe}} = 250\,\text{kJ/mole}$ and that for carbon diffusion in α-Fe is $E_{\text{C}} = 105\,\text{kJ/mole}$. Assuming that $D_0 \approx 10^{-5}\,\text{m}^2/\text{s}$ in both cases, we estimate that at $T = 700°\text{C}$, $D_{\text{Fe}} = 10^{-17}\,\text{m}^2/\text{s}$, and $D_{\text{C}} = 10^{-11}\,\text{m}^2/\text{s}$. Note that D_{C} is larger than the self-diffusion coefficient in most metals at their melting temperature ($\sim 10^{-12}\,\text{m}^2/\text{s}$).

10.3.2 Diffusion mechanisms in metals

The random walk model does not answer the question "What is the mechanism by which atoms hop?" Recall that at finite temperature, atoms vibrate around their equilibrium position with an amplitude that is much smaller than the nearest neighbor separation. Several different elementary diffusion mechanisms have been proposed. A few of these are shown in Fig. 10.4: (1) a simple exchange, in which a pair of neighboring atoms switch places, (2) a cyclic exchange, in which several atoms sequentially switch places (e.g. in a four- or six-member ring), (3) by exchanging with a vacancy (i.e. an empty lattice site), and (4) an interstitial jump in which an atom sitting in an interstice between lattice atoms jumps to a neighboring, empty interstitial site.

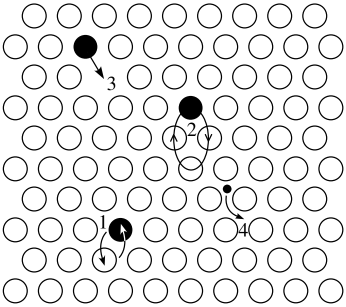

Fig. 10.4
Schematic illustration of the four diffusion mechanisms described in the text. The diffusing atom is shown in black.

Experiments show that the most commonly operating self-diffusion and hetero-diffusion in substitutial solutions is the vacancy mechanism, while the main mechanism of hetero-diffusion in interstitial solutions is the interstitial mechanism.

The vacancy mechanism was first proposed by Frenkel in the 1930s. Frenkel was also the first to propose that vacancies exist in equilibrium (the minimum in the free energy occurs at a finite vacancy concentration). In the vacancy mechanism of diffusion, an atom can hop only if it has a nearest neighbor vacancy into which it can jump. Therefore, the frequency with which a particular atom can jump is

$$\Gamma = x_v \omega, \tag{10.23}$$

where ω is the frequency with which the vacancy jumps and x_{v} is the vacancy concentration. Since $x_{\mathrm{v}} \ll 1$ (otherwise the crystal would simply fall apart), we must conclude that $\Gamma \ll \omega$. Inserting Eq. (10.23) into Eq. (10.20), we find

$$D = f\gamma\Delta^2 x_{\mathrm{v}}\omega. \tag{10.24}$$

The frequency with which the vacancy hops depends on the nature of the atomic interactions in the metal; unfortunately, this interesting topic is beyond the scope of this book. However, we can adopt a simplified model, in which an atom adjacent to a vacancy vibrates around its equilibrium position with a frequency ν.[5] In order to exchange places with the vacancy, a neighboring atom must pass over an energy barrier. This energy barrier is associated with necessity to push other atoms out of the way as the atom hops into the vacancy.[6] This process is similar to the activated complex theory we discussed in Section 8.1.4. Therefore, by analogy with Eq. (8.30), we write

$$\omega = \nu \mathrm{e}^{\Delta S_{\mathrm{v}}^{\mathrm{m}}/R} \mathrm{e}^{-\Delta H_{\mathrm{v}}^{\mathrm{m}}/RT}, \tag{10.25}$$

where $\Delta S_{\mathrm{v}}^{\mathrm{m}}$ and $\Delta H_{\mathrm{v}}^{\mathrm{m}}$ are the entropy and enthalpy of the vacancy migration.

We now derive an expression for the equilibrium vacancy concentration. Consider vacancies as the solute and the metal atoms as the solvent. Let the enthalpy of formation of the solution containing n_{v} moles of vacancies be

$$\Delta H_{\mathrm{f}} = \Delta H_{\mathrm{v}}^{\mathrm{f}} n_{\mathrm{v}}, \tag{10.26}$$

where $\Delta H_{\mathrm{v}}^{\mathrm{f}}$ is the enthalpy of formation of 1 mole of vacancies. Since the vacancy concentration is small, a vacancy rarely has a vacancy as a neighbor. Therefore, $\Delta H_{\mathrm{v}}^{\mathrm{f}}$ does not depend on the vacancy concentration (just as the partial enthalpy of a solute in an ideal dilute solution does not depend on solute concentration—see Section 3.2.1). The entropy of formation of the vacancy solution has two contributions: the first is associated with the fact that the formation of a vacancy modifies the vibrational frequencies of neighboring atoms, $\Delta S_{\mathrm{v}}^{\mathrm{f}}$, and the second is associated with the numbers of lattice sites where vacancies can be created. The last term is simply the entropy of mixing. Since we assume that the vacancy solution is an ideal dilute solution, this term should have the form

$$\Delta S_{\mathrm{mix}} = -R\left(n_1 \ln\frac{n_1}{n_1 + n_{\mathrm{v}}} + n_{\mathrm{v}} \ln\frac{n_{\mathrm{v}}}{n_1 + n_{\mathrm{v}}}\right), \tag{10.27}$$

---

[5] For simplicity we assume that all atoms vibrate with the same frequency. Of course, this is not really true, but you will have to read a book on condensed matter physics to find out why.

[6] Consider a tightly packed array of billiard balls on a billiards table. Remove one atom from the center and try to push one of the neighboring balls into this vacancy (you cannot lift the ball off the table because that would be cheating). You will see that this action pushes some of the other billiard balls away from the migration path.

where n_1 is the number of atoms. Combining these results, we obtain the following expression for the change in the Gibbs free energy associated with the formation of n_v vacancies in a lattice of n_1 atoms.

$$\Delta G_\mathrm{f} = \Delta H_\mathrm{v}^\mathrm{f} n_\mathrm{v} - T\Delta S_\mathrm{v}^\mathrm{f} n_\mathrm{v} + RT\left(n_1 \ln \frac{n_1}{n_1 + n_\mathrm{v}} + n_\mathrm{v} \ln \frac{n_\mathrm{v}}{n_1 + n_\mathrm{v}}\right). \quad (10.28)$$

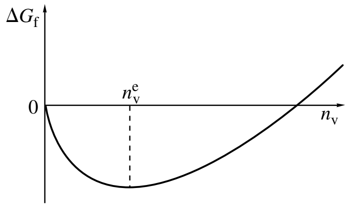

Fig. 10.5
The change in the Gibbs free energy associated with the formation n_v moles of vacancies.

As can be seen in Fig. 10.5, this expression has a minimum at a finite number of vacancies, n_v^e, which can be determined from the condition $(\partial\Delta G_\mathrm{f}/\partial n_\mathrm{v})_{n1,T}=0$. Using Eq. (10.25), we find

$$\frac{n_\mathrm{v}^\mathrm{e}}{n_1 + n_\mathrm{v}^\mathrm{e}} = \mathrm{e}^{\Delta S_\mathrm{v}^\mathrm{f}/R}\mathrm{e}^{-\Delta H_\mathrm{v}^\mathrm{f}/RT}$$

or

$$x_\mathrm{v}^\mathrm{e} = \mathrm{e}^{\Delta S_\mathrm{v}^\mathrm{f}/R}\mathrm{e}^{-\Delta H_\mathrm{v}^\mathrm{f}/RT}. \quad (10.29)$$

Experiments show that at $T \approx T_\mathrm{melt}$, $x_\mathrm{v}^\mathrm{e} \approx 10^{-4}$ in most metals. The value of $\Delta H_\mathrm{v}^\mathrm{f}$ in face-centered cubic metals is roughly $\Delta H_\mathrm{v}^\mathrm{f} \approx 10RT_\mathrm{melt}$. For example, for Al ($T_\mathrm{melt} = 933\,\mathrm{K}$), this estimate gives $\Delta H_\mathrm{v}^\mathrm{f} \approx 78$ kJ/mole as compared with experimental value of $\Delta H_\mathrm{v}^\mathrm{f} \approx 73$ kJ/mole and for Cu ($T_\mathrm{melt} = 1356\,\mathrm{K}$) we find $\Delta H_\mathrm{v}^\mathrm{f} \approx 113$ kJ/mole versus the experimental value $\Delta H_\mathrm{v}^\mathrm{f} \approx 113$ kJ/mole, respectively. Equation (10.29) implies that x_v^e grows rapidly with increasing temperature. For example, for Cu at T = 300 K, $x_\mathrm{v}^\mathrm{e} = 10^{-19}$ and at T = 1350 K it is $x_\mathrm{v}^\mathrm{e} = 1.3 \cdot 10^{-4}$.$\Delta S_\mathrm{v}^\mathrm{f}$ is typically quite small (usually, $0 \le \Delta S_\mathrm{v}^\mathrm{f} \le R$) and does not greatly influence the value of x_v^e. Note, that if we plot the temperature dependence of the vacancy concentration as $\ln x_\mathrm{v}^\mathrm{e}$ versus $1/T$ the values fall on a straight line with slope $-\Delta H_\mathrm{v}^\mathrm{f}/R$.

Inserting Eqs (10.25) and (10.29) into Eq. (10.24) we find

$$D = f\gamma\Delta^2\nu\mathrm{e}^{\left(\Delta S_\mathrm{v}^\mathrm{f}+\Delta S_\mathrm{v}^\mathrm{m}\right)/R}\mathrm{e}^{-\left(\Delta H_\mathrm{v}^\mathrm{f}+\Delta H_\mathrm{v}^\mathrm{m}\right)/RT}. \quad (10.30)$$

Comparison with the Arrhenius law (Eq. (10.21)) shows that the pre-exponential factor is

$$D_0 = f\gamma\Delta^2\nu\mathrm{e}^{\left(\Delta S_\mathrm{v}^\mathrm{f}+\Delta S_\mathrm{v}^\mathrm{m}\right)/R}. \quad (10.31)$$

The activation energy for diffusion in the case of the vacancy mechanism is the sum of the vacancy formation and the vacancy migration enthalpies

$$E = \Delta H_\mathrm{v}^\mathrm{f} + \Delta H_\mathrm{v}^\mathrm{m}. \quad (10.32)$$

This result can be checked experimentally, since all three variables (E, $\Delta H_\mathrm{v}^\mathrm{f}$, and $\Delta H_\mathrm{v}^\mathrm{m}$) can be independently determined. Table 10.2 presents the results for three face-centered cubic metals. The good agreement between the numbers in last two columns demonstrates that Eq. (10.32) and the assumption that diffusion in these systems is controlled by the vacancy mechanism is reasonable.

We now consider the mechanism of interstitial diffusion. For the case of self-diffusion, the physical picture is fundamentally identical to that for the

Table 10.2 The heat of vacancy formation $\Delta H_{\mathrm{v}}^{\mathrm{f}}$, the vacancy migration enthalpy $\Delta H_{\mathrm{v}}^{\mathrm{m}}$, the proposed activation energy for diffusion $\Delta H_{\mathrm{v}}^{\mathrm{f}} + \Delta H_{\mathrm{v}}^{\mathrm{m}}$, and the experimentally measured activation energy for diffusion E for several face-centered cubic metals

Metal	Energy (kJ/mole)			
	$\Delta H_{\mathrm{v}}^{\mathrm{f}}$	$\Delta H_{\mathrm{v}}^{\mathrm{m}}$	$\Delta H_{\mathrm{v}}^{\mathrm{f}} + \Delta H_{\mathrm{v}}^{\mathrm{n}}$	E
Ag	106	80	186	185
Al	73	60	133	143
Cu	113	77	190	199

vacancy mechanism: the diffusivity depends on both the equilibrium interstitial concentration and the rate at which an interstitial migrates. Therefore, by analogy with Eq. (10.30), we can write

$$D = f\gamma\Delta^2\nu \mathrm{e}^{(\Delta S_{\mathrm{i}}^{\mathrm{f}}+\Delta S_{\mathrm{i}}^{\mathrm{m}})/R}\mathrm{e}^{-(\Delta H_{\mathrm{i}}^{\mathrm{f}}+\Delta H_{\mathrm{i}}^{\mathrm{m}})/RT}, \tag{10.33}$$

where $\Delta H_{\mathrm{i}}^{\mathrm{f}}$ and $\Delta S_{\mathrm{i}}^{\mathrm{f}}$ are the changes in enthalpy and entropy associated with the formation of 1 mole of self-interstitials, and $\Delta H_{\mathrm{i}}^{\mathrm{m}}$ and $\Delta S_{\mathrm{i}}^{\mathrm{m}}$ are the energy and entropy of interstitial migration. Therefore the activation energy for interstitial diffusion is $E = \Delta H_{\mathrm{i}}^{\mathrm{f}} + \Delta H_{\mathrm{i}}^{\mathrm{m}}$. Experiments and computer simulations commonly show that $\Delta H_{\mathrm{i}}^{\mathrm{f}} + \Delta H_{\mathrm{i}}^{\mathrm{m}} > \Delta H_{\mathrm{v}}^{\mathrm{f}} + \Delta H_{\mathrm{v}}^{\mathrm{m}}$. This is why self-diffusion is usually controlled by the vacancy mechanism.

For the case of substitutional solid solutions, the fundamental mechanism of hetero-diffusion is the same as for self-diffusion—that is it occurs by the hopping of solute atoms into a vacancy. On the other hand, the physical picture for solute diffusion in interstitial solid solutions is quite different. Since the solutes are already in interstitial sites, interstitials need not be created. Hence, interstitial solute diffusion only has a contribution from interstitial migration

$$D_{\mathrm{i}} = f\gamma\Delta^2\nu \mathrm{e}^{\Delta S_{\mathrm{i}}^{\mathrm{m}}/R}\mathrm{e}^{-\Delta H_{\mathrm{i}}^{\mathrm{m}}/RT}. \tag{10.34}$$

In this case, the solute diffusivity can be much larger than the solvent diffusivity.

Example problem

1. Estimate $\Delta H_{\mathrm{v}}^{\mathrm{f}}$ and Γ for nickel. You can use the following handbook data:
   (1) copper is a face-centered cubic with a cubic lattice constant of $a = 0.355$ nm;
   (2) the melting temperature for copper is $T_{\mathrm{melt}} = 1355$ K;
   (3) the self-diffusivity of Ni can be described by $D = 1.9\mathrm{e}^{-285{,}000/RT}$ cm^2/s.

10.4 Diffusion in amorphous metals

In contrast with crystalline materials, amorphous alloys have no regular crystalline lattice. Atomic order in amorphous materials is rather more similar to that in liquids. However, diffusivities in amorphous materials are typically very small as compared with those in the corresponding liquids. Amorphous materials are generally metastable with respect to crystalline materials of the same composition. When an amorphous material is heated, it will crystallize at a temperature known as the crystallization temperature, T_{cr}. Note, since amorphous materials are metastable, they could, in principle, crystallize at any temperature. However, crystallization kinetics at low temperatures is very slow. The value of the crystallization temperature and the stability of amorphous alloys are controlled by kinetics, that is, diffusion. Below, we discuss the diffusion of metals and non-metals in classical amorphous metallic alloys. Such alloys consist of transition or noble metals (e.g. Fe, Co, Ni, Pd, Au) and non-metals (e.g. B, C, P, Si, Ge).[7]

Diffusivities in amorphous metals are sensitive to the manner in which they were fabricated. This is associated with the fact that amorphous materials do not have a unique structure, like crystals; there are very many different amorphous atomic arrangements. Not surprisingly, some of these are much more stable than others. When an amorphous material is heated, it undergoes some type of structural relaxation toward a more stable amorphous structure. Therefore, it is often difficult to separate the effects of diffusion from the effects of structural relaxation. In order to avoid this relaxation effect, amorphous materials are generally annealed at $T = 0.96/0.98\ T_{\mathrm{cr}}$ prior to performing a diffusion experiment at a lower temperature (below $0.9\ T_{\mathrm{cr}}$).

Experimental studies have shown that the temperature dependence of the diffusivity is usually well described by the Arrhenius law. This is a surprising result! Recall that in our development of the theory of diffusion, we have explicitly assumed that diffusion occurs through the formation and migration of point defects (Section 10.3). This is important since the regularity of the crystal lattice implies that the point defect formation and migration energies have unique values (all positions in the lattice are equivalent). In an amorphous structure, where the lattice is not regular, we should expect that the defect formation and migration energies are widely distributed. The observation that the Arrhenius law is still applicable for diffusion in amorphous alloys may be the result of the fact that most diffusion studies in these materials are performed over a relatively small temperature range (typically $\sim$100 K—the temperature must be high enough such that diffusion is measurable but not too close to the crystallization temperature). Typical diffusivities at $T = 0.85\ T_{\mathrm{cr}}$ in simple amorphous alloys are in the range 10^{-20}–$10^{-23}\ \mathrm{m^2/s}$. For example, at $T = 573\ \mathrm{K}$ ($0.85\ T_{\mathrm{cr}}$) the following data were obtained for the diffusivities in amorphous $\mathrm{Fe_{40}Ni_{40}B_{20}}$: $D_{\mathrm{B}} = 10^{-20}\ \mathrm{m^2/s}$, $D_{\mathrm{Fe}} = 10^{-23}\ \mathrm{m^2/s}$. At the same temperature $D_{\mathrm{B}} = 10^{-18}\ \mathrm{m^2/s}$ and $D_{\mathrm{Fe}} = 10^{-27}\ \mathrm{m^2/s}$ in crystal Fe.

Although several mechanisms for diffusion in amorphous alloys have been proposed, there is no consensus as to the dominant mechanism.

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[7] There are also amorphous alloys consisting of only metals (e.g. Ni–Zr, Fe–Zr).

According to one suggestion, the so-called quasi-vacancy mechanism, diffusion in amorphous alloys occurs by a mechanism akin to the vacancy mechanism in crystals. However, instead of real vacancies, amorphous materials have excess of free volume (the density of an amorphous state is less than that of the corresponding crystalline state) distributed over a spectrum of hole sizes or quasi-vacancies (they can be larger or smaller than the atoms of the alloy). The quasi-vacancy mechanism suggests that atoms can jump into these holes like atoms jump into vacancy sites in crystals (see Section 10.3 for a description but recall that each hole has its own formation and migration energy). In another suggested mechanism, the elementary diffusion event is thought to be a cooperative displacement of a group of neighboring atoms. Since many atoms participate in this cooperative displacement, the activation energy is a quantity representing an averaged over the entire group. This explains why there appears to be a single activation energy and why the activation energies for the diffusion of non-metals and metals are similar.

The experimental results for metal atom diffusion within amorphous semi-conductors are even more complicated. For example, the diffusivity of some metals (e.g. Li, Ni, Fe, Cu, Pd) in amorphous silicon is even slower than in crystalline silicon. This observation can be understood as follows: these metal atoms diffuse in crystalline silicon via an interstitial mechanism while in amorphous silicon these metal atoms can be trapped in a Si quasi-vacancy (recall that interstitial diffusion is typically much faster than substitutional diffusivity). However, some other metals (e.g. Au, Pt, Zr) diffuse in amorphous silicon faster than in crystalline silicon. This can be attributed to the fact that such metal atoms can occupy either lattice or interstitial sites in crystalline silicon. Therefore, the diffusion of these atoms includes fast migration through interstitials and trapping at Si sites. In amorphous silicon, such trapping is rarer than in crystalline silicon and hence diffusion is faster in amorphous silicon.

10.5 Diffusion in polymers

The last several decades have seen an explosion in the use of polymeric materials. The annual world production of polymeric materials (by volume or mass) has overtaken that of metals. Diffusion in polymeric materials is even more important than in metals since at moderate temperatures the diffusivities of atoms and small molecules (e.g. O_2, H_2O, CO_2, N_2) in natural rubber are $\sim 10^{-10}\,\mathrm{m}^2/\mathrm{s}$ at room temperature.

When small molecules penetrate into a polymer, the polymer chains can undergo a conformation change near these small molecules. The nature of the diffusion process is determined by the relative rates of the diffusion of the penetrant molecules and the conformational relaxation of the polymer chains. This can been described in terms of the **Deborah number** D_e, which is the ratio of the characteristic time τ_m of the conformational relaxation of the polymer chains and the characteristic diffusion time θ_D

$$D_\mathrm{e} = \tau_\mathrm{m}/\theta_\mathrm{D}. \qquad (1)$$

The characteristic time for diffusion through a polymeric film of thickness h can be defined as

$$\theta_D = h^2/D, \tag{10.35}$$

where D is the coefficient of mutual diffusion. If the Deborah number is small ($D_e < 0.1$), conformational relaxation is much faster than diffusion. If the Deborah number is large ($D_e > 10$), the polymer structure remains nearly static during the diffusion process. In both cases, the penetration can be described by Fick's laws. However, the situation is more complicated if the two times are similar, that is, $0.1 < D_e < 10$. In this case, the relaxation can lead to localized trapping of the penetrant molecules, and hence, Fick's second law is not directly applicable (the number of molecules that are free to diffuse is variable).

At present, no clear picture for diffusion of metals in polymers has emerged. For example, noble metals used in contacts in microelectronics diffuse more slowly than gas molecules of similar or even larger size. This suggests that either metal atoms diffuse as clusters which are considerably larger than single atoms or there is a strong interaction between noble metals and polymers.

10.6 Diffusion in multiphase systems

To this point, we have only considered diffusion in single phase systems. In such systems, the concentration profile, $c(x)$, is a smooth function. While it can be convex or concave, have inflection points, etc., neither it nor its derivatives exhibit discontinuities. In this section, we will consider diffusion in multiphase systems and find that such discontinuities are not only possible but are the rule. In particular, we will focus on the relation between the concentration profile and phase diagrams. We will not, however, consider diffusion along interfaces.

Consider the eutectic phase diagram shown in Fig. 10.6(a). At temperatures below the eutectic temperature, the diagram shows two solid solution regions (α and β) separated by a two-phase region. Consider diffusion at temperature T_1 in a very long bar, initially composed of a homogeneous α solid solution of B concentration c_0 ($c_0 < c_{\alpha\beta}$). The concentration of B is fixed at $c = c_s$ ($c_s > c_{\beta\alpha}$) on the left side of the sample, as shown in Fig. 10.6(b). The initial and boundary conditions for this problem are

$$c(x, 0) = c_0$$

$$c(0, t) = c_s; \qquad \left.\frac{\partial c}{\partial x}\right|_{x=\infty,\, t} = 0.$$

As B atoms diffuse from the left side into the sample, a β solid solution forms near that edge and grows during the diffusion anneal. The concentration of B in the β solid solution varies from c_s on the surface to $c_{\beta\alpha}$ at the point labeled ξ_1 in Fig. 10.6(b) (ξ_1 is the thickness of the β phase after some annealing time t_1). The B concentration cannot go below $c_{\beta\alpha}$, since

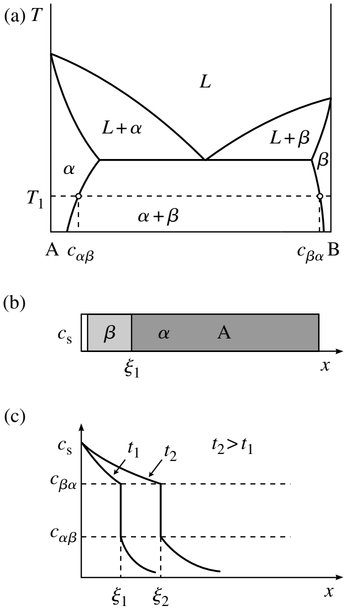

Fig. 10.6
(a) A eutectic phase diagram, (b) a semi-infinite bar that is initially composed of the α phase, where the concentration of B atoms at one end is fixed at c_s. As B atoms diffuse in, a section of the bar near the surface will transform to β while the remaining of the bar is α, (c) the B atom concentration profiles, where the variable ξ_i is the position of the β/α interface at time t_i.

the phase diagram shows that $c_{\alpha\beta} < \mathrm{c} < c_{\beta\alpha}$ is in the two-phase region of the diagram. At the point where $c = c_{\beta\alpha}$, an interface between α and β forms; the concentration of B in the α-phase near the interface is $c_{\alpha\beta}$. With increasing distance from the interface, the concentration of B atoms in the α-phase decreases monotonically. Note that the sample does not have a region containing both α and β. The point is that these two phases can co-exist only where they are both saturated in B ($c_{\alpha\beta}$ and $c_{\beta\alpha}$, respectively). Such a region cannot form by diffusion since the fact that these phases are saturated means there can be no flux through these phases (because no concentration gradient exists). Therefore, a vertical step in the concentration profile $c(x)$ corresponds to the two-phase region on the phase diagram. The height of this step, $c_{\beta\alpha} - c_{\alpha\beta}$, can be determined from the phase diagram and does not change during diffusion. The step will, however, move to the right as the β phase grows. In the region where the concentration of B is less than $c_{\alpha\beta}$, an α solid solution exists.

Wagner considered different limiting cases for the rate of growth of the β phase. For example, if we assume that the β phase growth is controlled by the rate of diffusion of B, the β phase thickens according to (cf. Eq. (10.18))

$$\xi = 2b\sqrt{D_{\mathrm{B}}t}, \tag{10.36}$$

where D_{B} is the diffusivity of B in β phase and b is a constant (see below).

Consider the special case in which the initial α solution is saturated ($c_0 = c_{\alpha\beta}$). The concentration profile for this case has the form shown in Fig. 10.7 after an annealing time t. In this case, diffusion occurs only in the β phase (since the α phase is saturated) and the concentration profile in β takes the following form (see Section 10.1.3):

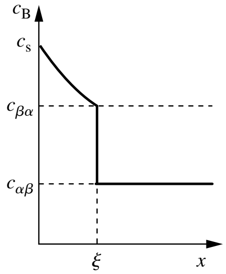

Fig. 10.7
Concentration profile for the case in which the initial α solution is saturated.

$$c(x,t) = A + B \cdot \mathrm{erf}\left(\frac{x}{2\sqrt{D_{\mathrm{B}}t}}\right). \tag{10.37}$$

The coefficients A and B can be found from the initial and boundary conditions:

$$c(0,t) = A = c_{\mathrm{s}}$$

$$c(\xi,t) = c_{\beta\alpha} = A + B \cdot \mathrm{erf}(b); \qquad B = \frac{c_{\mathrm{s}} - c_{\beta\alpha}}{\mathrm{erf}(b)}.$$

In general, the rate at which the β phase thickens is found by equating the amount of B required to grow the β phase and the rate at which B atoms are supplied to the α/β interface

$$(c_{\beta\alpha} - c_{\alpha\beta})\frac{\mathrm{d}\xi}{\mathrm{d}t} = -D_{\mathrm{B}}\left(\frac{\partial c}{\partial x}\right)_{\substack{x=\xi \\ c=c_{\beta\alpha}}}. \tag{10.38}$$

The derivatives $\mathrm{d}\xi/\mathrm{d}t$ and $(\partial c/\partial x)_{\substack{x=\xi \\ c=c_{\beta\alpha}}}$ can be found from Eqs (10.36) and (10.37), respectively. Inserting the results into Eq. (10.38), we obtain

$$\frac{c_{\mathrm{s}} - c_{\beta\alpha}}{c_{\beta\alpha} - c_{\alpha\beta}} = \sqrt{\pi}b \cdot \exp(b^2)\mathrm{erf}(b) = F(b). \tag{10.39}$$

This equation provides a means by which b can be determined. The function $F(b)$ is tabulated in Appendix IV. If $b \ll 1$, then $F(b) \approx 2b^2$ and Eq. (10.39) reduces to

$$b = \sqrt{\frac{1}{2}\frac{c_{\mathrm{s}} - c_{\beta\alpha}}{c_{\beta\alpha} - c_{\alpha\beta}}}. \tag{10.40}$$

Finally inserting this result into Eq. (10.36), we find

$$\xi = \sqrt{2\frac{c_{\mathrm{s}} - c_{\beta\alpha}}{c_{\beta\alpha} - c_{\alpha\beta}} D_{\mathrm{B}} t}. \tag{10.41}$$

This relation shows that the rate at which the new phase grows in a multicomponent system increases with increasing diffusivity and the difference between the concentration of B on the left-side of the sample and the solubility of A in β ($c_{\mathrm{s}} - c_{\beta\alpha}$ in the numerator) and with decreasing width of the two-phase region in the phase diagram ($c_{\beta\alpha} - c_{\alpha\beta}$ in the denominator).

Example problem

1. Consider an Ag–Zn alloy bar in which the α solution is saturated with Zn at $T = 600$°C (the phase diagram is shown in Fig. 10.8). The concentration of Zn on the left surface of a bar is fixed at 50%. The sample is annealed at $T = 600$°C for 10h. Estimate the thickness of the β phase formed. The handbook value of the diffusivity of Zn in the β solution at $T = 600$°C is $D_\beta = 7.2 \cdot 10^{-10}\,\mathrm{cm}^2/\mathrm{s}$.

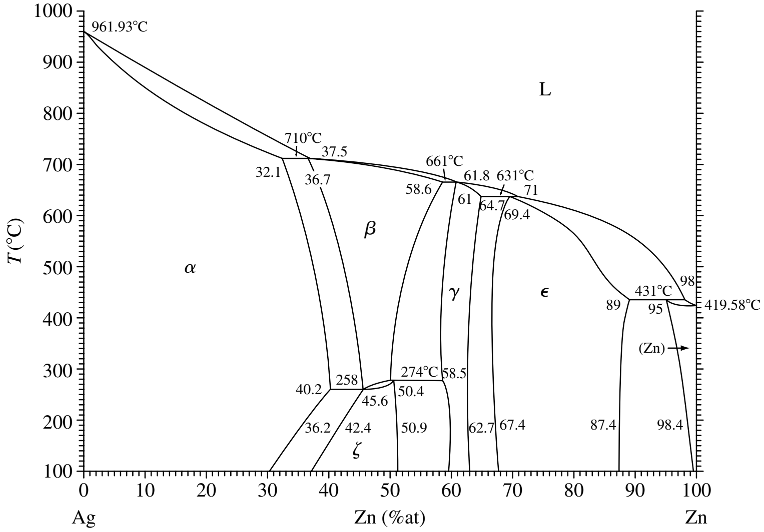

Fig. 10.8
The Ag–Zn phase diagram.

10.7 Thermal diffusion

In our discussion of diffusion, we have focused upon diffusion fluxes arising as a result of concentration gradients. However, as we know from the thermodynamics of irreversible processes (see Chapter 9), other thermodynamic forces can also give rise to a diffusion flux. Consider the following experiment. A sample prepared from a solution of C in α-Fe (a body-centered cubic lattice) is annealed for a long time such that the carbon concentration is constant throughout the sample. Next, the two ends of the sample are heated such that the temperatures of each are fixed at different values. This will, of course, produce a heat flux from the hotter end to the cooler end. This thermodynamic force that gives rise to heat flow can also create other fluxes as well, for example a diffusion flux. Indeed, experiments similar to that described here have been performed and showed that carbon tends to diffuse from the cooler to hotter end of the sample. If the sample is held under these conditions for a very long time, the diffusion flux stops, leaving behind a constant concentration gradient. This phenomenon is called **thermal diffusion**[8] and is an example of a cross-effect in the Onsager relation (Eq. (9.1)). We now analyze thermal diffusion within the framework of the thermodynamics of irreversible processes, as outlined in Section 9.7:

1. First, we determine which fluxes can occur in our system. In the present case, fluxes of C, Fe, vacancies, and heat are all possible. Since C is an interstitial in α-Fe, the C flux is much greater than either the Fe or vacancy flux. Therefore, it is reasonable to restrict our attention to fluxes of carbon and heat alone.
2. The appropriate acting thermodynamic forces are associated with gradients in the chemical potential for carbon and temperature.
3. The flux equations (see Section 9.6), according to the thermodynamics of irreversible processes, are

$$\begin{aligned} j_{\mathrm{C}} &= -L_{\mathrm{CC}}\nabla_T\mu_{\mathrm{C}} - L_{\mathrm{C}Q}\frac{\nabla T}{T} \\ j_Q &= -L_{Q\mathrm{C}}\nabla_T\mu_{\mathrm{C}} - L_{QQ}\frac{\nabla T}{T}. \end{aligned} \tag{10.42}$$

4. The diffusion of carbon toward the hot end leads to a concentration gradient and, hence, a chemical potential gradient. The chemical potential will also increase from the cooler to hotter end of the sample. According to Fick's first law, this chemical potential gradient should cause a diffusion flux directed from the hotter to cooler end of the sample. Steady-state is achieved when the C and temperature profiles no longer change. This happens when the carbon flux associated with the chemical potential gradient balances that due to the temperature gradient. Therefore, in steady-state, the first equation in Eq. (10.42) gives

$$(\nabla_T\mu_{\mathrm{C}})_{\text{steady-state}} = -\frac{L_{\mathrm{C}Q}}{L_{\mathrm{CC}}}\frac{\nabla T}{T}. \tag{10.43}$$

Note that in steady-state, there is still a flow of heat. Now, consider the case where no temperature gradient is imposed, but the chemical potential of carbon is fixed at different values on the two ends of the sample. In steady-state, Eq. (10.42) implies

$$\left(\frac{j_Q}{j_C}\right)_{\nabla T=0} = \frac{L_{QC}}{L_{CC}} = Q^*. \tag{10.44}$$

Since $J_Q = Q^* j_C$ we can interpret Q^* as the heat carried by 1 mole[9] of carbon atoms in an isothermal diffusion flux. This value is called the **heat of transport**. If the carbon forms an ideal dilute solution in α-Fe, the chemical potential for carbon is $\mu_C = \psi_C + RT \ln c_C$. Combining this relation with Eqs (10.43) and (10.44), gives

$$RT(\nabla_T c_C)_{\text{steady-state}} = -Q^* \frac{\nabla T}{T}$$

or

$$\left(\frac{\partial \ln c_C}{\partial T}\right)_{\text{steady-state}} = -\frac{Q^*}{RT^2}. \tag{10.45}$$

Since carbon diffuses to the heat end, its concentration increases with the increasing of the temperature, therefore, for given process the heat of transfer $Q^* < 0$. Experimentally measured value of the heat of transfer is $Q^* = -96\,\text{kJ/mole}$.

5. There are three kinetic coefficients in Eq. (10.42): L_{CC}, L_{CQ} and L_{QQ}. Therefore, we require three experimental measurements to determine these coefficients. Q^*, and hence the L_{QC}/L_{CC} ratio, can be determined using Eq. (10.45) by measuring $c(x)$ and $T(x)$ at steady-state. The coefficient L_{CC} can be found from a standard isothermal carbon diffusion experiment using the relation between the Onsager coefficient L_{CC} and the carbon diffusivity $L_{CC} = D_C c_C / RT$ (see Eq. (10.2)). Finally, measurement of the thermal conductivity λ_0 in the absence of a concentration gradient[10] using Fourier's law $j_Q = -\lambda_0 \nabla T$ allows us to determine L_{QQ} through $L_{QQ} = \lambda_0 T$.

Example problems

1. Show that at steady-state $j_{Q\text{steady-state}} = -\lambda_{\text{steady-state}} \nabla T$ and find the relation between $\lambda_{\text{steady-state}}$ and Q^*, D, and λ_0.
2. The thermal diffusion of hydrogen in α-Fe was investigated at $T = 300\,\text{K}$ in an experiment in which the average hydrogen concentration was $c_H = 0.01\%$. In an experiment in which the gradient of $\ln c_H$

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[8] Thermal diffusion in liquid solutions was discovered by Soret at the end of 19th century. Thermal diffusion can be used to separate isotopes.

[9] If the dimension of the flux is mole/(s m^2).

[10] The concentration gradient is initially zero but is established as a result of thermal diffusion. As any diffusion in solids, thermal diffusion requires a long time.

was 1 cm and the gradient of ln T (where T is in Kelvin) was -3.33 cm, the flux of hydrogen atoms was measured to be $j_{\mathrm{H}} = 5.7 \cdot 10^{14}$ atom/(cm^{2}s). Find the heat of transport. Use the following hand-book data: the density of α-Fe is 7.87 g/cm^3 and the hydrogen diffusivity in α-Fe is $D_{\mathrm{H}} = 2.4 \cdot 10^{-7}$ cm^2/s at 300 K.

11

Kinetics of heterogeneous processes

Most practical reactions that occur in synthesizing or processing materials are heterogeneous. These include oxidation, reduction reactions, dissolution of solids in liquids, and most solid-state phase transformations. Consider the oxidation of a metal by exposure of a solid metal to an atmosphere with a finite partial pressure of oxygen. In order for oxidation to occur, molecular oxygen must dissociate into atomic oxygen on the metal surface. In some cases, atomic oxygen diffuses into the metal and reacts to form an internal oxide, while in others, the reaction occurs at the surface. In the latter case, thickening of the oxide layer requires either metal or oxygen diffusion through the growing oxide layer. This example demonstrates that heterogeneous processes commonly involve several steps. The first step is usually the transport of a reactant through one of the phases to the interface. The second is the adsorption (segregation) or chemical reaction on the interface. Finally, the last third step is the diffusion of the products into the growing phase or the desorption of the product. Since the entire heterogeneous process is a type of complex reaction, there is usually one step that controls the rate of the process, that is, is the rate-determining step. Recall that the rate-determining step is the slowest (fastest) step for a consecutive (parallel) reaction (see Sections 8.2.1 and 8.2.2).

Consider the case of a consecutive heterogeneous reaction in which one of the reactants is transported through the fluid phase to the solid–fluid interface, where a first-order reaction takes place. The reaction rate ω_r in such a case is $\omega_r = kc_x$, where c_x is the concentration of the reactant on the interface. Since the reactant is consumed at the interface, c_x is smaller than the reactant concentration far from the interface, c_0 (see Fig. 11.1). It is usually easier to measure the reactant concentration in the bulk fluid. Therefore, it is convenient, to rewrite the reaction rate in terms of the bulk concentration in the fluid and an effective rate constant

$$\omega_r = kc_x = k_{\text{eff}}c_0. \tag{11.1}$$

It is easiest to see the relation between k_{eff} and k by considering the steady-state case. Steady-state occurs when the rate of transport of the reactant to the interface, ω_1, becomes equal to the chemical reaction rate, ω_r.

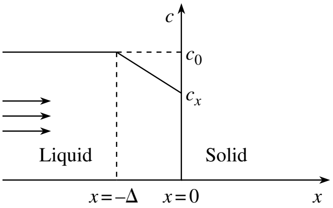


Fig. 11.1.
Concentration profile for the consecutive heterogeneous reaction considered in the text.

If we assume that the concentration decreases linearly from c_0 to c_x in the fluid over a distance Δ from the interface, then

$$\omega_1 = \beta(c_0 - c_x), \tag{11.2}$$

where β is the **mass-transfer coefficient**, with dimensionality per second. In steady-state $\omega_1 = \omega_r$, such that

$$\beta(c_0 - c_x) = k_{\text{eff}} c_0 = k c_x$$

or

$$c_x = \frac{\beta c_0}{\beta + k},$$

where we have used Eqs (11.1) and (11.2). Inserting this relation into Eq. (11.1), we find

$$\omega_r = k c_x = \frac{k \beta c_0}{\beta + k}.$$

Since, by definition, $\omega_r = k_{\text{eff}} c_0$, we finally obtain

$$k_{\text{eff}} = \frac{k\beta}{\beta + k}. \tag{11.3}$$

If $\beta \ll k$ (the rate-determining step is the transport of the reactant to the interface), then $k_{\text{eff}} = \beta$. If $\beta \gg k$ (the rate-determining step is the chemical reaction), then $k_{\text{eff}} = k$. In both cases, the overall rate of the process is controlled by the slowest step.

We now consider the case of a parallel heterogeneous reaction. Let the reactant concentration on the interface (at which the chemical reaction occurs) be constant ($c_x = \text{const}$) and the reactant is able to diffuse within the solid phase ($x > 0$ in Fig. 11.1). In this case, both reaction and diffusion can lead to the consumption of the reactant. The quantity q_r consumed by a first-order chemical reaction is

$$q_r = \omega_r t V = k c_x t A \delta \tag{11.4}$$

where t is time, V, A, and δ are the volume, interface area, and an effective interface thickness (typically measured to be of near atomic dimension). The quantity of reactant q_d which diffuses into the solid is (see Section 10.1.3)

$$q_d = \frac{2}{\sqrt{\pi}} c_x \sqrt{Dt} A. \tag{11.5}$$

Hence,

$$\frac{q_d}{q_r} = \frac{2}{\sqrt{\pi}} \frac{\sqrt{D/t}}{k\delta} \approx \frac{\sqrt{Dt}}{k\delta t}. \tag{11.6}$$

If $\sqrt{Dt} \ll k\delta t$, then $q_d \ll q_r$ and the reactant is consumed primarily by chemical reaction. If $k\delta t \ll \sqrt{Dt}$, then $q_r \ll q_d$ and most of the reactant diffuses into the solid. In both cases, while the rate of the total process depends on both steps, in very many cases, one of the steps contributes little.

As described above, heterogenous processes involve both transport of one or more species and a reaction. If the overall process is controlled by the reaction, such a process is described as **kinetics-limited**, while in the other case it is described as **transport-limited**. In the latter case, the limiting transport process can occur in either one of the two phases bounding the interface. If one of the phases is a fluid, this transport could occur by convection, turbulent mixing or diffusion, while in the solid, it is by diffusion. Whether the entire process is controlled by the interface reaction or by transport depends on such factors as temperature, pressure, and concentration. At low temperature, the process is usually kinetics-limited since the rate of chemical reactions commonly decreases more quickly with decreasing temperature than does the pertinent diffusivity (i.e. the activation energy for most chemical reactions is larger than that for diffusion). A typical plot of the effective rate constant versus temperature is shown schematically in Fig. 11.2.

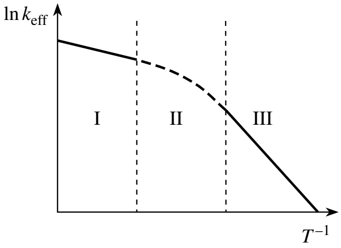


Fig. 11.2
A prototypical plot of the effective rate constant versus temperature. Regions I, II, and III correspond to the transport-limited, mixed, and kinetics-limited regimes, respectively.

If the process is limited by transport in the fluid, the rate of the process depends on the flux through the fluid, the rate of consumption of the reactant is proportional to time, the rate of the process is weakly temperature-dependent and may be influenced by convection. If the process is kinetics-limited, the rate of the process is independent of the flux through the fluid, the rate of consumption of the reactant depends on the order of the reaction, the rate of the process is strongly temperature-dependent and depends strongly on the type of reactants and their concentration. If the process is limited by diffusion in the solid, the rate of consumption of the reactant is proportional to the square root of time, the sensitivity of the rate of the process to temperature is intermediated between the other cases and the rate depends on the concentration of the reactant already in the solid and the structure of the solid.

12

Introduction to statistical thermodynamics of gases

As we discussed earlier in this book, thermodynamics provides very general relations between the properties of a system. On the other hand, thermodynamics is unable to predict any of the individual properties without the addition of either empirical or microscopic information. For example, we used thermodynamics to obtain Raoult's law from Henry's law, but we cannot derive Henry's law from thermodynamic principles. Statistical mechanics provides an approach to determine individual thermodynamic properties from microscopic considerations. When applied in the realm of physical chemistry, we refer to this approach as statistical thermodynamics. In this chapter, we provide a simplified derivation of the Gibbs distribution, which is the basis of much of statistical thermodynamics. We then use statistical mechanics to show how the properties of an ideal gas can be obtained from a small number of properties of the molecules in the gas. This will allow us to determine such quantities as the equilibrium and rate constants of gas phase chemical reactions. As a result, we will gain new insight into the phenomena which we have already considered on the basis of phenomenological thermodynamics or formal kinetics. This approach will also show how to determine some of the parameters we previously introduced as input data in our thermodynamic considerations.

12.1 Gibbs statistics

As we have already seen, a finite system will eventually come into equilibrium with its surroundings. We even showed that when thermodynamic equilibrium is established, the temperatures, pressures, and chemical potentials of the system and its surroundings are equal (see Section 1.5.2). However, we never discussed what equilibrium actually is. For example, does this mean that the energy of the system is truly constant or is it only constant on average? When the system has a particular energy, does this mean that it is in a unique physical state or can it be in any one of several states that have exactly the same energy? In the latter case, can we simply talk about the probability the system is in each of these states? If the energy can fluctuate, what is the probability that the system has a particular energy? A very general approach to these types of questions was suggested by Gibbs and is now known as **Gibbs statistics**.

In order to obtain the probability that the system is in a given state, we could observe the system over time and see what fraction of the time it spent in this state. Gibbs suggested another approach. He considered the system to be a member of a large ensemble of copies of our system. Let us assume that there are N systems in our ensemble and they interact only very weakly. This interaction is strong enough to ensure that thermal equilibrium is established between all of the systems in the ensemble, yet weak enough that it makes only a negligible contribution to the total energy of the ensemble of systems. This implies that the energy of the ensemble is simply

$$U_e = \sum_{i=1}^{N} U_i, \tag{12.1}$$

where U_i is the energy of system i. The main idea of Gibbs statistics is that the probability that a system is in a particular state is simply the fraction of the systems in the ensemble that are in this state. We can assume that N is so large that this fraction is independent of N.

Each member in our ensemble of N systems can be in microstate 1, 2, . . . ,k. These states are numbered in such a way that $U_{k+1} \geq U_k$, where U_k is the energy of the system in state k. The state of the ensemble can be characterized by the numbers of systems in each of these of microstates, that is, a_k systems in state k. How many different states of this ensemble are there? Elementary combinatorics shows that this number is

$$\Gamma = \frac{N!}{a_1!a_2!\ldots a_k!}. \tag{12.2}$$

In statistical mechanics, the ensemble entropy is related to the number of states, Γ as

$$S_{\mathrm{e}} = k_{\mathrm{B}} \ln \Gamma, \tag{12.3}$$

where k_{B} is the Boltzmann constant. This definition is consistent with the properties of entropy that we already know. Since Γ depends only on the state of the ensemble, $\ln \Gamma$ is obviously a state function. Consider now an ensemble consisting of two parts which are in thermal equilibrium with each other. Let Γ_1 and Γ_2 be the numbers of states associated with these two parts. The number of states associated with the entire ensemble is

$$\Gamma = \Gamma_1 \Gamma_2. \tag{12.4}$$

The total entropy is thus

$$S_{\mathrm{e}} = k_{\mathrm{B}} \ln \Gamma = k_{\mathrm{B}} \ln \Gamma_1 + k_{\mathrm{B}} \ln \Gamma_2 = S_1 + S_2,$$

therefore, we see that entropy is an extensive property. At $T = 0$, all systems should be in the state with the lowest energy, therefore, $\Gamma = 1$ and $S = 0$. This is in agreement with the third law of thermodynamics. Below, we will show that this definition of the entropy is consistent with the thermodynamic relations we found earlier on the basis of classical thermodynamics.

Since the ensemble is an isolated system, the entropy has a maximum in equilibrium. Therefore, in order to determine the number of systems in the ensemble that are in each state (i.e. a_k), we maximize S (Eq. (12.3)) subject to the constraints that the number of systems is fixed (at N) and the total energy is fixed (at U_e):

$$\sum_k a_k = N \tag{12.5}$$

$$\sum_k a_k U_k = U_e. \tag{12.6}$$

Thus, the condition of equilibrium takes the following form:

$$\delta S_e - \alpha \sum_k \delta a_k - \beta \sum_k U_k \delta a_k = 0, \tag{12.7}$$

where α and β are Lagrange multipliers and S_e is function of a_k. Since N is large, we can use Stirling's approximation

$$\ln N! \approx N \ln N - N = N \ln (N/e).$$

Inserting this expression into Eqs (12.2) and (12.3), we find

$$S_e = k_B N(\ln N - 1) - k_B \sum_k a_k(\ln a_k - 1). \tag{12.8}$$

Next, we employ this expression for S_e in Eq. (12.7) to find:

$$\begin{aligned} -k_B \sum_k \ln a_k \delta a_k - \alpha \sum_k \delta a_k - \beta \sum_k U_k \delta a_k \\ = -\sum_k (k_B \ln a_k + \alpha + \beta U_k)\delta a_k = 0. \end{aligned}$$

Since the coefficients a_k are independent variables, the multiplier in front of each δa_k must be zero. Therefore, we obtain:

$$a_k = e^{-(\alpha + \beta U_k)/k_B}.$$

The first Lagrange multiplier can be determined by inserting this expression into Eq. (12.5):

$$\sum_k e^{-(\alpha + \beta U_k)/k_B} = N; \qquad e^{-\alpha/k_B} = \frac{N}{\sum_k e^{-\beta U_k/k_B}}.$$

This implies that

$$a_k = N \frac{e^{-\beta U_k/k_B}}{\sum_k e^{-\beta U_k/k_B}}. \tag{12.9}$$

The energy and entropy of the ensemble can now be obtained by inserting this expression into Eqs (12.6) and (12.8), respectively:

$$U_\mathrm{e} = N\frac{\sum_k U_k \mathrm{e}^{-\beta U_k/k_\mathrm{B}}}{\sum_k \mathrm{e}^{-\beta U_k/k_\mathrm{B}}}, \tag{12.10}$$

$$\begin{aligned}
S_\mathrm{e} &= k_\mathrm{B}N(\ln N - 1) - K_\mathrm{B}\sum_k N\frac{\mathrm{e}^{-\beta U_k/k_\mathrm{B}}}{\sum_m \mathrm{e}^{-\beta U_m/k_\mathrm{B}}}\left(\ln \mathrm{N} + \ln\frac{\mathrm{e}^{-\beta U_k/k_\mathrm{B}}}{\sum_n \mathrm{e}^{-\beta U_n/k_\mathrm{B}}} - 1\right)\\
&= k_\mathrm{B}N(\ln\ N - 1) - \frac{k_\mathrm{B}N(\ln N - 1)}{\sum_m \mathrm{e}^{-\beta U_m/k_\mathrm{B}}}\sum_k \mathrm{e}^{-\beta U_k/k_\mathrm{B}}\\
&\quad + \frac{k_\mathrm{B}N}{\sum_m \mathrm{e}^{-\beta U_m/k_\mathrm{B}}}\sum_k \frac{\beta U_k}{k_\mathrm{B}}\mathrm{e}^{-\beta U_k/k_\mathrm{B}}\\
&\quad + \frac{k_\mathrm{B}N}{\sum_m \mathrm{e}^{-\beta U_m/k_\mathrm{B}}}\ln\sum_n \mathrm{e}^{-\beta U_n/k_\mathrm{B}}\sum_k \mathrm{e}^{-\beta U_k/k_\mathrm{B}}.
\end{aligned}$$

Since all of the sums in the last expression are independent we can replace the summation indices m and n by k. After some simple manipulations, we obtain:

$$S_\mathrm{e} = \frac{N\beta}{\sum_m \mathrm{e}^{-\beta U_m/k_\mathrm{B}}}\sum_k U_k \mathrm{e}^{-\beta U_k/k_\mathrm{B}} + k_\mathrm{B}N\ln\sum_k \mathrm{e}^{-\beta U_k/k_\mathrm{B}}.$$

Finally, using Eq. (12.10), we find:

$$S_\mathrm{e} = \beta U_\mathrm{e} + k_\mathrm{B}N\ \ln\sum_k \mathrm{e}^{-\beta U_k/k_\mathrm{B}}. \tag{12.11}$$

Although we have assumed that the ensemble is isolated in this derivation, the final expressions for the energy and entropy of the ensemble (Eqs (12.10) and (12.11)) are insensitive to this assumption. This must be the cases since both the energy and entropy are state functions. We now consider the case in which the ensemble is not isolated but rather is free to exchange heat with its surroundings such that the temperature T of the ensemble is fixed. We shall also work under the condition that the volume of the ensemble is constant. If we change the temperature of the surroundings, the energy levels U_k will not change (they depend only upon the internal structure of the systems and the volume). Therefore, changing temperature only changes the number of systems in each state (for example, if we add heat to the ensemble, some systems will go from lower energy to higher energy levels). Therefore, if the ensemble is brought into contact with some surroundings, the sum on the right hand side of Eq. (12.11) will not change. From Eq. (12.11), we obtain:

$$\left(\frac{\partial S_\mathrm{e}}{\partial U_\mathrm{e}}\right)_V = \beta.$$

Comparing this result with the combined statement of the first and second laws of thermodynamics (see Eq. (1.46)),

$$T\mathrm{d}S = \mathrm{d}U + p\mathrm{d}V,$$

we obtain

$$\beta = \frac{1}{T}. \tag{12.12}$$

Using this expression for the relation between the Lagrange multiplier β and the temperature in Eqs (12.9)–(12.11), we obtain

$$a_k = N \frac{e^{-U_k/k_B T}}{\sum_k e^{-U_k/k_B T}}, \tag{12.13}$$

$$U_e = N \frac{\sum_k U_k e^{-U_k/k_B T}}{\sum_k e^{-U_k/k_B T}}, \tag{12.14}$$

$$S_e = \frac{U_e}{T} + k_B N \ln \sum_k e^{-U_k/k_B T}. \tag{12.15}$$

These are the main equations of Gibbs statistics. Equation (12.13), which relates the occupancy of different states to their energies and temperature, is called the **Gibbs distribution law**. This result is *very* general—it does not depend on any physical characteristic of the system.

U_e and S_e in Eqs. (12.14) and (12.15) are properties of the entire ensemble, rather than any individual system within the ensemble. Equation (12.13) demonstrates that even in equilibrium we do not know which state any individual system is in or, therefore, what its properties are. However, statistical mechanics does tell us the probability (a_k/N) that the system is in a particular state (k). This probability can be used to determine the average properties of the system. This average can be thought of as the result of an ensemble average or, equivalently, a time average. The equivalence of ensemble and time averages is known as the **ergodic hypothesis**. These averages are the classical thermodynamics properties. Therefore, in order to obtain the thermodynamic energy and entropy of a system, we simply divide the energy and entropy of the entire ensemble by the number of copies of the system in the ensemble N:

$$U = \frac{\sum_k U_k e^{-U_k/k_B T}}{\sum_k e^{-U_k/k_B T}}, \tag{12.16}$$

$$S = \frac{U}{T} + k_B \ln \sum_k e^{-U_k/k_B T}. \tag{12.17}$$

In our discussion of thermodynamics in previous chapters, we often found it more convenient to work directly with the free energy, rather than other thermodynamic properties. Using the definition of the Helmholtz free energy,

$$A = U - TS,$$

and the expressions for the energy and entropy (Eqs (12.16) and (12.17)), we find:

$$A = -k_B T \ln \sum_k e^{-U_k/k_B T}. \tag{12.18}$$

We will use this expression as the starting point for the remainder of our discussions in this chapter.

Review question

1. What is U_k in the following equation:

$$A = -k_{\mathrm{B}}T \ln \sum_{k} \mathrm{e}^{-U_k/k_{\mathrm{B}}T}?$$

12.2 Statistical thermodynamics of an ideal gas

12.2.1 Partition function of an ideal gas

As a first application of the method of statistical thermodynamics, we will focus on the simple case of an ideal gas. Recall that the molecules of an ideal gas do not interact. This allows us to reduce the problem of determining the energy of an entire gas system of molecules to that of determining the energy of a single molecule. The state of an ideal gas can be described in terms of the set of states occupied by its individual constituent molecules. The energy of the kth state of the ideal gas system, U_k, can be related to the energies of the states that the individual molecules occupy ε_m:

$$\mathrm{e}^{-U_k/k_{\mathrm{B}}T} = \prod_{m} \mathrm{e}^{-\varepsilon_m/k_{\mathrm{B}}T}.$$

We shall assume that all molecules are identical such that states of all molecules are described by the same set of possible values of ε_m. Therefore, the sum over all states of the ideal gas system in Eq. (12.18) can be replaced by sums over all of the states that each molecule can occupy. Since each of the N molecules in the system is independent, the summation in Eq. (12.18) can be written as:

$$\sum_{k} \mathrm{e}^{-U_k/k_{\mathrm{B}}T} = \frac{1}{N!}\left(\sum_{m} \mathrm{e}^{-\varepsilon_m/k_{\mathrm{B}}T}\right)^{N}.$$

The factor $1/N!$ is used to take into account the fact that molecules in the system are physically indistinguishable from one another. In other words, if we exchange two molecules in the gas with each other, the new state is indistinguishable from the original one. Inserting this result into Eq. (12.18), we find

$$A = -Nk_{\mathrm{B}}T \ \ln \sum_{m} \mathrm{e}^{-\varepsilon_m/k_{\mathrm{B}}T} + k_{\mathrm{B}}T \ \ln \ N!.$$

Using Stirling's approximation

$$\ln N! = N \ln N - N = N \ln (N/e),$$

we obtain

$$A = -Nk_{\mathrm{B}}T \ \ln\left[\frac{e}{N}\sum_{m} \mathrm{e}^{-\varepsilon_m/k_{\mathrm{B}}T}\right] = -Nk_{\mathrm{B}}T \ \ln \frac{eZ}{N}, \qquad (12.19)$$

where $e = 2.718281828\ldots$ (i.e. $\ln e = 1$) and the quantity

$$Z = \sum_m \mathrm{e}^{-\varepsilon_m/k_\mathrm{B}T} \tag{12.20}$$

is called the **partition function** of the ideal gas.

It is interesting to note that Eq. (12.20) is sufficient to determine the equation of state of the ideal gas. First we note that in the absence of an external (gravitational, electric, magnetic, ...) field, the energy of a molecule in state m can be described by

$$\varepsilon_m = \frac{p_m^2}{2m} + \varepsilon'_m, \tag{12.21}$$

where the first term is the kinetic energy of the molecule and the second term is related to the internal structure of the molecule, the vibrations of the atoms within the molecule and its rotational momentum. This second term depends on neither the spatial location of the molecule nor the velocity of its center of mass. Therefore, the partition function of the ideal gas is

$$Z = \sum_m \mathrm{e}^{-\varepsilon_m/k_\mathrm{B}T} = \sum_m \mathrm{e}^{-\varepsilon'_m/k_\mathrm{B}T}\mathrm{e}^{-p_m^2/2mk_\mathrm{B}T}.$$

Since each state is characterized by the center of mass variables (momentum and position) and the internal variables, we could rewrite the sum over m as independent sums over the center of mass and internal variables. Next, we make use of the fact that the position of the molecules and their momenta are continuous variables by replacing the summation over the center of mass variables with integrals over position and momentum:

$$\sum \ldots \to \int \ldots \mathrm{d}\Gamma,$$

where

$$\mathrm{d}\Gamma = \frac{\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{p}}{(2\pi\hbar)^3}. \tag{12.22}$$

The normalization is a result of the Heisenberg uncertainty principle, as described in elementary quantum mechanics texts, and $\hbar$ is Planck's constant divided by 2π. Thus, the partition function can be written as

$$\begin{aligned} Z = \sum_m \mathrm{e}^{-\varepsilon_m/k_\mathrm{B}T} &= \sum_m \mathrm{e}^{-\varepsilon'_m/k_\mathrm{B}T} \int_V \int_p \frac{\mathrm{e}^{-p^2/2mk_\mathrm{B}T}}{(2\pi\hbar)^3}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{p} \\ &= \sum_m \mathrm{e}^{-\varepsilon'_m/k_\mathrm{B}T} \frac{V}{(2\pi\hbar)^3}\left(\int_{-\infty}^{+\infty} \mathrm{e}^{-p_x^2/2mk_\mathrm{B}T}\mathrm{d}p_x\right)^3 \\ &= \frac{V}{(2\pi\hbar)^3}\left(\sqrt{2\pi m k_\mathrm{B}T}\right)^3 \sum_m \mathrm{e}^{-\varepsilon'_m/k_\mathrm{B}T} = V\left(\frac{mk_\mathrm{B}T}{2\pi\hbar^2}\right)^{3/2}\sum_m \mathrm{e}^{-\varepsilon'_m/k_\mathrm{B}T}. \end{aligned}$$

Inserting this result into Eq. (12.19), we obtain:

$$A = -Nk_BT \ \ln\left[\frac{eV}{N}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\sum_m e^{-\varepsilon'_m/k_BT}\right]. \tag{12.23}$$

Since the molecules of the ideal gas do not interact, the summation

$$\sum_m e^{-\varepsilon'_m/k_BT}$$

is only a function of temperature (and the type of molecules). Therefore, Eq. (12.23) can be rewritten as

$$A = -Nk_BT \ \ln\frac{V}{N} + Nk_Bf(T). \tag{12.24}$$

Using Eq. (12.24), we can now derive all other thermodynamic properties. The equation of state is

$$p = -\left(\frac{\partial A}{\partial V}\right)_T = \frac{Nk_BT}{V}$$

or

$$pV = Nk_BT. \tag{12.25}$$

This is the classical ideal gas law. The other common thermodynamic properties are

$$G = A + pV = A + Nk_BT = -Nk_BT \ \ln\frac{Z}{N}, \tag{12.26}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = Nk_B \ \ln\frac{V}{N} - Nk_Bf'(T), \tag{12.27}$$

$$U = A + TS = Nk_Bf(T) - Nk_BTf'(T), \tag{12.28}$$

$$H = U + pV = Nk_Bf(T) - Nk_BTf'(T) + Nk_BT. \tag{12.29}$$

Equations (12.28) and (12.29) demonstrate that the internal energy and enthalpy of an ideal gas depend only upon temperature (we came to the same conclusion in Chapter 1). Since for an ideal gas, $H = U + Nk_BT$, we find

$$c_p = c_V + Nk_B \tag{12.30}$$

This can be rewritten per mole of molecules as $c_p = c_V + R$.

The thermodynamic properties can be related to the microscopic properties of the molecules through detailed consideration of the energy of a molecule in a particular state, ε. This energy can be represented as a sum over its internal energy, the energies associated with its rigid translation and rotation and the energy associated with the vibrations of the atoms within the molecule:

$$\varepsilon = \varepsilon_0 + \varepsilon_{\text{tran}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}}. \tag{12.31}$$

Therefore, the partition function and the Helmholtz free energy can be rewritten as:

$$Z = \mathrm{e}^{-\varepsilon_0/k_\mathrm{B}T} Z_\mathrm{tran} Z_\mathrm{rot} Z_\mathrm{vib} \tag{12.32}$$

$$\begin{aligned} A &= N\varepsilon_0 - Nk_\mathrm{B}T\ \ln Z_\mathrm{tran} - Nk_\mathrm{B}T\ \ln Z_\mathrm{rot} - Nk_\mathrm{B}T\ \ln Z_\mathrm{vib} \\ &= N\varepsilon_0 + A_\mathrm{tran} + A_\mathrm{rot} + A_\mathrm{vib} \end{aligned} \tag{12.33}$$

(the last two terms on the right hand side of Eq. (12.23) are absent for a monoatomic gas). As we discussed in Section 12.1, changing the temperature at constant volume does not change the energy spectrum but rather leads to a redistribution of the gas molecules between the available states. Therefore,

$$\left(\frac{\partial Z}{\partial T}\right)_V = \sum_m \frac{\varepsilon_m}{k_\mathrm{B}T^2} \mathrm{e}^{-\varepsilon_m/k_\mathrm{B}T} = \frac{Z}{k_\mathrm{B}T^2}\langle\varepsilon\rangle = \frac{Z}{k_\mathrm{B}T^2}\frac{U}{N}$$

or

$$U = Nk_\mathrm{B}T^2\left(\frac{\partial \ln Z}{\partial T}\right)_V. \tag{12.34}$$

Rewriting this expression using the separate contributions to the partition function associated with the different degrees of freedom (Eq. (12.32)), we find:

$$U = N\varepsilon_0 + U_\mathrm{tran} + U_\mathrm{rot} + U_\mathrm{vib} \tag{12.35}$$

$$c_V = c_{V\mathrm{tran}} + c_{V\mathrm{rot}} + c_{V\mathrm{vib}} \tag{12.36}$$

Review questions

1. When can the total energy of a system be represented as a sum of the energies of the molecules in the system?
2. What does the factor $1/N!$ in the expression $\sum_k \mathrm{e}^{-U_k/k_\mathrm{B}T} = \frac{1}{N!}\left(\sum_m \mathrm{e}^{-\varepsilon_m/k_\mathrm{B}T}\right)^N$ account for?

12.2.2 Effect of translational motion of gas molecules

Since the motion of the center of mass of a molecule in the absence of an external field is always classical, both classical and quantum mechanical treatments yield the same results. The translational partition function can be directly integrated as:

$$Z_\mathrm{tran} = \sum_m \mathrm{e}^{-p_m^2/2mk_\mathrm{B}T} = \int \mathrm{e}^{-p^2/2mk_\mathrm{B}T}\frac{\mathbf{drdp}}{(2\pi\hbar)^3}$$

$$Z_\mathrm{tran} = V\left(\frac{mk_\mathrm{B}T}{2\pi\hbar}\right)^{3/2}. \tag{12.37}$$

The contributions to the Helmholtz free energy and the other thermodynamic functions of the ideal gas can now be expressed as:

$$A_{\text{tran}} = -Nk_{\text{B}}T\ \ln\left[\frac{e}{N}Z_{\text{tran}}\right] = -Nk_{\text{B}}T\ \ln\left[\frac{eV}{N}\left(\frac{mk_{\text{B}}T}{2\pi\hbar}\right)^{3/2}\right] \tag{12.38}$$

$$U_{\text{tran}} = Nk_{\text{B}}T^2\left(\frac{\partial \ln Z_{\text{tran}}}{\partial T}\right)_V = \frac{3}{2}Nk_{\text{B}}T \tag{12.39}$$

$$\begin{aligned} S_{\text{tran}} &= Nk_{\text{B}}T\left(\frac{\partial \ln Z_{\text{tran}}}{\partial T}\right)_V + Nk_{\text{B}}\ln\left[\frac{e}{N}Z_{\text{tran}}\right] \\ &= Nk_{\text{B}}\ln\left[\frac{eV}{N}\left(\frac{mkT}{2\pi\hbar}\right)^{3/2}\right] + \frac{3}{2}Nk_{\text{B}} \end{aligned} \tag{12.40}$$

$$c_{V\text{tran}} = \left(\frac{\partial U_{\text{tran}}}{\partial T}\right)_V = \frac{3}{2}Nk_{\text{B}} \tag{12.41}$$

The heat capacity per mole is $c_{V\text{tran}} = 3/2R$.

12.2.3 Energy of diatomic molecules

The thermodynamic properties of a diatomic ideal gas differ from those of a monatomic ideal gas because a diatomic molecule can rotate and its constituent atoms can vibrate with respect to one another. These differences are manifested as rotational and vibrational contributions to the partition function. In order to determine these contributions, we must first obtain expressions for the vibrational and rotational contributions to the energy. This requires some knowledge of quantum mechanics. If you are not familiar with the basic notions of quantum mechanics, you may choose to skip ahead to the text immediately following Eq. (12.48), where we simply use the quantum mechanical results.

Since atomic nuclei are much heavier than electrons, we can use the **Born-Oppenheimer** or **adiabatic approximation**: we determine the energy levels of the electrons assuming that the nuclei are stationary. We can do this as a function of the distance between nuclei (i.e. determine $\varepsilon_e(r)$). We then allow the nuclei to move assuming that the electrons are always in equilibrium with respect to the instantaneous position of the nuclei. Therefore, the interaction between the nuclei can be described through $\varepsilon_e(r)$. The problem of the motion of two interacting particles can be described through classical mechanics. In this way, we can show that the energy of two interacting particles with masses m_1 and m_2 is

$$\varepsilon_m(r) = \varepsilon_e(r) + \frac{\mathbf{M}^2}{2m'r^2} \tag{12.42}$$

where **M** is the angular momentum of nuclei and

$$m' = \frac{m_1 m_2}{m_1 + m_2} \tag{12.43}$$

If the total spin of the molecule is zero, its total angular momentum, **J**, is the sum of the orbital momentum of the electrons, **L**, and angular momentum of the rotation of the nuclei, **M**. Therefore, Eq. (12.42) can be rewritten as

$$\varepsilon_m(r) = \varepsilon_e(r) + \left\langle \frac{|\mathbf{J} - \mathbf{L}|^2}{2m'r^2} \right\rangle \tag{12.44}$$

where the average implied by the angular brackets is performed in a state in which the square of the total rotational momentum $\mathbf{J}^2 = \hbar^2 J(J+1)$ and the projection of the electron angular momentum L_z along the axis of the molecule have particular values. Equation (12.44) can be rewritten as:

$$\varepsilon_m(r) = \varepsilon_e(r) + \frac{\hbar^2}{2m'r^2} J(J+1) - \frac{\mathbf{JL}}{m'r^2} + \frac{\mathbf{L}^2}{2m'r^2}$$

The last term is determined only by the electronic state, therefore, we can combine it with $\varepsilon_e(r)$. Let $\hat{z}$ be the unit vector in the direction of the molecule axis. Since, in the state under consideration, the projection of the angular momentum of the electrons onto the z-axis is defined, the average angular momentum **L** also points in this direction, $\langle \mathbf{L} \rangle = L_z \hat{\mathbf{z}}$. Classical mechanics states that the angular momentum of a system consisting of two particles is the product of the relative momentum of the particles and the vector connecting these particles:

$$\mathbf{M} = [\mathbf{r} \times \mathbf{p}] = r[\hat{\mathbf{z}} \times \mathbf{p}].$$

This definition implies that

$$\mathbf{M}\hat{\mathbf{z}} = 0$$

and, therefore,

$$(\mathbf{J} - \mathbf{L})\hat{\mathbf{z}} = 0; \qquad \mathbf{J}\hat{\mathbf{z}} = \mathbf{L}\hat{\mathbf{z}} = L_z; \qquad \mathbf{JL} = \mathbf{J}\hat{\mathbf{z}} L_z = L_z^2.$$

The last relation demonstrates that the term containing **JL** also depends only on the electronic state. Finally, we obtain,

$$\varepsilon_m(r) = \varepsilon(r) + \frac{\hbar^2}{2m'r^2} J(J+1). \tag{12.45}$$

The relative motion of the nuclei can be considered as a vibration along the direction between the two atoms, with equilibrium separation r_e. Introducing $\xi = r - r_\mathrm{e}$, we can rewrite the previous equation as

$$\varepsilon_m(r) = \varepsilon_0 + B\hbar J(J+1) + \frac{m'\omega^2}{2}\xi^2, \tag{12.46}$$

where

$$B = \frac{\hbar}{2m'r_e^2} = \frac{\hbar}{2I}, \tag{12.47}$$

is the so-called **rotational constant**, I is the moment of inertia and ω is the vibrational frequency. Since the last term in Eq. (12.46) is the energy of a harmonic oscillator, we can rewrite this equation as

$$\varepsilon_m(r) = \varepsilon_0 + B\hbar J(J+1) + \hbar\omega n, \tag{12.48}$$

where n is a non-negative integer (we included the energy of the zeroth vibrational state, ($\hbar/2$, in ε_0).

Equation (12.48) demonstrates that, in the Born–Oppenheimer/adiabatic approximation, the energy is the sum of three contributions: electronic (including the Coulomb interaction of the nuclei at $r = r_e$), rotational, and vibrational. Equation (12.48) can be used to explain the adsorption spectra and emission of diatomic molecules.

The only possible transitions in the rotational state satisfy

$$\Delta J = J' - J'' = \pm 1. \tag{12.49}$$

Therefore,

$$\begin{aligned}\Delta\varepsilon_{\text{rot}} &= \hbar B[J'(J'+1) - J''(J''+1)] = \hbar B[J'(J'+1) - (J'-1)J'] \\ &= 2\hbar BJ'.\end{aligned}$$

Since $\Delta\varepsilon_{\text{rot}} = \hbar\omega_{\text{rot}}$,

$$\omega_{\text{rot}} = 2BJ'. \tag{12.50}$$

This implies that the difference between two neighboring lines in the rotational spectrum (the set of possible rotational energies) is always $2B$; that is, the spectrum consists of equidistant lines. The equilibrium interatomic separation in a diatomic molecule can be determined from its rotational spectrum (see Eqs. (12.47) and (12.50)). The dipole momentum of a molecule can be found from the displacement of the spectrum lines in a homogeneous, external electric field (the Stark effect).

The only possible transitions in the vibrational state satisfy

$$\Delta n = n' - n'' = \pm 1. \tag{12.51}$$

Therefore,

$$\omega_{\text{vibration}} = \omega. \tag{12.52}$$

The vibrational spectrum of a harmonic oscillator contains only one line with a frequency that coincides with the vibrational frequency. However, anharmonicity introduces additional lines into the spectrum.

12.2.4 Rotational contributions to thermodynamic functions

In order to obtain the contribution to the partition function associated with the rotation of the gas molecules, we insert the expression for the rotational energy in Eq. (12.20) and account for the degeneracy of the rotational levels (i.e. the Jth rotational level is $(2J+1)$-fold degenerate):

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)\,\mathrm{e}^{-(\hbar^2/2Ik_{\mathrm{B}}T)\mathrm{J}(\mathrm{J}+1)}. \tag{12.53}$$

Table 12.1. The characteristic temperatures for some gases.[1]

Molecule	H_2	N_2	O_2	HCl	HI
T_c (K)	85.4	2.85	2.07	15.1	9.0
θ (K)	6000	3340	2230	4140	3200
T_{boil} (K)	20.4	77.4	90.2	188.1	237.8

This expression can be evaluated numerically. We can examine the rotational contribution to the partition function in the limits that $T \ll T_c$ and $T \gg T_c$, where T_c is the characteristic temperature:

$$T_c = \frac{\hbar^2}{2Ik_B}. \tag{12.54}$$

The values of T_c for some gases are given in Table 12.1. This table demonstrates that T_c is much smaller than room temperature for all gases.

In the $T \gg T_c$, limit, the summation in Eq. (12.53) can be replaced by the integration:[2]

$$Z_{\text{rot}} = \int_0^\infty (2x+1)e^{-(T_c/T)x(x+1)}\,dx.$$

Replacing x by $y = x(x+1)$, we can rewrite this integral as

$$Z_{\text{rot}} = \int_0^\infty e^{-(T_c/T)y}\,dy.$$

Performing the integration, we obtain:

$$Z_{\text{rot}} = \frac{T}{T_c}. \tag{12.55}$$

Using this result, we can derive expression for the contribution of molecular rotation to all thermodynamic functions:

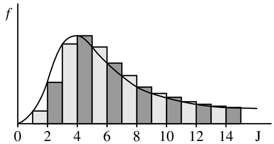
$$A_{\text{rot}} = -Nk_BT\ln\frac{T}{T_c} \tag{12.56}$$

$$S_{\text{rot}} = Nk_B\left(\ln\frac{T}{T_c}+1\right) \tag{12.57}$$

$$U_{\text{rot}} = NK_BT \tag{12.58}$$

$$C_{V\text{rot}} = NK_B. \tag{12.59}$$

The contribution to the heat capacity associated with the rotation per mole of molecules is $c_V = R$, or $R/2$ per rotational degree of freedom.



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[1] θ will be introduced in the next section.

[2] As the figure on the left demonstrates (where f is the integrand in Eq. (12.53)), replacing the sum by the integral is only a reasonable approximation at large T (see Eq. (12.55)), where only the large J contributions are significant.

At low temperature, $T \ll T_c$, we need only retain the first two terms in the sum in Eq. (12.53):

$$Z_{\text{rot}} = 1 + 3\mathrm{e}^{-2(T_c/T)}. \tag{12.60}$$

Therefore, in this limit, the thermodynamic functions are:

$$A_{\text{rot}} = -3Nk_BT\mathrm{e}^{-2(T_c/T)} \tag{12.61}$$

$$S_{\text{rot}} = 3Nk_Be^{-2(T_c/T)}\left(1 + 2\frac{T_c}{T}\right) \tag{12.62}$$

$$U_{\text{rot}} = Nk_BT^2\frac{\partial}{\partial T}\ln\left(1 + 3e^{-2(T_c/T)}\right) = \frac{Nk_BT^2}{\left(1 + 3\mathrm{e}^{-2(T_c/T)}\right)}3\mathrm{e}^{-2(T_c/T)}\frac{2T_c}{T^2};$$

$$U_{\text{rot}} = 6Nk_BT_c\mathrm{e}^{-2(T_c/T)} \tag{12.63}$$

$$c_{V\text{rot}} = 12Nk_B\left(\frac{T_c}{T}\right)^2\mathrm{e}^{-2(T_c/T)}. \tag{12.64}$$

These expressions demonstrate that as $T \to 0$, $S_{\text{rot}} \to 0$, and $c_{V\text{rot}} \to 0$. Moreover, the fact that $c_{V\text{rot}} \to 0$ implies that gases of diatomic molecules behave just like monoatomic gases in the $T \to 0$ limit.

The summation in Eq. (12.53) can be evaluated numerically at any finite temperature and hence all thermodynamic functions can be determined at any temperature. The variation of the rotational contribution to the heat capacity $c_{V\text{rot}}$ with temperature is shown in Fig. 12.1. Interestingly, the heat capacity is not a monotonic function: it exhibits a maximum at $T \approx 0.81T_c$ and then decays to Nk_B with increasing temperature.

In the case of homo-nuclear diatomic molecules, the expression for Z_{rot}, given above, should be divided by 2, since the rotation of a molecule by π around an axis perpendicular to the molecule axis is indistinguishable from its original orientation. Such a mirror symmetry will not change U_{rot} or $c_{V\text{rot}}$, but will decrease the entropy by $Nk_B \ln 2$.

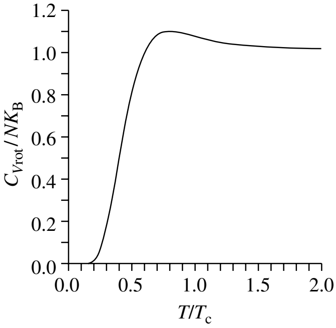

Fig. 12.1
The rotational contribution to the heat capacity of a diatomic gas as a function of temperature.

Example problem

1. As discussed above, the difference between neighboring rotational energy levels is the same for the entire rotational spectrum. However, the number of molecules at each rotational level is different. Find the most populated level for a gas of diatomic molecules at $T \gg T_c$.

12.2.5 Vibrational contributions to thermodynamic functions

Equations (12.48) and (12.20) imply

$$Z_{\text{vib}} = \sum_{n=0}^{\infty}\mathrm{e}^{-n\theta/T}, \tag{12.65}$$

where

$$\theta = \frac{\hbar\omega}{k_B}. \tag{12.66}$$

Values of θ for several diatomic gases are given in Table 12.1 of the previous section. Examination of the table shows that θ is much larger than room temperature.

Performing the summation in Eq. (12.65), we find:

$$Z_{\mathrm{vib}} = \frac{1}{1 - \mathrm{e}^{-\theta/T}}. \tag{12.67}$$

Using this relation, we can determine the other thermodynamic functions:

$$A_{\mathrm{vib}} = Nk_B T \ln\left(1 - \mathrm{e}^{-\theta/T}\right), \tag{12.68}$$

$$S_{\mathrm{vib}} = -Nk_B\left[\ln\left(1 - \mathrm{e}^{-\theta/T}\right) + \frac{\theta}{\mathrm{T}(\mathrm{e}^{\theta/\mathrm{T}} - 1)}\right], \tag{12.69}$$

$$U_{\mathrm{vib}} = -Nk_B T^2 \frac{\partial}{\partial \mathrm{T}} \ln\left(1 - \mathrm{e}^{-\theta/T}\right) = \frac{Nk_B\theta}{\mathrm{e}^{\theta/\mathrm{T}} - 1}, \tag{12.70}$$

$$c_{V\mathrm{vib}} = Nk_B\left(\frac{\theta}{T}\right)^2 \frac{\mathrm{e}^{\theta/T}}{\left(\mathrm{e}^{\theta/T} - 1\right)^2}. \tag{12.71}$$

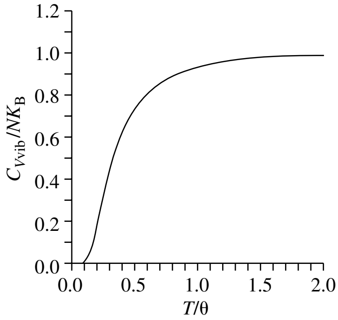

Fig. 12.2.
The temperature dependence of the vibrational contribution to the heat capacity of a diatomic gas.

The temperature dependence of $c_{V\mathrm{vib}}$ is shown in Fig. 12.2 At low temperature ($T \ll \theta$), Eq. (12.71) reduces to

$$c_{V\mathrm{vib}} = Nk_B\left(\frac{\theta}{T}\right)^2 \mathrm{e}^{-\theta/T} \tag{12.72}$$

and as $T \to 0$, $c_{V\mathrm{vib}} \to 0$. At high temperature ($T \gg \theta$),

$$c_{V\mathrm{vib}} = Nk_B\left(\frac{\theta}{T}\right)^2 \frac{1}{(\theta/T)^2} = Nk_B. \tag{12.73}$$

For 1 mole of diatomic molecules, we obtain $c_{V\mathrm{vib}} = R$ at high temperature; that is, the contribution from one vibrational degree of freedom to the heat capacity is R. However, since at typical temperatures $T \ll \theta$, $c_{V\mathrm{vib}} \approx 0$ such that the isochoric heat capacity of a diatomic gas is approximately $(5/2)R$ (a contribution of $(3/2)R$ from the translation motion and R from rotations) rather than $(7/2)R$ (the high temperature result). Interestingly, the low temperature heat capacity is different in quantum and classical mechanics (classically, the heat capacity is temperature independent).

Review question

1. An experiment shows that the contribution of one vibrational degree of freedom to the heat capacity of a gas can be larger than k_B. How can you explain this observation?

Example problems

1. The potential energy of a classical harmonic oscillator is

$$\varepsilon = \frac{\beta x^2}{2},$$

where x is the deviation of the atomic separation from its equilibrium value (e.g. in a diatomic molecule). If the amplitude of the vibration is not small, the oscillator will be anharmonic and more terms must be kept in the expansion of its energy:

$$\varepsilon = \frac{\beta x^2}{2} - \gamma x^3 - \delta x^4.$$

Find the heat capacity of this oscillator.

2. The linear coefficient of thermal expansion of an oscillator (see the previous Example problem) is defined as

$$\alpha = \frac{1}{a_0}\frac{\partial \bar{x}}{\partial T},$$

where a_0 is the equilibrium interatomic distance at $T = 0$. Find the linear coefficient of thermal expansion for the anharmonic oscillator of Example problem 1.

3. Calculate the heat capacity of CO at $p = 1$ atm and $T_1 = 298$ K and $T_2 = 800$ K. Use the following handbook data for CO: the equilibrium interatomic separation is $r = 1.128$ Å and the vibrational wavenumber[3] is $\tilde{\nu} = 2215$ cm.
4. Calculate the molar entropy of CO at $p = 1$ atm and $T = 298$ K. Use the handbook data from the previous example problem.

12.2.6 Polyatomic molecular gasses

Consider the case of a molecule containing v atoms. It has 3 translation degrees of freedom; the contribution of these degrees of freedom to the thermodynamic properties was discussed in Section 12.2.3. If the molecule is linear, it has 2 rotational degree of freedom; the contribution from these degrees of freedom was considered in Section 12.2.4. If the molecule is non-linear, it has 3 rotational degrees of freedom. We now derive an expression for Z_{rot} for this case. Since the moments of inertia for polyatomic molecules, I_1, I_2 and I_3 are always large, we can work in the $T \gg T_c$ limit. In this limit, the classical and quantum mechanical descriptions produce the same rotational energy:

$$\varepsilon_{\text{rot}} = \frac{M_1^2}{2I_1} + \frac{M_2^2}{2I_2} + \frac{M_3^2}{2I_3}, \tag{12.74}$$

---

[3] By definition, the wavenumber is , $\tilde{\nu} = \omega/(2\pi c)$ where c is the light speed. While this notation is widely used in spectroscopy, in many other situations the wavenumber is traditionally labeled as k or q.

where the subscripts identify the principal axes of inertia.[4] For the rotational contribution to the partition function, we obtain:

$$Z_{\mathrm{rot}} = \int' \mathrm{e}^{-\varepsilon_{\mathrm{rot}}/kT}\,\mathrm{d}\Gamma_{\mathrm{rot}}, \tag{12.75}$$

where the prime indicates that the integration should be performed over physically distinguishable states of the molecule. The number of physically indistinguishable orientations σ is equal to the number of ways a molecule can be rotated such that it appears, after rotation, unchanged (including rotations by 2π). However, it is convenient to perform this integration over the entire space and then to divide the result by σ. The element of this space is

$$\mathrm{d}\Gamma_{\mathrm{rot}} = \frac{1}{(2\pi\hbar)^3}\mathrm{d}M_1\mathrm{d}M_2\mathrm{d}M_3\mathrm{d}\varphi_1\mathrm{d}\varphi_2\mathrm{d}\varphi_3,$$

where the φ_i are the rotation angles around the principle axes. Integration over $\mathrm{d}\varphi_1\mathrm{d}\varphi_2$ gives a solid angle of 4π, while integration over $\mathrm{d}\varphi_3$ gives 2π. Hence,

$$\begin{aligned} Z_{\mathrm{rot}} &= \frac{1}{(2\pi\hbar)^3\sigma}4\pi\cdot 2\pi\prod_i\int_{-\infty}^{+\infty}\mathrm{e}^{-M_i^2/2I_ik_{\mathrm{B}}T}\,\mathrm{d}M_i \\ &= \frac{8\pi^2}{(2\pi\hbar)^3\sigma}(2I_1k_BT\pi\cdot 2I_2k_BT\pi\cdot 2I_3k_BT\pi)^{1/2} \end{aligned}$$

or

$$Z_{\mathrm{rot}} = \frac{(2k_{\mathrm{B}}T)^{3/2}(\pi I_1I_2I_3)^{1/2}}{\sigma\hbar^3} \tag{12.76}$$

$$A_{\mathrm{rot}} = -\frac{3}{2}Nk_{\mathrm{B}}T\ln T - Nk_{\mathrm{B}}T\ln\left[\frac{(8\pi k_{\mathrm{B}}^3I_1I_2I_3)^{1/2}}{\sigma\hbar^3}\right] \tag{12.77}$$

$$S_{\mathrm{rot}} = \frac{3}{2}Nk_{\mathrm{B}}(1+\ln T) + Nk_{\mathrm{B}}T\ln\left[\frac{(8\pi k_{\mathrm{B}}^3I_1I_2I_3)^{1/2}}{\sigma\hbar^3}\right] \tag{12.78}$$

$$U_{\mathrm{rot}} = Nk_{\mathrm{B}}T^2\frac{3}{2}\frac{1}{T} = \frac{3}{2}Nk_{\mathrm{B}}T \tag{12.79}$$

$$c_{V\mathrm{rot}} = \frac{3}{2}Nk_B. \tag{12.80}$$

---

[4] The tensor of inertia can be written, in general, as

$$I_{ik} = \sum m(x_1^2\delta_{ik} - x_ix_k),$$

where the summation is over all atoms of the molecule. This tensor is symmetric; therefore, it can be diagonalized by rotation of the coordinate system. The axes of this coordinate system, x_1, x_2 and x_3, are called the **principal axes of inertia** and the corresponding components of the tensor I_1, I_2 and I_3 are called the **principal moments of inertia**.

As in the case of diatomic molecules, we find that each rotational degree of freedom contributes $R/2$ to the heat capacity (per mole).

Since the total number of degrees of freedom is $3v$ and there are three translational degrees of freedom, we conclude that linear and non-linear molecules have $3v-5$ and $3v-6$ vibrational degrees of freedom, respectively. The contributions of vibrations within the molecules to the thermodynamic properties can be determined by summation over all vibrational degrees of freedom. The contributions from a particular degree of freedom can be calculated using formulas derived in the previous section. At high temperatures, each vibrational degree of freedom gives contribution R to the heat capacity (per mole).

12.2.7 Electronic contributions to thermodynamic functions

The partition function for the electronic degrees of freedom takes the following form:

$$Z_{\mathrm{el}} = g_0 + \sum_{k=1}^{\infty} g_k \mathrm{e}^{-\varepsilon_k/k_{\mathrm{B}}T}, \tag{12.81}$$

where g_k is the degeneracy of energy level k and we set the energy of the ground state to zero, $\varepsilon_0 = 0$. If the difference between neighboring energy levels is much larger than $k_{\mathrm{B}}T$, the sum in Eq. (12.81) can be neglected. If the ground state is not degenerate,

$$Z_{\mathrm{el}} = g_0 = 1,$$

and there is no electronic contribution to the thermodynamic functions. However, this is not always the case. For example, the ground state of alkaline metals is doubly degenerate. Equation (12.19) implies that, for this case, the Helmholtz free energy is reduced by

$$A_{\mathrm{el}} = -Nk_{\mathrm{B}}T \ln 2,$$

and the entropy is increased by

$$S_{\mathrm{el}} = Nk_{\mathrm{B}} \ln 2.$$

In some molecules, the ground state is a doublet with a small energy gap, Δ. For example, the ground state of NO is a doublet and each of these levels is doubly degenerate. The ground state of oxygen is a triplet where the gaps between levels is so small that they can be neglected (i.e. we can consider the ground state as one level which is triply degenerate). However, the next level is doubly degenerate and is close to the triplet ground state. In such cases, the electronic contributions to the thermodynamic functions are significant. If only the two lowest levels are of importance, we can write

$$Z_{\mathrm{el}} = g_0 + g_1 \mathrm{e}^{-\Delta/k_{\mathrm{B}}T}, \tag{12.82}$$

$$A_{\mathrm{el}} = -Nk_{\mathrm{B}}T \ln[g_0 + g_1 e^{-\Delta/k_{\mathrm{B}}T}]. \tag{12.83}$$

Review questions

1. Does the choice of the origin of the energy scale affect the partition function?
2. Which thermodynamic functions are affected by the degeneracy of the ground state?

Example problem

1. The energy gap between the ground state and next levels in NO is $\Delta = 15.4$ meV. Find the electronic contribution to the molar heat capacity at $T_1 = 50$ K and $T_2 = 500$ K.

12.2.8 Maxwell distribution

In the framework of classical mechanics, the energy of a molecule can always be represented as a sum of two terms: the kinetic energy $p^2/2m$, which depends only on the momentum and the potential energy U, which depends only on its position. This allows us to write the probability that the molecule has momentum in the range from $\mathbf{p}$ to $\mathbf{p}+\mathrm{d}\mathbf{p}$ and a position in the range from $\mathbf{r}$ to $\mathbf{r}+\mathrm{d}\mathbf{r}$ as

$$\mathrm{d}w = A\mathrm{e}^{-(p^2/2m+U)/k_\mathrm{B}T}\mathrm{d}\mathbf{p}\mathrm{d}\mathbf{r}. \tag{12.84}$$

Here A is a normalization factor that guarantees that

$$\int \mathrm{d}w = 1, \tag{12.85}$$

where the integration is performed over the entire phase space (all possible molecule positions and momenta).

It is easy to see that the right side of Eq. (12.84) contains two independent factors: the momentum distribution

$$\mathrm{d}w_\mathbf{p} = A_\mathbf{p}\mathrm{e}^{-p^2/2mk_\mathrm{B}T}\mathrm{d}\mathbf{p} \tag{12.86}$$

and the spatial distribution

$$\mathrm{d}w_\mathbf{r} = A_\mathbf{r}\mathrm{e}^{-U/k_\mathrm{B}T}\mathrm{d}\mathbf{r}, \tag{12.87}$$

such that

$$\mathrm{d}w = \mathrm{d}w_\mathbf{p}\mathrm{d}w_\mathbf{r}; \qquad \int \mathrm{d}w_\mathbf{p} = 1 \quad \text{and} \quad \int \mathrm{d}w_\mathbf{r} = 1. \tag{12.88}$$

Since $\mathbf{p} = m\mathbf{v}$, we can obtain the distribution of molecule velocities from Eq. (12.86):

$$\mathrm{d}w_\mathbf{v} = A_\mathbf{v}\mathrm{e}^{-mv^2/2k_\mathrm{B}T}\mathrm{d}\mathbf{v}. \tag{12.89}$$

This is known as the **Maxwell distribution** of velocities. While, for the sake of simplicity, we derived this velocity distribution for molecules in a gas, it also applies to molecules in condensed phases. This follows from the fact that the total energy can always be written as the sum of the kinetic and potential energies and the kinetic energy is always the sum of the kinetic energies of all of the molecules.

In Cartesian coordinates, $\mathrm{d}\mathbf{v}$ can be written as $\mathrm{d}\mathbf{v} = \mathrm{d}v_x \mathrm{d}v_y \mathrm{d}v_z$. Therefore, Eq. (12.89) can be rewritten in the following form:

$$\mathrm{d}w_{\mathbf{v}} = A_{\mathbf{v}} \mathrm{e}^{-mv_x^2/2k_\mathrm{B}T} \mathrm{d}v_x \mathrm{e}^{-mv_y^2/2k_\mathrm{B}T} \mathrm{d}v_y \mathrm{e}^{-mv_z^2/2k_\mathrm{B}T} \mathrm{d}v_z.$$

This implies that the distribution of the Cartesian components of the velocities are independent, such that

$$\mathrm{d}w_{\mathrm{v}_\alpha} = A_{\mathrm{v}_\alpha} \mathrm{e}^{-mv_\alpha^2/2k_\mathrm{B}T} \mathrm{d}v_\alpha; \qquad \int \mathrm{d}w_{\mathrm{v}_\alpha} = 1,$$

where α refers to one of the Cartesian coordinates. Performing the integration (see Eq. (AV.1)) to determine the normalization constant allows us to write

$$\mathrm{d}w_{\mathrm{v}_\alpha} = \sqrt{\frac{m}{2\pi k_\mathrm{B} T}}\, e^{-mv_\alpha^2/2k_B T} \mathrm{d}v_\alpha \tag{12.90}$$

and

$$\mathrm{d}w_{\mathbf{v}} = \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} \mathrm{e}^{-mv^2/2k_\mathrm{B}T} \mathrm{d}\mathbf{v}. \tag{12.91}$$

In spherical coordinates, $\mathrm{d}\mathbf{v} = 4\pi v^2 \mathrm{d}v$ such that Eq. (12.91) becomes

$$\mathrm{d}w_{\mathrm{v}} = 4\pi \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} \mathrm{e}^{-mv^2/2k_B T} v^2 \mathrm{d}v. \tag{12.92}$$

We now consider three important consequences of the Maxwell distribution: expressions for the mean velocity, the mean square velocity, and the mean velocity in a particular direction. The **mean velocity** is

$$\overline{v} = \frac{\int_0^\infty v \mathrm{e}^{-mv^2/2k_\mathrm{B}T} v^2 \mathrm{d}v}{\int_0^\infty \mathrm{e}^{-mv^2/2k_\mathrm{B}T} v^2 \mathrm{d}v} = \frac{\frac{1}{2} 4 (k_\mathrm{B} T)^2/m^2}{\frac{1}{4}\sqrt{8\pi (k_\mathrm{B} T)^3/m^3}} = \sqrt{\frac{8k_\mathrm{B} T}{\pi m}}. \tag{12.93}$$

The **mean square velocity** is

$$\overline{v^2} = \frac{\int_0^\infty v^2 \mathrm{e}^{-mv^2/2k_\mathrm{B}T} v^2\, \mathrm{d}v}{\int_0^\infty \mathrm{e}^{-mv^2/2k_\mathrm{B}T} v^2\, \mathrm{d}v} = \frac{\frac{3}{8}\sqrt{32\pi (k_\mathrm{B} T)^5/m^5}}{\frac{1}{4}\sqrt{8\pi (k_\mathrm{B} T)^3/m^3}} = 3k_\mathrm{B} T/m. \tag{12.94}$$

Since the average kinetic energy of a molecule is $\varepsilon_\mathrm{kin} = m\overline{v^2}/2$, we find

$$\varepsilon_\mathrm{kin} = m\overline{v^2}/2 = \frac{3}{2} k_B T. \tag{12.95}$$

The **mean velocity in a particular direction** can be evaluated as

$$\bar{v}_{\rightarrow} = \frac{\int_0^\infty v_x \mathrm{e}^{-mv_x^2/2k_\mathrm{B}T} \mathrm{d}v_x}{\int_0^\infty e^{-mv_x^2/2k_\mathrm{B}T} \mathrm{d}v_x} = \frac{1/2(2k_\mathrm{B}T/m)}{1/2\sqrt{(2\pi k_\mathrm{B}T/m}} = \sqrt{\frac{2k_\mathrm{B}T}{\pi m}} \qquad (12.96)$$

The Maxwell distribution is central to many important predictions in the kinetic theory of gases. Examples of this will be considered in the next two sections.

12.2.9 Collisions of gas molecules with a surface

In this section, we consider collisions of gas molecules with a surface. Our goal is to derive the number of such collisions per unit area per unit time. This is important for the theory of heterogeneous chemical reactions, adsorption, evaporation, and sublimation.

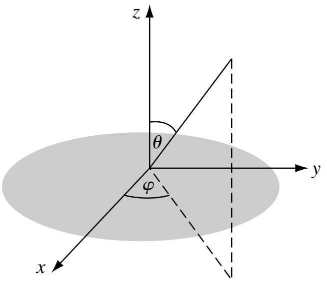

Fig. 12.3.
The coordinate system used to describe particle collisions with a solid surface.

Consider a surface such that $z < 0$ is a solid and $z > 0$ is a gas, as shown in Fig. 12.3. If all of the molecules in the gas have velocity v_z ($v_z < 0$), the number of molecules which hit the surface with area S during time dt is

$$v_z \mathrm{d}t S \frac{N}{V},$$

where N/V is the gas density. The number of molecules that hit a unit area of the surface in a unit time is

$$v_z \frac{N}{V}.$$

However, in reality the molecule velocities are not all the same, but are described by the Maxwell distribution (see Eq. (12.91)). Therefore, the number of collisions per unit area of the surface per unit time is

$$\Lambda = \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} \int v_z \frac{N}{V} \mathrm{e}^{-mv^2/2k_\mathrm{B}T} \mathrm{d}v_x \mathrm{d}v_y \mathrm{d}v_z.$$

In spherical coordinates (see Fig. 12.3) this is

$$\begin{aligned}\Lambda &= \frac{N}{V}\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} \int \mathrm{e}^{-mv^2/2k_\mathrm{B}T} v \cos\theta v^2 \sin\theta \, \mathrm{d}v \mathrm{d}\theta \mathrm{d}\varphi \\ &= \frac{2\pi N}{V}\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} \int_0^{\pi/2} \cos\theta \sin\theta \, \mathrm{d}\theta \int_0^\infty \mathrm{e}^{-mv^2/2k_\mathrm{B}T} v^3 \, \mathrm{d}v.\end{aligned}$$

Evaluating these integrals (see Eq. (AV.5)), we find

$$\Lambda = \frac{N}{V}\sqrt{\frac{k_\mathrm{B}T}{2\pi m}}. \qquad (12.97)$$

Since, for an ideal gas, $pV = Nk_\mathrm{B}T$ we obtain

$$\Lambda = \frac{p}{\sqrt{2\pi m k_\mathrm{B}T}}. \qquad (12.98)$$

Comparing Eqs (12.97) and (12.96), we find that

$$\Lambda = \frac{N}{V}\frac{\bar{v}_{\rightarrow}}{2} \tag{12.99}$$

This equation has a simple interpretation. If the molecules can only move up or down with speed $\bar{v}_{\rightarrow}$, then in a time dt half of the molecules with $0 \leq z \leq \bar{v}_{\rightarrow}\mathrm{d}t$ hit the surface. Since the number of molecules within $0 \leq z \leq \bar{v}_{\rightarrow}\mathrm{d}t$ is $\bar{v}_{\rightarrow}\mathrm{d}tSN/V$, we obtain Eq. (12.99).

Equation (12.98) is a fundamental result that is used in many applications. Here we consider just one, namely, the rate of evaporation. In equilibrium, the vapor pressure over any surface is equal to the saturated vapor pressure p_s (this is the definition of p_s). On the other hand, in equilibrium the number of molecules which leave the surface is equal to the number of molecules which condense from the gas. If we assume that all gas molecules which hit the surface stick there, the rate of evaporation must be

$$\omega = \frac{p_s}{\sqrt{2\pi m k_\mathrm{B} T}} \tag{12.100}$$

Example problem

1. A sample of liquid Cs was placed on a balance in a closed chamber. One of the chamber walls has a very small circular hole (diameter $d = 0.7$ mm). The sample was annealed for $t = 80$ s at $T = 773$ K. The sample mass decreased by $\Delta w = 604$ mg during annealing. Find the pressure of the saturated vapor over liquid Cs at $T = 773$ K.

12.2.10 Collisions of gas molecules

Any chemical reaction in a gas proceeds via the collisions of molecules. Therefore, in order to develop a kinetic theory describing chemical reactions, we must first discuss the collisions of molecules per se. Consider a gas consisting of molecules of two types. Let the density of the molecules of type i be $n_i = N_i/V$ and their molecular mass be m_i. We now derive an expression for the number of molecules of type j which hit a molecule of type i in a unit time. We can describe the motion of two molecules as the sum of the motions of their centers of mass and their relative motion. Obviously, only the their relative motion matters in our consideration of collisions. The energy associated with the relative motion of the centers of mass is:

$$\varepsilon = \frac{m_{ij} v_{ij}^2}{2}, \tag{12.101}$$

where

$$m_{ij} = \frac{m_i m_j}{m_i + m_j}, \qquad \mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j. \tag{12.102}$$

and $\mathbf{v}_i$ is the velocity of the center of mass of the molecule of type i. The probability that a molecule of type j has relative velocity v_{ij} with respect to a molecule of type i is

$$\mathrm{d}w_{ij} = \left(\frac{m_{ij}}{2\pi k_B T}\right)^{3/2} 4\pi e^{-m_{ij}v_{ij}^2/2k_B T} v_{ij}^2\, \mathrm{d}v_{ij}.$$

Consider now molecules of type j moving in the same direction with a relative velocity v_{ij} with respect to a given molecule of type i. We will use a coordinate system in which the molecules of type j are fixed and the molecule of type i moves with velocity v_{ij}. In a unit time, this molecule will hit all molecules j which are in a cylinder with height v_{ij} and with a base of area σ_{ij}. σ_{ij} is called the **collision cross-section** (we discuss this term in more detail in the next section). The number of such molecules of type j is $n_j\sigma_{ij}v_{ij}\mathrm{d}w_{\vec{ij}}$. The integration over all possible directions replaces $\mathrm{d}w_{\vec{ij}}$ by $\mathrm{d}w_{\mathrm{ij}}$. Therefore, the number of molecules of type j with which a molecule of type i collides in a unit time is

$$\begin{aligned} z_{ij} &= \int_0^\infty n_j\sigma_{ij}\left(\frac{m_{ij}}{2\pi k_\mathrm{B} T}\right)^{3/2} 4\pi e^{-m_{ij}v_{ij}^2/2k_\mathrm{B} T} v_{ij}^3\, \mathrm{d}v_{ij} \\ &= n_j\sigma_{ij}\left(\frac{m_{ij}}{2\pi k_B T}\right)^{3/2} 4\pi \frac{1}{2}\left(\frac{2k_\mathrm{B} T}{m_{ij}}\right)^2 \\ z_{ij} &= 4\sigma_{ij}n_j\left(\frac{k_\mathrm{B} T}{2\pi m_{ij}}\right)^{1/2} \end{aligned} \qquad (12.103)$$

The number of collisions of molecules (per unit time and volume) of types i and j is simply the product of the number of collisions per molecule and the density of molecules:

$$Z_{ij} = \begin{cases} n_i z_{ij} = 4\sigma_{ij}n_i n_j\left(\frac{k_\mathrm{B} T}{2\pi m_{ij}}\right)^{1/2}, & i \neq j \\ \frac{1}{2}n_i z_{ii} = 2\sigma_{ii}n_i^2\left(\frac{k_B T}{2\pi m_{ij}}\right)^{1/2} \end{cases} \qquad (12.104)$$

The total number of collisions which a molecule of type i suffers in a unit time is

$$z_{ii} + z_{ij} = 4\left(\frac{\sigma_{ii}}{\sqrt{m_{ii}}}n_i + \frac{\sigma_{ij}}{\sqrt{m_{ij}}}n_j\right)\left(\frac{k_B T}{2\pi}\right)^{1/2}$$

The inverse of this quantity is the average time between collisions. The average distance which a molecule goes between two subsequent collisions is the **mean free path**. It is the product of the mean molecule velocity (Eq. (12.93)) and the average time between collisions:

$$\lambda_i = \frac{\bar{v}_i}{4\left((\sigma_{ii}/\sqrt{m_{ii}})n_i + (\sigma_{ij}/\sqrt{m_{ij}})n_j\right)}\left(\frac{2\pi}{k_B T}\right)^{1/2}$$

Inserting the expression for the mean velocity (Eq. (12.93)), we find

$$\lambda_i = \frac{1}{\sqrt{2}\sigma_{ii}n_i + \sigma_{ij}n_j\left(1 + (m_i/m_j)\right)^{1/2}} \qquad (12.105)$$

In the case of a one-component gas, this equation reduces to

$$\lambda = \frac{1}{\sqrt{2}\sigma n}. \tag{12.106}$$

We can consider the physical meaning of the mean free path from another perspective. Consider the probability $w(L)$ that a molecule travels along a path of length L without suffering any collisions. The probability that the molecule continues along its path to $L + \mathrm{d}L$ without any collisions is

$$w(L + \mathrm{d}L) = w(L)w(\mathrm{d}L). \tag{12.107}$$

Since the path length $\mathrm{d}L$ is infinitesimal, the molecule cannot suffer more than one collision in this distance. The probability that the molecule will collide with another in this distance is $1 - w(\mathrm{d}L)$. Obviously, this probability should be proportional to the length of this path, $\mathrm{d}L$. Therefore, $1\text{-}w(\mathrm{d}L) = a\mathrm{d}L$, where a is a proportionality constant. Comparing this result with Eq. (12.107), we find

$$\begin{aligned} w(L + \mathrm{d}L) &= w(L)(1 - a\mathrm{d}L) \\ \frac{\mathrm{d}w}{w} &= -a\mathrm{d}L \\ w &= Ae^{-aL} \end{aligned}$$

If $L \to 0$, then $w \to 1$. This implies $A = 1$ and

$$w = \mathrm{e}^{-aL}$$

By definition, the mean free path can be represented as

$$\lambda = \int_0^\infty L\,\mathrm{d}P(L)$$

where $\mathrm{d}P(L)$ is the probability that the molecule travels a distance L without collisions but does suffer a collision in the additional infinitesimal distance $\mathrm{d}L$. The probability of this is

$$\mathrm{d}P(L) = w(L)a\mathrm{d}L.$$

Inserting this result in the previous expression for the mean free path, we find:

$$\lambda = a\int_0^\infty L\mathrm{e}^{-aL}\,\mathrm{d}L = \frac{1}{a}.$$

Thus, the probability that a molecule travels a distance L without collisions is

$$w = \mathrm{e}^{-L/\lambda} \tag{12.108}$$

and the probability that the molecule will suffer its first collision at a distance L from where it starts is

$$\mathrm{d}P(L) = \frac{1}{\lambda}\mathrm{e}^{-L/\lambda}\mathrm{d}L. \tag{12.109}$$

We will use this important result below.

12.2.11 Cross-sections

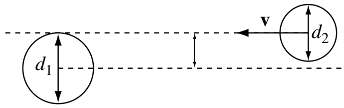

Fig. 12.4
Collision of two hard sphere molecules.

In this section, we return to consider the cross-sections in more detail. We model all molecules as hard spheres with diameters d_1 and d_2. A collision occurs if the **target distance** r is less than or equal to half of the sum of the diameters (see Fig. 12.4):

$$r \leq r_{\max} = (d_1 + d_2)/2.$$

Therefore, we can define the cross-section as

$$\sigma_{12} = \pi r_{\max}^2 = \frac{\pi}{4}(d_1 + d_2)^2. \tag{12.110}$$

According to the definition of the flux, the number of molecules that will pass through the area σ_{ij} per unit time[5] is $j_{ij}\sigma_{ij}$. Therefore, the cross-section σ_{ij} is the number of collisions between molecules of types i and j per unit time ($j_{ij}\sigma_{ij}$) divided by the relative molecular flux j_{ij}. By analogy, we define the **cross-section of a process** as the number of elementary events divided by the relative molecular flux, j_{ij}. This generalization accounts for the observation that not all collisions between the gas molecules result in the occurrence of the event of interest (e.g. not all collisions result in a chemical reaction between the molecules).

The number of molecules of type j with target distances in the range from r to $r + \mathrm{d}r$ which will collide in a unit time is $j_{ij}2\pi r\mathrm{d}r$. Let $P_{ij}(r,v)$ be the probability that an elementary event occurs as a result of the collision. Therefore, the number of elementary events per unit time is $j_{ij}2\pi P_{ij}(r,v)r\mathrm{d}r$. The total number of elementary events is $2\pi j_{ij}\int_0^\infty P_{ij}(r,v)r\,\mathrm{d}r$ and, therefore,

$$\sigma_{ij} = 2\pi\int_0^\infty P_{ij}(r,v)r\,\mathrm{d}r. \tag{12.111}$$

In the case of collisions of hard spheres, the elementary event is the collision itself which always occurs provided that $r \leq (d_1 + d_2)/2$. This implies that

$$P(r,v) = \begin{cases} 1, & \text{at} \quad r \leq (d_1 + d_2)/2 \\ 0, & \text{at} \quad r > (d_1 + d_2)/2 \end{cases}$$

Inserting this result into Eq. (12.111), we find

$$\sigma_{ij} = 2\pi\int_0^{(d_1+d_2)/2} r\,\mathrm{d}r = 2\pi\frac{1}{2}\left(\frac{d_1 + d_2}{2}\right)^2 = \frac{\pi}{4}(d_1 + d_2)^2.$$

This result coincides with Eq. (12.110).

---

[5] In reality, the relative velocities are pointed in all possible directions, however this is not important for the phenomenon under consideration. This is equivalent to considering first all pairs with relative velocities in one direction and then integration over all directions—as we did in the previous section.

In some processes, the cross-section depends on the velocity v. For example, **active collisions** refer to events that only occur if

$$\frac{m_{ij}v_n^2}{2} \geq E, \tag{12.112}$$

where v_n is the projection of the relative velocity onto the line connecting the centers of mass of the molecules and E is a critical or threshold energy for the event to occur. Examination of Fig. 12.5 shows that

$$\left(\frac{v_n}{v}\right)^2 = \cos^2\theta = 1 - \sin^2\theta = 1 - \frac{r^2}{[(d_1+d_1)/2]^2} = \frac{[(d_1+d_1)/2]^2 - r^2}{[(d_1+d_1)/2]^2}.$$

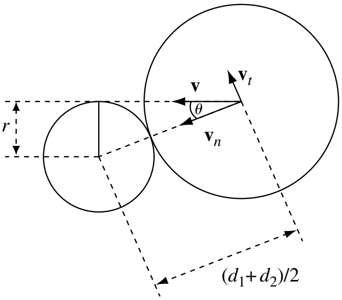

Fig. 12.5
The geometry of the collision of two hard sphere molecules of different sizes.

Inserting this result into Eq. (12.112), we find

$$\frac{m_{ij}v^2}{2}\frac{[(d_1+d_1)/2]^2 - r^2}{[(d_1+d_1)/2]^2} \geq E.$$

Therefore, an active collision event will occur provided that

$$r^2 \leq \left(\frac{d_1+d_2}{2}\right)^2\left(1 - \frac{2E}{m_{ij}v^2}\right).$$

In this case, the cross-section defined in Eq. (12.111) can be rewritten as

$$\sigma_{12} = 2\pi\int_0^{(d_1+d_2)/2\sqrt{1-(2E/m_{ij}v^2)}} r\,\mathrm{d}r = 2\pi\frac{1}{2}\left(\frac{d_1+d_2}{2}\right)^2\left(1 - \frac{2E}{m_{ij}v^2}\right)$$

or

$$\sigma_{ij} = \sigma_{ij}^{\infty}\left(1 - \frac{2E}{m_{ij}v^2}\right), \tag{12.113}$$

where $\sigma_{ij}^{\infty} = (\pi/4)(d_i + d_j)^2$..

We can now find the number of active collisions. By analogy with the derivation of Eq. (12.103), we obtain[6]

$$z_{ij} = \int_{\sqrt{2E/m_{ij}}}^{\infty} n_j\sigma_{ij}^{\infty}\left(1 - \frac{2E}{m_{ij}v^2}\right)\left(\frac{m_{ij}}{2\pi k_B T}\right)^{3/2} 4\pi e^{-m_{ij}v^2/2k_B T} v^3\,\mathrm{d}v.$$

Evaluation of the integral yields

$$z_{ij} = n_j\sigma_{ij}^{\infty}4\pi\frac{1}{2}\left(\frac{2k_B T}{m_{ij}}\right)^2\left(\frac{m_{ij}}{2\pi k_B T}\right)^{3/2}\mathrm{e}^{-E/k_B T} = z_{ij}^0\mathrm{e}^{-E/k_B T}.$$

Therefore, the number of active collisions per unit time is

$$Z_{aij} = Z_{0ij}\mathrm{e}^{-E/k_B T}, \tag{12.114}$$

where Z_{0ij} is determined by Eq. (12.104).

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[6] The collision is not active if $m_{ij}v^2/2 < \mathrm{E}$.

Example problems

1. The kinetic diameter of a molecule is defined as.

$$d = \sqrt{\frac{\sigma}{\pi}}.$$

   The kinetic diameter of Ne is $d = 2.04$ Å. Find the number of collisions which one Ne atom suffers during 1 s at $T = 600$ K and $p = 1$ atm.
2. Experiment shows that for H_2 at $T = 0^{\circ}$C and $p = 1$ atm, the mean free path is $\lambda = 128$ nm. Find the kinetic diameter of H_2 molecule under these conditions.
3. Find the number of molecule collisions per unit volume and unit time in a gas of density n and temperature T for which the relative velocity of the molecules is larger than v_0.

12.3 Statistical theory of chemical reactions

12.3.1 Calculation of the equilibrium constant from spectroscopic data

In Chapter 5, we already discussed how to calculate the equilibrium constant for a chemical reaction from thermodynamic data. This obviously requires us to first obtain such data from experiment (e.g., from calorimetric experiment) and this is not always simple. Fortunately, we can also determine the equilibrium constant from spectroscopic data (i.e. the intensity of the light emitted from or absorbed by the gas as a function of wavelength).

Consider the following reaction

$$a\mathrm{A} + b\mathrm{B} = c\mathrm{C} + d\mathrm{D}, \tag{12.115}$$

where all species are gases. In equilibrium the following relation must be satisfied:

$$\Delta G = d\mu_{\mathrm{D}} + c\mu_{\mathrm{C}} - a\mu_{\mathrm{A}} - b\mu_{\mathrm{B}} = 0. \tag{12.116}$$

The Gibbs free energy can be expressed via the partition function as (see Eq. (12.26))

$$G = -Nk_{\mathrm{B}}T \ln \frac{Z}{N}. \tag{12.117}$$

The partition function is proportional to volume (see Eq. (12.37)) since it includes integration over the three translation degrees of freedom of a molecule (the translational degrees of freedom are independent of all other degrees of freedom). Therefore, it is convenient to normalize the partition function by the volume of the gas

$$P = \frac{Z}{V}, \tag{12.118}$$

where P is the **reduced partition function**. Using this definition, we rewrite Eq. (12.117) as

$$G = -Nk_{\mathrm{B}}T \ln\left(\frac{V}{N}P\right). \tag{12.119}$$

Since N/V is the concentration of the molecules in the gas, n, and $\mu = G/N$ for a pure material, we find

$$\mu_i = -k_\mathrm{B} T \ln (P_i/n_i). \tag{12.120}$$

Finally, inserting this expression into Eq. (12.116), we obtain

$$\frac{P_\mathrm{D}^d P_\mathrm{C}^c}{P_\mathrm{A}^a P_\mathrm{B}^b} = \frac{n_\mathrm{D}^d n_\mathrm{C}^c}{n_\mathrm{A}^a n_\mathrm{B}^b} = K_\mathrm{c}. \tag{12.121}$$

Note that the concentrations in this equation are expressed in molecules/m^3.

When calculating the partition function of a gas, it is convenient to choose the zero of an energy to be that of the molecules at $T = 0$. This is, of course, an arbitrary choice but since no experimentally measurable thermodynamics quantities depend on it, we can choose any zero we like. However, when calculating the equilibrium constant, we must describe the energy levels of all species consistently. If we have a gas containing many types of molecules, we must choose the same zero of energy for all of the species. This introduces additional terms into the energies for each species i, ε_0^i. This, in turn, leads to additional factors in the partition functions, $\mathrm{e}^{-\varepsilon_0^i/k_\mathrm{B}T}$. It is easy to see that the combination of these factors in Eq. (12.121) simply gives a composite factor $\mathrm{e}^{-\Delta U_0/k_\mathrm{B}T}$, where ΔU_0 is the heat of reaction at $T = 0$. Now Eq. (12.121) can be rewritten as

$$K_c = \frac{P_\mathrm{D}^d P_\mathrm{C}^c}{P_\mathrm{A}^a P_\mathrm{B}^b} \mathrm{e}^{-\Delta U_0/k_\mathrm{B}T}. \tag{12.122}$$

Since for an ideal gas $H = U + Nk_\mathrm{B}T$, we find that $\Delta U_0 = \Delta H_0$. This enthalpy of reaction can be found in thermodynamic databases from the heats of formations of all species at $T = 0$ ($\Delta H_{f,0}^0$).

Example problem

1. The vapor over a liquid Na sample consists of Na atoms and dimers ($\mathrm{Na_2}$). Analysis of the spectroscopic data implies that the dimer has a singlet ground state, an equilibrium interatomic separation at $T = 0$ of $r = 2.18$ Å and a vibrational wavenumber of $\tilde{\nu} = 159.2$ cm. The energy of dissociation of this molecule is $\Delta E_\mathrm{d} = 0.73$ eV. Find the molar fraction of the dimers in the saturated vapor over Na at its boiling temperature (1163 K).

12.3.2 Theory of active collisions

Consider the bimolecular reaction

$$\mathrm{A} + \mathrm{B} = \mathrm{C} \tag{12.123}$$

The **theory of active collisions** states that molecules A and B react with each other if their collision energy is larger than the activation energy E for the reaction. The total angular momentum must be conserved in the collision of the molecules. In the system of coordinates fixed to molecule A, the total angular momentum is equal to $m_{12}v_t(d_1 + d_2)/2$ (see Fig. 12.5). If we make the reasonable approximation that the molecule diameters do not change during collision, the only part of the translational (kinetic) energy which is available to aid the reaction is $m_{12}v_n^2/2$ (again, see Fig. 12.5). Therefore, the chemical reaction will occur as a result of the collision of molecules A and B provided that

$$\frac{m_{12}v_n^2}{2} \geq E. \tag{12.124}$$

Strictly speaking, this conclusion is valid only in the case where A and B are atoms. The situation is more complex if A or B are polyatomic molecules. Recall that in addition to translational degrees of freedom, such molecules also have rotational and vibrational degrees of freedom. The energy associated with these degrees of freedom can also contribute to the energy available for the chemical reaction. Therefore, the chemical reaction could occur even if Eq. (12.124) is not satisfied. On other hand, part of the energy $m_{12}v_n^2/2$ can be transferred from the translational degree of freedom into the rotational or vibrational degrees of freedom during collisions. This part of $m_{12}v_n^2/2$ will not be available to aid the chemical reaction. If these two effects compensate each other, Eq. (12.124) will still be reasonable.

Equation (12.114) implies that the number of active collisions between molecules A and B in a unit time is

$$Z_a = Z_0 e^{-E/RT} = 4\sigma_{AB} n_A n_B \left(\frac{k_B T}{2\pi}\right)^{1/2} \left(\frac{1}{m_A} + \frac{1}{m_B}\right)^{1/2} e^{-E/RT}$$

or

$$Z_a = \pi (r_A + r_B)^2 \left(\frac{1}{m_A} + \frac{1}{m_B}\right)^{1/2} \left(\frac{8k_B T}{\pi}\right)^{1/2} e^{-E/RT} n_A n_B. \tag{12.125}$$

where r_i is the radius of molecule i. Recall that in Section 8.1.1, we saw that formal kinetics suggest that the rate of the elementary bimolecular reaction, ω, is

$$\omega = k n_A n_B, \tag{12.126}$$

where

$$k = A e^{-E/RT}. \tag{12.127}$$

Comparison of Eqs (12.125) and (12.127) shows that

$$A = \pi (r_A + r_B)^2 \left(\frac{1}{m_A} + \frac{1}{m_B}\right)^{1/2} \left(\frac{8k_B T}{\pi}\right)^{1/2}. \tag{12.128}$$

Thus, we were able to show that statistical thermodynamics can be used to derive the kinetic equation which we simply postulated in our discussion of formal kinetics. Moreover, statistical thermodynamics provides a means to determine the rate constant from microscopic characteristics of the molecules participating in the chemical reaction (this was a necessary input parameter in the formal kinetic theory). Note that according to the theory of active collisions, the pre-exponential factor A depends on temperature, but only very weakly compared with the exponential Arrhenius dependence in the rate constant.

Unfortunately, the pre-exponential factor calculated using Eq. (12.128) is very seldom in agreement with experimental data. In fact, it commonly overestimates the experimental value by 3–4 orders of magnitude. In order to explain this disagreement, we introduce the so-called **steric factor** as the ratio of the experimental and theoretical values of the pre-exponential factor:

$$\sigma = \frac{A_{\text{exp}}}{A_{\text{theory}}}. \tag{12.129}$$

When this factor is smaller than unity, it can be interpreted as the probability that the molecules are favorably oriented at the moment of the collision for the reaction to occur. In order to illustrate this idea, we examine the results of quantum–mechanical calculations for the energy surface for the reaction $Cl + HI = HCl + I$, shown in Fig. 12.6. This figure shows that the activation energy for the chemical reaction actually depends on the angle of attack of the Cl atom. The reaction will occur only if the angle of attack is within a $\sim 30°$ window centered on the H atom. This is a reason why the steric factor can be less than unity. However, there are some reactions for which the steric factor is larger than unity. We cannot, of course, rely on arguments based on the angle of attack to explain these. Our theory of active collisions is clearly too simplistic to provide a rigorous determination of the steric factor.

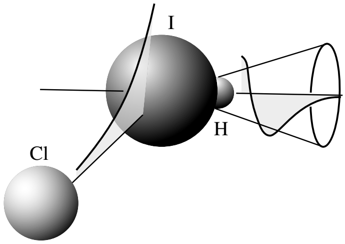

Fig. 12.6
Schematic illustration of the impact of a Cl atom and a HI molecule. The plots show the energy as a function of separation for the Cl impacting the HI molecule at the I atom and at the H atom. Note that in the first case the Cl atom is repelled while the energy versus separation curve has a minimum in the second case when the Cl impacts the H (i.e. the reaction can occur only in the latter case).

Example problem

1. The following rate constant data were measured for the gas phase reaction

$$C_5H_5N + CH_3I = C_5H_5NCH_3I:$$

T (K)	293.1	323.2
k (10^2/[mole (min)])	0.713	5.89

The densities of liquid C_5H_5N and CH_3I at room temperature are $\rho = 0.98$ g/cm^3 and $\rho = 2.28$ g/cm^3, respectively. Estimate the steric factor.

12.3.3 Theory of the activated complex

As we saw in the previous section, the theory of active collisions gives a qualitative explanation of the laws of formal kinetics but is not capable of providing accurate predictions of the rate constant. The main reason why this theory does not show better agreement with experiment is that it does not consider what is actually happening during collisions. The theory of the activated complex, developed by Eyring is an attempt to answer this question. In this section, we first present a qualitative picture of what is happening during a bimolecular chemical reaction. We will show that the discussion of such a reaction is greatly simplified by the introduction of the concept of a reaction path. We will then apply a statistical mechanics approach to describe the motion of the system along the reaction path. Finally, we will show how to predict the rate constant from microscopic characteristics of the molecules participating in the chemical reaction.

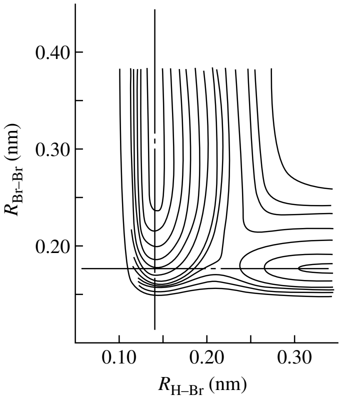

Fig. 12.7.
Energy contours as a function of the distances between the Br atoms $R_{\text{Br–Br}}$ and between the H atom and the closest Br atoms $R_{\text{H–Br}}$ for the special case in which the Br_2 molecule axis and the direction of the H atom movement are colinear.

12.3.3.1 Reaction path

In analyzing the reaction path, we will again make use of the so-called adiabatic approximation (see Section 12.2.3). Recall that the main idea of this approximation is that the electrons move much faster than the nuclei, such that they are always in equilibrium with the slowly moving nuclei. In this approximation, the total energy can be written as

$$E = E_{\text{k}} + E_{\text{e}}^{(0)} + U_{\text{n}}, \tag{12.130}$$

where E_{k} is the kinetic energy of the nuclei, $E_e^{(0)}$ is the ground state energy of the electrons and U_{n} is the interaction energy of the nuclei with each other. The two last terms are functions of the coordinates of the nuclei, $q_1, \ldots, q_{3\nu\text{-}6(5)}$ (see Section 12.2.6), and hence can be combined into a single function $U(q_1, \ldots, q_{3\nu-6(5)})$. Figure 12.7 shows an example of such a function for the reaction

$$\text{H} + \text{Br}_2 = \text{HBr} + \text{Br},$$

in the special case where the hydrogen approaches the Br_2 molecule along its axis.

The set of all of the states through which the system passes as it goes from reactants to products is called the **reaction path**. Obviously, there could be many possible reaction paths for the same reaction. The shortest path from any point on the energy surface to the energy minimum is a line which is normal to the constant energy contours. Starting from an arbitrary point in the reaction coordinates (e.g. the coordinates in Fig. 12.7), minimization of the energy can lead to either the products or the reactants. The groups of paths that lead to reactants and those that lead to products are separated from each other by a **dividing surface** (in the case of Fig. 12.7, this is just a curve). Any path that takes the system from reactants to products necessarily crosses this dividing surface. If that path intersects the dividing surface at a right angle, the intersection point corresponds to the maximum energy along that path. One of these points has a lower energy than all other points; this point is the **saddle point**. We refer to the system at the saddle point as the **activated complex**. Let x be the coordinate along the reaction path that crosses the dividing surface at right angle at the saddle point. The potential energy U as a function of x is shown in Fig. 12.8(a). In Fig. 12.8(b), we add the energy of the zeroth vibrational mode of the system to the potential energy to obtain $E(x)$. In this figure, E_0, E_0' and $E_0^{\ddagger}$ are the total energies of the reactants, products, and the activated complex, respectively. E_a is the activation energy[7] (i.e. the energy that must be provided in going from reactants to the activated complex) and ΔU_0 is the heat of the reaction at $T=0$ (i.e. the difference in energy between the products and reactants).

12.3.3.2 Calculation of the rate constant

In determining the rate of a reaction, we consider the rate at which the system traverses the reaction path from reactants to products. It is sufficient to simply discuss the rate at which the system crosses the activated complex. In the classical theory of the activated complex, we make a number of simplifying assumptions that help us determine the rate at which the system crosses the saddle point. In so doing, it is convenient to think of the system as a set of reactants, as a set of products, or as a special molecule corresponding to the state of the system at the activated complex. This allows us to ignore the whole reaction path and just focus on these three states. We now make three specific assumptions:

1. All reaction paths cross the saddle point on the dividing surface at which point the system is the activated complex.
2. The concentration of activated complexes can be determined from Gibbs statistics.
3. The motion of the system along the reaction path is a form of translational motion.

The first assumption asserts that we can focus on only one reaction path and, more importantly, one point along that path (rather than the entire energy surface). The second assumption allows us to determine the concentration of activated complexes using the approach developed for reactions in Section 12.3.1. Finally, the third assumption provides a method (see Section 12.2.8) for determining how quickly the system moves along the reaction path.

We will derive the main equations in the theory of the activated complex by considering the following prototypical reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C}, \tag{12.131}$$

for which we will assume the following mechanism

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \mathrm{AB}^{\ddagger} \xrightarrow{k_2} \mathrm{C}, \tag{12.132}$$

where $\mathrm{AB}^{\ddagger}$ is the activated complex. The rate of the reaction in Eq. (12.131) can be described as

$$\omega = \frac{n_{\mathrm{AB}^{\ddagger}}}{\tau}, \tag{12.133}$$

where τ is the average lifetime of the activated complex. Therefore, we need to derive expressions for the concentration of the activated complexes and for their average lifetime.

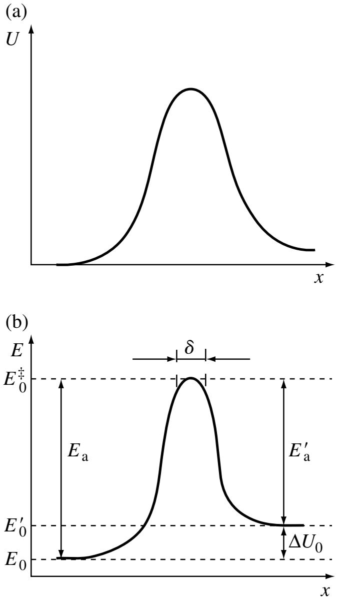

Fig. 12.8.
(a) The potential energy U along the reaction path, (b) the energy (potential plus the energy of the zeroth vibrational mode) E along the reaction path. E_0, E'_0, $E^{\ddagger}_0$, E_a, and ΔU_0 are the energy of the reactants, energy of the products, energy of the activated complex, activation energy, and $T=0$ heat of reaction, respectively.

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[7] In Section 12.3.3.3, we will show that this quantity is not exactly the same as the activation energy obtained from experiment using the Arrhenius law.

In order to address the first issue, we assume that the reactants and the activated complex are in equilibrium with respect to each other (see Eq. (12.132)). This equilibrium is described by the following equilibrium constant

$$K_{\mathrm{c}}^{\ddagger}=\frac{n_{\mathrm{AB}^{\ddagger}}}{n_{\mathrm{A}}n_{\mathrm{B}}}=\frac{P_{\mathrm{AB}^{\ddagger}}}{P_{\mathrm{A}}P_{\mathrm{B}}}\mathrm{e}^{-E_{\mathrm{a}}/RT}, \tag{12.134}$$

where $\mathrm{E_a}$ is the activation energy.

In order to derive an expression for the average lifetime of the activated complex, it is useful to consider the activated state as having four translational degrees of freedom. These are the three usual translational degrees of freedom associated with motion in three-dimensional space and one translational degree of freedom associated with the motion of the system along the reaction path. Since the total number of degrees of freedom of molecule containing ν atoms is 3ν, we conclude the activated complex has $3\nu-7$ vibrational degrees of freedom ($3\nu-6$ for a linear molecule); that is, it has one vibrational degree of freedom less than a garden variety molecule. The average lifetime can be expressed via the width of the activated state, δ, and the average velocity along the reaction path

$$\tau=\frac{\delta}{\bar{u}}. \tag{12.135}$$

Of course, δ is not a well defined quantity. Fortunately, it will cancel out of the final expressions so its value is irrelevant. Using the molecular theory of gases, we write the average velocity along the reaction path as (see Eq. (12.96))

$$\bar{u}=\sqrt{\frac{2k_{\mathrm{B}}T}{\pi m_{\mathrm{AB}^{\ddagger}}}}. \tag{12.136}$$

We can also evaluate the part of partition function associated with the motion along the reaction path. For one dimensional translational motion, we can write the partition function as follows:

$$Z=\frac{1}{h}\int_0^{\delta}\mathrm{d}x\int_0^{\infty}\mathrm{e}^{-mv^2/2k_{\mathrm{B}}T}\mathrm{d}(mv)=\frac{\delta}{h}m\frac{1}{2}\sqrt{\frac{2\pi k_{\mathrm{B}}T}{m}}=\frac{\delta}{2}\frac{\sqrt{2\pi m k_{\mathrm{B}}T}}{h}.$$

Therefore, the part of the partition function associated with the motion along the reaction path takes the following form:

$$P_{\mathrm{AB}^{\ddagger}}^{\mathrm{path}}=\frac{\delta}{2}\frac{\sqrt{2\pi m_{\mathrm{AB}^{\ddagger}}k_{\mathrm{B}}T}}{h}. \tag{12.137}$$

Combining Eqs (12.133)–(12.137), we obtain

$$\omega=\frac{K_{\mathrm{c}}^{\ddagger}n_{\mathrm{A}}n_{\mathrm{B}}}{\tau}=\frac{P'_{\mathrm{AB}^{\ddagger}}}{P_{\mathrm{A}}P_{\mathrm{B}}}\mathrm{e}^{-E_{\mathrm{a}}/RT}n_{\mathrm{A}}n_{\mathrm{B}}\frac{\delta}{2}\frac{\sqrt{2\pi m_{\mathrm{AB}^{\ddagger}}k_{\mathrm{B}}T}}{h}\frac{1}{\delta}\sqrt{\frac{2k_{\mathrm{B}}T}{\pi m_{\mathrm{AB}^{\ddagger}}}}$$

or

$$\omega = \frac{k_\mathrm{B}T}{h}\frac{P'_{\mathrm{AB}^\ddagger}}{P_\mathrm{A}P_\mathrm{B}}\mathrm{e}^{-E_\mathrm{a}/RT}n_\mathrm{A}n_\mathrm{B}, \tag{12.138}$$

where $P'_{\mathrm{AB}^\ddagger}$ is the partition function of the activated complex excluding the contribution of the motion along the reaction path. Therefore, the rate constant is

$$k = \frac{k_\mathrm{B}T}{h}\frac{P'_{\mathrm{AB}^\ddagger}}{P_\mathrm{A}P_\mathrm{B}}\mathrm{e}^{-E_\mathrm{a}/RT}. \tag{12.139}$$

This is the main result of the theory of the activated complex. In some cases, this theory allows us to calculate the rate constant of a bimolecular reaction in reasonable agreement with experiments. However, as mentioned at the beginning of this section, this theory is based on some oversimplifications. We now discuss some of the effects of these oversimplifications.

First, we note the theory of the activated complex does not consider the fate of the reactants (molecule C in Eq. (12.131)) after the reaction. Since the potential energy of the product is lower than that of the activated complex, the product has an excess energy. It can loose this energy either by emission of light, or by collision with another molecule or the chamber wall. All of these processes require a finite time. During this time, there is a chance that the inverse reaction will occur (deactivation). Consider the mechanism where molecule C transfers excess energy to a molecule M of an inert gas:

$$\begin{cases} \mathrm{A} + \mathrm{B} \xrightarrow{k_\mathrm{a}} \mathrm{AB}^\ddagger & \text{(activation)} \\ \mathrm{AB}^\ddagger \xrightarrow{k_\mathrm{d}} \mathrm{A} + \mathrm{B} & \text{(deactivation)} \\ \mathrm{AB}^\ddagger \xrightarrow{k_\mathrm{p}} \mathrm{C}^* & \text{(formation of energetic molecule C*)} \\ \mathrm{C}^* \xrightarrow{k_{-\mathrm{p}}} \mathrm{AB}^\ddagger & \text{(return from C* to the activated complex)} \\ \mathrm{C}^* + \mathrm{M} \xrightarrow{k_\mathrm{s}} \mathrm{C} + \mathrm{M}^* & \text{(stabilization of the molecule C)} \end{cases} \tag{12.140}$$

where * indicates a high energy state.

Note that in the derivation of Eq. (12.139), we only considered the first three stages. Consider now all stages from the point of view of formal kinetics. The rate of reaction in Eq. (12.131) is

$$\omega = k_\mathrm{s}[C^*][M].$$

In steady state, the concentrations of $\mathrm{AB}^\ddagger$ and C* should be constant, therefore, we can write

$$\frac{\mathrm{d}[\mathrm{AB}^\ddagger]}{\mathrm{d}t} = k_\mathrm{a}[\mathrm{A}][\mathrm{B}] - k_\mathrm{d}[\mathrm{AB}^\ddagger] - k_\mathrm{p}[\mathrm{AB}^\ddagger] + k_{-\mathrm{p}}[\mathrm{C}^*] = 0$$

$$\frac{\mathrm{d}[C^*]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{AB}^\ddagger] - k_{-\mathrm{p}}[\mathrm{C}^*] - k_\mathrm{s}[\mathrm{C}^*][\mathrm{M}] = 0,$$

from which we obtain

$$[\mathrm{AB}^{\ddagger}] = \frac{k_{-p}[\mathrm{C}^*] + k_{\mathrm{s}}[\mathrm{C}^*][\mathrm{M}]}{k_p}$$

$$[\mathrm{C}^*] = \frac{k_{\mathrm{a}}[\mathrm{A}][\mathrm{B}]}{(k_{\mathrm{d}}k_{-p}/k_p) + (k_{\mathrm{d}}k_{\mathrm{s}}/k_p)[\mathrm{M}] + k_{\mathrm{s}}[\mathrm{M}]}.$$

Inserting the last result into the equation for the rate of the reaction in Eq. (12.131), we obtain

$$\omega = \frac{k_{\mathrm{s}}k_{\mathrm{p}}k_{\mathrm{a}}[\mathrm{A}][\mathrm{B}][\mathrm{M}]}{k_{\mathrm{d}}k_{-p} + k_{\mathrm{s}}\left(k_{\mathrm{d}} + k_p\right)[\mathrm{M}]}. \tag{12.141}$$

Since the theory of the activated complex considered only the first three stages of the reaction in Eq. (12.140), the rate constant can be determined from the constants k_{a}, k_{d}, and k_{p} alone. Equation (12.141) shows that when the concentration of M is very large, this is true:

$$\omega = \frac{k_{\mathrm{p}}k_{\mathrm{a}}[\mathrm{A}][\mathrm{B}]}{k_{\mathrm{d}} + k_{\mathrm{p}}}. \tag{12.142}$$

However, this is a special case. If the concentration of M is small, Eq. (12.141) reduces to

$$\omega = \frac{k_{\mathrm{s}}k_{\mathrm{p}}k_{\mathrm{a}}}{k_{\mathrm{d}}k_{-p}}[\mathrm{M}][\mathrm{A}][\mathrm{B}], \tag{12.143}$$

where the rate constant also depends on k_{s} and k_{-p}. Since the concentration of M is constant in steady state, we can consider Eq. (12.143) as the kinetic equation for a second order reaction. This agrees with our original theory of the activated complex result (Eq. (12.138)). However, the rate constant in our extended theory (Eq. (12.143)) depends on the rate constants for each stage of the reaction in Eq. (12.140) and the concentration of M (k_{s}, $k_{-\mathrm{p}}$, and [M] are absent in the original theory). Therefore, it is not surprising that the original theory of the activated complex does not accurately predict experimentally measured rate constants.

In the derivation of Eq. (12.139), we assumed that the probability that a chemical reaction occurs is unity if the system reaches the activated state and zero if it does not. Strictly speaking, neither of these assumptions are valid. Even after reaching the activated state, the system can return to the original state and a system with energy less than the activation barrier E_{a} can react through a process known as **tunneling**. There are even more complicated cases, such as when there is a quantum mechanical transition that takes the system from one potential energy surface to another. Consider the following example reaction

$$\mathrm{CO} + \mathrm{O} \rightarrow \mathrm{CO_2}.$$

The oxygen atom has two unpaired electrons with parallel spins in its ground state, while CO and $\mathrm{CO_2}$ molecules each have zero net spin. Therefore, the reaction can only occur if one of the spins flip. However, this means that the electronic state of the system changes abruptly and the system jumps from one potential energy surface to another.

We can account for the disagreements between the theory of the activated complex and experiment by writing the reaction rate as

$$k = \kappa \frac{\mathrm{k}T}{h} \frac{P'_{\mathrm{AB}^{\ddagger}}}{P_{\mathrm{A}} P_{\mathrm{B}}} \mathrm{e}^{-E_{\mathrm{a}}/RT}, \tag{12.144}$$

where we have combined all of these disappointments into a new constant, the **transmission coefficient** κ. Of course, the theory of the activated complex is silent on the value of the transmission coefficient.

Review question

1. The reaction $O + CO \rightarrow CO_2$ has a linear activated complex O–C–O. How many vibrational degrees of freedom does this activated complex have?
2. The reaction $C_2H_4 + Cl \rightarrow C_2H_4Cl$ has the following activated complex CH_2–CH_2Cl. How many vibrational degrees of freedom does this activated complex have?

12.3.3.3 Theory of the activated complex versus the Arrhenius law

The rate constant in the theory of the activated complex is expressed in terms of the partition functions of the reacting molecules and the activated complex. We can provide a rough estimate of the temperature dependence of these partition functions at room temperature. The translational partition function is proportional to $T^{3/2}$ (see Eq. (12.37)). The rotational partition function is proportional to T in the case of linear molecules (see Eq. (12.55)) or $T^{3/2}$ in the case of non-linear molecules (see Eq. (12.76)). Finally, the vibrational partition function is only very weakly temperature dependent at room temperature, where $T \ll \theta$ (see Eq. (12.67)). Therefore, Eq. (12.139) can be rewritten as

$$k = AT^{m} \mathrm{e}^{-E_a/RT},$$

where A is a temperature independent constant and the power, m, depends on the structure of the reacting molecules and the activated complex. This result implies that

$$\ln k = \ln A + m \ln T - \frac{E_a}{RT}; \qquad \frac{\mathrm{d} \ln k}{\mathrm{d}T} = \frac{m}{T} + \frac{E_{\mathrm{a}}}{RT^2} = \frac{E_{\mathrm{a}} + mRT}{RT^2}.$$

On the other hand, the Arrhenius law takes the following form:

$$\frac{\mathrm{d} \ln k}{\mathrm{d}T} = \frac{E}{RT^2},$$

where E is the experimentally observed activation energy. Comparing this equation with the previous one, we find

$$E_{\mathrm{a}} = E - mRT. \tag{12.145}$$

Therefore, the measured activation energy need not be the true activation energy.

12.3.3.4 Thermodynamic form of the theory of the activated complex

If we consider the activated complex as a regular molecule, we can write the expression for the equilibrium constant for the reaction

$$A + B \rightarrow AB^{\ddagger} \tag{12.146}$$

as (see Eq. (12.122))

$$K_{\mathrm{c}}^{\ddagger\prime} = \frac{P'_{\mathrm{AB}^{\ddagger}}}{P_{\mathrm{A}}P_{\mathrm{B}}}\mathrm{e}^{-E_{\mathrm{a}}/RT}. \tag{12.147}$$

Inserting this expression into Eq. (12.139), we find

$$k = \frac{k_{\mathrm{B}}T}{h}K_{\mathrm{c}}^{\ddagger\prime}. \tag{12.148}$$

In physics, we commonly express concentrations in molecules/m^3, while in chemistry we commonly express it in mole/l. Equation (12.248) is unchanged on going from physics to chemistry (as long as we are consistent). In the rest of this chapter, we will be chemists and express the concentration in mole/l. We will use the state in which the partial pressures of all species are 1 atm as our standard state. In this case (see Section 5.2)

$$K_{\mathrm{p}} = K_{\mathrm{c}}(R'T)^{-1},$$

where $R' = 0.0821$ (l · atm)/(K mole). Since $-RT \ln K_{\mathrm{p}} = \Delta G$, we obtain

$$K_{\mathrm{p}} = K_{\mathrm{c}}(R'T)^{-1},$$

where $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are the change of the Gibbs free energy, enthalpy, and entropy at formation of the activated complex. Inserting this result into Eq. (12.148), we obtain:

$$k = \frac{k_{\mathrm{B}}T}{h}R'T\mathrm{e}^{-\Delta H^{\ddagger}/RT}\mathrm{e}^{\Delta S^{\ddagger}/R}, \tag{12.149}$$

where the rate constant has the dimension l/(mole s). This equation can be transformed as follows

$$\ln k = 2\ln T - \frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \text{const}; \qquad \frac{E}{RT^2} = \frac{2}{T} + \frac{\Delta H^{\ddagger}}{RT^2}$$

or

$$\Delta H^{\ddagger} = E - 2RT. \tag{12.150}$$

Inserting this expression into Eq. (12.149), we obtain:

$$k = \frac{k_{\mathrm{B}}T}{h}e^2\mathrm{e}^{\Delta S^{\ddagger}/R}R'T\mathrm{e}^{-E/RT}. \tag{12.151}$$

Note that both R and R' are the ideal gas constants, but are in different units. Recall that in the theory of active collisions

$$k = \sigma A\mathrm{e}^{-E/RT}, \tag{12.152}$$

where

$$A = \pi (r_{\mathrm{A}} + r_{\mathrm{B}})^2 \left(\frac{8 k_{\mathrm{B}} T}{\pi m_{\mathrm{AB}}} \right)^{1/2} \qquad (12.153)$$

Comparing Eqs (12.151) and (12.152), we obtain the following relationship:

$$\sigma = \frac{1}{A} \frac{k_{\mathrm{B}} T}{h} e^2 R' T \mathrm{e}^{\Delta S^{\ddagger}/R}. \qquad (12.154)$$

Obviously, the factor A has the same order of magnitude for all bimolecular reactions. Therefore, the steric factor σ is determined by the entropy of the formation of the activated complex. According to the theory of active collisions, all bimolecular reactions fall into one of the following three categories:

$\sigma > 1$-“fast reactions”;
$\sigma \approx 1$-“normal reactions”
$\sigma > 1$-“slow reactions”.

Inserting reasonable numbers into Eq. (12.153), we find that $A \sim 10^{11}$ l/(mole s). The factor $(1/A)(k_{\mathrm{B}} Th)e^2 R' T$ is $\sim 10^4$ at room temperature. Ignoring the steric factor in Eq. (12.152) (i.e. $\sigma \approx 1$) is equivalent to assuming that $\Delta S^{\ddagger} \approx -80$ J/(K mole). For this value of $\Delta S^{\ddagger}$, the theory of active collisions should work. We can estimate $\Delta S^{\ddagger}$ as follows. At room temperature, the vibrational degrees of freedom do not make a significant contribution to the entropy. In the case of bimolecular reactions, the reacting molecules together have six translational degrees of freedom and 4–6 rotational degrees of freedom. The activated complex has four translational degrees of freedom and 2–3 rotational degrees of freedom. Therefore, $\Delta S^{\ddagger}$ has contributions from two translational degrees of freedom (~ 50 J/(K mole) per degree) and 1–3 rotational degrees of freedom (~ 20 J/(K mole) per degree) and overall, $\Delta S^{\ddagger} < -100$ J/(K mole). This is why most bimolecular reactions are “slow reactions” and the theory of active collisions overestimates the rate constants.

13

Introduction to statistical thermodynamics of condensed matter

In this Chapter we apply statistical thermodynamics to condensed matter. We start with a description of the structure of liquids and the relation between this structure and its thermodynamic properties. Taking the low density limit, we derive a general equation of state appropriate for both liquids and gases. Next, we turn to a statistical thermodynamic description of solids. Finally, we consider the statistical theory of solutions.

13.1 Introduction to liquid theory

13.1.1 Correlation functions

Recall that interactions between molecules in an ideal gas can be ignored for the purpose of determining thermodynamic properties. Therefore, we can assume that the spatial position of a molecule is independent of the positions of all of the other molecules in the gas. In real gases under high pressure and, even more so, in condensed matter, the intermolecular interactions play an important role and the positions of molecules are not independent. In other words, intermolecular interactions lead to the formation of correlations in the location of the molecules or, equivalently, to the development of structure. The energy of the system and the other thermodynamic properties depend on this structure. Therefore, we now turn to a discussion of structure. There are two distinct approaches to this problem. The first approach is designed for crystalline materials and is based upon a description of crystal symmetry. The description of this method is outside the scope of this text. The second is based upon the introduction of probability functions for atom locations and is applicable to disordered systems such as dense gases, liquids, and amorphous solids.

Consider, as we are apt to do, the ideal gas. In this case, the probability of finding s molecules at points $\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_s}$ is simply

$$\mathrm{d}w(\mathbf{r_1}, \ldots, \mathbf{r_s}) = \frac{1}{V^s}\mathrm{d}\mathbf{r_1} \ldots \mathrm{d}\mathbf{r_s}.$$

In contrast with the ideal gas, the positions of molecules in high density gases or condensed matter are not independent of each other. Therefore, we write

$$\mathrm{d}w(\mathbf{r_1}, \ldots, \mathbf{r_s}) = \frac{1}{V^s} F_s(\mathbf{r_1}, \ldots, \mathbf{r_s})\mathrm{d}\mathbf{r_1} \ldots \mathrm{d}\mathbf{r_s}, \tag{13.1}$$

where $F_s(\mathbf{r_1}, \ldots, \mathbf{r_s})$ is called the **s-particle correlation function**. Note three obvious properties of such functions. First, the system does not change when we exchange two molecules. This implies that the correlation functions should be symmetric with respect to their arguments. For example, two-particle correlation functions are invariant upon switching indices:

$$F_2(\mathbf{r_1}, \mathbf{r_2}) = F_2(\mathbf{r_2}, \mathbf{r_1}).$$

The second property is associated with the fact that correlation functions are probability distributions and, hence, must be normalized:

$$\frac{1}{V^s} \int F_s(\mathbf{r_1}, \ldots, \mathbf{r_s})\mathrm{d}\mathbf{r_1} \ldots \mathrm{d}\mathbf{r_s} = 1. \tag{13.2}$$

Finally, we can find any of the lower order correlation functions from the any higher order correlation function, for example,

$$F_s(\mathbf{r_1}, \ldots, \mathbf{r_s}) = \frac{1}{V} \int F_{s+1}(\mathbf{r_1}, \ldots, \mathbf{r_s}, \mathbf{r_{s+1}})\mathrm{d}\mathbf{r_{s+1}}. \tag{13.3}$$

Below, we primarily focus on homogeneous systems. In this case, the probability of finding a single molecule at any point is the same. Therefore,

$$\mathrm{d}w_1 = \frac{1}{V}\mathrm{d}\mathbf{r_1}$$

or

$$F_1(\mathbf{r}) = 1. \tag{13.4}$$

It is often useful to write the conditional probability $\mathrm{d}w_{\mathbf{r_{s+1}}, \ldots, \mathbf{r_{s+p}}}(\mathbf{r_1}, \ldots, \mathbf{r_s})$ that s molecules are at points $\mathbf{r_1}, \ldots, \mathbf{r_s}$, while p other molecules are at points $\mathrm{r}_{s+1}, \ldots, \mathrm{r}_{s+p}$. It is obvious that

$$\mathrm{d}w(\mathbf{r_1}, \ldots, \mathbf{r_{s+p}}) = \mathrm{d}w(\mathbf{r_{s+1}}, \ldots, \mathbf{r_{s+p}})\mathrm{d}w_{\mathbf{r_{s+1}}, \ldots, \mathbf{r_{s+p}}}(\mathbf{r_1}, \ldots, \mathbf{r_s}).$$

Inserting Eq. (13.1) into this relation, we obtain:

$$\begin{aligned}&\frac{1}{V^{s+p}} F_{s+p}(\mathbf{r_1}, \ldots, \mathbf{r_{s+p}})\mathrm{d}\mathbf{r_1} \ldots \mathrm{d}\mathbf{r_{s+p}} \\ &\quad = \frac{1}{V^p} F_p(\mathbf{r_{s+1}}, \ldots, \mathbf{r_{s+p}})\mathrm{d}\mathbf{r_{s+1}} \ldots \mathrm{d}\mathbf{r_{s+p}}\mathrm{d}w_{\mathbf{r_{s+1}}, \ldots, \mathbf{r_{s+p}}}(\mathbf{r_1}, \ldots, \mathbf{r_s})\end{aligned}$$

or

$$\mathrm{d}w_{\mathbf{r_{s+1}}, \ldots, \mathbf{r_{s+p}}}(\mathbf{r_1}, \ldots, \mathbf{r_s}) = \frac{1}{V^s} \frac{F_{s+p}(\mathbf{r_1}, \ldots, \mathbf{r_{s+p}})}{F_p(\mathbf{r_{s+1}}, \ldots, \mathbf{r_{s+p}})}\mathrm{d}\mathbf{r_1} \ldots \mathrm{d}\mathbf{r_s}. \tag{13.5}$$

Another approach is to describe the structure of a homogeneous disordered system through pair correlation functions. If the system is homogeneous, the probability of finding molecule 2 at a distance r from molecule 1 does not depend on the position of molecule 1. If the system is an ideal gas then this probability is simply $4\pi r^2 \mathrm{d}r/V$. In the case of condensed matter, we must introduce a new factor that accounts for the correlation between the positions of molecules:

$$\mathrm{d}w(r) = \frac{4\pi r^2\, \mathrm{d}r}{V} g(r). \tag{13.6}$$

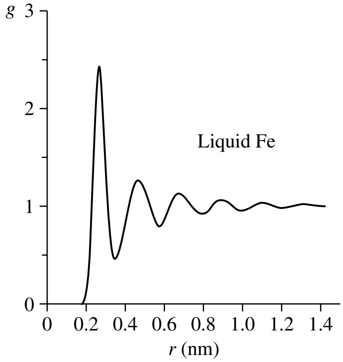


Fig. 13.1
The pair correlation function of liquid iron at $T = 1873$ K.

The function $g(r)$ is called the **pair correlation function**. For an ideal gas, $g(r) = 1$. However, if the molecules repel each other at short distances (as quantum mechanics tells us they must), molecule 2 cannot approach too close to molecule 1. Therefore, at small distances $g(r) = 0$. In disordered systems (liquids, amorphous solids), there is no correlation between molecule positions at large r; hence, $g(r) = 1$ at large distances. Figure 13.1 shows a typical pair correlation function for liquid metals.

We can also describe the probability of finding molecule 2 at a distance r from molecule 1 using the correlation functions introduced earlier (see Eq. 13.5):

$$\begin{aligned} \mathrm{d}w_{\mathbf{r}_1}(\mathbf{r}_2) &= \frac{1}{V}\frac{F_2(\mathbf{r}_2, \mathbf{r}_1)}{F_1(\mathbf{r}_1)}\mathrm{d}\mathbf{r}_2 = \frac{1}{V}\frac{F_2(\mathbf{r}_1, \mathbf{r}_2)}{F_1(\mathbf{r}_1)}\mathrm{d}(\mathbf{r}_2 - \mathbf{r}_1) \\ &= F_2(\mathbf{r}_1, \mathbf{r}_2)\frac{4\pi|\mathbf{r}_2 - \mathbf{r}_1|^2 \mathrm{d}|\mathbf{r}_2 - \mathbf{r}_1|}{V}. \end{aligned}$$

Comparing this result with Eq. (13.6) and taking into account that $r = |\mathbf{r}_2 - \mathbf{r}_1|$, we find:

$$F_2(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|). \tag{13.7}$$

Therefore, the two-particle correlation function for homogeneous system only depends on the scalar separation between molecules. We note, without derivation, that this function can be determined from diffraction experiments.

Review questions

1. What is $\mathrm{d}w(\mathbf{r}_1, \ldots, \mathbf{r}_\mathbf{s}) = (1/V^s)F_s(\mathbf{r}_1, \ldots, \mathbf{r}_\mathbf{s})\mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_\mathbf{s}$?
2. What is $\mathrm{d}w_{\mathbf{r}_{s+1},\ldots,\mathbf{r}_{s+p}}(\mathbf{r}_1, \ldots, \mathbf{r}_\mathbf{s}) = (1/V^s)\frac{F_{s+p}(\mathbf{r}_1,\ldots,\mathbf{r}_{s+p})}{F_p(\mathbf{r}_{s+1},\ldots,\mathbf{r}_{s+p})}\mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_\mathbf{s}$?
3. For which systems is the following relation $F_2(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|)$ valid?

13.1.2 Determination of thermodynamic properties

Since our goal is to obtain the thermodynamic properties from a microscopic description of the system, we now consider how to determine such properties from the correlation functions and molecular interactions (and external parameters). Since the correlation functions (structure) are themselves determined by the molecular interactions, our first step is to relate the correlation functions to the molecular interactions. The most natural approach is to use Gibbs statistics. Recall that the partition function takes the following form:

$$Z_N = \frac{1}{N!}\int \mathrm{e}^{-\left[U_N(\mathbf{r}_1,\ldots,\mathbf{r}_\mathrm{N})+\sum\limits_{i=1}^{N} p_i^2/2m\right]/k_\mathrm{B}T}\mathrm{d}\Gamma, \tag{13.8}$$

where $U_\mathrm{N}(\mathbf{r}_1,\ldots,\mathbf{r}_\mathbf{N})$ is the interaction energy of the molecules (atoms) and

$$\mathrm{d}\Gamma = \frac{\mathrm{d}\mathbf{r}_1\ldots\mathrm{d}\mathbf{r}_\mathbf{N}\mathrm{d}\mathbf{p}_1\ldots\mathrm{d}\mathbf{p}_\mathbf{N}}{(2\pi\hbar)^{3N}}. \tag{13.9}$$

The integration over momenta in Eq. (13.8) can be separated from the integration over molecule positions. This allows us to rewrite Eq. (13.8) as

$$Z_N = \left(\frac{mk_\mathrm{B}T}{2\pi\hbar^2}\right)^{3N/2}\frac{Q_N}{N!}, \tag{13.10}$$

where the quantity

$$Q_N = \int \mathrm{e}^{-U_N(\mathbf{r}_1,\ldots,\mathbf{r}_\mathrm{N})/k_\mathrm{B}T}\mathrm{d}\mathbf{r}_1\ldots\mathrm{d}\mathbf{r}_\mathbf{N}, \tag{13.11}$$

is called the **configuration integral** or **configurational partition function**.

In the case of an ideal gas $U_N \equiv 0$ and, therefore, $Q_N = V^N$. Thus, we can rewrite the partition function for an arbitrary system in terms of that for an ideal gas Z_N^0 and the configuration integral:

$$Z_N = Z_N^0\frac{Q_N}{V^N}. \tag{13.12}$$

Since

$$A = -k_\mathrm{B}T\ \ln Z_N$$

we can rewrite Eq. (13.12) as

$$A = A_0 - k_\mathrm{B}T\ \ln\frac{Q_N}{V^N}, \tag{13.13}$$

where A_0 is the Helmholtz free energy of an ideal gas of N molecules at the same temperature and volume.

The probability that N molecules are at points $\mathbf{r}_1,\ldots,\mathbf{r}_\mathbf{N}$ is

$$\mathrm{d}w_N(\mathbf{r}_1,\ldots,\mathbf{r}_\mathbf{N}) = \frac{1}{Q_N}\mathrm{e}^{-U_N(\mathbf{r}_1,\ldots,\mathbf{r}_\mathrm{N})/k_\mathrm{B}T}\mathrm{d}\mathbf{r}_1\ldots\mathrm{d}\mathbf{r}_\mathbf{N}. \tag{13.14}$$

Comparing this result with Eq. (13.1), we find:

$$F_N(\mathbf{r}_1,\ldots,\mathbf{r}_\mathbf{N}) = \frac{V^N}{Q_N}\mathrm{e}^{-U_N(\mathbf{r}_1,\ldots,\mathbf{r}_\mathrm{N})/k_\mathrm{B}T} \tag{13.15}$$

Other correlation functions can be found using Eq. (13.3) and will be discussed in Section 13.1.4.

Now imagine that we know the correlation functions. How can we use this information to determine thermodynamic functions? We recall that any measurable thermodynamic property is, by definition, an averaged quantity. Any quantity that is a function of atomic coordinates can be written as a sum over the s-body interactions

$$M_s(\mathbf{r_1},\ldots,\mathbf{r_N}) = \sum_{i_1=1}^{N-1}\sum_{i_2=i_1+1}^{N-2}\cdots\sum_{i_s=i_{s-1}+1}^{N-s} f(\mathbf{r_{i_1}},\ldots,\mathbf{r_{i_s}}). \tag{13.16}$$

In principle $s = N$, but in many cases it is sufficient to describe the interactions as simply two-body (pairwise) or three-body (bond bending) interactions. The average of this quantity M_s (i.e. the thermodynamic quantity) is simply a weighted average of all possible molecular positions:

$$\overline{M}_s = \int M_s\,\mathrm{d}w_N = \frac{1}{Q_N}\int M_s(\mathbf{r_1},\ldots,\mathbf{r_N})\mathrm{e}^{-U_N(\mathbf{r}_1,\ldots,\mathbf{r_N})/k_\mathrm{B}T}\mathrm{d}\mathbf{r_1}\ldots\mathrm{d}\mathbf{r_N}.$$

Inserting Eqs (13.15) and (13.16) into this relation, yields

$$\begin{aligned}\overline{M}_s &= \frac{N!}{s!(N-s)!}\frac{1}{Q_N}\int f(\mathbf{r_1},\ldots,\mathbf{r_s})\mathrm{e}^{-U_N(\mathbf{r}_1,\ldots,\mathbf{r_N})/k_\mathrm{B}T}\mathrm{d}\mathbf{r_1}\ldots\mathrm{d}\mathbf{r_N}\\ &= \frac{N!}{s!(N-s)!}\int f(\mathbf{r_1},\ldots,\mathbf{r_s})F_N(\mathbf{r_1},\ldots,\mathbf{r_s})V^{-N}\mathrm{d}\mathbf{r_1}\ldots\mathrm{d}\mathbf{r_N}\\ &= \frac{N!}{s!(N-s)!}\frac{1}{V^s}\int f(\mathbf{r_1},\ldots,\mathbf{r_s})F_s(\mathbf{r_1},\ldots,\mathbf{r_s})\mathrm{d}\mathbf{r_1}\ldots\mathrm{d}\mathbf{r}_s.\end{aligned}$$

Since we usually work with $s \ll N$, this equation reduces to

$$\overline{M}_s = \left(\frac{N}{V}\right)^s\frac{1}{s!}\int f(\mathbf{r_1},\ldots,\mathbf{r_s})F_s(\mathbf{r_1},\ldots,\mathbf{r_s})\mathrm{d}\mathbf{r_1}\ldots\mathrm{d}\mathbf{r_s}. \tag{13.17}$$

As an example, consider a system in which the molecules only interact through a pairwise potential $\varphi(r)$, that is a potential that only depends on the distance between molecules. In this case, the instantaneous potential energy is

$$U_N(\mathbf{r_1},\ldots,\mathbf{r_N}) = \sum_{1\le i<\,\ldots\,<j\le N}\varphi\left(\left|\mathbf{r_i}-\mathbf{r_j}\right|\right). \tag{13.18}$$

Equation (13.17) implies that the mean potential energy is

$$\overline{U}_N = \left(\frac{N}{V}\right)^2\frac{1}{2}\int \varphi(|\mathbf{r_1}-\mathbf{r_2}|)F_2(\mathbf{r_1},\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}.$$

If the system is homogeneous, this reduces to

$$\overline{U}_N = \left(\frac{N}{V}\right)^2\frac{1}{2}\int \varphi(r)g(r)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r_2} = \frac{1}{2}\left(\frac{N}{V}\right)^2 V\int \varphi(r)g(r)4\pi r^2\mathrm{d}r$$

and, finally,

$$\overline{U}_N = 2\pi N\frac{N}{V}\int_0^\infty \varphi(r)g(r)r^2\mathrm{d}r. \tag{13.19}$$

This example relates a thermodynamic function to the molecular interactions, the structure and an external parameter, the density.

Review questions

1. What approximations were used to derive the following expression:

$$\overline{M}_s = \left(\frac{N}{V}\right)^s \frac{1}{s!} \int f(\mathbf{r_1}, \ldots, \mathbf{r_s}) \mathrm{F}_s(\mathbf{r_1}, \ldots, \mathbf{r_s}) \mathrm{d}\mathbf{r_1} \ldots \mathrm{d}\mathbf{r_s}$$

   for the average value of a quantity $M_s(\mathbf{r_1}, \ldots, \mathbf{r_N}) = \sum_{i_1=1}^{N-1} \Sigma_{i_2=i_1+1}^{N-2} \cdots \sum_{i_s=i_{s-1}+1}^{N-s} f(\mathbf{r_{i_1}}, \ldots, \mathbf{r_{i_s}})$?
2. What approximations were used to derive the following expression for the average value of the potential energy, $\overline{U}_N = 2\pi N(N/V) \int_0^\infty \varphi(r) g(r) r^2 \mathrm{d}r$?

13.1.3 Equation of state of non-crystalline matter

The equation of state can be obtained from the following thermodynamic relation:

$$p = -\left(\frac{\partial A}{\partial V}\right)_T.$$

Inserting Eq. (13.13) into this relation, we obtain

$$p = -\left(\frac{\partial A_0}{\partial V}\right)_T + k_\mathrm{B} T \left(\frac{\partial \ln Q_N}{\partial V}\right)_T - k_\mathrm{B} T \frac{\partial \ln V^N}{\partial V}.$$

The first term is the equation of state of an ideal gas ($p = Nk_\mathrm{B}T/V$) and is exactly canceled by the last term. Therefore,

$$p = k_\mathrm{B} T \left(\frac{\partial \ln Q_N}{\partial V}\right)_T. \tag{13.20}$$

For simplicity, in the remainder of this section, we consider the special case in which the molecular interactions are strictly pairwise. In this case, we can express the potential energy as

$$U_N(\mathbf{r_1}, \ldots, \mathbf{r_N}) = \sum_{1 \le i < \ldots < j \le N} \varphi(|\mathbf{r_i} - \mathbf{r_j}|).$$

It is convenient to scale all of the atomic coordinates by a parameter, λ, such that

$$V(\lambda) = \lambda^3 V.$$

Differentiating both sides of this expression, we find:

$$\mathrm{d}V(\lambda) = 3\lambda^2 \mathrm{d}\lambda V = \frac{3\,\mathrm{d}\lambda}{\lambda} V$$

or

$$\frac{\mathrm{d}V}{V} = \frac{3\mathrm{d}\lambda}{\lambda}.$$

Introduction of this scaling parameter also leads to the following changes in the potential energy and the configuration integral:

$$U_N(\lambda\mathbf{r_1},\ldots,\lambda\mathbf{r_N})=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\varphi(\lambda|\mathbf{r_i}-\mathbf{r_j}|)=\sum_{i<j}^{N}\varphi(\lambda|\mathbf{r_i}-\mathbf{r_j}|)$$

$$Q_N(\lambda)=\lambda^{3N}\int \mathrm{e}^{-U_N(\lambda\mathbf{r_1},\ldots,\lambda\mathbf{r_N})/k_\mathrm{B}T}\mathrm{d}\mathbf{r_1}\ldots\mathrm{d}\mathbf{r_N}$$

Inserting these results into Eq. (13.10), we obtain:

$$\begin{aligned}
p &= k_\mathrm{B}T\left(\frac{\partial\ln Q_N(\lambda)}{\partial V}\right)\bigg|_{\lambda=1}=k_\mathrm{B}T\frac{1}{3V}\left[\frac{\lambda}{Q_N}\frac{\partial Q_N(\lambda)}{\partial\lambda}\right]_{\lambda=1}\\
&=\frac{k_\mathrm{B}T}{3V}\frac{1}{Q_N}\Bigg[3N\lambda^{3N-1}\int \mathrm{e}^{-U_N(\lambda\mathbf{r_1},\ldots,\lambda\mathbf{r_N})/k_\mathrm{B}T}\mathrm{d}\mathbf{r_1}\ldots\mathrm{d}\mathbf{r_N}\\
&\quad-\lambda^{3N}\sum_{i<j}^{N}\int\frac{\partial\varphi(\lambda|\mathbf{r_i}-\mathbf{r_j}|)}{\partial|\mathbf{r_i}-\mathbf{r_j}|}\frac{|\mathbf{r_i}-\mathbf{r_j}|}{k_\mathrm{B}T}\mathrm{e}^{-U_N(\lambda\mathbf{r_1},\ldots,\lambda\mathbf{r_N})/k_\mathrm{B}T}\mathrm{d}\mathbf{r_1}\ldots\mathrm{d}\mathbf{r_N}\Bigg]_{\lambda=1}\\
&=\frac{k_\mathrm{B}T}{3V}\frac{1}{Q_N}3NQ_N\\
&\quad-\frac{k_\mathrm{B}T}{3V}\frac{1}{Q_N}\frac{1}{k_\mathrm{B}T}\sum_{i<j}^{N}\int\frac{\partial\varphi(|\mathbf{r_i}-\mathbf{r_j}|)}{\partial|\mathbf{r_i}-\mathbf{r_j}|}|\mathbf{r_i}-\mathbf{r_j}|\mathrm{e}^{-U_N(\mathbf{r_1},\ldots,\mathbf{r_N})/k_\mathrm{B}T}\mathrm{d}\mathbf{r_1}\ldots\mathrm{d}\mathbf{r_N}\\
&=\frac{Nk_\mathrm{B}T}{V}-\frac{1}{3V}\left\langle\sum_{i<j}^{N}\frac{\partial\varphi(|\mathbf{r_i}-\mathbf{r_j}|)}{\partial|\mathbf{r_i}-\mathbf{r_j}|}|\mathbf{r_i}-\mathbf{r_j}|\right\rangle.
\end{aligned}$$

The average in the final expression can be evaluated using Eq. (13.17):

$$\begin{aligned}
p &= \frac{Nk_\mathrm{B}T}{V}-\frac{1}{3V}\left(\frac{N}{V}\right)^2\frac{1}{2}\int\frac{\partial\varphi(|\mathbf{r_1}-\mathbf{r_2}|)}{\partial|\mathbf{r_1}-\mathbf{r_2}|}|\mathbf{r_1}-\mathbf{r_2}|F_2(\mathbf{r_1},\mathbf{r_2})\mathrm{d}\mathbf{r_1}d\mathbf{r_2}\\
&=\frac{Nk_\mathrm{B}T}{V}-\frac{1}{3V}\left(\frac{N}{V}\right)^2\frac{1}{2}V4\pi\int\frac{\partial\varphi(r)}{\partial r}g(r)r^3\mathrm{d}r
\end{aligned}$$

and finally

$$p=\frac{Nk_\mathrm{B}T}{V}-\frac{2\pi}{3}\left(\frac{N}{V}\right)^2\int\varphi'(r)g(r)r^3\mathrm{d}r, \qquad (13.21)$$

where the prime indicates that a derivative is taken with respect to r. This is the equation of state for non-crystalline matter in which the molecules interact via a pairwise potential, φ. The first term corresponds to an ideal gas and the second is determined by the molecular interactions. In the low density limit, this equation reduces to the equation of state of an ideal gas. We return to this equation in Section 13.2.1.

Review questions

1. Under what conditions does the equation $p = (Nk_\mathrm{B}T/V) - (2\pi/3)\times\,(N/V)^2 \int \varphi'(r)g(r)r^3\mathrm{d}r$ reduce to the equation of state of an ideal gas?
2. Is it possible to derive an equation of state for a non-ideal gas from the following equation $p = (Nk_\mathrm{B}T/V) - (2\pi/3)(N/V)^2 \int \varphi'(r)g(r)r^3\mathrm{d}r$?

13.1.4 Born–Green–Bogoliubov equation

We have already derived expressions for the potential energy (Eq. 13.19) and the pressure (Eq. 13.21) in non-crystalline matter. Both expressions require the knowledge of the molecular interactions and the pair correlation function (assuming that the interactions are strictly pairwise). The intermolecular potential can be fitted to either quantum-mechanical results and/or experimentally measurable quantities. While a large corpus of intermolecular potentials exists, a discussion of this issue is outside the scope of this text. If the intermolecular potential is known, the pair correlation function can easily be determined using atomistic computer simulation—unfortunately, this is also outside the scope of this text. While such an approach has clear advantages, it does not yield pair correlation functions in an analytical form. On the other hand, the modern theory of liquids, while producing analytical results, does not predict accurate pair correlation functions. Nonetheless, such theories are useful both conceptually and in practice in some special cases. The remainder of this section will be devoted to the theory of liquids. This theory will play a pivotal role in our discussion of non-ideal gases in the next section.

We will again limit our discussion to the case in which the interactions between molecules is pairwise. In order to derive the relation between the pair potential and pair correlation function, we start from the general relation between the correlation functions (see Eq. 13.3):

$$F_s(\mathbf{r_1}, \ldots, \mathbf{r_s}) = \frac{1}{V}\int F_{s+1}(\mathbf{r_1}, \ldots, \mathbf{r_s}, \mathbf{r_{s+1}})\mathrm{d}\mathbf{r_{s+1}}.$$

This relation allows us to express the correlation function of any order through the N-particle correlation function:

$$F_s(\mathbf{r_1}, \ldots, \mathbf{r_s}) = \frac{1}{V^{N-s}}\int F_N(\mathbf{r_1}, \ldots, \mathbf{r_N})\mathrm{d}\mathbf{r_{s+1}} \ldots \mathrm{d}\mathbf{r_N}.$$

Note that we have an exact expression only for the N-particle correlation function (Eq. 13.15):

$$F_N(\mathbf{r_1}, \ldots, \mathbf{r_N}) = \frac{V^N}{Q_N}\mathrm{e}^{-U_N(\mathbf{r_1},\ldots,\mathbf{r_N})/k_\mathrm{B}T}.$$

Inserting this expression into the preceding equation, we obtain

$$F_s(\mathbf{r_1}, \ldots, \mathbf{r_s}) = \frac{V^s}{Q_N}\int \mathrm{e}^{-U_N(\mathbf{r_1},\ldots,\mathbf{r_N})/k_\mathrm{B}T}\mathrm{d}\mathbf{r_{s+1}} \ldots \mathrm{d}\mathbf{r_N}. \tag{13.22}$$

This, in principle, provides an exact expression for any correlation function. In practice, however, this expression is not particularly useful.

For example, in order to calculate the two-particle correlation function, we must perform integration over $N-2$ coordinates. Since N can be *very* large, this would be tedious. We can obtain a more practical relation by taking derivatives of both sides of Eq. (13.22) with respect to the position of molecule 1:

$$\begin{aligned}\nabla_{\mathbf{1}} F_s &= -\frac{V^s}{Q_N}\int \frac{\nabla_{\mathbf{1}} U_N}{k_{\mathrm{B}} T}\mathrm{e}^{-U_N/k_{\mathrm{B}}T}\mathrm{d}\mathbf{r}_{\mathbf{s+1}}\ldots\mathrm{d}\mathbf{r}_{\mathbf{N}}\\ &= -\frac{V^s}{k_{\mathrm{B}}TQ_N}\sum_{i=2}^{s}\nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{i}}|)\int \mathrm{e}^{-U_N/k_{\mathrm{B}}T}\mathrm{d}\mathbf{r}_{\mathbf{s+1}}\ldots\mathrm{d}\mathbf{r}_{\mathbf{N}}\\ &\quad -\frac{V^s}{k_{\mathrm{B}}TQ_N}\sum_{i=s+1}^{N}\int \nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{i}}|)\mathrm{e}^{-U_N/k_{\mathrm{B}}T}\mathrm{d}\mathbf{r}_{\mathbf{s+1}}\ldots\mathrm{d}\mathbf{r}_{\mathbf{N}}\\ &= -\frac{1}{k_{\mathrm{B}}T}\sum_{i=2}^{s}\nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{i}}|)\frac{V^s}{Q_N}\int \mathrm{e}^{-U_N/k_{\mathrm{B}}T}\mathrm{d}\mathbf{r}_{\mathbf{s+1}}\ldots\mathrm{d}\mathbf{r}_{\mathbf{N}}\\ &\quad -\frac{1}{k_{\mathrm{B}}T}\frac{N-s}{V}\int \nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{s+1}}|)\mathrm{d}\mathbf{r}_{\mathbf{s+1}}\frac{V^{s+1}}{Q_N}\int \mathrm{e}^{-U_N/k_{\mathrm{B}}T}\mathrm{d}\mathbf{r}_{\mathbf{s+2}}\ldots\mathrm{d}\mathbf{r}_{\mathbf{N}},\end{aligned}$$

where ∇_1 implies the derivative with respect to the position of molecule 1, that is, $\partial/\partial\mathbf{r}_{\mathbf{1}}$. We can replace the integrals on the right hand side of this expression using the correlation functions F_s and F_{s+1} (Eq. 13.22):

$$\begin{aligned}\nabla_{\mathbf{1}} F_s(\mathbf{r}_{\mathbf{1}},\ldots,\mathbf{r}_{\mathbf{s}}) &= -\frac{1}{k_{\mathrm{B}}T}F_s(\mathbf{r}_{\mathbf{1}},\ldots,\mathbf{r}_{\mathbf{s}})\sum_{i=2}^{s}\nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{i}}|)\\ &\quad -\frac{1}{k_{\mathrm{B}}T}\frac{N-s}{V}\int \nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{s+1}}|)F_{s+1}(\mathbf{r}_{\mathbf{1}},\ldots,\mathbf{r}_{\mathbf{s+1}})\mathrm{d}\mathbf{r}_{\mathbf{s+1}}\end{aligned}$$

or

$$\begin{aligned}k_B T\nabla_{\mathbf{1}} F_s(\mathbf{r}_{\mathbf{1}},\ldots,\mathbf{r}_{\mathbf{s}}) &= -F_s(\mathbf{r}_{\mathbf{1}},\ldots,\mathbf{r}_{\mathbf{s}})\sum_{i=2}^{s}\nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{i}}|)\\ &\quad -\frac{N-s}{V}\int \nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{s+1}}|)F_{s+1}(\mathbf{r}_{\mathbf{1}},\ldots,\mathbf{r}_{\mathbf{s+1}})\mathrm{d}\mathbf{r}_{\mathbf{s+1}}.\end{aligned}\tag{13.23}$$

This is the **Born–Green–Bogoliubov equation**. For $s=2$, it reduces to

$$\begin{aligned}k_{\mathrm{B}}T\nabla_{\mathbf{1}}\ln g(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{2}}|) &= -\nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{2}}|)\\ &\quad -\frac{N}{V}\int \nabla_{\mathbf{1}}\varphi(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{3}}|)\frac{F_3(\mathbf{r}_{\mathbf{1}},\mathbf{r}_{\mathbf{2}},\mathbf{r}_{\mathbf{3}})}{g(|\mathbf{r}_{\mathbf{1}}-\mathbf{r}_{\mathbf{2}}|)}\mathrm{d}\mathbf{r}_{\mathbf{3}}.\end{aligned}\tag{13.24}$$

This expression gives the relationship between the pair potential, the pair correlation function, and the three-body correlation function. This equation is exact. Unfortunately, Eq. (13.24) cannot be solved unless we know the three-body correlation function. To make it useful, we need another equation that express the three-particle correlation function in terms of the pair correlation function. Unfortunately, at present, no such exact expression is known. The simplest approximate form can be found using the **superposition approximation**. In this approximation, we assert

$$F_3(\mathbf{r}_{\mathbf{1}},\mathbf{r}_{\mathbf{2}},\mathbf{r}_{\mathbf{3}}) = F_2(\mathbf{r}_{\mathbf{1}},\mathbf{r}_{\mathbf{2}})F_2(\mathbf{r}_{\mathbf{1}},\mathbf{r}_{\mathbf{3}})F_2(\mathbf{r}_{\mathbf{2}},\mathbf{r}_{\mathbf{3}}).\tag{13.25}$$

Inserting this into Eq. (13.24), we obtain

$$k_B T \nabla_1 \ln g(|\mathbf{r}_1 - \mathbf{r}_2|) = -\nabla_1 \varphi(|\mathbf{r}_1 - \mathbf{r}_2|) \\ - \frac{N}{V}\int \nabla_1 \varphi(|\mathbf{r}_1 - \mathbf{r}_3|)\, g(|\mathbf{r}_1 - \mathbf{r}_3|) g(|\mathbf{r}_2 - \mathbf{r}_3|) \mathrm{d}\mathbf{r}_3. \qquad (13.26)$$

In order to evaluate the pair correlation function from this expression, it is convenient to introduce a new function:

$$E(x) = \int_\infty^x \varphi'(t) g(t) \mathrm{d}t. \qquad (13.27)$$

Taking derivatives of both sides of this equation, we obtain:

$$\nabla_1 E(|\mathbf{r}_1 - \mathbf{r}_3|) = \nabla_1 \varphi(|\mathbf{r}_1 - \mathbf{r}_3|) g(|\mathbf{r}_1 - \mathbf{r}_3|).$$

Inserting this relation into Eq. (13.26) yields

$$k_B T \nabla_1 \ln g(|\mathbf{r}_1 - \mathbf{r}_2|) = -\nabla_1 \varphi(|\mathbf{r}_1 - \mathbf{r}_2|) - \frac{N}{V}\int \nabla_1 E(|\mathbf{r}_1 - \mathbf{r}_3|) g(|\mathbf{r}_2 - \mathbf{r}_3|) \mathrm{d}\mathbf{r}_3.$$

Integrating this equation shows

$$k_B T \ln g(r) = -\varphi(r) - \frac{N}{V}\int E(|\mathbf{r} - \mathbf{r}'|) g(r') \mathrm{d}\mathbf{r}' + \text{const}. \qquad (13.28)$$

We can determine the value of the integration constant by considering what happens at large r. In this limit, ln g(r) → 0 and $\varphi(r) \to 0$. This implies

$$\text{const} = \frac{N}{V}\int E(|\mathbf{r} - \mathbf{r}'|) g(r') \mathrm{d}\mathbf{r}'. \qquad (13.29)$$

Since $E(x)$ is non-zero at small x, $E(|\mathbf{r} - \mathbf{r}'|)$ at $r \to \infty$ is only non-zero near $\mathbf{r}' \approx \mathbf{r}$. We now use the fact that $g(r') = 1$ at large r' to write

$$\text{const} = \frac{N}{V}\int E(|\mathbf{r} - \mathbf{r}'|) \mathrm{d}\mathbf{r}'.$$

Inserting this result into Eq. (13.28), we find:

$$k_B T \ln g(r) = -\varphi(r) - \frac{N}{V}\int E(|\mathbf{r} - \mathbf{r}'|)[g(r') - 1] \mathrm{d}\mathbf{r}'. \qquad (13.30)$$

In order to simplify the volume integral, we rewrite this expression in spherical coordinates:

$$k_B T \ln g(r) = -\varphi(r) - \frac{2\pi N}{V}\int_0^\infty [g(r') - 1] r'^2 \mathrm{d}r' \\ \times \int_0^\pi E\left(\sqrt{r^2 + r'^2 - 2rr'\cos\theta}\right) \sin\theta \, \mathrm{d}\theta.$$

This can be further simplified by switching the integration variable from θ to $t = \sqrt{r^2 + r'^2 - 2rr'\cos\theta}$:

$$k_B T \ln g(r) = -\varphi(r) - \frac{2\pi N}{V}\frac{1}{r}\int_0^\infty [g(r') - 1] r' \mathrm{d}\mathbf{r}' \int_{|r-r'|}^{r+r'} E(t) t \, \mathrm{d}t. \qquad (13.31)$$

This expression is an implicit equation for the pair correlation function in terms of only the pair potential, temperature, and density. It yields accurate results at low density but is poor at high densities.

13.2 Theory of non-ideal gases

To this point, when we worked with gases, we mainly focused on ideal gases. At room temperature and atmosphere pressure, most real gases behave as if they are ideal. However, at high pressure, this is not the case. Moreover, as we mentioned in Section 2.1, there is no difference between gases and liquids above the critical point. Obviously, the equation of state ($pV = NRT$) and other thermodynamic properties derived for ideal gases should not be applied under these conditions. In this section, we derive more general equations for gases and consider the critical point in more detail.

13.2.1 Van der Waals equation of state

We start by deriving the equation of state for a non-ideal gas. Since the case of simultaneous collision of three molecules in a gas (even a dense one) is rare, we can justifiably limit our consideration to pairwise interactions of gas molecules. As discussed in the previous sections, we can write the pair correlation function in the Born–Green–Bogoliubov formalism as

$$k_B T \ln g(r) = -\varphi(r) + \frac{N}{V} F(r),$$

where $F(r)$ is a function that only weakly depends on T and N/V (via the pair correlation function). We will consider only the low density (small N/V) limit. In this case, the previous equation can be rewritten as:

$$g(r) = \mathrm{e}^{-\varphi(r)/k_B T} \mathrm{e}^{(N/V)F(r)/k_B T} \approx \mathrm{e}^{-\varphi(r)/k_B T} \left(1 + \frac{N}{V k_B T} F(r)\right).$$

Inserting this expression into the exact equation of state (Eq. (13.21)),

$$p = \frac{N k_B T}{V} - \frac{2\pi}{3} \left(\frac{N}{V}\right)^2 \int_0^\infty \varphi'(r) g(r) r^3 \mathrm{d}r,$$

we find

$$\begin{aligned} p = \frac{N k_B T}{V} &- \frac{2\pi}{3} \left(\frac{N}{V}\right)^2 \int_0^\infty \varphi'(r) \mathrm{e}^{-\varphi(r)/kT} r^3 \mathrm{d}r \\ &- \frac{2\pi}{3} \left(\frac{N}{V}\right)^3 \frac{1}{k_B T} \int_0^\infty \varphi'(r) \mathrm{e}^{-\varphi(r)/k_B T} F(r) r^3 \mathrm{d}r. \end{aligned}$$

The first term on the right-hand side of this equation gives the equation of state of an ideal gas. The next two terms represent the first two corrections as we expand in powers of the density. Keeping only the first of these (i.e. that proportional to the square of the density), we obtain:

$$p = \frac{N k_B T}{V} - \frac{2\pi}{3} \left(\frac{N}{V}\right)^2 \int_0^\infty \varphi'(r) \mathrm{e}^{-\varphi(r)/k_B T} r^3 \mathrm{d}r.$$

Integration by parts gives

$$p = \frac{Nk_\mathrm{B}T}{V} + \frac{2\pi}{3}\left(\frac{N}{V}\right)^2 k_\mathrm{B}Tr^3(\mathrm{e}^{-\varphi(r)/k_\mathrm{B}T} - 1)\Big|_0^\infty - \frac{2\pi 3k_\mathrm{B}TN^2}{3V^2}$$
$$\times \int_0^\infty (\mathrm{e}^{-\varphi(r)/k_\mathrm{B}T} - 1)r^2\mathrm{d}r = \frac{Nk_\mathrm{B}T}{V} - \frac{2\pi N^2k_\mathrm{B}T}{V^2}\int_0^\infty (\mathrm{e}^{-\varphi(r)/k_\mathrm{B}T} - 1)r^2\mathrm{d}r.$$

Introducing a new constant

$$\beta_1 = 4\pi\int_0^\infty (\mathrm{e}^{-\varphi(r)/k_\mathrm{B}T} - 1)r^2\mathrm{d}r, \tag{13.32}$$

we obtain the equation of state in the following form:

$$p = \frac{Nk_\mathrm{B}T}{V} - \frac{N^2k_\mathrm{B}T}{2V^2}\beta_1. \tag{13.33}$$

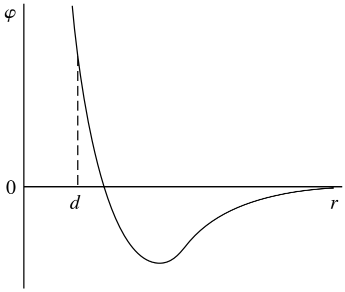


Fig. 13.2
A typical pair potential.

The parameter β_1 in this equation does not depend on density but does depend on temperature and the pair potential. We now attempt to simplify this equation by making some generic assumptions about the interatomic potential. For example, at very small r, $\varphi(r) \gg k_\mathrm{B}T$ (see Fig. 13.2) such that $\mathrm{e}^{-\varphi(r)/k_\mathrm{B}T} \approx 0$. At very large r, $|\varphi(r)| \ll k_\mathrm{B}T$ such that $\mathrm{e}^{-\varphi(r)/k_\mathrm{B}T} \approx 1 - \varphi(r)/k_\mathrm{B}T$. We now assume that for any r, we are in either one or the other of these limits. In this way, we can rewrite Eq. (13.32) as

$$\beta_1 = -4\pi\int_0^d r^2\,\mathrm{d}r - 4\pi\int_\mathrm{d}^\infty \frac{\varphi(r)}{k_\mathrm{B}T}r^2\,\mathrm{d}r = -\frac{4\pi d^3}{3} - \frac{4\pi}{k_\mathrm{B}T}\int_d^\infty \varphi(r)r^2\,\mathrm{d}r,$$

where d is the intermolecular separation where we divide between these two limits. Clearly, d is a measure of the molecule diameter. It is convenient to introduce two new constants

$$a = -2\pi\int_d^\infty \varphi(r)r^2\,\mathrm{d}r; \qquad b = \frac{2\pi d^3}{3} = 4v_0, \tag{13.34}$$

such that

$$\beta_1 = -2b + \frac{2a}{k_\mathrm{B}T}, \tag{13.35}$$

where v_0 is a measure of the volume of a molecule. The constants a and b depend only on inherent molecule properties and do not depend on the external parameters (V and T). The first constant characterizes the intermolecular interaction: $-N(N/V)a$ is the potential energy of a gas in which the molecules are in random locations but interact through the pair potential $\varphi(r)$. Since the potential energy of a non-ideal gas is lower than the potential energy of an ideal gas under the same conditions (our reference state), we conclude that $a > 0$. The second constant simply tells us the size of the molecules and hence $b > 0$. Inserting Eq. (13.35) into Eq. (13.33), we obtain the famous **van der Waals equation of state**:

$$p = \frac{Nk_\mathrm{B}T}{V} + \frac{N^2k_\mathrm{B}T}{V^2}b - \frac{N^2}{V^2}a. \tag{13.36}$$

The first term on the right side of this equation corresponds to an ideal gas; it is proportional to the gas density. The next two terms are corrections that are proportional to the square of the gas density. The first correction is associated with the fact that molecules have a finite volume; this decreases the volume in which the molecules are free to move and therefore, increases the pressure. This explains why this correction is always positive. The second correction is associated with the interaction between the gas molecules; this interaction provides some degree of bonding between gas molecules. Since any bonding between the molecules decreases the fraction of the time the molecules can move through the volume, this leads to a decrease in pressure (i.e. $a > 0$).

Review question

1. What is the physical meaning of parameters a and b in the van der Waals equation $p = (Nk_BT/V) + (N^2k_BT/V^2)b - (N^2/V^2)a$?

Example problem

1. Construct an expression for the Gibbs free energy of 1 mole of O_2 using the following handbook data: interatomic separation in O_2 is $r = 1.20735$ Å; the vibrational wavenumber is $\bar{\nu} = 1579.78$ cm; the van der Waals parameters are $a = 0.138$ J $m^3/mole^2$ and $b = 3.258 \cdot 10^{-5}\,m^3/mole$.

13.2.2 Critical point

We have already discussed the phase diagram of a one-component system (see Fig. 2.1 in Section 2.1) and derived the Clausius–Clapeyron equation, which describes the two-phase coexistence lines in the phase diagram, except for the gas–liquid line near the critical point. We now focus on the critical point. Since there is no difference between a gas and a liquid above the critical point, they must have the same equation of state there. Unfortunately, we have not yet found an equation of state for a liquid. On the other hand, the van der Waals equation,

$$p = \frac{Nk_BT}{V}\left(1 + \frac{Nb}{V}\right) - \frac{N^2a}{V^2}, \tag{13.37}$$

describes a non-ideal gas at high pressure. This expression does not account for the well-known fact that the pressure in a liquid gets extremely large when it is compressed by only a few percent from its equilibrium density (in this equation, $p \to \infty$ only when the density goes to infinity).

We can correct this problem by using a mathematical slight of hand. Recall that in our derivation of the van der Waals equation, we performed an expansion in small values of the density, N/V, only retaining the leading order term. To the same level of approximation, we can rewrite Eq. (13.37) as

$$p = \frac{Nk_{\mathrm{B}}T}{V(1-(Nb/V))} - \frac{N^2a}{V^2}, \tag{13.38}$$

since both Eqs (13.37) and (13.38) are exactly identical to leading order in the density. This new version of the van der Waals equation of state has the feature that $p \to \infty$ as $V/N \to b$. Thus, Eq (13.38) reduces to the van der Waals equation at low density and exhibits small compressibility at large densities. Therefore, we will use this equation to describe fluids in general, that is, both gases and liquids.

Figure 13.3 shows the isotherms predicted by Eq. (13.38) at several temperatures. At high temperature, the isotherms are monotonically decreasing functions of volume and at low temperature, the isotherms exhibit two extrema. The interesting feature is that at low temperature, there are conditions for which $(\partial p/\partial V)_T > 0$ (segment *BCD* in Fig. 13.3). $(\partial p/\partial V)_T > 0$ is indicative of a thermodynamic instability. Therefore, we are forced to conclude that at low temperatures, the isotherms must each split into two separate parts: the high density branch *AB* corresponds to a liquid and the low density branch *DE* corresponds to a gas. This means that if we construct a system with an intermediate volume in the range *BD*, the system will phase separate into a liquid and a gas.

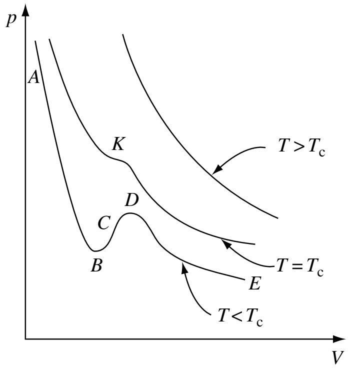


Fig. 13.3
Isotherms obtained from Eq. (13.38).

The critical temperature is the temperature at which the liquid and gas are indistinguishable. This occurs when the extrema in Fig. 13.3 disappear upon heating the system. At any temperature below T_{c}, we can find the two extrema (V_1, V_2) by setting $\partial p/\partial V = 0$. The critical temperature is the temperature for which $V_1 = V_2 = V_{\mathrm{c}}$. At this point, $\partial^2 p/\partial V^2 = 0$. Inserting Eq. (13.38) into these relations implies

$$\frac{\partial p}{\partial V} = -\frac{Nk_{\mathrm{B}}T_c}{(V_{\mathrm{c}} - Nb)^2} + \frac{2N^2a}{V_{\mathrm{c}}^3} = 0; \qquad \frac{\partial^2 p}{\partial V^2} = \frac{2Nk_{\mathrm{B}}T_{\mathrm{c}}}{(V_{\mathrm{c}} - Nb)^3} - \frac{6N^2a}{V_{\mathrm{c}}^4} = 0.$$

Solving these equations for T_{c} and V_{c}, we find:

$$T_{\mathrm{c}} = \frac{8}{27}\frac{a}{bk_{\mathrm{B}}} \tag{13.39}$$

and

$$V_{\mathrm{c}} = 3Nb. \tag{13.40}$$

Inserting these values back into Eq. (13.38), demonstrates that

$$p_{\mathrm{c}} = \frac{1}{27}\frac{a}{b^2}. \tag{13.41}$$

All three quantities, T_{c}, V_{c}, and p_{c} can be obtained from experiment. Any two of these can be used to determine *a* and *b* from the van der Waals equation. The third parameter provides a consistency check on the validity of the van der Waals equation of state. Usually, the agreement is within an order of magnitude. This shows that the van der Waals equation is reasonable, although not quantitatively accurate. This comes as no surprise given all of the assumptions we made to get here.

Example problem

1. For oxygen, $V_c = 97.74\ \text{cm}^3/\text{mole}$ and $T_c = -118.82°\text{C}$. Find p_c.

13.2.3 Principle of corresponding states

Since the critical point parameters (T_c, p_c, V_c) can be determined from experiment, it is convenient to recast the van der Waals equation in a form where the external parameters are scaled by these quantities. First, we introduce the following dimensionless variables:

$$\pi = \frac{p}{p_c}; \qquad \tau = \frac{T}{T_c}; \qquad \omega = \frac{V}{V_c}. \tag{13.42}$$

The state parameters can be written as (see Eqs (13.39)–(13.41)):

$$\begin{aligned} p &= \pi p_c = \frac{1}{27}\frac{a}{b^2}\pi \\ T &= \tau T_c = \frac{8}{27}\frac{a}{k_B b}\tau \\ V &= \omega V_c = 3Nb\omega. \end{aligned} \tag{13.43}$$

Using these relations, we can rewrite Eq. (13.38) as

$$8\tau = \left(\pi + \frac{3}{\omega^2}\right)(3\omega - 1). \tag{13.44}$$

This result is fascinating because it contains no materials parameters. It implies that all fluids can be described using the same universal equation of state. The fact that all fluids at the same dimensionless volume and temperature have the same dimensionless pressure is a statement of the **principle of corresponding states.** While we derived this result based upon the van der Waals equation of state, the same statement can be made on the basis of more sophisticated equations of state. Although this principle is not a mathematically exact statement, it is found to work surprisingly well for a very large variety of gases. In the next section, we will use this principle to solve a practical problem.

13.2.4 Fugacity

When we considered the thermodynamics of gas phase reactions in Section 5.2, we derived the van't Hoff isotherm from the following form of the chemical potential

$$\mu = \mu^0 + RT \ln p, \tag{13.45}$$

which was in turn obtained from the equation of state of ideal gases

$$pV = NRT, \tag{13.46}$$

Table 13.1 Experimental data for the reaction in Eq. (13.47)

p(atm)	1	10	30	50	100	300	600	1000
$p^2_{NH_3}/(p^3_{H_2}p_{N_2})$	42.1	42.9	45.0	47.1	51.8	76.3	163.8	519.8

(see Section 1.5.1). Since we already know that this equation is not valid at high pressure, all equations based upon it are suspect at high pressures. As an example, consider the following reaction

$$N_2 + 3H_2 \rightarrow 2NH_3. \tag{13.47}$$

If all species were ideal gases, the equilibrium constant of this reaction would take the following form:

$$K_p^0 = \frac{p^2_{NH_3}}{p^3_{H_2}p_{N_2}} = \frac{1}{p^2}\frac{x^2_{NH_3}}{x^3_{H_2}x_{N_2}}, \tag{13.48}$$

where the superscript 0 implies that we are only confident in the validity of this expression at low pressure. Experimental values of the $p^2_{NH_3}/(p^3_{H_2}p_{N_2})$ at equilibrium at $T = 450°C$ are shown in Table 13.1. These data show that $p^2_{NH_3}/(p^3_{H_2}p_{N_2})$ is nearly independent of the total pressure for $p < 10$ atm, but varies strongly with pressure at large total pressure. Hence, we cannot determine the equilibrium constant as in Eq. (13.48) at high pressure.

In order to adopt the thermodynamic equations to the high pressures, we introduce a new thermodynamic function, the **fugacity** f, as

$$\mu = \mu^0 + RT \ln f. \tag{13.49}$$

This equation must reduce to Eq. (13.45) in the $p \rightarrow 0$ limit, where all gases are ideal. Therefore, $f \rightarrow p$ in this limit. Now, consider a mixture of two gases. In spite of the fact that the gases are not ideal, we will assume that they form an ideal solution, that is,

$$\begin{aligned} &\Delta H_{mix} = 0; \qquad \Delta V_{mix} = 0; \\ &\Delta S_{mix} = -(n_1 + n_2)RT(x_1 \ln x_1 + x_2 \ln x_2), \end{aligned} \tag{13.50}$$

where n_i and x_i are number of moles and molar fraction of component i in the gas. The Gibbs free energy of this mixture is

$$\begin{aligned} G = {} & n_1\left(\mu_1^0 + RT \ln f_1^0\right) + n_2\left(\mu_2^0 + RT \ln f_2^0\right) \\ & + (n_1 + n_2)RT(x_1 \ln x_1 + x_2 \ln x_2). \end{aligned}$$

Differentiating this expression with respect to n_i at constant $n_{j \neq i}$, we obtain:

$$\mu_i = \mu_i^0 + RT \ln f_i^0 + RT \ln x_i = \mu_i^0 + RT \ln f_i \tag{13.51}$$

where

$$f_i = x_i f_i^0, \tag{13.52}$$

and f_i^0 is the fugacity of pure i at the pressure which is equal to the total pressure in the mixture. Comparison of Eqs (13.45) and (13.51) suggests that the only change in going from ideal to non-ideal gases is to replace the partial pressure with the fugacity.

By analogy with the activity coefficient in solutions (see Eq. (3.68)), we can also define the **fugacity coefficient** as

$$\gamma_i = f_i / p_i. \tag{13.53}$$

Using this new variable, we can write the equilibrium constant of the reaction in Eq. (13.47) as

$$K_p = \frac{p^2_{\mathrm{NH_3}}}{p^3_{\mathrm{H_2}} p_{\mathrm{N_2}}} \frac{\gamma^2_{\mathrm{NH_3}}}{\gamma^3_{\mathrm{H_2}} \gamma_{\mathrm{N_2}}}. \tag{13.54}$$

Note that this expression reduces to Eq. (13.48) when $p \to 0$.

Although we now have a more robust thermodynamic description of reactions in gases at high pressures, it is of little practical consequence until we learn how to determine the fugacity. As always, phenomenological thermodynamics provides no guidance in such situations, so we will have to resort to other means to determine the fugacity. We discuss two such approaches below: a method based upon the van der Waals equation of state and a more practical method based upon the principle of corresponding states.

The van der Waals equation of state for 1 mole of a gas takes the following form (cf. Eq. (13.38)):

$$p = \frac{RT}{V-b} - \frac{a}{V^2}, \tag{13.55}$$

where V and b are expressed in $\mathrm{m^3}$/mole and a in $(\mathrm{J\ m^3})/\mathrm{mole^2}$. In order to find the fugacity, we start from the following general thermodynamic relation:

$$\left(\frac{\partial A}{\partial V}\right)_T = -p.$$

For an ideal gas

$$\left(\frac{\partial A_{\mathrm{ideal}}}{\partial V}\right)_T = -p_{\mathrm{ideal}},$$

where p_{ideal} is the pressure in an ideal gas at the same V and T. Subtracting the second relation from the first, we find

$$\left(\frac{\partial (A - A_{\mathrm{ideal}})}{\partial V}\right)_T = -(p - p_{\mathrm{ideal}}).$$

Integrating both sides of this equation, we obtain

$$\int_0^{A - A_{\mathrm{ideal}}} \mathrm{d}(A - A_{\mathrm{ideal}}) = \int_\infty^V (p_{\mathrm{ideal}} - p)\,\mathrm{d}V$$

$$A = A_{\mathrm{ideal}} + \int_\infty^V \left(\frac{RT}{V} - \frac{RT}{V-b} + \frac{a}{V^2}\right)\mathrm{d}V = A_{\mathrm{ideal}} + RT \ln \frac{V}{V-b} - \frac{a}{V},$$

where we used the fact that $(A - A_{\text{ideal}}) \to 0$ as $V \to \infty$. Since we calculated the Helmholtz free energy per mole of a pure substance, the Gibbs free energy and chemical potential (these are identical since we are working with 1 mole of a pure substance) can be obtained by adding pV:

$$\mu = A + pV = A_{\text{ideal}} + RT \ln \frac{V}{V-b} - \frac{a}{V} + pV.$$

For an ideal gas, $pV = RT$, hence,

$$\mu_{\text{ideal}} = A_{\text{ideal}} + pV = A_{\text{ideal}} + RT$$

$$A_{\text{ideal}} = \mu_{\text{ideal}} - RT = \mu^0 + RT \ln\, p - RT = \mu^0 + RT \ln \frac{RT}{V} - RT.$$

Inserting this result into the expression for μ yields

$$\begin{aligned}\mu &= \mu^0 + RT \ln \frac{RT}{V} - RT + RT \ln \frac{V}{V-b} - \frac{a}{V} + \frac{RTV}{V-b} - \frac{a}{V}\\ &= \mu^0 + RT \ln \frac{RT}{V-b} + RT \frac{b}{V-b} - \frac{2a}{V}.\end{aligned}$$

Finally, comparing this result with Eq. (13.49) leads to the conclusion that

$$\ln f = \ln \frac{RT}{V-b} + \frac{b}{V-b} - \frac{2a}{VRT}. \tag{13.56}$$

Since this expression is based upon the van der Waals equation of state, it too must be viewed as approximate. We could, however, apply the same approach for any equation of state.

Another approach to determining the fugacity uses the principle of corresponding states. An obvious extension of this principle leads to the conclusion that if two gases have the same values of π and τ, they also have the same fugacities. Many handbooks tabulate the coefficients of fugacity obtained from experimental data in this manner. In order to illustrate this method we return to the reaction in Eq. (13.47). Table 13.2 provides the requisite data for all species participating in this reaction. π and τ are calculated for $T = 450°\text{C}$ and $p = 300$ atm. Assuming that $K_p = 42.1$ (the value at the smallest pressure in Table 13.1), we obtain:

$$\frac{p^2_{\text{NH}_3}}{p^3_{\text{H}_2} p_{\text{N}_2}} = K_p \left(\frac{\gamma^2_{\text{NH}_3}}{\gamma^3_{\text{H}_2} \gamma_{\text{N}_2}} \right)^{-1} = 42.1 \frac{1.13 \cdot 1.12^2}{0.91^3} = 80.7.$$

This value is close to that in Table 13.1 for $p = 300$ atm.

Table 13.2 Handbook data for the species participating in the reaction in Eq. (13.47)

Species	p_c (atm)	T_c (K)	π	τ	γ
N_2	33.6	126.3	8.9	5.73	1.13
H_2	12.7	33.0	23.6	21.9	1.12
NH_3	111.4	405.5	2.7	1.78	0.91

Review question

1. Consider the following reaction

$$\mathrm{CO} + \mathrm{H_2} \rightarrow \mathrm{HCOH}.$$

At small pressures, its equilibrium constant takes the following form:

$$K_p = \frac{\mathrm{p_{HCOH}}}{\mathrm{p_{CO}p_{H_2}}}$$

and at high pressure the equilibrium constant is

$$K_f = \frac{f_{\mathrm{HCOH}}}{f_{\mathrm{CO}}f_{\mathrm{H_2}}}.$$

What is the relation between these two quantities?

13.3 Statistical thermodynamics of solids

13.3.1 Lattice vibrations

In contrast with liquids and gases, the most important contribution of the motion of atoms in crystals to the thermodynamic functions is associated with their vibrations around their equilibrium lattice sites. The same applies to amorphous materials, except that the equilibrium sites are not arranged in a periodic manner. Therefore, we can consider any solid consisting of N atoms as a set of $3N$ independent oscillators.[1] Therefore, we can express the Helmholtz free energy of a solid as (cf. Eq. 12.68)):

$$A = N\varepsilon_0 + k_{\mathrm{B}}T\sum_{\alpha} \ln\left(1 - \mathrm{e}^{-\hbar\omega_\alpha/k_{\mathrm{B}}T}\right), \qquad (13.57)$$

where $N\varepsilon_0$ is the energy of the atoms sitting still on their equilibrium positions and the summation is performed over all $3N$ vibrational degrees of freedom. All of the other thermodynamic functions can be obtained from this expression provided that we know the vibrational spectrum (the set of ω_α). However, this spectrum depends on the symmetry of the crystal lattice (or the structure of an amorphous material) and the interatomic bonding. The determination of this spectrum is a topic in condensed matter physics and is, to our great sadness, beyond the scope of this text. Our goal here is much more modest. We will examine the low and high temperature limiting cases and then interpolate between them, as suggested by Debye (1912).

13.3.2 Low temperature limit

At low temperatures, the only vibrational frequencies that make a significant contribution to the free energy are those for which $\omega_\alpha \sim k_{\mathrm{B}}T/\hbar$ or

---

[1] Strictly speaking the number of oscillators is $3N-6$. The six missing degrees of freedom are associated with translation and rotation of the whole crystal. Since $N \gg 6$, it is often neglected relative to $3N$. Although the vibrations of an atom and its neighbors are not independent, there are $3N-6$ independent collective vibrational modes.

less (see Eq. (13.57)). These low frequencies correspond to sound waves with the wavelength $\lambda \sim c/\omega$, where c is the speed of sound. Therefore, in this approach, we define low temperatures as

$$T \approx \frac{\hbar\omega}{k_{\mathrm{B}}} \approx \frac{\hbar c}{k_{\mathrm{B}}\lambda} \ll \frac{\hbar c}{k_{\mathrm{B}}a}, \tag{13.58}$$

where a is a typical nearest neighbor separation. For simplicity, we will assume that the solid is isotropic (this applies to amorphous materials, but rarely to crystals). In the isotropic case, there is one longitudinal sound wave (velocity c_1) and two transverse sound waves (c_{t}).[2] The corresponding vibrational frequencies are $\omega_1 = c_1\mathrm{k}$ and $\omega_{\mathrm{t}} = c_{\mathrm{t}}\mathrm{k}$, where $\mathbf{k}$ is the wave vector. In our analysis, we ignore the discrete atomic structure of the solid and view it as a continuous medium. It is important to remember that this is reasonable for the long wavelengths ($\lambda \gg a$)/low frequencies discussed here.

Consider a solid sample in the form of a parallelepiped with edges A, B, and C. If the system is a perfect crystal, we assume that this sample is periodically repeated through all of space (i.e. we use periodic boundary conditions).[3] This is reasonable also for an amorphous material provided that these edge lengths are very much larger than the typical intermolecular spacing. A plane wave $\mathrm{e}^{ik_x x}$ must satisfy the following periodicity requirement:

$$\mathrm{e}^{ik_x x} = \mathrm{e}^{ik_x(x+A)}.$$

Therefore,

$$\mathrm{e}^{ik_x A} = 1$$

and

$$k_x = \frac{2\pi n_x}{A}, \tag{13.59}$$

where n_x is an integer. This equation demonstrates that the number of possible values of k_x in the interval $\mathrm{d}k_x$ is not infinite but equal to $\mathrm{d}n_x = (A/2\pi)\mathrm{d}k_x$. The number of possible wave vectors between $\mathbf{k}$ to $\mathbf{k} + \mathrm{d}\mathbf{k}$ is

$$\mathrm{d}n = \mathrm{d}n_x\mathrm{d}n_y\mathrm{d}n_z = \frac{ABC}{(2\pi)^3}\mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z.$$

Rewriting this expression in spherical coordinates yields

$$\mathrm{d}n = \frac{V}{2\pi^2}k^2\mathrm{dk}, \tag{13.60}$$

where $ABC = V$. Since there are one longitudinal and two transverse sound waves corresponding to each wave vector in the interval, the total number of vibrational states in this range is

$$\mathrm{d}n = \frac{V}{2\pi^2}\left(\frac{\omega^2}{c_l^2}\frac{\mathrm{d}\omega}{c_l} + \frac{2\omega^2}{c_{\mathrm{t}}^2}\frac{\mathrm{d}\omega}{c_t}\right).$$

---

[2] Elastic theory of vibrations in crystals is not explicitly considered herein.

[3] The atoms on the top of the parallelepiped interact with atoms on its bottom, atoms on the right edge interact with atoms on the left edge, etc., as in a torus.

Introducing the average sound velocity

$$\frac{3}{\bar{c}^3} = \frac{1}{c_l^3} + \frac{2}{c_t^3}, \tag{13.61}$$

we obtain the following phonon (vibrational) spectrum

$$\mathrm{d}n = \frac{3V}{2\pi^2\bar{c}^3}\omega^2\mathrm{d}\omega. \tag{13.62}$$

Note that this formula is also valid for crystals even though the averaging must be performed differently because of anisotropy.

As discussed above, at low temperatures, only the low frequency end of the vibrational spectrum is important in determining thermodynamic properties. This is given by Eq. (13.62). Inserting Eq. (13.62) into Eq. (13.57) and replacing the summation by an integration, we find

$$A = N\varepsilon_0 + kT\frac{3V}{2\pi^2\bar{u}^3}\int_0^{\omega_{\max}} \ln\left(1 - \mathrm{e}^{-\hbar\omega/k_\mathrm{B}T}\right)\omega^2\mathrm{d}\omega. \tag{13.63}$$

Since the integral converges quickly, we need not be concerned about the value of $\omega_{\max}$ and can set it to infinity. We can integrate the second term on the right in Eq. (13.63) by parts to obtain

$$\begin{aligned}\int_0^\infty \ln\left(1 - \mathrm{e}^{-\hbar\omega/k_\mathrm{B}T}\right)\omega^2\mathrm{d}\omega &= \frac{\omega^3}{3}\ln\left(1 - \mathrm{e}^{-\hbar\omega/k_\mathrm{B}T}\right)\Big|_0^\infty \\ &\quad - \frac{\hbar}{3k_\mathrm{B}T}\int_0^\infty \frac{\mathrm{e}^{-\hbar\omega/k_\mathrm{B}T}}{1 - \mathrm{e}^{-\hbar\omega/k_\mathrm{B}T}}\,\omega^3\mathrm{d}\omega.\end{aligned}$$

The first term on the right side is zero. The second term is

$$\begin{aligned}\int_0^\infty \frac{\mathrm{e}^{-\hbar\omega/kT}}{1 - \mathrm{e}^{-\hbar\omega/kT_\mathrm{B}}}\,\omega^3\mathrm{d}\omega &= \int_0^\infty \frac{\omega^3}{\mathrm{e}^{\hbar\omega/k_\mathrm{B}T} - 1}\mathrm{d}\omega \\ &= \left(\frac{k_\mathrm{B}T}{\hbar}\right)^4\int_0^\infty \frac{x^3}{\mathrm{e}^x - 1}\mathrm{d}x = \left(\frac{k_\mathrm{B}T}{\hbar}\right)^4\frac{\pi^4}{15}.\end{aligned}$$

Inserting this into Eq. (13.63), we finally find

$$A = N\varepsilon_0 - \frac{\pi^2k_\mathrm{B}^4}{30(\hbar\bar{u})^3}VT^4. \tag{13.64}$$

Other thermodynamic functions can be determined as

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = \frac{2\pi^2k_\mathrm{B}^4}{15(\hbar\bar{u})^3}VT^3 \tag{13.65}$$

$$U = A + TS = N\varepsilon_0 + \frac{\pi^2k_\mathrm{B}^4}{10(\hbar\bar{u})^3}VT^4 \tag{13.66}$$

$$c_\mathrm{V} = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{2\pi^2k_\mathrm{B}^4}{5(\hbar\bar{u})^3}VT^3. \tag{13.67}$$

That $c_\mathrm{V} \sim T^3$ is a well-known result seen in experiments at low temperatures.

13.3.3 High temperature limit

By analogy with Eq. (13.58), the high temperature limit applies when

$$k_{\mathrm{B}}T \gg \hbar\omega. \tag{13.68}$$

Expanding the exponential in Eq. (13.57) and retaining only the leading order term, we find:

$$A = N\varepsilon_0 + kT\sum_{\alpha} \ln \frac{\hbar\omega_\alpha}{k_{\mathrm{B}}T}. \tag{13.69}$$

Introducing the mean frequency as

$$\ln \overline{\omega} = \frac{1}{3N}\sum_{\alpha} \ln \omega_\alpha, \tag{13.70}$$

we can rewrite Eq. (13.69) as

$$\begin{aligned} A &= N\varepsilon_0 + k_{\mathrm{B}}T\left(\sum_{\alpha} \ln \frac{\hbar}{k_{\mathrm{B}}T} + 3N\ \ln \overline{\omega}\right) \\ &= N\varepsilon_0 + 3Nk_{\mathrm{B}}T \ln \frac{\hbar}{k_{\mathrm{B}}} - 3Nk_{\mathrm{B}}T \ln T + 3Nk_{\mathrm{B}}T \ln \bar{\omega} \end{aligned}$$

or

$$A = N\varepsilon_0 - 3Nk_{\mathrm{B}}T \ln T + 3Nk_{\mathrm{B}}T \ln \frac{\hbar\overline{\omega}}{k_{\mathrm{B}}}. \tag{13.71}$$

The other thermodynamic functions can be obtained from this:

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = 3Nk_{\mathrm{B}}(1 + \ln T) - 3Nk_{\mathrm{B}} \ln \frac{\hbar\overline{\omega}}{k_{\mathrm{B}}}$$

or

$$S = 3Nk_{\mathrm{B}} \ln T - 3Nk_{\mathrm{B}} \ln \frac{\hbar\overline{\omega}}{k_{\mathrm{B}}e} \tag{13.72}$$

$$U = A + TS = N\varepsilon_0 + 3Nk_{\mathrm{B}}T \tag{13.73}$$

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_V = 3Nk_{\mathrm{B}}. \tag{13.74}$$

The last expression is exactly the classical result: each vibrational degree of freedom contributes k_{B} to the heat capacity.

13.3.4 Debye's interpolation

Now that we have derived expressions for the contributions to the thermodynamic properties of solids at high and low temperatures, it is of interest to determine these properties at intermediate temperatures.

While this requires the determination of the entire vibrational spectrum of the solid (which is not discussed in this text), we will employ a simpler, interpolation method proposed by Debye. We start by recalling that the low temperature results follow simply from the form of the phonon spectrum in Eq. (13.62). At high temperatures, the only important point is that the total number of oscillators is $3N$. The simplest way to retain both of these features is to describe the phonon spectrum using Eq. (13.62) but to cut it off at a maximum frequency $\omega_{\max}$, which is determined from the condition that the total number of vibrational modes is $3N$. This condition takes the following form:

$$3N = \frac{3V}{2\pi^2 \bar{c}^3} \int_0^{\omega_{\max}} \omega^2 \, \mathrm{d}\omega = \frac{3V}{2\pi^2 \bar{c}^3} \frac{\omega_{\max}^3}{3}$$

or

$$\omega_{\max} = \left(\frac{6\pi^2 N}{V} \right)^{1/3} \bar{c}. \tag{13.75}$$

Introducing the Debye temperature, Θ, as

$$\Theta = \frac{\hbar \omega_{\max}}{k_{\mathrm{B}}}, \tag{13.76}$$

we can rewrite Eq. (13.57):

$$A = N\varepsilon_0 + k_{\mathrm{B}} T \int_0^{\omega_{\max}} \frac{3V}{2\pi^2 \, \bar{c}^3} \ln\left(1 - \mathrm{e}^{-\hbar\omega/k_{\mathrm{B}}T}\right) \omega^2 \mathrm{d}\omega.$$

Using Eq. (13.75), we can then make the following substitution:

$$\frac{3V}{2\pi^2 \bar{c}^3} = \frac{9N}{\omega_{\max}^3}.$$

Next, we switch integration variables from ω to

$$z = \frac{\hbar\omega}{k_{\mathrm{B}} T},$$

such that the Helmholtz free energy becomes

$$\begin{aligned} A &= N\varepsilon_0 + k_{\mathrm{B}} T \frac{9N}{\omega_{\max}^3} \left(\frac{k_{\mathrm{B}} T}{\hbar} \right)^3 \int_0^{\Theta/T} \ln(1 - \mathrm{e}^{-z}) \, z^2 \mathrm{d}z \\ &= N\varepsilon_0 + 9Nk_{\mathrm{B}} T \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \ln(1 - \mathrm{e}^{-z}) \, z^2 \mathrm{d}z. \end{aligned}$$

Integration by parts yields

$$A = N\varepsilon_0 + 9NkT \left(\frac{T}{\Theta} \right)^3 \left(\frac{z^3}{3} \ln(1 - \mathrm{e}^{-z}) \Big|_0^{\Theta/T} - \frac{1}{3} \int_0^{\Theta/T} \frac{z^3}{\mathrm{e}^z - 1} \mathrm{d}z \right).$$

In order to write this expression in a simpler form, we introduce the Debye function

$$D(x) = \frac{3}{x^3}\int_0^x \frac{z^3}{\mathrm{e}^z - 1}\,\mathrm{d}z. \tag{13.77a}$$

Its derivative is

$$D'(x) = -\frac{9}{x^4}\int_0^x \frac{z^3}{\mathrm{e}^z - 1}\,\mathrm{d}z + \frac{3}{x^3}\frac{x^3}{\mathrm{e}^x - 1} = -\frac{3}{x}D(x) + \frac{3}{\mathrm{e}^x - 1}. \tag{13.77b}$$

Replacing the remaining integral in the Helmholtz free energy using the Debye function yields

$$A = N\varepsilon_0 + Nk_\mathrm{B}T\left\{3\ln\left(1 - \mathrm{e}^{-\Theta/T}\right) - D\left(\frac{\Theta}{T}\right)\right\}. \tag{13.78}$$

From this, we obtain the energy:

$$U = -T^2\left(\frac{\partial A/T}{\partial T}\right)_V = N\varepsilon_0 - Nk_\mathrm{B}T^2\left\{-\frac{3}{\mathrm{e}^{\Theta/T} - 1}\frac{\Theta}{T^2} - D'\left(\frac{\Theta}{T}\right)\right\}.$$

The derivative in this expression can be rewritten using

$$\frac{\partial}{\partial T} = \frac{\partial}{\partial(\Theta/T)}\frac{\mathrm{d}\Theta/T}{\mathrm{d}T} = -\frac{\Theta}{T^2}\frac{\partial}{\partial(\Theta/T)}.$$

This identity, together with Eq. (13.77b) allows us to write

$$U = N\varepsilon_0 + Nk_\mathrm{B}\Theta\frac{3}{\mathrm{e}^{\Theta/T} - 1} + Nk_\mathrm{B}T^2\left\{-\frac{3D(\Theta/T)}{\Theta/T} + \frac{3}{\mathrm{e}^{\Theta/T} - 1}\right\}\left(-\frac{\Theta}{T^2}\right)$$

or

$$U = N\varepsilon_0 + 3Nk_\mathrm{B}TD\left(\frac{\Theta}{T}\right). \tag{13.79}$$

Finally,

$$c_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_\mathrm{B}\left\{D\left(\frac{\Theta}{T}\right) + T\frac{\partial}{\partial T}D\left(\frac{\Theta}{T}\right)\right\}$$

or

$$c_V = 3Nk_\mathrm{B}\left\{D\left(\frac{\Theta}{T}\right) - \frac{\Theta}{T}D'\left(\frac{\Theta}{T}\right)\right\}. \tag{13.80}$$

Figure 13.4 shows the heat capacity as a function of temperature. The Debye temperature is a materials property and is given in Table 13.3 for

Table 13.3 The Debye temperature for several solids

Substance	Pb	Ag	KBr	NaCl	Diamond	H_2O
θ (K)	90	210	180	280	2000	192

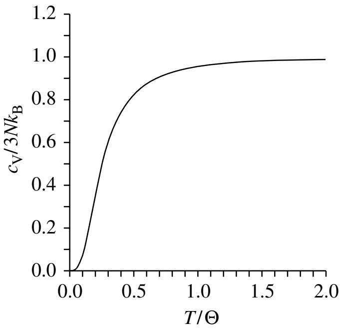


Fig. 13.4
The heat capacity in the Debye model.

several materials. Examination of this table shows that the Debye temperature for most condensed systems is below room temperature (although there are notable exceptions) and therefore, the high temperature limit is widely applicable. This is in agreement with the empirical rule proposed by Dulong and Petit: the heat capacity of 1 mole of atoms of any condensed substance is approximately $3R = 24.9$ J/(mole K) (see also Section 1.4.2).

13.4 Statistical thermodynamics of solutions

In this section, we consider several statistical theories for the thermodynamic properties of solutions. Some of these theories were already discussed in Chapter 3. In such cases, our goal is to derive some of the fundamental equations that we simply postulated above. This should provide new insight into the physical nature of solutions. We then discuss some (hopefully) interesting extensions to these theories.

13.4.1 Ideal dilute solutions

Recall that the main idea underlying the theory of ideal dilute solutions is that the probability two solute molecules come in contact with one another is sufficiently small that it can be ignored, such that solute molecules only have solvent molecule nearby. This means that the change in energy $\alpha(p,T,N_1)$ associated with the addition of a single solute molecule to the solution does not depend on the number of solute molecules already present. In order to construct an expression for the Gibbs free energy, we must be cognizant of the fact that solute molecules are indistinguishable. This decreases the number of physically distinguishable states by a factor of $N_2!$ and, therefore, decreases the partition function by a factor of $\mathrm{N}_2!$. Since $A = -k_\mathrm{B}T \ln Z$, indistinguishability increases the free energy of the solution by $kT \ln N_2!$. Therefore, the Gibbs free energy of the solution can be written as:

$$G = N_1\mu_1^0(p,T) + N_2\alpha(p,T,N_1) + k_\mathrm{B}T \ln N_2!, \tag{13.81}$$

where $\mu_1^0(p,T)$ is the chemical potential of the pure solvent (recall that the Gibbs free energy of a one-component system is always the product of the chemical potential and the number of atoms (of moles)—see Section 1.5.1). Applying Stirling's approximation, $\ln N! = N \ln N - N = N \ln(N/e)$, we obtain:

$$G = N_1\mu_1^0(p,T) + N_2 k_\mathrm{B}T \ln\left\{\frac{N_2}{e}\,\mathrm{e}^{\alpha(p,T,N_1)/k_\mathrm{B}T}\right\}.$$

In order to find the corresponding chemical potentials, the Gibbs free energy should be written as an explicit function of the number of atoms. To this end, we note that as with any extensive property, the Gibbs free energy must be a homogeneous function of the numbers of moles of all of its components (see Section 3.1). We can satisfy this requirement, if and only if

$$\mathrm{e}^{\alpha(p,T,N_1)/k_\mathrm{B}T} = \beta(p,T)/N_1,$$

where $\beta(p,T)$ is a function that depends on the properties of the solvent and solute but not on the solute concentration. Therefore,

$$G = N_1\mu_1^0(p,T) + N_2k_BT\ln\frac{N_2}{eN_1} + N_2k_BT\ln\beta(p,T).$$

Introducing a new function

$$\psi(p,T) = k_BT\ln\beta(p,T), \tag{13.82}$$

we obtain:

$$G = N_1\mu_1^0(p,T) + N_2k_BT\ln\frac{N_2}{eN_1} + N_2\psi(p,T). \tag{13.83}$$

We can now, write the chemical potential of the solvent as

$$\mu_1 = \left(\frac{\partial G}{\partial N_1}\right)_{p,T,N_2} = \mu_1^0 - k_BT\frac{N_2}{N_1} \approx \mu_1^0 - k_BTx_2 \approx \mu_1^0 + k_BT\ln(1-x_2)$$

or

$$\mu_1 = \mu_1^0 + k_BT\ln x_1 \tag{13.84}$$

In the equation preceding Eq. (13.84), we replaced $-x_2$ with $\ln(1-x_2)$ to get the result into a form that is widely seen in phenomenological thermodynamics (this substitution works because x_2 is small). For the chemical potential of the solute, we obtain:

$$\mu_2 = \left(\frac{\partial G}{\partial N_2}\right)_{p,T,N_1} = k_BT\ln\frac{N_2}{eN_1} + k_BT + \psi = \psi + k_BT\ln\frac{N_2}{N_1}$$

or

$$\mu_2 = \psi + k_BT\ln x_2. \tag{13.85}$$

These chemical potentials are exactly those obtained in Section 3.2.1, except that these are expressed per atom rather than per mole. In Section 3.2.1 these results were a consequence of the Henry law, which was postulated based upon a wide range of experimental observations. Recall that all remaining properties of ideal dilute solutions can be obtained from these expressions for the chemical potentials (see Section 3.2).

Review question

1. What is the meaning of the term $k_BT\ln N_2!$ in the expression for the Gibbs free energy for ideal dilute solutions $G = N_1\mu_1^0(p,T) + N_2\alpha(p,T,N_1) + k_BT\ln N_2!$?

13.4.2 Substitutional solutions

In this section, we focus on substitutional solutions. Such solutions usually form in systems in which the solute and solvent atoms (molecules) have approximately the same size. In our discussion of such solutions, we will follow the theory of substitutional solutions described by Guggenheim. First, we will describe a general model of substitutional solutions that in well-defined limits yields the ideal and regular solution models. Then, we will consider an extension of the regular solution model. While in our analysis we will assume that the material is a crystalline solid solution, the results will be equally applicable to amorphous materials and liquids.

13.4.2.1 Basic assumptions

We assume that the energy of the system can be written as the sum of terms associated with the internal degrees of freedom of the molecules and that with the positions of the molecules. Therefore, the partition function takes the following form:

$$Z = Q_{\text{internal}} Q_{\text{translational}}. \tag{13.86}$$

The second term can, in turn, be divided into two parts: an acoustic part associated with the vibration of molecules near their equilibrium sites and a configurational part associated with the occupancy of these sites by molecules of different types, Ω:

$$Q_{\text{translational}} = Q_{\text{acoustic}} \Omega. \tag{13.87}$$

We will further assume that the internal and acoustic partition functions do not change upon adding the solute to the solvent. In this case, the change in the Helmholtz free energy associated with the formation of 1 mole of the solution from its pure components is

$$\Delta A_{\text{mix}} = -RT\left(\ln \Omega - x_{\text{A}} \ln \Omega_{\text{A}}^{0} - x_{\text{B}} \ln \Omega_{\text{B}}^{0}\right), \tag{13.88}$$

where Ω_i^0 is the configurational partition function of 1 mole of component i.

By definition, the configurational partition function is

$$\Omega = \sum \mathrm{e}^{-U/k_{\text{B}}T}, \tag{13.89}$$

where the configurational energy U is the potential energy of the system when all molecules are sitting still at their equilibrium positions (their vibrations are taken into account in Q_{acoustic}). We will assume that the molecular interactions are pairwise and only extend over nearest neighbor lattice sites. The number of nearest neighbors of a site (coordination number) is z, which we will assume to be the same for both pure components and the solution. The configurational energy of pure component i is proportional to the number of molecules, that is, $-N_i\chi_i$ (since the configurational energy is set to zero when the molecules are infinitely separated and the condensed phase is stable, $\chi_{\text{i}} > 0$). The energy per bond in pure component i is (there are $N_i z/2$ nearest neighbor bonds)

$$\frac{-N_i\chi_i}{N_i z/2} = -\frac{2\chi_i}{z}.$$

Consider now two pure components, A and B. We take 1 molecule from A and 1 molecule from B and exchange them. We denote the change in the configurational energy associated with this exchange as

$$\Delta U = 2\omega. \tag{13.90}$$

On other hand, this change in the energy can be expressed in terms of the number of A–A, B–B and A–B bonds:

$$\Delta U = z\varepsilon_{AB} + z\varepsilon_{AB} - \left(z\frac{-2\chi_A}{z} + z\frac{-2\chi_B}{z} \right),$$

where ε_{AB} is the A–B bond energy and, of course, the A–A and B–B bond energies are $\varepsilon_{AA} = -2\chi_A/z$ and $\varepsilon_{BB} = -2\chi_B/z$, respectively. Inserting this result into Eq. (13.90), we obtain:

$$2\omega = 2z\varepsilon_{AB} + 2\chi_A + 2\chi_B$$

or

$$\varepsilon_{AB} = \frac{-\chi_A - \chi_B + \omega}{z}. \tag{13.91}$$

Finally, we note that since pV is small for condensed phases in typical laboratory situations (see Section 1.1.4), we neglect the difference between U and H and between A and G.

13.4.2.2 Ideal solutions

By definition, ideal solutions are formed from pure components without absorbing or emitting heat, that is, $\omega = 0$ for such solutions. Therefore, for an ideal solution, the A–B bond energy is (see Eq. (13.91)):

$$\varepsilon_{AB} = \frac{-\chi_A - \chi_B}{z} = \frac{1}{2}\left(\frac{-2\chi_A}{z} + \frac{-2\chi_B}{z} \right).$$

This is the arithmetic mean of the A–A and B–B bond energies. The key feature of ideal solutions is that if we exchange two arbitrary molecules A and B, there will be no change in the energy of the solution. If you remain unconvinced of this statement, we can prove it as follows. Assume an A molecule has z_A^A neighbors of type A and z_B^A neighbors of type B and a B molecule has z_B^B and z_A^B like and unlike neighbors, respectively. Since the total number of neighbors is always z,

$$z_A^A + z_B^A = z_A^B + z_B^B.$$

The change in the solution energy associated with exchange two arbitrary A and B molecules is

$$\begin{aligned}
\Delta U &= -z_A^B \frac{2\chi_A}{z} - z_B^B \frac{\chi_A + \chi_B}{z} - z_B^A \frac{2\chi_B}{z} - z_A^A \frac{\chi_A + \chi_B}{z} \\
&\quad - \left(-z_A^A \frac{2\chi_A}{z} - z_B^A \frac{\chi_A + \chi_B}{z} - z_B^B \frac{2\chi_B}{z} - z_A^B \frac{\chi_A + \chi_B}{z} \right) \\
&= \frac{1}{z}\left(-2\chi_A z_A^B - \chi_A z_B^B - \chi_B z_B^B - 2\chi_B z_B^A - \chi_A z_A^A - \chi_B z_A^A \right. \\
&\quad \left. + 2\chi_A z_A^A + \chi_A z_B^A + \chi_B z_B^A + 2\chi_B z_B^B + \chi_A z_A^B + \chi_B z_A^B \right) \\
&= \frac{1}{z}\left[\chi_A\left(-2z_A^B - z_B^B - z_A^A + 2z_A^A + z_B^A + z_A^B \right) \right. \\
&\quad \left. + \chi_B\left(-z_B^B - 2z_B^A - z_A^A + z_B^A + 2z_B^B + z_A^B \right) \right] \\
&= \frac{1}{z}\left[\chi_A\left(-z_A^B - z_B^B + z_A^A + z_B^A \right) + \chi_B\left(-z_B^A - z_A^A + z_B^B + z_A^B \right) \right] = 0.
\end{aligned}$$

Since an ideal solution is formed from its pure components with no change in energy, its configurational energy is simply the sum of the energies of its pure components:

$$U = -Nx_A\chi_A - Nx_B\chi_B. \tag{13.92}$$

There are

$$\frac{N!}{(Nx_A)!(Nx_B)!},$$

physically distinguishable ways to arrange the molecules in this solution and all of these configurations have exactly the same energy. Therefore, the partition function of this solution can be represented as:

$$\Omega = \sum e^{-U/kT} = \frac{N!}{(Nx_A)!(Nx_B)!} e^{(Nx_A\chi_A + Nx_B\chi_B)/k_BT}$$

and its Helmholtz free energy is:

$$\begin{aligned} A &= -k_BT \ln\Omega = -k_BT \ln N! + k_BT \ln(Nx_A)! + k_BT \ln(Nx_B)! \\ &\quad - Nx_A\chi_A - Nx_B\chi_B \\ &= -Nk_BT \ln N + Nk_BT + Nx_Ak_BT \ln Nx_A - Nx_Ak_BT \\ &\quad + Nx_Bk_BT \ln Nx_B - Nx_BkT - Nx_A\chi_A - Nx_B\chi_B \\ &= -Nx_A\chi_A - Nx_B\chi_B + Nk_BT(x_A \ln x_A + x_B \ln x_B). \end{aligned}$$

In a pure component, there is just one physically distinguishable configuration, therefore, its partition function takes the following form:

$$\Omega_i^0 = e^{Nx_i\chi_i/k_BT}$$

and its Helmholtz free energy is

$$A_i^0 = -Nx_i\chi_i.$$

Thus, the change of the Helmholtz free energy upon the formation of an ideal solution from its pure components is

$$\Delta A_{\text{mix}} = Nk_BT(x_A \ln x_A + x_B \ln x_B). \tag{13.93}$$

The chemical potential is, therefore,

$$\mu_i = \mu_i^0 + k_BT \ln x_i. \tag{13.94}$$

This expression is the definition of ideal solutions that we postulated in Section 3.3.

13.4.2.3 Regular solutions

In the previous section, we developed the theory of ideal solutions based on the fact that in such solutions $\omega = 0$. In contrast with ideal solutions, $\omega \neq 0$ in regular solutions. In this section, we derive general (albeit difficult to apply) relations for such solutions. In the next two sections, we will consider two approximations that simplify the regular solution theory. As usually in statistical thermodynamics, we start by deriving an expression for the partition function. Consider a configuration of the solution with zX A–B pairs. The total number of neighbors of all A molecules is zN_A.

Table 13.4 The number of bonds, the energy per bond, and the total energy associated with different bond types in a regular solution

Bond	Number of bonds	Energy per bond	Energy of all bonds
A–A	$z(N_A - X)/2$	$-2\chi_A/z$	$-(N_A - X)\chi_A$
A–B	zX	$(-\chi_A - \chi_B + \omega)/z$	$X(-\chi_A - \chi_B + \omega)$
B–B	$z(N_B - X)/2$	$-2\chi_B/z$	$-(N_B - X)\chi_B$
All	$z(N_A + N_B)/2$	–	$-N_A\chi_A - N_B\chi_B + X\omega$

Therefore, there are $z(N_A - X)/2$ A–A bonds (the factor of 2 arises from the fact that two A atoms share an A–A bond). By analogy, we can calculate the number of all other pairs and the energy associated with these pairs. The results are presented in Table 13.4.

The configurational partition function is:

$$\Omega = e^{N_A\chi_A/k_BT} e^{N_B\chi_B/k_BT} \sum e^{-X\omega/k_BT}, \tag{13.95}$$

where the summation is performed over the $N!/(N_A!N_B!)$ physically distinguishable configurations. Introducing an unconventional average value of X $\left(\overline{\overline{X}}\right)$ as follows:

$$\sum e^{-X\omega/k_BT} = \frac{N!}{N_A!N_B!} e^{-\overline{\overline{X}}\omega/k_BT}, \tag{13.96}$$

we can rewrite Eq. (13.95) as:

$$\Omega = e^{N_A\chi_A/k_BT} e^{N_B\chi_B/k_BT} \frac{N!}{N_A!N_B!} e^{-\overline{\overline{X}}\omega/k_BT}. \tag{13.97}$$

The configurational part of the Helmholtz free energy is

$$A = -k_BT \ln\Omega = -N_A\chi_A - N_B\chi_B - k_BT \ln\frac{N!}{N_A!N_B!} + \overline{\overline{X}}\omega.$$

If we expand the logarithm using Stirling's equation,

$$\begin{aligned} \ln\frac{N!}{N_A!N_B!} &= N\ln N - N - N_A\ln N_A + N_A - N_B\ln N_B + N_B \\ &= -N_A\ln x_A - N_B\ln x_B, \end{aligned}$$

we can express the Helmholtz free energy as:

$$A = -N_A\chi_A - N_B\chi_B + Nk_BT(x_A\ln x_A + x_B\ln x_B) + \overline{\overline{X}}\omega. \tag{13.98}$$

Note that if $\omega = 0$, this expression reduces to the Helmholtz free energy of an ideal solution (see the previous section).

The experimentally observed configurational energy of a regular solution can be written as (see Table 13.4)

$$U = -N_A\chi_A - N_B\chi_B + \overline{X}\omega, \tag{13.99}$$

where $z\overline{X}$ is the usual statistical average of the number of A–B bonds. In order to find the relation between $\overline{X}$ and $\overline{\overline{X}}$, we use the Gibbs–Helmholtz equation:

$$U = A - T\frac{\partial A}{\partial T}.$$

Inserting Eqs (13.98) and (13.99) into this expression, we find:

$$-N_{\mathrm{A}}\chi_{\mathrm{A}} - N_{\mathrm{B}}\chi_{\mathrm{B}} + \overline{X}\omega = -N_{\mathrm{A}}\chi_{\mathrm{A}} - N_{\mathrm{B}}\chi_{\mathrm{B}} + Nk_{\mathrm{B}}T(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}}) + \overline{\overline{X}}\omega - Nk_{\mathrm{B}}T(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}}) - T\omega\frac{\partial\overline{\overline{X}}}{\partial T}$$

or

$$\overline{X} = \overline{\overline{X}} - T\frac{\partial\overline{\overline{X}}}{\partial T} = -T^2\frac{\partial\left(\overline{\overline{X}}/T\right)}{\partial T} = -T^2\frac{\partial\left(\overline{\overline{X}}/T\right)}{\partial(1/T)}\frac{\mathrm{d}(1/T)}{\mathrm{d}T} = \frac{\partial\left(\overline{\overline{X}}/T\right)}{\partial(1/T)}.$$

Integration of this equation yields

$$\int_0^{\overline{\overline{X}}/T}\mathrm{d}\left(\frac{\overline{\overline{X}}}{T}\right) = \int_0^{1/T}\overline{X}\mathrm{d}\left(\frac{1}{T}\right),$$

where we took into account that $\overline{\overline{X}}/T \to 0$ at $T \to \infty$ (the number of A–B bonds must always be finite). Evaluation of the left side of this equation, shows that

$$\overline{\overline{X}} = T\int_0^{1/T}\overline{X}\mathrm{d}\left(\frac{1}{T}\right). \tag{13.100}$$

This is the central equation of the theory of regular solutions. While we are not interested in $\overline{\overline{X}}$ per se, if we know $\overline{\overline{X}}$, we can determine the Helmholtz free energy (through Eq. (13.98)). Of course, if we know A, we then know all thermodynamic properties.

13.4.2.4 Theory of regular solutions: 0th approximation

In the 0th approximation, we assume that the molecules of type A or B randomly occupy the crystal lattice sites, despite the fact that $\omega \neq 0$. In this case, A molecules will have, on average, $zN_{\mathrm{B}}/(N_{\mathrm{A}}+N_{\mathrm{B}})$ B neighbors. Therefore, the total number of A–B bonds is

$$z\overline{X} = N_{\mathrm{A}}z\frac{N_{\mathrm{B}}}{N_{\mathrm{A}}+N_{\mathrm{B}}}$$

and

$$\overline{X} = \frac{N_{\mathrm{A}}N_{\mathrm{B}}}{N_{\mathrm{A}}+N_{\mathrm{B}}}. \tag{13.101}$$

Note that in this approximation, the average number of A–B bonds is independent of temperature. Inserting Eq. (13.101) into (13.100), we find:

$$\overline{\overline{X}} = \overline{X} = \frac{N_{\mathrm{A}}N_{\mathrm{B}}}{N_{\mathrm{A}}+N_{\mathrm{B}}}. \tag{13.102}$$

Inserting this result into Eq. (13.98) yields

$$A = -N_{\mathrm{A}}\chi_{\mathrm{A}} - N_{\mathrm{B}}\chi_{\mathrm{B}} + Nk_{\mathrm{B}}T(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}}) + N\omega x_{\mathrm{A}}x_{\mathrm{B}}.$$

The other thermodynamic functions are, therefore,

$$\Delta A_{\text{mix}} = Nk_{\text{B}}T(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}) + N\omega x_{\text{A}} x_{\text{B}} \qquad (13.103)$$

$$\Delta S_{\text{mix}} = -\frac{\partial A}{\partial T} = -Nk_{\text{B}}T(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}) \qquad (13.104)$$

$$\Delta H_{\text{mix}} = \Delta U_{\text{mix}} = A_{\text{mix}} + TS_{\text{mix}} = N\omega x_{\text{A}} x_{\text{B}} \qquad (13.105)$$

$$\mu_{\text{A}} = \left(\frac{\partial A}{\partial N_{\text{A}}}\right)_{N_{\text{B}}} = \mu_{\text{A}}^0 + k_{\text{B}}T \ln x_{\text{A}} + \omega x_{\text{B}}^2 \qquad (13.106)$$

$$\gamma_{\text{A}} = \mathrm{e}^{(\mu_{\text{A}} - \mu_{\text{A}}^0 - k_{\text{B}}T \ln x_{\text{A}})/k_{\text{B}}T} = \mathrm{e}^{\omega x_{\text{B}}^2/kT}. \qquad (13.107)$$

These thermodynamic properties exactly coincide with those obtained in our phenomenological thermodynamic theory of regular solutions in Section 3.5. In other words, the regular solution theory we referred to previously, is simply the 0th approximation to the statistical thermodynamic regular solution theory. This is not surprising since both derivations are based on the assumption that A and B molecules randomly occupy the lattice sites.

13.4.2.5 Theory of regular solutions: 1st approximation

The regular solution theory in the 0th approximation is not self-consistent. On one hand, we explicitly use the fact that $\omega \neq 0$. This implies that the energies of different configurations are not the same. On the other hand, we assume that A and B molecules occupy the lattice sites at random. Clearly, we could lower the energy of the system by imposing some type of ordering on the configuration of the molecules. However, this will invariably decrease the entropy of the system. Hence, this ordering makes two competing contributions to the free energy of the system. Therefore, it is not clear whether such ordering is favorable. Further, if ordering is favorable, how does it modify the thermodynamic properties of the solution? These questions are the subject of this section.

Again, consider the impact of exchanging a molecule of type A and a molecule of type B. Originally the A molecule has z_{A}^{A} neighbors of type A and z_{B}^{A} neighbors of type B, that is, it has z_{A}^{A} A–A bonds and z_{B}^{A} A–B bonds (similarly for the B molecule). After the exchange, the A molecule will have z_{B}^{B} A–B bonds and z_{A}^{B} A–A bonds. Therefore, this exchange can be written, by analogy with chemical reactions, as follows:

$$\begin{aligned} &z_{\text{A}}^{\text{A}}(\text{A}-\text{A}) + z_{\text{B}}^{\text{A}}(\text{A}-\text{B}) + z_{\text{A}}^{\text{B}}(\text{A}-\text{B}) + z_{\text{B}}^{\text{B}}(\text{B}-\text{B}) \\ &\qquad \to z_{\text{A}}^{\text{A}}(\text{A}-\text{B}) + z_{\text{B}}^{\text{A}}(\text{B}-\text{B}) + z_{\text{A}}^{\text{B}}(\text{A}-\text{A}) + z_{\text{B}}^{\text{B}}(\text{A}-\text{B}). \end{aligned}$$

We can formally rewrite this equation as follows:

$$\left(z_{\text{A}}^{\text{A}} - z_{\text{A}}^{\text{B}}\right)(\text{A}-\text{A}) + \left(z_{\text{B}}^{\text{B}} - z_{\text{B}}^{\text{A}}\right)(\text{B}-\text{B}) \to \left(z_{\text{A}}^{\text{A}} + z_{\text{B}}^{\text{B}} - z_{\text{B}}^{\text{A}} - z_{\text{A}}^{\text{B}}\right)(\text{A}-\text{B}).$$

Since

$$z_{\text{A}}^{\text{A}} - z_{\text{A}}^{\text{B}} = z - z_{\text{B}}^{\text{A}} - z_{\text{A}}^{\text{B}} = z_{\text{B}}^{\text{B}} - z_{\text{B}}^{\text{A}},$$

we can divide both sides of the previous expression by $\left(z^{\mathrm{A}}_{\mathrm{A}} - z^{\mathrm{B}}_{\mathrm{A}}\right)$ to find a simplified chemical reaction equation for this exchange process

$$(\mathrm{A}-\mathrm{A}) + (\mathrm{B}-\mathrm{B}) \rightarrow 2(\mathrm{A}-\mathrm{B}). \tag{13.108}$$

The equilibrium constant for this reaction takes the form (see Table 13.4 in Section 13.4.2.3)

$$K = \frac{\overline{X}^2}{\left(N_{\mathrm{A}} - \overline{X}\right)\left(N_{\mathrm{B}} - \overline{X}\right)} \tag{13.109}$$

and the van't Hoff isobar is

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{2\omega}{zk_{\mathrm{B}}T^2}.$$

Integrating this equation yields

$$\ln K = C - \frac{2\omega}{zk_{\mathrm{B}}T}, \tag{13.110}$$

where C is an integration constant. When $\omega/k_{\mathrm{B}}T \rightarrow 0$, the molecules will be randomly occupy the lattice sites. This is the 0th approximation, for which we found

$$\overline{X} = \frac{N_{\mathrm{A}}N_{\mathrm{B}}}{N_{\mathrm{A}} + N_{\mathrm{B}}},$$

(see Eq. (13.101)). We can transform this relation as follows:

$$N_{\mathrm{A}}N_{\mathrm{B}} - \overline{X}(N_{\mathrm{A}} + N_{\mathrm{B}}) = 0$$

$$\overline{X}^2 = \overline{X}^2 + N_{\mathrm{A}}N_{\mathrm{B}} - \overline{X}(N_{\mathrm{A}} + N_{\mathrm{B}})$$

and finally,

$$\overline{X}^2 = \left(\overline{X} - N_{\mathrm{A}}\right)\left(\overline{X} - N_{\mathrm{B}}\right). \tag{13.111}$$

Comparing this result with Eq. (13.109), we find that when $\omega/k_{\mathrm{B}}T \rightarrow 0$ (the condition for which Eq. (13.111) is valid), $K \rightarrow 1$. Therefore, $C = 0$. Inserting this value into Eq. (13.110) and combining it with Eq. (13.109) yields:

$$\overline{X}^2 = \left(N_{\mathrm{A}} - \overline{X}\right)\left(N_{\mathrm{B}} - \overline{X}\right)\mathrm{e}^{-2\omega/zk_{\mathrm{B}}T}. \tag{13.112}$$

This equation differs from Eq. (13.111) by the factor $\mathrm{e}^{-2\omega/zk_{\mathrm{B}}T}$.

Equation (13.112) is an implicit expression for the average site occupancy. In order to determine $\overline{X}$, the average number of A–B bonds, it is convenient to write it in the form:

$$\overline{X} = \frac{N_{\mathrm{A}}N_{\mathrm{B}}}{N_{\mathrm{A}} + N_{\mathrm{B}}}\frac{2}{\beta + 1}, \tag{13.113}$$

where β is a parameter to be determined. Inserting Eq. (13.113) into Eq. (13.112) yields:

$$\frac{N_{\mathrm{A}}^2 N_{\mathrm{B}}^2}{(N_{\mathrm{A}} + N_{\mathrm{B}})^2}\frac{4}{(\beta+1)^2} = \left(N_{\mathrm{A}} - \frac{N_{\mathrm{A}}N_{\mathrm{B}}}{N_{\mathrm{A}} + N_{\mathrm{B}}}\frac{2}{\beta+1}\right)\left(N_{\mathrm{B}} - \frac{N_{\mathrm{A}}N_{\mathrm{B}}}{N_{\mathrm{A}} + N_{\mathrm{B}}}\frac{2}{\beta+1}\right)\mathrm{e}^{-2\omega/zk_{\mathrm{B}}T}.$$

Solving this equation for β gives:

$$\beta^2 = 1 + 4x_A x_B \left(e^{2\omega/zk_BT} - 1\right) \tag{13.114}$$

or

$$\beta = \sqrt{1 + 4x_A x_B (e^{2\omega/zk_BT} - 1)}. \tag{13.115}$$

Equations (13.113) and (13.115) show how interactions between A and B atoms modify the average number of A–B bonds, $\overline{X}$.

Our next goal is to determine the free energy of the solution from Eq. (13.98). To this end, we must obtain $\overline{\overline{X}}$. Equation (13.100) provides a means of determining $\overline{\overline{X}}$ from $\overline{X}$. First, we should express $d(1/T)$ in terms of $d\beta$. Recall that Eq. (13.100) was derived from the Gibbs–Helmholtz equation at constant x_i. Using Eq. (13.114), we find:

$$\frac{2\omega}{zk_B} d\left(\frac{1}{T}\right) = d\,\ln\frac{\beta^2 - 1 + 4x_A x_B}{4x_A x_B} = \frac{2\beta\, d\beta}{\beta^2 - 1 + 4x_A x_B}.$$

Inserting this into Eq. (13.100), we obtain:

$$\overline{\overline{X}} = T\int_0^{1/T} \overline{X} d\left(\frac{1}{T}\right) = N x_A x_B \frac{zk_BT}{2\omega}\int_1^{\beta} \frac{4\beta\, d\beta}{(\beta^2 - 1 + 4x_A x_B)(\beta + 1)}.$$

The lower limit in the last integral was obtained by realizing that $1/T = 0$ (lower limit in the intermediate integral) implies infinite temperature and $\omega/kT = 0$. This is the case where the 0th approximation is valid. Comparing Eqs (13.115) and (13.113) demonstrates that $\beta = 1$ in the 0th approximation. Evaluating the integral in the previous expression yields:

$$\overline{\overline{X}} = \frac{Nzk_BT}{2\omega}\left\{x_A \ln\frac{\beta + 1 - 2x_B}{x_A(\beta + 1)} + x_B \ln\frac{\beta + 1 - 2x_A}{x_B(\beta + 1)}\right\}. \tag{13.116}$$

Inserting this result into Eq. (13.98), we are able to write the change in the Helmholtz free energy upon formation of the solution from the pure components as:

$$\begin{aligned}\Delta A_{\text{mix}} = {} & Nk_BT(x_A \ln x_A + x_B \ln x_B)\\ & + \frac{1}{2}Nzk_BT\left\{x_A \ln\frac{\beta + 1 - 2x_B}{x_A(\beta + 1)} + x_B \ln\frac{\beta + 1 - 2x_A}{x_B(\beta + 1)}\right\}.\end{aligned} \tag{13.117}$$

The corresponding chemical potential and the activity coefficient are:

$$\mu_A = \mu_A^0 + \left(\frac{\partial A_{\text{mix}}}{\partial N_A}\right)_{T,N_B} = \mu_A^0 + kT\,\ln x_A + \frac{1}{2}zkT\,\ln\frac{\beta + 1 - 2x_B}{x_A(\beta + 1)}, \tag{13.118}$$

$$\gamma_A = e^{(\mu_A - \mu_A^0 - k_BT\,\ln x_A)/k_BT} = \left[\frac{\beta + 1 - 2x_B}{x_A(\beta + 1)}\right]^{z/2} \tag{13.119}$$

Equations (13.117)–(13.119) describe the influence of the interaction between A and B atoms on the thermodynamic properties of the solution (i.e. the 1st approximation). Unfortunately, these equations are not particularly transparent.

In order to simplify these equations, we recall that the theory of regular solutions in the 1st approximation reduces to the theory of regular solutions in the 0th approximation when $\omega/k_{\mathrm{B}}T \to 0$. Therefore, it is reasonable to consider $\omega/k_{\mathrm{B}}T$ as a small parameter. Expansion of the Helmholtz free energy with respect to $\omega/k_{\mathrm{B}}T$ yields:

$$\Delta A_{\mathrm{mix}} = Nk_{\mathrm{B}}T(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}}) + N\omega x_{\mathrm{A}}x_{\mathrm{B}} - N\frac{\omega^2}{zk_{\mathrm{B}}T}x_{\mathrm{A}}^2 x_{\mathrm{B}}^2 \ldots \tag{13.120}$$

The first term on the right side of this equation corresponds to an ideal solution, which forms from the pure components with no change in energy. The second term gives the regular solution in the 0th approximation that forms from the pure components with a finite change in energy for the case that the molecules are randomly located on the lattice sites. Finally, the third term is the leading order correction to the free energy of mixing that accounts for ordering in the solution. Whether the deviation from ideality is positive ($\omega > 0$) or negative ($\omega < 0$), this ordering always lowers the Helmholtz free energy.

The leading order corrections to the entropy and enthalpy of mixing can be obtained from Eq. (13.120) as follows:

$$\Delta S_{\mathrm{mix}} = -\left(\frac{\partial A_{\mathrm{mix}}}{\partial T}\right)_{N_{\mathrm{A}},N_{\mathrm{B}}} = -Nk_{\mathrm{B}}(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}}) - \frac{N\omega^2 x_{\mathrm{A}}^2 x_{\mathrm{B}}^2}{zk_{\mathrm{B}}T^2} \tag{13.121}$$

and

$$\Delta H_{\mathrm{mix}} = \Delta A_{\mathrm{mix}} + T\Delta S_{\mathrm{mix}} = N\omega x_{\mathrm{A}}x_{\mathrm{B}} - \frac{2N\omega^2 x_{\mathrm{A}}^2 x_{\mathrm{B}}^2}{zk_{\mathrm{B}}T}. \tag{13.122}$$

The first term on the right side of Eq. (13.121) corresponds to the change of entropy upon formation of an ideal solution from its pure components. The change of the entropy in the theory of regular solutions in the 0th approximation is the same as in ideal solutions, therefore, this theory does not provide any corrections to the entropy of mixing. The last term in Eq. (13.121) is a correction from the theory of regular solutions in the 1st approximation. It is associated with ordering and is always negative. Recall that ideal solutions form from their pure components with no change in energy. This implies that for ideal solutions, $\Delta H_{\mathrm{mix}} = 0$. The first term in Eq. (13.122) is from the theory of regular solutions in the 0th approximation. It can be either negative or positive depending on the sign of ω. The second term is associated with ordering (1st approximation) and always lowers the energy of mixing. Comparing Eqs (13.121) and

(13.122) with Eq. (13.120), we find the following relations for the corrections associated with the ordering:

$$\Delta A^{(1)}_{\text{mix}} = \frac{1}{2}\Delta H^{(1)}_{\text{mix}}$$

$$T\Delta S^{(1)}_{\text{mix}} = \frac{1}{2}\Delta H^{(1)}_{\text{mix}},$$

where the superscript (1) indicates that this is the leading order term in the correction associated with ordering in the regular solution model in the 1st approximation. These relations demonstrate that half of the decrease in the enthalpy of mixing associated with ordering is compensated in the free energy by a decrease in the entropy associated with the same ordering.

Review questions

1. What is the difference between the 0th and 1st approximations of the theory of regular solutions?
2. Which regular solution approximation predicts lower solution enthalpy?
3. Which regular solution approximation predicts lower solution entropy?

13.4.3 Interstitial solutions

In this section, we briefly discuss a statistical model for interstitial solutions. In particular, we focus on the well-known case of carbon in face-centered cubic (γ) iron (see Fig. 13.5). In this model, proposed by Schwartsman and Temkin, the carbon can occupy any of the octahedral interstitial sites, but carbon atoms cannot occupy neighboring octahedral sites simultaneously. Examination of the central octahedral site in Fig. 13.5 will convince you that carbon can occupy at most one site per cubic unit cell. Since there are four Fe atoms per unit cell, this implies that the maximum number of carbon atoms in this structure is a quarter of the number of Fe atoms, $N_{\text{Fe}}/4$. Alternatively, we can state that the number of sites accessible to the carbon atoms is $N_{\text{Fe}}/4$. Assuming that all interstitial sites are energetically equivalent, we obtain the following expression for the configurational energy of the solid solution:

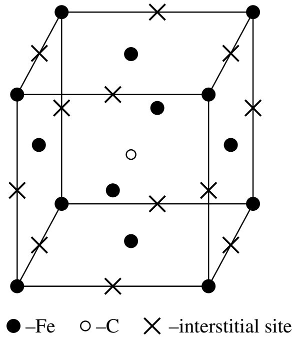


Figure 13.5
The Schwartsman–Temkin model of carbon in γ-Fe, where the filled circles are the positions of the Fe atoms, the open circle is an octahedral interstitial site occupied by carbon and the xs are unoccupied interstitial sites.

$$U = N_{\text{Fe}}U_0 + N_{\text{C}}\dot{U}_{\text{C}}, \tag{13.123}$$

where U_0 is the configurational energy of pure iron per atom and $\dot{U}_{\text{C}}$ is the change of energy of the system upon addition of one carbon atom. Recall from Section 3.2 that the dot implies that $\dot{U}_{\text{C}}$ is independent of the carbon concentration.

Taking into account the number of physically distinguishable states, we obtain the following expression for the partition function:

$$\Omega = \frac{(N_{\text{Fe}}/4)!}{N_{\text{C}}!((N_{\text{Fe}}/4) - N_{\text{C}})!}\mathrm{e}^{-U/k_{\text{B}}T}. \tag{13.124}$$

The configurational part of the Helmholtz free energy can be determined as:

$$A = -k_BT\ \ln\Omega = N_{Fe}U_0 + N_C\dot{U}_C - k_BT\left\{\ln\left(\frac{N_{Fe}}{4}\right)! - \ln N_C! - \ln\left(\frac{N_{Fe}}{4} - N_C\right)!\right\}$$
$$= N_{Fe}U_0 + N_C\dot{U}_C - k_BT\frac{N_{Fe}}{4}\ln\frac{N_{Fe}}{4} + k_BT\frac{N_{Fe}}{4} + k_BTN_C\ln N_C - k_BTN_C + k_BT\left(\frac{N_{Fe}}{4} - N_C\right)\ln\left(\frac{N_{Fe}}{4} - N_C\right) - k_BT\left(\frac{N_{Fe}}{4} - N_C\right).$$

The chemical potential of carbon takes the following form:

$$\mu_C = \dot{U}_C + k_BT(1 + \ln N_C) - k_BT - k_BT\left(\ln\left(\frac{N_{Fe}}{4} - N_C\right) - 1\right) + k_BT$$
$$= \dot{U}_C + k_BT\ln\frac{N_C}{(N_{Fe}/4) - N_C} = \dot{U}_C + k_BT\ \ln\frac{4x_C}{x_{Fe} - 4x_C}$$

or

$$\mu_C = \psi_C + k_BT\ \ln\frac{x_C}{1 - 5x_C}. \tag{13.125}$$

If we choose the standard state of carbon to be the standard solution with unit carbon concentration (see Section 3.4.1), we find the following expression for the carbon activity coefficient:

$$f_C = \frac{1}{1 - 5x_C}. \tag{13.126}$$

This result is in good agreement with experiment.

Analogously, the chemical potential and activity coefficient for iron are:

$$\mu_{Fe} = U_0 - \frac{k_BT}{4}\left(1 + \ln\frac{N_{Fe}}{4}\right) + \frac{k_BT}{4} + kT\left(\frac{1}{4} + \frac{1}{4}\ln\left(\frac{N_{Fe}}{4} - N_C\right)\right) - \frac{k_BT}{4}$$
$$= U_0 + \frac{k_BT}{4}\ln\frac{N_{Fe} - 4N_C}{N_{Fe}} = U_0 + \frac{k_BT}{4}\ln\frac{x_{Fe} - 4x_C}{x_{Fe}}$$

$$\mu_{Fe} = \mu^0_{Fe} + \frac{k_BT}{4}\ \ln\frac{1 - 5x_C}{1 - x_C}, \tag{13.127}$$

$$\gamma_{Fe} = \frac{(1 - 5x_C)^{1/4}}{(1 - x_C)^{5/4}}. \tag{13.128}$$

13.4.4 Dilute ionic solutions

We previously considered the thermodynamics of ionic solutions in Section 3.7. We stated that the reason why ionic solutions show deviations from ideality is the existence of long-range Coulombic interactions between solute ions. We then derived a very important relation between the activity coefficient and the freezing temperature, based upon the general experimental observation that the logarithm of the activity coefficient is proportional to the square root of the solute concentration in the solvent

$$\ln f_i = L_i\sqrt{c_{\mathrm{B}}},$$

where L_i is a constant (independent of the solute concentration) for ion i. Note that the value of this constant is sensitive to the charge on the ion. In this section, we discuss the Debye–Hückel theory, which provides a theoretical explanation for this relation and a method to calculate L_i.

Since the reason for the deviation from ideality in ionic solution is the Coulombic interactions between ions, we first determine the contribution to the Gibbs free energy from these interactions. Then, we will use this Gibbs free energy to derive expressions for the chemical potentials and the activity coefficients.

The Coulombic interaction energy is simply the product of the charge on the ions and the electrostatic potential into which they are embedded. Therefore, the first step is to determine the electrostatic potential field associated with the distribution of ions. The distribution of ions in the solution establishes an electrostatic potential field given by the Poisson equation:

$$\Delta\varphi = \nabla^2\varphi = -\frac{4\pi}{\varepsilon}\sum_{\alpha} e_\alpha \delta(\mathbf{r}-\mathbf{r}_\alpha),$$

where the sum is over all ions, α, in the solution, e_α is the charge on ion α, and ε is the dielectric constant of the solution. Averaging this equation over all ions of type i we can rewrite this expression in terms of the density of ions of type j, measured with respect to the position of an ion of type i, $n_{ij}(r)$:

$$\Delta\varphi_i = -\frac{4\pi}{\varepsilon}\sum_{j} n_{ij}(r)e_j. \tag{13.129}$$

If the ion concentration is small, we can write $n_{ij}(r)$ using the Born–Green–Bogoliubov equation (see Section 13.2.1) as:

$$n_{ij}(r) = n_j \mathrm{e}^{-e_j\varphi_i(r)/k_{\mathrm{B}}T},$$

where n_j is the average density of ions of type j. Assuming that $e\varphi \ll k_{\mathrm{B}}T$, we expand the exponential to first order to find:

$$n_{ij}(r) = n_j\left(1-\frac{e_j\varphi_i(r)}{k_{\mathrm{B}}T}\right). \tag{13.130}$$

Inserting this expression into Eq. (13.129), we obtain:

$$\Delta\varphi_i = -4\pi\sum_{j=1}^{k} n_j e_j/\varepsilon + 4\pi\sum_{j=1}^{k} n_j e_j^2\varphi_i/\varepsilon k_{\mathrm{B}}T.$$

The first term is zero in electrically neutral solution. Introducing

$$\kappa^2 = \frac{4\pi}{\varepsilon k_{\mathrm{B}}T}\sum_{j=1}^{k} n_j e_j^2, \tag{13.131}$$

Eq. (13.129) reduces to

$$\Delta\varphi_i = \kappa^2\varphi_i. \qquad (13.132)$$

Assuming that the potential is, on average, symmetric around ion *i*, the Laplacian can be written explicitly to yield

$$\frac{1}{\mathrm{r}^2}\frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r}^2\frac{\partial\varphi_i}{\partial \mathrm{r}}\right) = \kappa^2\varphi_i.$$

The general form of the solution of this differential equation is

$$\varphi_i(r) = \frac{A\mathrm{e}^{-\kappa r}}{r} + \frac{A'\mathrm{e}^{\kappa r}}{r}.$$

Since $\varphi_\mathrm{i} \to 0$ in the $r \to \infty$ limit, A' must be zero. Therefore, the electrostatic potential as a function of distance away from an ion of type *i*, on average, is

$$\varphi_i(r) = \frac{A\mathrm{e}^{-\kappa r}}{r}. \qquad (13.133)$$

The potential in Eq. (13.129) contains contributions from each ion and all its neighbors. Let φ_i^* be the value of this electrostatic potential at the position of an ion of type *i* (from Eq. (13.129)) minus the contribution from the ion itself (and averaged over all ions of type *i*). Then, the energy associated with the Coulombic interactions is

$$U^{\mathrm{Coulomb}} = V\frac{1}{2}\sum_i n_i e_i \varphi_i^*. \qquad (13.134)$$

We now find the relationship between φ_i (Eq. (13.133)) to φ_i^* by assuming that each ion is a conducting ball of radius *a*, with dielectric constant ε and charge e_i located at its center. Then the potential inside the ion is:

$$\varphi_i(r) = \frac{e_i}{\varepsilon r} + \varphi_i^*, \qquad (13.135)$$

where the first term is the Coulomb potential of the point charge and the second term is the Coulomb potential at $r = a$, associated with the other ions in the system. The two expressions for φ_i (Eqs (13.133 and 13.135)) and their first derivatives must be identical at $r = a$. From these two conditions, we find:

$$\varphi_i(r) = \frac{e_i}{\varepsilon r}\frac{e^{-\kappa(r-a)}}{1+\kappa a}, \qquad (13.136)$$

$$\varphi_i^* = -\frac{e_i}{\varepsilon}\frac{\kappa}{1+\kappa a}. \qquad (13.137)$$

Inserting this result into Eq. (13.134), we obtain an expression for the Coulombic contribution to the internal energy:

$$U^{\mathrm{Coulomb}} = -\frac{V}{2\varepsilon}\frac{\kappa}{1+\kappa a}\sum_i n_i e_i^2. \qquad (13.138)$$

In order to find the corresponding part of the Helmholtz free energy, we use the Gibbs–Helmholtz equation:

$$\frac{\partial (A^{\mathrm{Coulomb}}/T)}{\partial T} = -\frac{U^{\mathrm{Coulomb}}}{T^2}.$$

Integration of this expression yields:

$$A^{\mathrm{Coulomb}} = \mathrm{const}\cdot T - T\int \frac{U^{\mathrm{Coulomb}}}{T^2}\mathrm{d}T, \tag{13.139}$$

where the constant is temperature independent.

The only quantity that depends upon T in Eq. (13.138) is κ. It is convenient to rewrite Eqs (13.131) and (13.138) as:

$$U^{\mathrm{Coulomb}} = A\frac{\kappa}{1+\kappa a};\quad \kappa = BT^{-1/2},$$

where A and B do not depend on T. Now, we can rewrite the integral in Eq. (13.139) as:

$$T\int \frac{U^{\mathrm{Coulomb}}}{T^2}\mathrm{d}T = AT\int \frac{\kappa}{T^2(1+\kappa a)}\mathrm{d}T.$$

Since $T=(B/\kappa)^2$, we find that $\mathrm{d}T = -(2B^2/\kappa^3)\mathrm{d}\kappa$. Therefore, the integral can be evaluated as:

$$\begin{aligned}
T\int \frac{U^{\mathrm{Coulomb}}}{T^2}\mathrm{d}T &= -AT\int \frac{\kappa}{1+\kappa a}\left(\frac{\kappa}{B}\right)^4\frac{2B^2}{\kappa^3}\mathrm{d}\kappa \\
&= -\frac{2AT}{B^2}\int \frac{\kappa^2}{1+\kappa a}\mathrm{d}\kappa = -\frac{2AT}{B^2}\int \frac{1}{a^2}\frac{(\kappa a)^2-1+1}{1+\kappa a}\mathrm{d}\kappa \\
&= -\frac{2A}{\kappa^2}\frac{1}{a^2}\left(\frac{1}{a}\ln(1+\kappa a)+\frac{\kappa^2 a}{2}-\kappa\right) \\
&= -\frac{2}{3}A\kappa\frac{3}{(\kappa a)^3}\left(\ln(1+\kappa a)+\frac{(\kappa a)^2}{2}-\kappa a\right).
\end{aligned}$$

Inserting this result into Eq. (13.139) and introducing the function:

$$\tau(x) = \frac{3}{x^3}\left(\ln(1+x)+\frac{x^2}{2}-x\right), \tag{13.140}$$

we obtain:

$$\begin{aligned}
A^{\mathrm{Coulomb}} &= \mathrm{const}\cdot T + \frac{2}{3}A\kappa\tau(\kappa a) = \mathrm{const}\cdot T - \frac{2}{3}\frac{V}{2\varepsilon}\sum_i n_i e_i^2 \kappa\tau(\kappa a) \\
&= \mathrm{const}\cdot T - \frac{\kappa V}{3\varepsilon}\tau(\kappa a)\sum_i n_i e_i^2.
\end{aligned}$$

When $T\to\infty$, the ion arrangement becomes random, and A^{coulomb} is no longer a function of temperature. This implies that the integration constant is zero and we finally obtain:

$$A^{\mathrm{Coulomb}} = -\frac{\kappa V}{3\varepsilon}\tau(\kappa a)\sum_i n_i e_i^2. \tag{13.141}$$

Note that combination of Eqs (13.138) and (13.141) yields:

$$\begin{aligned} TS^{\text{Coulomb}} &= U^{\text{Coulomb}} - A^{\text{Coulomb}} \\ &= -\frac{\kappa V}{\varepsilon}\sum_i n_i e_i^2\left(\frac{1}{2(1+\kappa a)} - \frac{1}{3}\tau(\kappa a)\right). \end{aligned} \tag{13.142}$$

It is easy to show that the function in the brackets is always positive and, therefore, the Coulombic interaction contribution to the entropy $S^{\text{Coulomb}} < 0$. This is not surprising, since the Coulombic interactions between ions should lead to some form of ion ordering.

Since we consider a condensed phase, we can use the approximation that $H^{\text{Coulomb}} = U^{\text{Coulomb}}$ and, therefore, $G^{\text{Coulomb}} = A^{\text{Coulomb}}$. Using Eq. (13.141), we find:

$$G^{\text{Coulomb}} = -\frac{\kappa V}{3\varepsilon}\tau(\kappa a)\sum_i n_i e_i^2. \tag{13.143}$$

Now we can obtain an expression for the chemical potential. For the solvent (water), we find:

$$\begin{aligned} \mu_1^{\text{Coulomb}} &= \left(\frac{\partial G^{\text{Coulomb}}}{\partial N_1}\right)_{N_i} = \left(\frac{\partial G^{\text{Coulomb}}}{\partial \kappa}\right)_{N_i}\left(\frac{\partial \kappa}{\partial N_1}\right)_{N_i} \\ &= \left(\frac{\partial G^{\text{Coulomb}}}{\partial \kappa}\right)_{N_i}\left(\frac{\partial \kappa}{\partial V}\right)_{N_i}\left(\frac{\partial V}{\partial N_1}\right)_{N_i}. \end{aligned} \tag{13.144}$$

In order to evaluate the first derivative on the right, we rewrite Eq. (13.143) in an explicit form as:

$$G^{\text{Coulomb}} = -\frac{1}{3\varepsilon}\sum_i N_i e_i^2 \cdot \kappa\frac{3}{(\kappa a)^3}\left(\ln(1+\kappa a) + \frac{1}{2}(\kappa a)^2 - \kappa a\right).$$

Differentiating this expression with respect to κ, we find:

$$\left(\frac{\partial G^{\text{Coulomb}}}{\partial \kappa}\right)_{N_i} = -\frac{1}{3\varepsilon}\sum_i N_i e_i^2\frac{3}{(\kappa a)^3}\left(-2\ln(1+\kappa a) + \kappa a + 1 - \frac{1}{1+\kappa a}\right)$$

or, introducing the function

$$\sigma(x) = \frac{3}{x^3}\left(1 + x - \frac{1}{1+x} - 2\ln(1+x)\right), \tag{13.145}$$

we obtain:

$$\left(\frac{\partial G^{\text{Coulomb}}}{\partial \kappa}\right)_{N_i} = -\frac{1}{3\varepsilon}\sum_i N_i e_i^2 \sigma(\kappa a). \tag{13.146}$$

The second derivative on the right in Eq. (13.144) can be found from Eq. (13.131) (which can be written as $\kappa = AV^{-1/2}$) and, therefore,

$$\left(\frac{\partial \kappa}{\partial V}\right)_{N_i} = -\frac{1}{2}AV^{-3/2}$$

or

$$\left(\frac{\partial\kappa}{\partial V}\right)_{N_i} = -\frac{\kappa}{2V}. \tag{13.147}$$

Finally, the third derivative on the right in Eq. (13.144) is simply the partial molar volume of the solvent. Combining all of these results, we obtain the following correction to the chemical potential of the solvent associated with the Coulombic interaction between ions in the solution:

$$\mu_1^{\text{Coulomb}} = \frac{1}{3\varepsilon}\sum_i N_i e_i^2 \sigma(\kappa a)\frac{\kappa}{2V}\bar{V}_1. \tag{13.148}$$

This equation implies that $\mu_1^{\text{Coulomb}} > 0$, that is we find that the deviation from ideality for the solvent should be positive.

For the chemical potential of the ions of type i, we obtain:

$$\begin{aligned}
\mu_i^{\text{Coulomb}} &= \left(\frac{\partial G^{\text{Coulomb}}}{\partial N_i}\right)_{N_1,N_j} \\
&= \left(\frac{\partial G^{\text{Coulomb}}}{\partial N_i}\right)_{N_1,N_j,\kappa} + \left(\frac{\partial G^{\text{Coulomb}}}{\partial \kappa}\right)_{N_1,N_j}\left(\frac{\partial\kappa}{\partial N_i}\right)_{N_1,N_j} \\
&= \left(\frac{\partial G^{\text{Coulomb}}}{\partial N_i}\right)_{N_1,N_j,\kappa} \\
&\quad + \left(\frac{\partial G^{\text{Coulomb}}}{\partial \kappa}\right)_{N_1,N_j}\left(\frac{\partial\kappa}{\partial V}\right)_{N_1,N_i}\left(\frac{\partial V}{\partial N_i}\right)_{N_1,N_j} \\
&\quad + \left(\frac{\partial G^{\text{Coulomb}}}{\partial \kappa}\right)_{N_1,N_j}\left(\frac{\partial\kappa}{\partial N_i}\right)_{N_1,N_j,V}.
\end{aligned} \tag{13.149}$$

The first term on the right in the final expression can be evaluated using Eq. (13.143):

$$\left(\frac{\partial G^{\text{Coulomb}}}{\partial N_i}\right)_{N_1,N_j,\kappa} = -\frac{e_i^2}{3\varepsilon}\kappa\tau(\kappa a).$$

The second term looks like the right side of Eq. (13.144). Therefore, we can obtain this term from the right side of Eq. (13.148) by replacing $\overline{V_1}$ with $\overline{V_i}$. Finally, in order to evaluate the third term, we rewrite Eq. (13.131) as:

$$\ln\kappa = \frac{1}{2}\left(\ln\frac{4\pi}{\varepsilon kTV} + \ln\sum_i N_i e_i^2\right).$$

Differentiating this with respect to N_i, we obtain:

$$\left(\frac{\partial\kappa}{\partial N_i}\right)_{N_1,N_j,V} = \kappa\left(\frac{\partial\ln\kappa}{\partial N_i}\right)_{N_1,N_j,V} = \frac{\kappa e_i^2}{2\sum_j N_j e_j^2}.$$

Now combining the first and third terms on the right side of Eq. (13.149), we obtain:

$$\left(\frac{\partial G^{\text{Coulomb}}}{\partial N_i}\right)_{N_1,N_j,\kappa} + \left(\frac{\partial G^{\text{Coulomb}}}{\partial \kappa}\right)_{N_1,N_i}\left(\frac{\partial \kappa}{\partial N_i}\right)_{N_1,N_j,V}$$
$$= -\frac{e_i^2}{3\varepsilon}\kappa\tau(\kappa a) - \frac{1}{3\varepsilon}\sum_j N_j e_j^2 \sigma(\kappa a)\frac{\kappa e_i^2}{2\sum_j N_j e_j^2} = -\frac{e_i^2}{3\varepsilon}\kappa\left(\tau(\kappa a) + \frac{1}{2}\sigma(\kappa a)\right).$$

Combination of Eqs (13.140) and (13.145) yields:

$$\tau(x) + \frac{1}{2}\sigma(x) = \frac{3}{x^3}\left(\ln(1+x) + \frac{x^2}{2} - x + \frac{1}{2} + \frac{x}{2} - \frac{1}{2(1+x)} - \ln(1+x)\right)$$
$$= \frac{3}{2(1+x)}.$$

Using all of these results, Eq. (13.149) reduces to:

$$\mu_i^{\text{Coulomb}} = -\frac{e_i^2\kappa}{2\varepsilon}\frac{1}{1+\kappa a} + \frac{1}{3\varepsilon}\sum_j N_j e_j^2 \sigma(\kappa a)\frac{\kappa}{2V}\overline{V}_i. \tag{13.150}$$

Recall that the activity coefficient can be determined as:

$$RT\ln f_i = \mu_i^{\text{Coulomb}} = -\frac{e_i^2\kappa}{2\varepsilon}\frac{1}{1+\kappa a} + \frac{1}{3\varepsilon}\sum_j N_j e_j^2 \sigma(\kappa a)\frac{\kappa}{2V}\overline{V}_i. \tag{13.151}$$

If the solute concentration is small, the second term on the right side of Eq. (13.150) can be neglected. In a case in which the solution contains only one type of salt, Eqs (13.151) and (13.131) imply that the logarithm of the activity coefficient of the solute is proportional to the square root of the solute concentration. This is in good agreement with experimental observations. Moreover, now we can obtain a numerical value for the parameter L_i. For example, in a salt in which each ion carries one elementary charge (e.g. NaCl) at $T = 298$ K, Eqs (13.131) and (13.151) imply:

$$\ln f_i = -1.18\sqrt{c}. \tag{13.152}$$

Table 13.5 The activity coefficient of NaCl at $T = 298$ K

c (M)	f_i (Experiment)	f_i (Calculation)
0.001	0.98	0.96
0.01	0.92	0.89
0.1	0.77	0.67

Table 13.5 shows a comparison of the activity coefficients of NaCl obtained from experiment and calculated using Eq. (13.152). Overall, the theory provides reasonable agreement with experiment.

If the solution contains more than one type of solute, the situation is more complex. In this case, it is convenient to introduce the so-called **ionic strength** of the solution:

$$I = \frac{1}{2}\sum_i c_i z_i^2, \tag{13.153}$$

where z_i is the charge on the ion of type i (in units of the elementary charge) and c_i is its molarity. Equation (13.132) can then be rewritten as:

$$\kappa = \sqrt{\frac{8\pi e^2 N_A}{1000 k_B}}\sqrt{\frac{I}{\varepsilon T}}. \tag{13.154}$$

Inserting this result into Eq. (13.152) demonstrates that the activity coefficient of ions of a given type depends on the ionic strength of the entire solution rather than just on the concentration of that ion. This is a surprising result. For example, consider a solution containing two salts consisting of different ions (e.g. KCl and $NaNO_3$). The theory described above predicts that if we keep the concentration of one of the salts fixed and decrease concentration of the second, the activity coefficients of the second solute ions will go to some finite limit, determined by the first solute concentration.

Appendices

The appendices below provide a brief discussion of some of the important mathematical points employed within this book. Since this is not a mathematics text, rather than providing rigorous mathematical derivations, the presentation is guided by the need for transparency and simplicity.

Appendix I. Working with partial derivatives

We frequently deal with partial derivatives in thermodynamics. Therefore, we often need to relate different partial derivatives of thermodynamic functions. The most convenient approach is through the Jacobian.

The **Jacobian** $\partial(u, v)/\partial(x, y)$ is given by the following determinant:

$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{vmatrix} = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial v}{\partial y}\right)_x - \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial v}{\partial x}\right)_y, \tag{AI.1}$$

where u and v are two functions of the variables x and y. The Jacobian has the following obvious properties:[1]

$$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)}, \tag{AI.2}$$

$$\frac{\partial(u,y)}{\partial(x,y)} = \left(\frac{\partial u}{\partial x}\right)_y, \tag{AI.3}$$

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(s,t)}\frac{\partial(s,t)}{\partial(x,y)}. \tag{AI.4}$$

Consider three physical variables x, y, and z which are related through $f(x,y,z) = 0$, where f is some, as of now, unspecified function. Using the previous three equations, we can write:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\partial(x,z)}{\partial(y,z)} = \frac{\partial(x,z)}{\partial(x,y)}\frac{\partial(x,y)}{\partial(y,z)} = -\frac{\partial(z,x)}{\partial(y,x)}\frac{\partial(x,y)}{\partial(z,y)}$$

---

[1] It is a useful exercise to derive these for yourself.

or

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y . \tag{AI.5}$$

For example, using the equation of state $f(p,V,T)=0$, we can show that:

$$\left(\frac{\partial p}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial p}{\partial T}\right)_V . \tag{AI.6}$$

This is valid for any system and any equation of state.

As a second example, we derive the relation between the isochoric and isobaric heat capacities. First, from the definition of the isochoric heat capacity (Eq. (1.49)) and formal mathematical transformations we find:

$$\begin{aligned} c_{\mathrm{V}} &= T\left(\frac{\partial S}{\partial T}\right)_V = T\frac{\partial(S,\ V)}{\partial(T,\ V)} = T\frac{\partial(S,\ V)}{\partial(T,\ p)}\frac{\partial(T,\ p)}{\partial(T,\ V)} \\ &= T\left[\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial V}{\partial p}\right)_T - \left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\right]\left(\frac{\partial p}{\partial V}\right)_T \\ &= T\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial p}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial V}\right)_T . \end{aligned}$$

Using the definition of the isobaric heat capacity (Eq. (1.49)) and the relationship $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$ (see Eq. (1.74)), we obtain:

$$c_{\mathrm{V}} = c_{\mathrm{p}} + T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial V}\right)_T$$

or

$$c_{\mathrm{p}} - c_{\mathrm{V}} = -T\left(\frac{\partial V}{\partial T}\right)_p^2\left(\frac{\partial p}{\partial V}\right)_T . \tag{AI.7}$$

Appendix II. Tensors

Some physical variables (e.g. the mass or the free energy) are characterized only by their magnitude. Such variables are called **scalars**. Other variables (e.g. force or velocity) must be characterized by both a magnitude and a direction. Such values are called **vectors**. In three dimension, a vector can be described by three **components**. Note that the components of a vector are numbers but not scalars. This is related to the fact that rotation of the coordinate system has no effect on scalars or the magnitude and direction of a vector (these are physical variables), but does change the representation or components of a vector. For example, the radius-vector **r**, drawn from the origin of the coordinate system to a specified point, has components x, y, and z. If we rotate the coordinate system about the z-axis, as shown in Fig. AII.1, the vector **r**, of course, will not change, but its

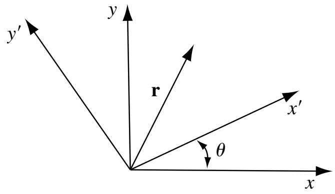


Fig. AII.1
Rotation of the coordinate system around the z-axis.

components will:

$$
\begin{aligned}
x' &= x\cos\theta + y\sin\theta \\
y' &= y\cos\theta - x\sin\theta \\
z' &= z
\end{aligned}
$$

Consider an equation describing some physical phenomenon that contains both scalars and vectors, for example, Newton's second law:

$$\mathbf{F} = m\mathbf{a}.$$

We can explicitly write the components of the vector force as:

$$
\begin{aligned}
F_x &= ma_x \\
F_y &= ma_y \\
F_z &= ma_z.
\end{aligned}
$$

Clearly, the physics cannot change if we choose to translate or rotate the coordinate system. Since m is a scalar, it does not change upon rotation of the coordinate system. Therefore, the components of the vectors **F** and **a** must transform in exactly the same way. This is true for any vector, including the radius vector we discussed above. Hence, we can define a vector (in three dimensions) as a set of three values which changes upon rotation of the coordinate system in exactly the same way as the components of the radius-vector.

A tensor of rank n in three dimensions is defined as a set of 3^n components which change upon rotation of the coordinate system in the same way as products of n the same components of the radius vector. For example, consider the component ε_{xy} of the second-rank tensor ε_{ij}. If we rotate the coordinate system, the value of ε_{xy} changes by the same factor as does the product xy. According to this definition, scalars and vectors are tensors of rank zero and one, respectively.

A widely used convention for describing sums of components of a tensor is known as the **Einstein summation rule**: if in an expression containing tensors, an index is repeated in the same term, we sum over all values of this index. Consider the following examples,

$$Q_j = a_i b_{ij} \equiv \sum_{i=1}^{3} a_i b_{ij} = a_x b_{xj} + a_y b_{yj} + a_z b_{zj}$$

$$R_{mn} = \varepsilon_{mn} + \varepsilon_{im}\varepsilon_{in} \equiv \varepsilon_{mn} + \sum_{i=1}^{3} \varepsilon_{im}\varepsilon_{in} = \varepsilon_{mn} + \varepsilon_{xm}\varepsilon_{xn} + \varepsilon_{ym}\varepsilon_{yn} + \varepsilon_{zm}\varepsilon_{zn}.$$

The dot product of two vectors can be written as:

$$\mathbf{ab} = a_i b_i \equiv a_x b_x + a_y b_y + a_z b_z. \tag{AII.1}$$

It is also convenient to introduce two special tensors:

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \tag{AII.2}$$

and

$$\varepsilon_{ijk} = -\varepsilon_{jik}; \qquad \varepsilon_{ijk} = -\varepsilon_{kji}; \qquad \varepsilon_{ijk} = -\varepsilon_{ikj}$$
$$\left|\varepsilon_{ijk}\right| = \begin{cases} 0 & \text{if} \quad i = j \text{ or } i = k \text{ or } j = k \\ 1 & \text{if} \quad i \neq j \text{ and } i \neq k \text{ and } j \neq k. \end{cases} \qquad \text{(AII.3)}$$

δ_{ij} is known as the Kronecker delta and ε_{ijk} is the Levi–Civita epsilon. It can be shown that the components of these two tensors do not change upon rotation of the coordinate system. Manipulation of these definitions shows that:

$$\varepsilon_{kij}\varepsilon_{klm} = \delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}, \qquad \text{(AII.4)}$$

where, of course, we sum over k.

The dot and vector products of two vectors can be defined in terms of these tensors as follows:

$$\mathbf{a} \cdot \mathbf{b} = a_i b_i = \delta_{ij} a_i b_j, \qquad \text{(AII.5)}$$

$$(\mathbf{a} \times \mathbf{b})_k = \varepsilon_{kij} a_i b_j, \qquad \text{(AII.6)}$$

where the index k in the last equation implies the kth component of the vector. Note that the dot product of two vectors is a scalar and does not depend upon the orientation of the coordinate system. While $a_i b_j$ is a tensor of second rank and, hence, depends on the orientation of the coordinate system, its **trace** $a_i b_i$, is identical to the dot product $\mathbf{a} \cdot \mathbf{b}$ and is independent of the orientation of the coordinate system. This conclusion is valid for the trace of any second-rank tensor.

In Chapters 7 and 9, we encounter the **gradient** operator, ∇. We can consider this operator as a vector with components $\partial/\partial x$, $\partial/\partial y$, and $\partial/\partial z$. We can then write the following definitions:

$$(\mathrm{grad} f)_k = (\nabla f)_k = \frac{\partial f}{\partial x_k}, \qquad \text{(AII.7)}$$

$$\mathrm{div}\mathbf{a} = \nabla \cdot \mathbf{a} = \frac{\partial a_i}{\partial x_i}, \qquad \text{(AII.8)}$$

$$(\mathrm{curl}\mathbf{a})_k = (\nabla \times \mathbf{a})_k = \varepsilon_{kij} \frac{\partial a_j}{\partial x_i}, \qquad \text{(AII.9)}$$

$$\Delta f = \nabla^2 f = (\nabla\nabla) f = \frac{\partial^2 f}{\partial x_i \partial x_i} = \frac{\partial^2 f}{\partial x_i^2}, \qquad \text{(AII.10)}$$

$$(\Delta \mathbf{a})_k = (\nabla^2 \mathbf{a})_k = (\nabla\nabla) a_k = \frac{\partial^2 a_k}{\partial x_i \partial x_i} = \frac{\partial^2 a_k}{\partial x_i^2}, \qquad \text{(AII.11)}$$

where f is a scalar and $\mathbf{a}$ is a vector.

In order to demonstrate how to work with these operators, we derive several useful expressions used in this book:

$$f \frac{\partial a_i}{\partial x_i} = \frac{\partial (f a_i)}{\partial x_i} - a_i \frac{\partial f}{\partial x_i}$$

or

$$f\nabla\cdot\mathbf{a}=\nabla\cdot(f\mathbf{a})-\mathbf{a}\cdot\nabla f, \tag{AII.12}$$

$$\frac{\partial}{\partial x_i}\left(\frac{\partial^2 a_i}{\partial x_j\partial x_j}\right)=\frac{\partial^2}{\partial x_j\partial x_j}\left(\frac{\partial a_i}{\partial x_i}\right)$$

or

$$\nabla\cdot(\Delta\mathbf{a})=\Delta(\nabla\cdot\mathbf{a}), \tag{AII.13}$$

and

$$\begin{aligned}(\nabla\times(\nabla\times\mathbf{a}))_k&=\varepsilon_{kij}\frac{\partial}{\partial x_i}\varepsilon_{jlm}\frac{\partial a_m}{\partial x_l}=\varepsilon_{jki}\varepsilon_{jlm}\frac{\partial^2 a_m}{\partial x_i\partial x_l}=(\delta_{kl}\delta_{im}-\delta_{km}\delta_{il})\frac{\partial^2 a_m}{\partial x_i\partial x_l}\\&=\frac{\partial}{\partial x_k}\left(\frac{\partial a_m}{\partial x_m}\right)-\frac{\partial^2 a_k}{\partial x_i\partial x_i}=(\nabla\cdot(\nabla\cdot\mathbf{a}))_k-\Delta\mathbf{a}_k\end{aligned}$$

or

$$\nabla\cdot(\nabla\cdot\mathbf{a})=\Delta\mathbf{a}+\nabla\times(\nabla\times\mathbf{a}). \tag{AII.14}$$

Finally, we recall the statement of the **Gauss theorem**:

$$\int_V\frac{\partial b_j}{\partial x_j}\,\mathrm{d}V=\oint_A b_j n_j\,\mathrm{d}a, \tag{AII.15}$$

where **b** is a vector, V is a volume, and A is the surface surrounding this volume.

Appendix III. Continuity equation

There are several extensive quantities, such as the number of atoms or the total electrical charge in the system that typically remains constant during any process. The conservation law for such quantities can be expressed through continuity equations. In this appendix, we derive such an equation for the number of atoms of component i.

Consider an arbitrary volume V inside a system. The number of atoms of component i in this volume is

$$N_i=\int_V c_i\,\mathrm{d}V,$$

where c_i is the concentration expressed in mole/m^3. The number of atoms of component i, which leave volume V through its surface element da in unit time is $\mathbf{j_i}\cdot\mathbf{n}\mathrm{d}a$, where $\mathbf{j_i}$ is the flux of atoms of component i and **n** is the normal to the surface element da. Therefore, the number of atoms of component i, which leaves the entire volume V in unit time is:

$$\oint_a \mathbf{j_i}\mathbf{n}\,\mathrm{d}a.$$

The number of atoms leaving the unit volume per unit time can also be expressed as $-\partial N_i/\partial t$. Equating these two expressions, we find:

$$-\frac{\partial}{\partial t}\int_V c_i\,\mathrm{d}V = \oint_a \mathbf{j_i n}\,\mathrm{d}a.$$

Using the Gauss theorem (Eq. (AII.15)) to evaluate the integral on the right, we can rewrite this equation as:

$$\int_V \frac{\partial c_i}{\partial t}\mathrm{d}V + \int_V \nabla\cdot\mathbf{j_i}\,\mathrm{d}V = 0.$$

Since this equality is valid for any arbitrary volume V, we obtain:

$$\frac{\partial c_i}{\partial t} + \nabla\cdot\mathbf{j_i} = 0. \qquad \text{(AIII.1)}$$

This relation is known as the **continuity equation**.

Appendix IV. Functions erf(*z*) and *F*(*z*)

In this appendix, we describe several functions, which frequently occur in the solution of the diffusion equation. The first is called the **error function**:

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^\infty \mathrm{e}^{-\xi^2}\mathrm{d}\xi. \qquad \text{(AIV.1)}$$

It is tabulated in Table AIV.1 for convenience. erf(z) has the following properties:

$$\mathrm{erf}(0) = 0; \qquad \mathrm{erf}(\infty) = 1 \qquad \text{(AIV.2)}$$

$$\mathrm{erf}(-z) = -\mathrm{erf}(z) \qquad \text{(AIV.3)}$$

$$[\mathrm{erf}(z)]' = \frac{2}{\sqrt{\pi}}\mathrm{e}^{-z^2}. \qquad \text{(AIV.4)}$$

The **complimentary error function**, erfc(z) is defined as:

$$\mathrm{erfc}(z) = 1 - \mathrm{erf}(z). \qquad \text{(AIV.5)}$$

Both of these functions are plotted in Fig. AIV.1.

Another important function that occurs in solutions of diffusion equations is:

$$F(z) = \sqrt{\pi}z\cdot\exp(z^2)\mathrm{erf}(z). \qquad \text{(AIV.6)}$$

For $z \ll 1$, $F(z) \approx 2z^2$. The function is also tabulated in Table AIV.1.

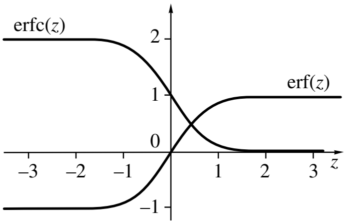


Fig. AIV.1
A plot of the functions erf(z) and erfc(z).

Table AIV.1 The functions erf(z) and $F(z)$

z	erf(z)	$F(z) = \sqrt{\pi}z\mathrm{e}^{z^2}\,\mathrm{erf}(z)$
0.00	0.000	0.000
0.05	0.056	0.006
0.10	0.112	0.020
0.15	0.168	0.044
0.20	0.223	0.082
0.25	0.276	0.13
0.30	0.329	0.19
0.35	0.379	0.26
0.40	0.428	0.36
0.45	0.475	0.47
0.50	0.520	0.59
0.60	0.604	0.92
0.70	0.678	1.36
0.80	0.742	2.00
0.90	0.797	2.82
1.00	0.843	4.06
1.20	0.910	8.19
1.40	0.952	16.65

Appendix V. Integrals that frequently occur in statistical mechanics

Two types of integrals appear frequently in statistical mechanics problems:

$$\int_{-\infty}^{+\infty} x^{2n}\mathrm{e}^{-\alpha x^2}\mathrm{d}x$$

and

$$\int_0^{\infty} x^{2n+1} \mathrm{e}^{-\alpha x^2} \mathrm{d}x,$$

where n is integer. The first of these can be evaluated using the Poisson formula:

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \sqrt{\frac{\pi}{\alpha}}. \tag{AV.1}$$

Taking derivatives of both sides of this equation with respect to α yields:

$$\int_{-\infty}^{+\infty} x^2 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}}. \tag{AV.2}$$

Repeating this procedure gives:

$$\int_{-\infty}^{+\infty} x^4 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{3}{4}\sqrt{\frac{\pi}{\alpha^5}}, \tag{AV.3}$$

and so forth.

In order to evaluate the second type of integral, we note that

$$\int_0^{\infty} x \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{2\alpha}. \tag{AV.4}$$

Then, taking derivatives of both sides of this equation with respect to α, we obtain:

$$\int_0^{\infty} x^3 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{2\alpha^2}. \tag{AV.5}$$

Example problem solutions

Before providing the solutions to the Example problems in the text, a few remarks are in order. Solving the Example problems will serve as a good test to ensure that you understand the material in the section containing the problem. It is strongly recommended that you follow the problem all of the way through until you have obtained a numerical answer. A numerical answer has no meaning unless the units are fully specified. Before checking your answer, you should apply the reasonableness test. That is, determine whether your answer is plausible. Note that the examples in the text contain either real experimental data or reasonable estimates of the requisite quantities.

Chapter 1

1.1.2.1. It is obvious that the equilibrium temperature must be between 273.2 K and 373.2 K (initial temperatures of the ice and water, respectively). Since the system is in an adiabatic container, it does not exchange heat with its surrounding, therefore $\Delta H = 0$. The following three processes occur:

(1) the ice melts;
(2) the water produced from the melting ice warms up to the equilibrium temperature T_e;
(3) the 100°C water that was initially part of the system cools down to the equilibrium temperature T_e.

In order to find the equilibrium state, it does not matter in which order these processes proceed. Rather, we simply sum the change in enthalpy for each of the processes and insist that the change in the total enthalpy is zero. In this way, we obtain:

$$0 = \Delta H = \frac{m_{\mathrm{ice}}}{M}\Delta H_{\mathrm{melt}} + \frac{m_{\mathrm{ice}}}{M} c_{\mathrm{p}}\left(T_{\mathrm{e}} - T_{\mathrm{melt}}\right) + \frac{m_{\mathrm{water}}}{M} c_{\mathrm{p}}\left(T_{\mathrm{e}} - T_{\mathrm{boil}}\right),$$

where M is the molecular weight of water, m_{ice} and m_{water} are the initial masses of ice and water, respectively. Solving this equation for the equilibrium temperature yields:

$$T_e = \frac{c_p\left(m_{\text{ice}}T_{\text{melt}} + m_{\text{water}}T_{\text{boil}}\right) - m_{\text{ice}}\Delta H_{\text{melt}}}{c_p\left(m_{\text{ice}} + m_{\text{water}}\right)}$$
$$= \frac{75.3(1 \cdot 273.2 + 10 \cdot 373.2) - 1 \cdot 6010}{75.3(1+10)} = 356.9 \text{ K}.$$

1.1.3.1. Since the gas is heated at constant pressure, it will expand and, therefore, perform work. Hence, the answer must be positive. The ideal gas law and Eq. (1.20) can then be used to obtain the work performed by the gas:

$$W = nR\Delta T = \frac{p_1V_1R\Delta T}{RT_1} = \frac{p_1 m\Delta T}{T_1\rho_1}$$
$$= \frac{1.013 \cdot 10^5 \cdot 2 \cdot 1}{273.2 \cdot 0.00129 \cdot 10^6} = 0.575 \text{ J}.$$

1.1.3.2. Since the gas expands, it performs (positive) work. The internal energy of an ideal gas does not change during an isothermal process. Therefore, all of the heat added to the gas is converted into work, that is, $Q = W > 0$. Applying Eq. (1.19) to the present situation yields

$$Q = W = nRT \ln\frac{p_1}{p_2} = p_1V_1 \ln\frac{p_1}{p_2}$$
$$= 5 \cdot 1.013 \cdot 10^5 \cdot 2 \cdot 10^{-3} \ln\frac{5}{1} = 1630 \text{ J}.$$

1.1.3.3. Since the gas contracts, the work performed by the gas must be negative. Application of Eqs (1.23), (1.22), and (1.21) shows:

$$W = -nc_V\Delta T = -\frac{m}{M}c_V\Delta T$$

$$\left.\begin{array}{r} pV^{\gamma} = \text{const} \\ pV = nRT \end{array}\right\} \Rightarrow TV^{\gamma-1} = \text{const}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}; \qquad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\gamma = \frac{c_p}{c_V} = \frac{c_V + R}{c_V} = \frac{7}{5} = 1.4$$

$$T_2 = 290\left(\frac{8}{5}\right)^{1.4-1} = 350 \text{ K}$$

$$W = -\frac{10}{28.02}2.5 \cdot 8.314 \cdot (350 - 290) = -445 \text{ J}.$$

1.1.3.4. Since the internal energy is a state function, it does not change when we go around a complete circuit. Therefore, the first law of thermodynamics reduces to $Q = W$. Writing expressions for the work associated with each process, we find:

$$Q = W = nR(T_2 - T_1) + nRT_2 \ln\frac{p_1}{p_2} + nR(T_1 - T_2)$$
$$+ nRT_1 \ln\frac{p_2}{p_1} = nR(T_2 - T_1) \ln\frac{p_1}{p_2}.$$

1.1.4.1. Equation (1.31) implies:

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta c_\mathrm{p} \mathrm{d}T$$

where

$$\Delta c_\mathrm{p} = \Delta a + \Delta b \cdot 10^{-3} T + \Delta \mathrm{c} \cdot 10^5 T^{-2}.$$

Performing the integration, we obtain:

$$\Delta H_T^0 = \Delta H_{298}^0 + \Delta a(T - 298) + \frac{\Delta b}{2} \cdot 10^{-3}(T^2 - 298^2)$$
$$- \Delta c \cdot 10^5 \left(\frac{1}{T} - \frac{1}{298}\right).$$

Using the data provided in the problem, we find:

$$\Delta H_{298}^0 = 2 \cdot (-241.81) + 3 \cdot 0 - 2 \cdot (-110.53)$$
$$- (-74.60) = -187.96 \text{ kJ/mole}$$
$$\Delta a = 2 \cdot 30.00 + 3 \cdot 16.86 - 2 \cdot 28.41 - 42.06 = 11.7$$
$$\Delta b = 2 \cdot 10.71 + 3 \cdot 4.77 - 2 \cdot 4.10 - 31.50 = -3.97$$
$$\Delta c = 2 \cdot 0.33 + 3 \cdot (-8.54) - 2 \cdot (-0.46)$$
$$- (-17.29) = -6.75$$
$$\Delta H_{1100}^0 = -182.45 \text{ kJ/mole}.$$

Note that the value of the standard enthalpy at $T = 1100$ K is not very different from that at $T = 298$ K. Is this always true? We can analyze how strongly ΔH_T^0 depends on temperature as follows. The heat capacity of inorganic substances per mole usually does not exceed $20R$. Therefore, for a reaction involving inorganic substances $\Delta c_\mathrm{p} \sim 10R$ and the change of ΔH_T^0 is $\sim 10R(T - 298)$. At high temperatures (~1000 K), this gives approximately 50 kJ/mole (note, this is an upper bound—usually, $\Delta c_\mathrm{p} < 10R$). Therefore, the heat of reaction changes with temperatures by only 10 kJ/mole. Since the heat of reaction is typically 100 kJ/mole, its value at $T = 298$ K is a good approximation for the heat of reaction at other temperatures (of course, if you know the heat capacities of all of the species you need not make this assumption). If in solving a problem you found that the heat of reaction changes by >100 kJ/mole with temperature, you probably made a mistake—in any case, this is a hint that you had better check your calculations one more time.

1.1.4.2. The heat of a reaction occurring at constant volume is ΔU_T^0. For the reaction under consideration $\Delta U_T^0 = \Delta H_T^0 + RT$. The heat of this reaction, if it occurred at constant pressure, can be found from the data provided, as in Example problem 1.1.4.1. You should obtain $\Delta H_{700}^0 = -910$ kJ/mole and $\Delta U_{700}^0 = -904$ kJ/mole. Note, that even for reactions involving gases, the difference between the heats of reaction at constant pressure and at constant volume is small in comparison with the values of the heat of reaction.

1.2.1.1. The processes prohibited by Thomson's and Clausius's postulates are called Thomson's and Clausius's processes (surprising but true), respectively. We must prove that the impossibility of one process follows from the impossibility of the other process.

1. Assume that Clausius's process is possible. Let a medium receive heat $|Q_\mathrm{h}|$ from a heater, give up heat $|Q_\mathrm{c}|$ to a cooler and performs work $W = |Q_\mathrm{h}| - |Q_\mathrm{c}|$. Using Clausius's process we can take heat $|Q_\mathrm{c}|$ from the cooler and give it to the heater (no other changes will happen during this process!). As a result, we obtain a circuit in which the state of the cooler was not changed, the heater gave up heat $|Q_\mathrm{h}| - |Q_\mathrm{c}|$ in order for the medium to perform work $W = |Q_\mathrm{h}| - |Q_\mathrm{c}|$ and there are no other changes in the universe. However, this is Thomson's process! Therefore in order to prohibit Thomson's process we must also prohibit Clausius's process.

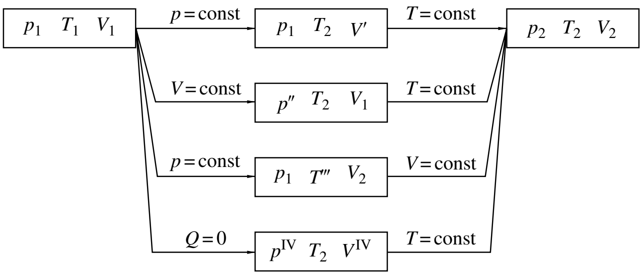
2. Now assume that Thomson's process is possible. Let a medium take heat from the cooler and perform a circuit in which a weight is lifted. No other change occurs in the universe. The potential energy of the lifted weight can be easily converted in heat, for example via friction. We can return the weight to its initial state and give up the resulting heat to the heater. The only change in the universe as a result of the entire process was the transfer of heat from the cooler to the heater. However, this is Clausius's process. Therefore in order to prohibit Clausius's process we must also prohibit Thomson's process.

1.2.6.1. We now continue considering Example problem 1.1.2.1 and find the change of entropy associated with the equilibration of the system. Since equilibration is a spontaneous process and the system is adiabatic, the entropy should increase and therefore its change should be positive. We need not worry about how the system actually reaches the equilibrium state, since the entropy is a state function and its change does not depend on path. As in Example problem 1.1.2.1, we consider the change of the entropy of the system as a sum of contributions from the three processes:

$$\Delta S = \frac{m_{\text{ice}}}{M}\Delta S_{\text{melt}} + \frac{m_{\text{ice}}}{M} c_{\text{p}} \ln\frac{T_{\text{e}}}{T_{\text{melt}}} + \frac{m_{\text{water}}}{M} c_{\text{p}} \ln\frac{T_{\text{e}}}{T_{\text{boil}}}$$
$$= \frac{1}{M}\left(m_{\text{ice}}\frac{\Delta H_{\text{melt}}}{T_{\text{melt}}} + m_{\text{ice}}c_{\text{p}} \ln\frac{T_{\text{e}}}{T_{\text{melt}}} + m_{\text{water}}c_{\text{p}} \ln\frac{T_{\text{e}}}{T_{\text{boil}}}\right)$$
$$= 0.471 \text{ J/K}.$$

1.2.6.2. Since 1 mole of any ideal gas has a volume of 22.4 l under normal conditions ($T = 0°\text{C}$ and $p = 1$ atm), 2 moles of a gas at $T_1 = 25°\text{C}$ and $p_1 = 1$ atm takes approximately 50 l. Hence, as a result of the process under consideration in this example problem, the gas expands and gets hotter. The entropy increases as a result of this expansion and heating and, therefore, overall the change in entropy must be positive.

The change in entropy depends only on the initial and final states of a system and does not depend on path. Therefore, we can consider any process that leads from the initial state to the final one described in the problem. Of course, we should choose a path for which we can calculate the change in entropy at each step. The figure shows four examples of such processes.



Here we calculate the change in entropy using the uppermost path. Application of Eqs (1.48) and (1.52) yields:

$$\Delta S = \Delta S_p + \Delta S_{\text{T}} = n\int_{T_1}^{T_2}\frac{c_{\text{p}}}{T}\text{d}T + nR \ln\frac{p_1}{p_2}$$
$$= n\left\{c_{\text{p}} \ln\frac{T_2}{T_1} + R \ln\frac{p_1 V_2}{nRT_2}\right\}$$
$$= 2\left\{3.5 \cdot 8.314 \ln\frac{473.2}{298.2} + R \ln\frac{1.013 \cdot 10^5 \cdot 100 \cdot 10^{-3}}{2 \cdot 8.314 \cdot 473.2}\right\}$$
$$= 31.06 \text{ J/K}.$$

In order to test your skills, calculate the change in entropy associated with the remaining paths and convince yourself that all paths give the same change in entropy.

1.2.6.3. This problem can be solved using Eq. (1.53):

$$\Delta S_{\text{mix}} = n_1 R \ln \frac{V}{V_1} + n_2 R \ln \frac{V}{V_2}.$$

However, when deriving this equation, we assumed that the temperatures and pressures of both gases are the same before and after mixing. Therefore, first we should calculate the change of entropy associated with changing the pressure of the oxygen to 1 atm. If the oxygen pressure is decreased at constant temperature to 1 atm, its volume will be $V_2' = V_2(p_2/p_1) = 4$ l. The change of entropy associated with this process is $\Delta S_{\text{T}} = n_2 R \ln (V_2'/V_2)$. The change of entropy as a result of entire process (including mixing) is, therefore,

$$\begin{aligned}\Delta S = \Delta S_{\text{T}} + \Delta S_{\text{mix}} &= n_2 R \ln \frac{V_2'}{V_2} - R\left\{ n_1 R \ln \frac{V_1}{V_1 + V_2'} \right.\\ &\qquad \left. + n_2 R \ln \frac{V_2'}{V_1 + V_2'} \right\}\\ &= \frac{p_1 V_2'}{T} \ln \frac{V_2'}{V_2} - \frac{p_1 V_1}{T} \ln \frac{V_1}{V_1 + V_2'} - \frac{p_1 V_2'}{T} \ln \frac{V_2'}{V_1 + V_2'}\\ &= \frac{p_1}{T} \left\{ V_2' \ln \frac{V_1 + V_2'}{V_2} + V_1 \ln \frac{V_1 + V_2'}{V_1} \right\}\\ &= \frac{1.013 \cdot 10^5}{298.2} 10^{-3} \left\{ 4 \ln \frac{1+4}{2} + 1 \ln \frac{1+4}{1} \right\} = 1.79 \text{ J/K}.\end{aligned}$$

1.2.6.4. Using Eq. (1.48), we can write:

$$\Delta S_{\text{T}}^0 = \Delta S_{298}^0 + \Delta a \ln \frac{T}{298} + \Delta b \cdot 10^{-3}(T - 298) - \frac{\Delta c \cdot 10^5}{2} \left(\frac{1}{T^2} - \frac{1}{298^2} \right).$$

Applying this expression to the reaction under consideration yields:

$$\Delta S_{298}^0 = -186.70 \text{ J/(mole K)}; \qquad \Delta S_{1100}^0 = -178.13 \text{ J/(mole K)}$$

1.3.2.1. The entropy increases with increasing temperature (the heat capacity is always positive) and also during the $\alpha \rightarrow \beta$ transformation (since $\Delta H_{\alpha \rightarrow \beta} > 0$). Using Eqs (1.48) and (1.51), we find:

$$\begin{aligned}S_{T_{\alpha\rightarrow\beta}}^0(\beta - \text{Fe}) &= S_{298}^0(\alpha - \text{Fe}) + \int_{298}^{T_{\alpha\rightarrow\beta}} \frac{c_{\text{p}}}{T} \mathrm{d}T + \frac{\Delta H_{\alpha\rightarrow\beta}}{T_{\alpha\rightarrow\beta}}\\ &= 27.15 + 17.3 \ln \frac{1041}{298}\\ &\quad + 2.67 \cdot 10^{-2}(1041 - 298) + \frac{1530}{1041}\\ &= 70.10 \text{ J/(mole K)}.\end{aligned}$$

1.4.2.1. In order to determine the pressure, we must first derive the equation of state. This equation can be obtained using Eq. (1.70):

$$V = \left(\frac{\partial G}{\partial p}\right)_T = \frac{nRT}{p} + nb - \frac{an}{RT}$$

or

$$p = \frac{nRT}{V - nb + (an/RT)}.$$

For the conditions specified in the example problem, we find $p = 23.9$ atm.

Note, that for these conditions, $bn/V = 0.03$ and $an/RTV = 0.06$. Expanding the equation of state in a series in these two small parameters and retaining only the first-order terms, we obtain:

$$pV = \frac{nRT}{1 - (nb/V) + (an/RTV)} \approx nRT\left(1 + \frac{nb}{V}\right) - \frac{an^2}{V}.$$

This is the **van der Waals equation** (see Example problems 13.2.1.1 and 13.2.2.1). According to the molecular theory of gases, $b/4$ is the volume of a molecule and the coefficient a is associated with the interaction between molecules. If $b = 0$ (the molecule volume is negligible) and $a = 0$ (there is no interaction between molecules) the van der Waals equation reduces to the ideal gas law $pV = nRT$. Note that the expression for the Gibbs free energy given in the example problem corresponds to oxygen in the van der Waals approximation.

In order to find the entropy, we use Eq. (1.69):

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = 3.5nR(1 + \ln T) - nR \ln p + 12.73nR - \frac{nap}{RT^2}$$

$$= nR[3.5(1 + \ln T) - \ln p + 12.73] - \frac{nap}{RT^2}.$$

Since the deviations from ideality are related to non-zero values of the coefficients a and b, we conclude that the first term in this expression is the entropy of the ideal gas and the second term represents the deviations from ideality. For the given conditions: $S = 178.50 - 0.45 = 178.05$ J/(mole K).

In order to calculate the isobaric heat capacity, we use Eq. (1.49):

$$c_p = T\left(\frac{\partial S}{\partial T}\right)_p = 3.5nR + \frac{2nap}{RT^2} = 29.10 + 0.91 = 30.00 \text{ J/(mole K)}.$$

In order to calculate the isothermal compressibility we note that:

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2}$$

and therefore,

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{nRT}{p^2 V} = 4.23 \cdot 10^{-7}\ \mathrm{Pa}^{-1}.$$

For the coefficient of thermal expansion, we obtain:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{nR}{p} + \frac{an}{RT^2}\right) = 3.62 \cdot 10^{-3}\ \mathrm{K}^{-1}.$$

Finally, for the isochoric heat capacity, we use Eq. (1.75):

$$c_\mathrm{V} = c_\mathrm{p} - \frac{TV\alpha^2}{\chi_T} = 30.00 - 9.23 = 20.77\ \mathrm{J/(mole\,K)}.$$

From this example problem, we see that if we have the Gibbs free energy as a function of p and T (or the Helmholtz free energy as function of V and T), we can calculate any thermodynamic property of the system under consideration. Further, we will see that in the case of a solution we also need to know the dependence of the free energy on the concentrations of the components. This example problem demonstrates the most common approach for developing a thermodynamic description of any homogeneous system. First, we construct an expression for the Gibbs free energy (or the Helmholtz free energy) using some theoretical ideas or experimental observation. Then, we derive all other thermodynamic properties of the system using this function.

1.4.2.2. Equation (1.46) implies

$$\Delta U = \int T\,\mathrm{d}S - \int p\,\mathrm{d}V.$$

In order to calculate the first term on the right side of this expression (the heat absorbed by the system as a result of a reversible process), we use Eq. (1.74)

$$(\mathrm{d}S)_T = -\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p.$$

Integration of this equation gives:

$$\begin{aligned}
\int T\mathrm{d}S &= -\int_{p_1}^{p_2} T\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p \\
&= -\int_{p_1}^{p_2} T(4.5 \cdot 10^{-3} + 1.4 \cdot 10^{-6} p)\mathrm{d}p \\
&\approx -T\left(4.5 \cdot 10^{-3} p_2 + 1.4 \cdot 10^{-6} p_2^2\right) = -1550\ \mathrm{cm^3\,atm} \\
&= -1550 \cdot 10^{-6} \cdot 1.013 \cdot 10^5\ \mathrm{J} = -157.0\ \mathrm{J}
\end{aligned}$$

(we neglected the pressure p_1 in comparison with pressure p_2). Calculation of the second term (work performed by the system) gives:

$$\begin{aligned}\int_{p_1}^{p_2} p\,\mathrm{d}V &= \int_{p_1}^{p_2} p\left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p\\ &= \int_{p_1}^{p_2} (-7.15\cdot 10^{-4}p + 9.2\cdot 10^{-8}p^2)\mathrm{d}p\\ &\approx -\frac{7.15\cdot 10^{-4}}{2}p_2^2 + \frac{9.2\cdot 10^{-8}}{3}p_2^3\\ &= -327\ \mathrm{cm}^3\ \mathrm{atm} = -33.1\ \mathrm{J}.\end{aligned}$$

Finally, for the change of the internal energy, we obtain:

$$\Delta U = -157.0 + 33.1 = -123.9\ \mathrm{J}.$$

Chapter 2

2.2.1. From Eq. (2.7), we obtain:

$$\frac{\mathrm{d}p}{\mathrm{d}T_{\mathrm{melt}}} = \frac{\Delta H_{\mathrm{melt}}}{T_{\mathrm{melt}}(V_{\mathrm{L}} - V_{\mathrm{S}})}$$

or

$$\int \mathrm{d}T_{\mathrm{melt}} = \int \frac{T_{\mathrm{melt}}(V_{\mathrm{L}} - V_{\mathrm{S}})}{\Delta H_{\mathrm{melt}}}\mathrm{d}p.$$

Since the properties of condensed phases that appear in the integrand only weakly depend on pressure, we can assume that they are constant and take them outside of the integral. We obtain:

$$\begin{aligned}\Delta T_{\mathrm{melt}} &= \frac{T_{\mathrm{melt}}(V_{\mathrm{L}} - V_{\mathrm{S}})}{\Delta H_{\mathrm{melt}}}\Delta p = \frac{T_{\mathrm{melt}}M((1/d_{\mathrm{L}}) - (1/d_{\mathrm{S}}))\Delta p}{\Delta H_{\mathrm{melt}}}\\ &= \frac{(231.9 + 273.2)\cdot 118.7\cdot 10^{-6}((1/6.988) - (1/7.184))\cdot 99\cdot 1.013\cdot 10^5}{7070}\\ &= 0.33\ \mathrm{K}.\end{aligned}$$

This result supports our assumption that large increases in pressure produce only small changes in the melting temperature.

2.2.2. Since the saturated vapor pressure monotonically increases with increasing temperature and is equal to 1 atm at the boiling temperature, the pressure must be less than 1 atm. Equation (2.9) can be rewritten as:

$$\int_0^{\ln p} \mathrm{d}\ln p = \int_{T_{\mathrm{boil}}}^{T} \frac{\Delta H_{\mathrm{evap}}}{RT^2}\mathrm{d}T,$$

(we used the fact that $p = 1$ atm at T_{boil}—that is, normal conditions). Performing the integration, we obtain:

$$\ln p = \frac{1}{R}\left\{-45860\left(\frac{1}{333} - \frac{1}{348}\right) - 44.06\ln\frac{333}{348}\right\} = -0.480.$$

Therefore, $p = 0.62$ atm.

2.2.3. If we neglect the temperature dependence of ΔH_{subl}, integration of Eq. (2.10) yields:

$$\ln p = \ln p_1 + \frac{\Delta H_{\mathrm{subl}}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right).$$

Therefore, in order to calculate the saturated vapor pressure over a solid at a given temperature T we need to know the saturated vapor pressure p_1 at some other temperature T_1 and ΔH_{subl}. The only temperature in the input data related to the solid is the melting temperature. At this temperature, the solid argon is in equilibrium with liquid argon:

$$\mathrm{Ar}_{(\mathrm{S})} = \mathrm{Ar}_{(\mathrm{L})}.$$

Since, by definition, the saturated vapor is a vapor which is in equilibrium with its corresponding condensed phase, this equation implies that at the melting temperature the saturated vapors over the solid and liquid phases must be in equilibrium with each other. This means that the vapor pressure above the two condensed phases at the melting temperature must be the same. Therefore, now we should find the saturated vapor pressure over the liquid phase at the melting temperature. We can do this using the fact that the saturated vapor pressure over a liquid at the normal boiling temperature is 1 atm. Analogously to the previous example problem we obtain:

$$\ln p_{\mathrm{melt}} = \frac{\Delta H_{\mathrm{evap}}}{R}\left(\frac{1}{T_{\mathrm{boil}}} - \frac{1}{T_{\mathrm{melt}}}\right).$$

Therefore, the saturated vapor pressure over the solid phase is:

$$\ln\ p = \frac{\Delta H_{\mathrm{subl}}}{R}\left(\frac{1}{T_{\mathrm{melt}}} - \frac{1}{T}\right) + \frac{\Delta H_{\mathrm{evap}}}{R}\left(\frac{1}{T_{\mathrm{boil}}} - \frac{1}{T_{\mathrm{melt}}}\right).$$

We now estimate the heat of sublimation ΔH_{subl} from ΔH_{evap} and ΔH_{melt}. These three quantities are equal to the heats of the following reactions:

$$\begin{array}{lll} (1) & \mathrm{Ar}_{(\mathrm{S})} = \mathrm{Ar}_{(\mathrm{V})}, & \Delta H_{\mathrm{subl}} \\ (2) & \mathrm{Ar}_{(\mathrm{L})} = \mathrm{Ar}_{(\mathrm{V})}, & \Delta H_{\mathrm{evap}} \\ (3) & \mathrm{Ar}_{(\mathrm{S})} = \mathrm{Ar}_{(\mathrm{L})}, & \Delta H_{\mathrm{melt}}. \end{array}$$

The first reaction can be written as the sum of the second and third reactions (recall, that we assumed that the heats do not depend on temperature), therefore,

$$\Delta H_{\mathrm{subl}} = \Delta H_{\mathrm{evap}} + \Delta H_{\mathrm{melt}}.$$

Using the handbook data, we obtain: $\Delta H_{\mathrm{subl}} = 7.69$ kJ/mole and $p = 4.0 \cdot 10^{-4}$ atm.

The experimental value for the saturated vapor pressure over solid argon at $T = 50$ K is $p = 3.4 \cdot 10^{-4}$ atm. This is in reasonable agreement with our estimate.

Chapter 3

3.1.1. The relation between weight and molar fractions can be found as follows:

$$x_i = \frac{n_i}{\sum_{j=1}^{k} n_j} = \frac{q_i/M_i}{\sum_{j=1}^{k} q_j/M_j} = \frac{[i]/M_i}{\sum_{j=1}^{k} [j]/M_j} = \frac{[\%i]/M_i}{\sum_{j=1}^{k} [\%j]/M_j}.$$

The inverse relation can be obtained analogously:

$$[i] = \frac{x_i M_i}{\sum_{j=1}^{k} x_j M_j}.$$

Note that from these relations, it follows that the molar fraction of the component with the smallest molecular (atomic) weight is always larger than its weight fraction and the molar fraction of the component with the largest molecular weight is always smaller than its weight fraction.

For the molar fractions of the components of the alloy considered in the example problem, we obtain:

$$x_{\mathrm{Ni}} = \frac{70/58.7}{70/58.7 + 25/27.0 + 5/47.9} = 0.536$$

$$x_{\mathrm{Al}} = \frac{25/27.0}{70/58.7 + 25/27.0 + 5/47.9} = 0.417$$

$$x_{\mathrm{Ti}} = \frac{5/47.9}{70/58.7 + 25/27.0 + 5/47.9} = 0.047.$$

Of course, we could calculate the final molar fraction from the fact that $x_{\mathrm{Ni}} + x_{\mathrm{Al}} + x_{\mathrm{Ti}} = 1$. However, if we made a numerical error in the calculation of the first two molar fractions, we would probably not see it. It is better to use this relation to check the results, rather than obtain them. Indeed, the sum of the above three values is 1.

3.1.2. From the Gibbs–Duhem equation, we obtain:

$$V = n_1 \overline{V}_1 + n_2 \overline{V}_2 = \frac{q_1}{M_1}\overline{V}_1 + \frac{q_2}{M_2}\overline{V}_2$$
$$= \frac{q}{100}\left(\frac{[\%1]}{M_1}\overline{V}_1 + \frac{[\%2]}{M_2}\overline{V}_2\right).$$

Simple transformations yield:

$$\frac{1}{\rho} = \frac{1}{100}\left(\frac{[\%1]}{M_1}\overline{V}_1 + \frac{[\%2]}{M_2}\overline{V}_2\right)$$

$$\overline{V}_2 = \left(\frac{100}{\rho} - \frac{[\%1]}{M_1}\overline{V}_1\right)\frac{M_2}{[\%2]} = 39.85\ \mathrm{cm}^3/\mathrm{mole}.$$

3.1.3. In order to solve this problem, we use the Gibbs–Duhem equation (Eq. (3.16)):

$$x_1\left(\frac{\partial \overline{V}_1}{\partial x_1}\right)_{p,T} = x_2\left(\frac{\partial \overline{V}_2}{\partial x_2}\right)_{p,T}.$$

Since this equation is expressed in terms of molar fraction we should re-express it in terms of molarity:

$$m_2 = \frac{n_2}{q_1} = \frac{n_2}{n_1 M_1/1000} = \frac{1000}{M_1}\frac{x_2}{x_1} = \frac{1000}{M_1}\frac{x_2}{1 - x_2}.$$

Now, integrating the Gibbs–Duhem equation, we find:

$$x_1 \frac{\partial \overline{V}_1}{\partial x_1} = x_2 \frac{\partial \overline{V}_2}{\partial x_2} = x_2 \frac{1000b}{M_1}\frac{1}{(1 - x_2)^2}$$

$$\int_{V_1^0}^{\overline{V}_1} \mathrm{d}\overline{V}_1 = \int_1^{x_1} \frac{1000b}{M_1}\frac{1 - x_1}{x_1^3}\mathrm{d}x_1$$

$$\overline{V}_1 = V_1^0 + \frac{1000b}{M_1}\left(-\frac{1}{2x_1^2} + \frac{1}{x_1}\right)\Bigg|_1^{x_1} = V_1^0 + \frac{1000b}{M_1}\left(-\frac{1}{2x_1^2} + \frac{1}{x_1} - \frac{1}{2}\right)$$
$$= V_1^0 - \frac{1000b}{2M_1}\frac{x_1^2 - 2x_1 + 1}{x_1^2} = V_1^0 - \frac{1000b}{2M_1}\frac{x_2^2}{x_1^2} = V_1^0 - \frac{M_1}{2000}bm_2^2.$$

3.2.1.1. The Raoult law implies that the saturated vapor pressure over the glass of pure water is larger than the saturated vapor pressure over the glass containing a solution of urea. Therefore, the water vapor will diffuse from the glass with pure water toward the glass with the solution. This will lead to a water vapor pressure above the glass of the solution that is in excess of its saturated vapor pressure; therefore, some of this water vapor will condense. Analogously, some water will evaporate from the glass of pure water.

The same result can be obtained without consideration of the evaporation–condensation mechanism. Consider the following process:

$$H_2O_{(\mathrm{pure})} \to H_2O_{(\mathrm{solution})}.$$

The change of the Gibbs free energy associated with this process is:

$$\Delta G = \mu_{H_2O}^{\mathrm{solution}} - \mu_{H_2O}^{0} < 0,$$

(the chemical potential of any pure solvent is larger than the chemical potential of the solvent in a solution). Therefore, the process under consideration will go in the forward direction.

3.2.3.1. The molar fraction of sulfur in this solution is

$$x_S \approx \frac{n_S}{n_{Fe}} = \frac{q_S/M_S}{q_{Fe}/M_{Fe}} = \frac{M_{Fe}}{100 M_S}[\%S] = \frac{55.8}{100 \cdot 32.1}1 = 0.017.$$

Using Eq. (3.47), we obtain:

$$\Delta T_{\mathrm{freeze}} = \frac{8.314 \cdot 1813^2 \cdot 0.017}{262.5 \cdot 55.8} = 32.4\ \mathrm{K}.$$

The experimental value is 32 K.

3.2.4.1. The mass of iodine which can be extracted from the water is equal to the mass of iodine dissolved at equilibrium in CCl_4. From the partition law, we obtain:

$$L = \frac{c_{I_2}^{CCl_4}}{c_{I_2}^{H_2O}} = \frac{n_{I_2}^{CCl_4}}{n_{I_2}^{H_2O}} \frac{V^{H_2O}}{V^{CCl_4}} = \frac{q_{I_2}^{CCl_4}}{q_{I_2}^{H_2O}} \frac{V^{H_2O}}{V^{CCl_4}} = \frac{q_{I_2}^{CCl_4}}{\left(q_{I_2}^{H_2O}\right)^{\text{init}} - q_{I_2}^{CCl_4}} \frac{V^{H_2O}}{V^{CCl_4}}$$

$$q_{I_2}^{CCl_4} = \frac{L\left(q_{I_2}^{H_2O}\right)^{\text{init}}}{L + V^{H_2O}/V^{CCl_4}} = \frac{85.1 \cdot 0.1}{85.1 + 500/80} = 0.0932 \text{ g.}$$

3.3.1. The molar fraction of the saturated vapor of component i over a solution is:

$$x_i = \frac{p_i}{\sum_{j=1}^{k} p_j} = \frac{p_i^0 x_{[i]}}{\sum_{j=1}^{k} p_j^0 x_{[j]}},$$

where $x_{[i]}$ is the molar fraction of component i in solution. For the molar fraction of CH_3OH in the solution we find:

$$\begin{aligned} x_{[CH_3OH]} &= \frac{n_{[CH_3OH]}}{n_{[CH_3OH]} + n_{[C_2H_5OH]}} \\ &= \frac{q_{[CH_3OH]}/M_{CH_3OH}}{q_{[CH_3OH]}/M_{CH_3OH} + q_{[C_2H_5OH]}/M_{C_2H_5OH}} \\ &= \frac{\rho_{[CH_3OH]} V_{[CH_3OH]}/M_{CH_3OH}}{\rho_{[CH_3OH]} V_{[CH_3OH]}/M_{CH_3OH} + \rho_{[C_2H_5OH]} V_{[C_2H_5OH]}/M_{C_2H_5OH}} \\ &= \frac{\rho_{[CH_3OH]}/M_{CH_3OH}}{\rho_{[CH_3OH]}/M_{CH_3OH} + 2\rho_{[C_2H_5OH]}/M_{C_2H_5OH}} \\ &= \frac{0.9715/32.04}{0.9715/32.04 + 2 \cdot 0.7894/46.07} = 0.4189. \end{aligned}$$

Finally, the molar fraction of CH_3OH in the saturated vapor is

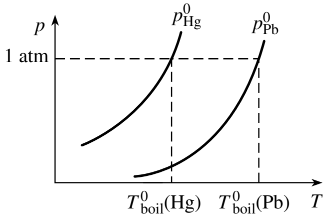
$$x_{CH_3OH} = \frac{96 \cdot 0.4189}{96 \cdot 0.4189 + 44 \cdot (1 - 0.4189)} = 0.611.$$

Note that the fraction of the more volatile component (i.e. the pure component which has the larger saturated vapor pressure) in the gas phase is larger than its fraction in the solution. In other words, the gas phase is enriched in the more volatile component.

3.3.2. In order to solve this problem, we shall use Eq. (3.39):

$$\ln x_1 = \frac{\Delta H_{\text{evap}}^0}{R}\left(\frac{1}{T_{\text{boil}}} - \frac{1}{T_{\text{boil}}^0}\right) = -\frac{\Delta H_{\text{boil}}^0}{R\left(T_{\text{boil}}^0\right)^2} \Delta T_{\text{boil}}.$$

However, this equation was obtained for ideal dilute solutions. Can we use this equation for ideal solutions? In order to answer this question, recall the assumptions which were used to derive Eq. (3.55). First, we used the fact that the chemical potential of the first component can be written as $\mu_1 = \mu_1^0 + RT \ln x_1$. This expression is also valid for ideal solutions. Second, we assumed that the saturated vapor pressure of the second component is negligible in comparison with that of the first component. This is obviously true for dilute solutions where $x_2 \to 0$. However, this is not the case for ideal solutions where all components have comparable concentrations. Since we were unable to make any general statement, we must consider our specific case more carefully. Note that the Clausius–Clapeyron equation implies that the saturated vapor pressure increases monotonically with increasing temperature, as shown in the figure. At the normal melting temperature, the saturated vapor pressure is 1 atm. Since $T^0_{\text{boil}}(\text{Hg}) \ll T^0_{\text{boil}}(\text{Pb})$, we conclude that $p^0_{\text{Hg}} \gg p^0_{\text{Pb}}$ at $T^0_{\text{boil}}(\text{Hg})$. If the boiling temperature for the solution is not very different from that of pure mercury (as will be supported by the calculation below), $p^0_{\text{Hg}} \gg p^0_{\text{Pb}}$ at the boiling temperature of the solution. Since the gas phase over the solution is enriched in mercury (see the previous example problem), we can conclude that $p_{\text{Hg}} \gg p_{\text{Pb}}$. Therefore, we can use Eq. (3.39).



We calculate the molar fraction of mercury in the solution (see Example problem 3.1.1) as:

$$x_{\text{Hg}} = \frac{[\%\text{Hg}]/M_{\text{Hg}}}{[\%\text{Hg}]/M_{\text{Hg}} + [\%\text{Pb}]/M_{\text{Pb}}} = 0.842.$$

For the boiling temperature of the solution, we find:

$$\Delta T_{\text{boil}} = -\frac{R\left(T^0_{\text{boil}}(\text{Hg})\right)^2}{\lambda(\text{Hg}) M_{\text{Hg}}} \ln x_{\text{Hg}} = 10.4 \text{ K},$$

and $T_{\text{boil}} = 357 + 10.4 = 367.4$°C.

3.4.1.1. We solve this problem, using the Gibbs–Duhem equation:

$$x_{\text{Bi}} \left(\frac{\partial \ln \gamma_{\text{Bi}}}{\partial x_{\text{Bi}}} \right)_{p,T} = x_{\text{Pb}} \left(\frac{\partial \ln \gamma_{\text{Pb}}}{\partial x_{\text{Pb}}} \right)_{p,T} = x_{\text{Pb}} \ln 10 \cdot 0.64 \cdot (1 - x_{\text{Pb}}).$$

We can integrate this equation using the fact that $\mathrm{d}x_{\mathrm{Pb}} = -\mathrm{d}x_{\mathrm{Bi}}$ (since $x_{\mathrm{Pb}} + x_{\mathrm{Bi}} = 1$):

$$\int_0^{\ln\gamma_{\mathrm{Bi}}} \mathrm{d}\ln\gamma_{\mathrm{Bi}} = -\ln\,10 \cdot 0.64 \int_0^{x_{\mathrm{Pb}}} x_{\mathrm{Pb}}\mathrm{d}x_{\mathrm{Pb}}$$

$$\ln\gamma_{\mathrm{Bi}} = -\ln\,10 \cdot 0.32 \cdot x_{\mathrm{Pb}}^2$$

$$\ln\gamma_{\mathrm{Bi}} = -0.32(1 - x_{\mathrm{Bi}})^2.$$

For $x_{\mathrm{Bi}} = 0.4$, we obtain $\gamma_{\mathrm{Bi}} = 0.77$.

3.4.1.2. Equation (3.6) implies:

$$\begin{aligned}\Delta G_{\mathrm{mix}} &= G - \sum_i n_i G_i^0 = \sum_i n_i\mu_i - \sum_i n_i\mu_i^0 = \sum_i n_i\left(\mu_i - \mu_i^0\right)\\ &= \sum_i n_i\left(\mu_i^0 + RT\ln a_i - \mu_i^0\right) = RT\sum_i n_i \ln a_i\\ &= nRT\sum_i x_i \ln a_i.\end{aligned}$$

For the equi-molar solution, we obtain:

$$\Delta G_{\mathrm{mix}} = \frac{q}{(M_{\mathrm{SnCl_4}} + M_{\mathrm{CCl_4}})/2} RT\frac{1}{2}(\ln a_{\mathrm{SnCl_4}} + \ln a_{\mathrm{CCl_4}})$$

$$\begin{aligned}\ln a_{\mathrm{CCl_4}} &= \frac{(M_{\mathrm{SnCl_4}} + M_{\mathrm{CCl_4}})}{qRT}\Delta G_{\mathrm{mix}} - \ln a_{\mathrm{SnCl_4}}\\ &= -\frac{(260.5 + 153.8)}{500 \cdot 8.314 \cdot 500}7030 - \ln 0.52 = -0.747\\ a_{\mathrm{CCl_4}} &= 0.474; \qquad \gamma_{\mathrm{CCl_4}} = 0.947.\end{aligned}$$

3.4.1.3. It is not difficult to show that the relative partial molar quantities are related to each other by the same relations as the corresponding extensive quantities. Since $G = H - TS$, we can write:

$$\mu_{\mathrm{Mg}}^{\mathrm{M}} = \overline{H}_{\mathrm{Mg}}^{\mathrm{M}} - T\overline{S}_{\mathrm{Mg}}^{\mathrm{M}}$$

or

$$\overline{S}_{\mathrm{Mg}}^{\mathrm{M}} = \frac{1}{T}\left(\overline{H}_{\mathrm{Mg}}^{\mathrm{M}} - \mu_{\mathrm{Mg}}^{\mathrm{M}}\right).$$

Since pure Mg is considered as the standard state here, we can write:

$$\mu_{\mathrm{Mg}} = \mu_{\mathrm{Mg}}^0 + RT\ln a_{\mathrm{Mg}}$$

or

$$\mu_{\mathrm{Mg}}^M = RT\ln a_{\mathrm{Mg}}.$$

Thus,

$$\overline{S}_{\mathrm{Mg}}^{\mathrm{M}} = \frac{1}{T}\left(\overline{H}_{\mathrm{Mg}}^{\mathrm{M}} - RT\ln a_{\mathrm{Mg}}\right) = \frac{\overline{H}_{\mathrm{Mg}}^{\mathrm{M}}}{T} - R\ln(x_{\mathrm{Mg}}\gamma_{\mathrm{Mg}})$$
$$= 0.64\ \mathrm{J/(mole\,K)}.$$

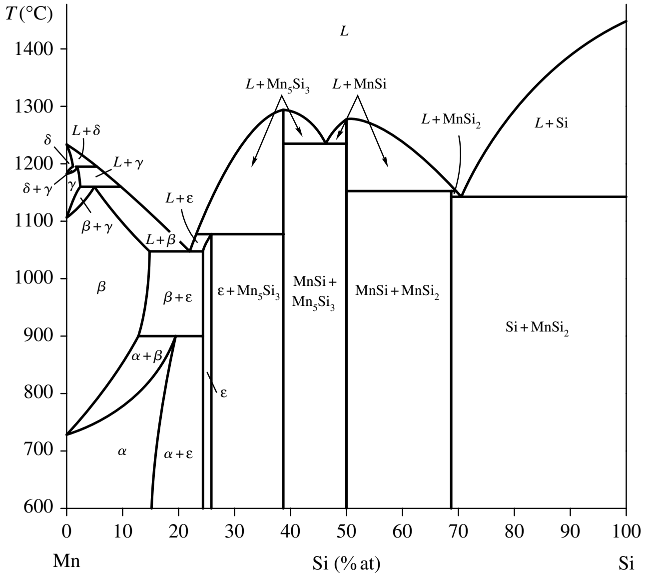
3.4.1.4. Since pure silicon is chosen as the standard state for both solutions, Eq. (3.51) implies that the partition coefficient is $L = 1$. Therefore, $a_{\mathrm{Si}}^{\mathrm{Fe}} = a_{\mathrm{Si}}^{\mathrm{Ag}}$ and

$$\gamma_{\mathrm{Si}}^{\mathrm{Fe}} = \frac{x_{\mathrm{Si}}^{\mathrm{Ag}}}{x_{\mathrm{Si}}^{\mathrm{Fe}}}\gamma_{\mathrm{Si}}^{\mathrm{Ag}} = 0.0040.$$

Chapter 4

4.2.1. In order to calculate the temperature and concentration at the eutectic point, both equations (4.4) should be solved simultaneously. The numerical solution gives $T_{\mathrm{eutectic}} = 408\ \mathrm{K}$ and $x_{\mathrm{Bi}}^{\mathrm{eutectic}} = 0.448$. Experiment shows that $T_{\mathrm{eutectic}} = 417\ \mathrm{K}$ and $x_{\mathrm{Bi}}^{\mathrm{eutectic}} = 0.45$.

4.8.1. The phases in each of the fields of the diagram (and for each compound) are shown in the figure below.



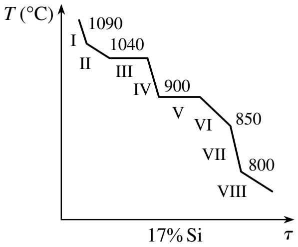
4.8.2 There is only one phase, the β-solid solution, in the alloy at $T = 1000$°C and 10% Si. The composition of this solid solution coincides with the alloy composition. There are two phases, a liquid and the chemical compound Mn_3Si_5 in the alloy at

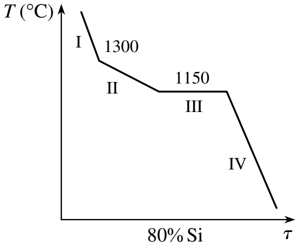
$T = 1200$°C and 35% Si. The composition of the liquid is 29% Si and 71% Mn, the composition of the chemical compound is 37.5% Si and 62.5% Mn (percents are atomic).

4.8.3. The cooling curves are shown in the figure.

The cooling curve for the alloy with 17% Si consists of several segments characterized by:

I. no phase transformations;
II. the formation of the β solid solution from the liquid;
III. the eutectic reaction $L \to \beta + \varepsilon$;
IV. the ε solid solution is formed from the β solid solution;
V. the peritectic reaction $\beta + \varepsilon \to \alpha$;
VI. the α solid solution is formed from the β solid solution;
VII. no phase transformations (only a single phase is present, α);
VIII. the ε solid solution forms from the α solid solution.



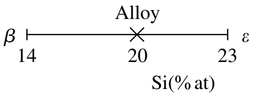


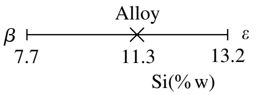
The cooling curve for the alloy with 80% Si consists of four segments characterized by:

I. no phase transformations;
II. crystals of pure Si form from the liquid;
III. the eutectic reaction $L \to \mathrm{MnSi}_2 + \mathrm{Si}$ proceeds;
IV. no phase transformations.

4.8.4. There is only a β-phase in the alloy at $T = 1000$°C and 10% Si with the same composition and weight as the alloy.

Both β and ε phases are present in the alloy at $T = 950$°C and 20% Si. Since the present diagram provides only atomic fraction we should calculate the weight fraction. The results are shown in the figure below.





Using the lever rule we find:

$$Q_\beta = \frac{13.2 - 11.3}{13.2 - 7.7} 200 = 69.1 \text{ g}$$

$$Q_\varepsilon = \frac{11.3 - 7.7}{13.2 - 7.7} 200 = 130.9 \text{ g}$$

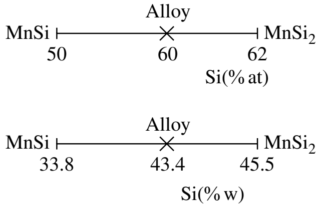
$$Q_{\mathrm{Si}}^{\beta} = \frac{7.7}{100} 69.1 = 5.3 \text{ g}$$

$$Q_{\mathrm{Mn}}^{\beta} = \frac{100 - 7.7}{100} 69.1 = 63.8 \text{ g}$$

$$Q_{\mathrm{Si}}^{\varepsilon} = \frac{13.2}{100} 130.9 = 17.3 \text{ g}$$

$$Q_{\mathrm{Mn}}^{\varepsilon} = \frac{100 - 13.2}{100} 130.9 = 113.6 \text{ g.}$$

4.8.5. There are two phases (MnSi and $\mathrm{MnSi_2}$) in the 60% Si alloy at $T = 1200°\mathrm{C}$. If we add more Si, the alloy will have only one phase when its composition corresponds to $\mathrm{MnSi_2}$. Using the lever rule (see figure) we find:



$$0.455 = \frac{300 \cdot 0.434 + Q_{\mathrm{Si}}^{\mathrm{add}}}{300 + Q_{\mathrm{Si}}^{\mathrm{add}}}$$

$$Q_{\mathrm{Si}}^{\mathrm{add}} = \frac{300(0.455 - 0.434)}{1 - 0.455} = 11.6 \text{ g}$$

In order to obtain the compound MnSi, we should add more Mn:

$$1 - 0.338 = \frac{300 \cdot (1 - 0.434) + Q_{\mathrm{Mn}}^{\mathrm{add}}}{300 + Q_{\mathrm{Mn}}^{\mathrm{add}}}$$

$$Q_{\mathrm{Mn}}^{\mathrm{add}} = \frac{300(0.434 - 0.338)}{0.338} = 85.2 \text{ g.}$$

Chapter 5

5.2.1 The degree of dissociation at constant pressure does not depend on the total number of moles. Therefore, for simplicity, we assume that at the initial moment, the system consisted of 1 mole of $\mathrm{PCl_5}$ and 0 moles of $\mathrm{PCl_3}$ and $\mathrm{Cl_2}$. According to the definition of the degree of dissociation, α moles of $\mathrm{PCl_5}$ will be consumed before the system reaches the equilibrium. The number of moles of each of the species in the system at the initial moment and at equilibrium can be written as:

Species	PCl_5	PCl_3	Cl_2
Initial	1	0	0
Equilibrium	$1-\alpha$	α	α
$\sum_i n_i$		$1-\alpha+\alpha+\alpha=1+\alpha$	

Using Eq. (5.15), we find:

$$K_p = \frac{p}{1+\alpha}\frac{\alpha\cdot\alpha}{1-\alpha} = \frac{p\alpha^2}{1-\alpha^2}.$$

$$\alpha = \sqrt{\frac{1}{1+p/K_{\mathrm{p}}}} = 0.32.$$

5.2.2. If the system initially contained 1 mole of PCl_3 and 1 mole of Cl_2 and z moles of PCl_5 were produced during the equilibration of the system, we can indicate the number of moles of each species as:

Species	PCl_5	PCl_3	Cl_2
Initial	0	1	1
Equilibrium	z	$1-z$	$1-z$
$\sum_i n_i$		$z+1-z+1-z=2-z$	

The total pressure in equilibrium is:

$$p = \frac{p_{\mathrm{PCl_5}}}{x_{\mathrm{PCl_5}}} = p_{\mathrm{PCl_5}}\frac{2-z}{z}.$$

The equilibrium constant can be written as:

$$K_p = p_{\mathrm{PCl_5}}\frac{2-z}{z}\frac{1}{2-z}\frac{(1-z)(1-z)}{z} = p_{\mathrm{PCl_5}}\frac{(1-z)^2}{z^2}$$

and, therefore,

$$z = \frac{1}{1+(K_p/p_{\mathrm{PCl_5}})^{1/2}} = 0.414.$$

Using $pV=nRT$, we find:

$$\frac{p_0}{p} = \frac{2}{2-z} \quad \text{or} \quad p_0 = 4.29 \text{ atm}.$$

5.2.3. In this example problem, we consider the following reactions:

$$\text{(a) } H_2 + Cl_2 = 2HCl$$

$$\text{(b) } H_2O = H_2 + \frac{1}{2}O_2$$

$$\text{(c) } 4HCl + O_2 = 2H_2O + 2Cl_2.$$

Since $c = -(2 \times a) - (2 \times b)$, we find $\Delta G_T^{0\text{c}} = -2\Delta G_T^{0\text{a}} - 2\Delta G_T^{0\text{b}}$ and, therefore,

$$K_p^{\text{c}} = \frac{1}{(K_p^{\text{a}} K_p^{\text{b}})^2}.$$

For the first reaction, $K_p^{\text{a}} = K_c^{\text{a}}$. The equilibrium constant of the second reaction can be expressed through the total pressure and the degree of dissociation. Analogously to Example problem (5.2.1) we obatin:

Species	H_2O	H_2	O_2
Initial	1	0	0
Equilibrium	$1-\alpha$	α	0.5α
$\sum_i n_i$		$1-\alpha+\alpha+0.5\alpha = 1+0.5\alpha$	

$$K_p^{\text{b}} = \frac{p^{1/2}}{(1+0.5\alpha)^{1/2}} \frac{\alpha \cdot (0.5\alpha)^{1/2}}{1-\alpha} = \frac{\sqrt{0.5}p\alpha^{3/2}}{(1-\alpha)(1+0.5\alpha)^{1/2}} = 3.07 \cdot 10^{-12}$$

$$K_p^{\text{c}} = 1.014.$$

5.2.4 For this reaction, the van't Hoff isotherm takes the following form:

$$\Delta G_T = -RT \ln K_p + RT \ln \frac{p_{NH_3}^2}{p_{H_2}^3 p_{N_2}}.$$

Using the data given in the example problem, we find $\Delta G_T = 11.43$ kJ/mole. Therefore, the reaction will proceed in the backward direction.

5.2.5 By analogy with Example problem 5.2.1, we obtain the following table:

Species	H_2	I_2	HI
Initial	1	1	0
Equilibrium	$1-z$	$1-z$	$2z$
$\sum_i n_i$		$1-z+1-z+2z = 2$	

The variable z can be found from the expression for the equilibrium constant:

$$K_p = \frac{(2z)^2}{(1-z)(1-z)} = \frac{(2z)^2}{(1-z)^2}$$

$$z = \frac{\sqrt{K_p}}{2+\sqrt{K_p}} = 0.78.$$

Now we can find the partial pressures as follows:

$$p_{H_2} = p_{I_2} = \frac{1-z}{2}\frac{RT}{V} = 6.5 \text{ atm}$$

$$p_{HI} = \frac{2z}{2}\frac{RT}{V} = 46.0 \text{ atm.}$$

5.3.1. We use results of Example problems 1.1.4.1 and 1.2.6.4 in order to calculate ΔG_T^0:

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 = 13.46 \text{ kJ/mole.}$$

Note that at standard conditions, this reaction proceeds in the backward direction. Using the van't Hoff isotherm, we obtain:

$$\Delta G_T = \Delta G_T^0 + RT\ln\left[\frac{1}{p}\frac{x_{H_2O}^2}{x_{CO}^2 x_{CH_4}}\right] = -8.28 \text{ kJ/mole.}$$

Therefore, at the conditions specified in the example problem, this reaction proceeds in the forward direction.

5.3.2. Since only two gases participate in the present reaction, there is no need to create a table as we did in Example problem 5.2.1. The point is that in this case the equilibrium composition of the gas phase does not depend on its initial composition. This conclusion follows from the expression for the equilibrium constant:

$$K_p = \frac{p_{HI}^2}{p_{H_2S}} = p\frac{x_{HI}^2}{x_{H_2S}} = p\frac{x_{HI}^2}{1-x_{HI}}.$$

Using this expression, we find $x_{HI} = 1.15 \cdot 10^{-2}$.

Note the fact that the equilibrium composition of the gas phase is independent of its initial composition can be also derived from the Gibbs phase rule. Indeed, in this case, the number of component is $C = 4 - 1 = 3$ (four species and one chemical reaction relating them). The number of phases is $P = 3$ (two solid phases and one gas phase). The number of degrees of freedom is $F = (C + 2) - P = (3 + 2) - 3 = 2$. Therefore, if we specify two parameters (temperature and total pressure), we uniquely determine the equilibrium composition of the gas phase.

5.4.1. In this example problem we deal with the following reaction:

$$N_2 = 2[N].$$

The van't Hoff isotherm for this reaction takes the following form:

$$\Delta G_T = -RT\ln K_p + RT\ln\frac{[\%N]^2}{p_{N_2}}.$$

Since, by definition, the solubility is the equilibrium concentration of solute at the specified solute partial pressure in the gas phase, we can find the equilibrium constant as follows:

$$K_p = \frac{0.06^2}{0.01} = 0.36.$$

The change of the Gibbs free energy at the conditions specified in the example problem is

$$\Delta G_T = -RT \ln 0.36 + RT \ln \frac{0.5^2}{0.5} = 2.38 \text{ kJ/mole}.$$

Therefore, at these conditions, nitrogen will be extracted from cobalt.

5.4.2. The following reaction proceeds in a water vapor atmosphere:

$$[\mathrm{Ni}] + \mathrm{H_2O} = \mathrm{NiO} + \mathrm{H_2}.$$

The standard change of the Gibbs free energy for this reaction can be calculated from the standard change of the Gibbs free energy for the two reactions given in the example problem:

$$\Delta G_T^0 = \Delta G_T^{0(1)} - \Delta G_T^{0(2)} = 43.65 \text{ kJ/mole}$$

Therefore, the equilibrium constant for the reaction in the example problem is $K_p = 5.25 \cdot 10^{-3}$. The equilibrium constant relates the equilibrium concentrations as follows:

$$K_p = \frac{x_{\mathrm{H_2}}}{x_{\mathrm{H_2O}} x_{[\mathrm{Ni}]} \gamma_{[\mathrm{Ni}]}}.$$

Using this expression, we find $\gamma_{[\mathrm{Ni}]} = 6.7$.

5.4.3. Equation (5.23) implies

$$\frac{\mathrm{d} \ln h}{\mathrm{d}T} = -\frac{\overline{H}_{\mathrm{Ag}} - H^0_{\mathrm{Ag(G)}}}{RT^2} = -\frac{\overline{H}_{\mathrm{Ag}} - H^0_{\mathrm{Ag(L)}} + H^0_{\mathrm{Ag(L)}} - H^0_{\mathrm{Ag(G)}}}{RT^2}$$
$$= -\frac{\overline{H}^M_{\mathrm{Ag}}}{RT^2} + \frac{\Delta H^0_{\mathrm{evapAg}}}{RT^2}.$$

Using the Clausius–Clapeyron equation (Eq. (2.9)), we find:

$$\overline{H}^M_{\mathrm{Ag}} = RT^2 \left(\frac{\mathrm{d} \ln p^0_{\mathrm{Ag}}}{\mathrm{d}T} - \frac{\mathrm{d} \ln h}{\mathrm{d}T} \right) = -12.06 \text{ kJ/mole}.$$

5.4.4. In this example problem, we have the following reaction:

$$[\mathrm{C}] + 2\mathrm{H_2} = \mathrm{CH_4}.$$

The equilibrium constant for this reaction is:

$$K_p = \frac{p_{\mathrm{CH_4}}}{p^2_{\mathrm{H_2}}} \frac{1}{x_{[\mathrm{C}]} \gamma_{[\mathrm{C}]}}.$$

Using this expression, we find:

$$\gamma_{[C]} = \left(\frac{0.227 \cdot 10^{-3}}{0.233 \cdot 10^{-2}}\right)^{-1} \frac{5.31 \cdot 10^{-3}}{4.10 \cdot 10^{-2}} = 1.33.$$

Chapter 6

6.1.1.1. The solution of this example problem differs from the derivation of the Langmuir isotherm in Section 6.1.1 in two important ways. First, in order for a gas molecule to adsorb, there must be two empty nearest neighbor sites on the adsorbent surface. The probability of this event is proportional to $(1-\theta)^2$. Second, two adsorbate atoms must be nearest neighbors in order for them to desorb as a molecule. The probability of this event is proportional to θ^2. Therefore, Eqs (6.1) and (6.2) should be rewritten as follows:

$$\omega_\downarrow = k_\downarrow p(1-\theta)^2; \qquad \omega_\uparrow = k_\uparrow \theta^2$$

$$\omega_\downarrow = \omega_\uparrow; \qquad k_\downarrow p(1-\theta)^2 = k_\uparrow \theta^2.$$

Introducing $b^2 = k_\downarrow / k_\uparrow$, we obtain:

$$\theta = \frac{b\sqrt{p}}{1 + b\sqrt{p}}.$$

Note that at small adsorbate pressures, this equation reduces to $\Gamma = Zb\sqrt{p}$. This is the analog of the Sieverts law for adsorption (recall that the Sieverts law for dissolving a diatomic gas was derived assuming that the gas molecules dissociate before penetrating into a metal).

6.1.2.1. Introducing $x = p/p_s$ and inserting $\Gamma = Z$ in Eq. (6.20), we obtain:

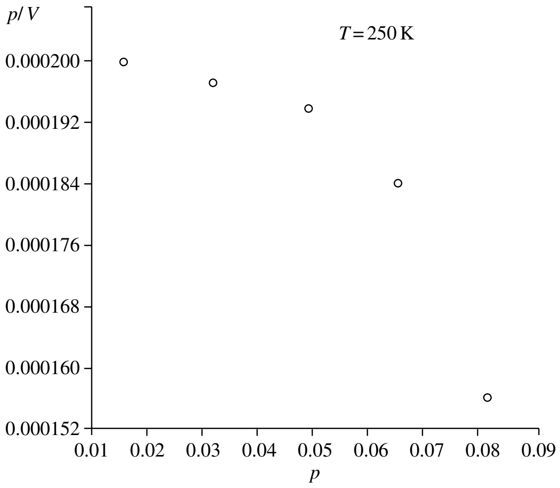
$$1 = \frac{gx}{(1 + gx - x)(1 - x)}.$$

Using this equation, we find that if $g = 1$, $x = 1/2$, and if $g = 100$, $x = 1/11$. Equation (6.16) implies that the fraction of unoccupied sites on the adsorbent surface is:

$$\theta_0 = \frac{1 - x}{1 + gx - x}.$$

If $g = 1$, the fraction of unoccupied sites is 0.5. In other words, in spite of the fact that the number of adsorbed molecules is equal to the number of sites on the adsorbent surface, half of these sites are still not occupied. At $g = 100$, the fraction of such sites is 0.082. In other words, for the same conditions 92% of the sites are occupied.

6.1.2.2. First, we determine if it is appropriate to describe these data within the framework of the Langmuir theory. In order to check, we plot the data in the coordinates p/V versus p. The figure shows that data do *not* fall on a straight line. Moreover, if we determine $1/Z$ as the average slope of this curve, we would find that $Z < 0$.



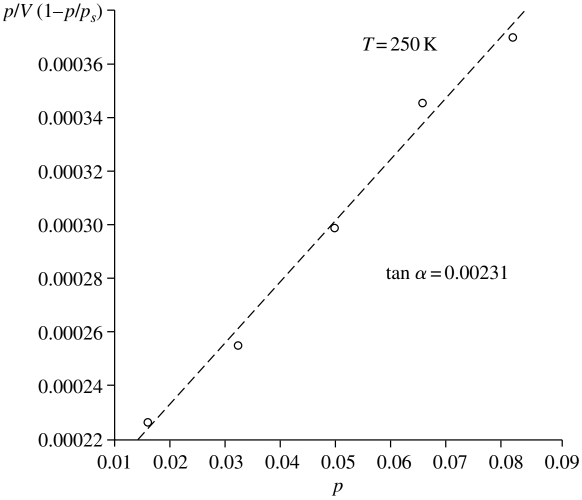
We now try to describe these data with the BET isotherm:

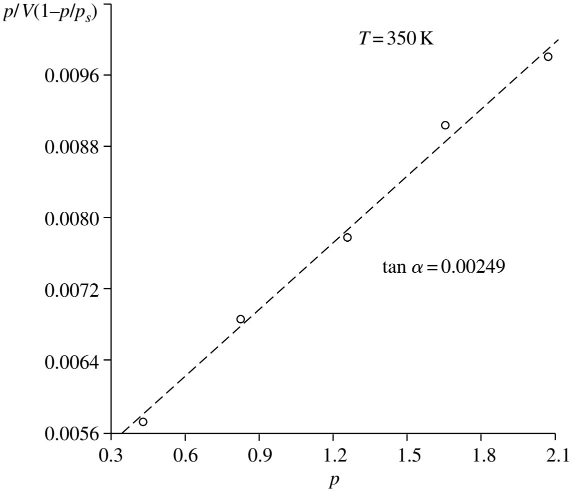
$$V = \frac{V_{\max} b p}{(1 + bp - p/p_s)(1 - p/p_s)}.$$

In order to do this, we should plot the data in $p/(V(1 - p/p_s))$ versus p coordinates. Since this requires knowledge of the saturated vapor pressure, we estimate this quantity using the Clausius–Clapeyron equation:

$$\ln p_s = \frac{\Delta H_{\text{evap}}}{R}\left(\frac{1}{T_{\text{boil}}} - \frac{1}{T}\right).$$

At $T = 250$ K and $T = 350$ K, we obtain 0.140 atm and 4.07 atm, respectively. The two plots show that the data fall on straight lines at both temperatures. Therefore, these data can indeed be described in the BET theory framework. From these plots, we find that at $T = 250$ K, $b = 20$ cm^3/atm, and $V_{\max} = 270$ cm^3 and at $T = 350$ K, $b = 0.77$ cm^3/atm, and $V_{\max} = 273$ cm^3. Note that in the BET theory $V_{\max}$ does not depend on temperature. We can attribute the small discrepancy in $V_{\max}$ to experimental errors (when in doubt, blame the experimentalist—everyone else does).





The surface area of 12 g of the adsorbent can be estimated from $V_{\max}$ as follows:

$$S = 12\frac{1.013 \cdot 10^5 \cdot 271 \cdot 10^{-6}}{8.314 \cdot 273.2} 19.4 \cdot 10^{-20} \cdot 6.02 \cdot 10^{23}$$
$$= 16.9 \cdot 10^3 \text{ m}^2$$

The heat of adsorption can be calculated from the temperature dependence of b as follows:

$$\Delta H_{\text{ads}} = \frac{R \ln (b_2/b_1)}{1/T_1 - 1/T_2} = -23.7 \text{ kJ/mole.}$$

6.2.1. The Gibbs adsorption equation implies:

$$\Gamma_2 = -\frac{c_2}{RT}\frac{\partial\sigma}{\partial c_2} \approx -\frac{c_2}{RT}\frac{\Delta\sigma}{c_2} = 4.16 \cdot 10^{-6} \text{ mole/m}^2$$
$$= 4.16 \cdot 10^{-8} \text{ mole/l.}$$

Assuming that the surface layer is a homogeneous plate, we obtain:

$$c_2^\pi = c_2 + \Gamma_2/\delta = 0.1 + \frac{4.16 \cdot 10^{-8}}{10^{-8}} = 4.26 \text{ mole/l.}$$

Chapter 7

7.3.2.1 In order to express C_{ijkl} in terms of μ and B, we compare the versions of Hooke's law for anisotropic and isotropic solids. For σ_{xx}, we obtain from Eqs (7.24) and (7.28):

$$\sigma_{xx} = C_{xxxx}\varepsilon_{xx} + 2C_{xxxy}\varepsilon_{xy} + 2C_{xxxz}\varepsilon_{xz} + C_{xxyy}\varepsilon_{yy}$$
$$+2C_{xxyz}\varepsilon_{yz} + C_{xxzz}\varepsilon_{zz}$$

$$\sigma_{xx} = 2\mu\left[\varepsilon_{xx} - \tfrac{1}{3}(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})\right] + B(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})$$
$$= \left(B + \tfrac{4}{3}\mu\right)\varepsilon_{xx} + \left(B - \tfrac{2}{3}\mu\right)\varepsilon_{yy} + \left(B - \tfrac{2}{3}\mu\right)\varepsilon_{zz}.$$

For an isotropic system, these equations must be equivalent for any set of strains ε_{ij}. This is true if and only if:

$$C_{11} = C_{xxxx} = B + 4\mu/3$$
$$C_{12} = C_{xxyy} = B - 2\mu/3$$
$$C_{13} = C_{xxzz} = B - 2\mu/3$$
$$C_{14} = C_{xxyz} = 0$$
$$C_{15} = C_{xxxz} = 0$$
$$C_{16} = C_{xxxy} = 0.$$

Since the x, y, and z-directions are equivalent in an isotropic solid, expressions for components C_{2j} and C_{3j} are equal to C_{1j}. Therefore, we need only obtain C_{4j}, C_{5j}, and C_{6j}. To this end, we compare expressions for σ_{xy}:

$$\sigma_{xy} = C_{xyxx}\varepsilon_{xx} + 2C_{xyxy}\varepsilon_{xy} + 2C_{xyxz}\varepsilon_{xz} + C_{xyyy}\varepsilon_{yy}$$
$$+ 2C_{xyyz}\varepsilon_{yz} + C_{xyzz}\varepsilon_{zz}$$

$$\sigma_{xy} = 2\mu\varepsilon_{xy}.$$

These equations are valid for arbitrary ε_{ij} if and only if:

$$C_{61} = C_{xyxy} = 0$$
$$C_{62} = C_{xyyy} = 0$$
$$C_{63} = C_{xyzz} = 0$$
$$C_{64} = C_{xyyz} = 0$$
$$C_{65} = C_{xyxz} = 0$$
$$C_{66} = C_{xyxy} = \mu.$$

Since the x, y, and z-directions are equivalent in an isotropic solid, $C_{66}=C_{55}=C_{44}$. Using these relations, we see that in an isotropic solid

$$C_{44} = (C_{11} - C_{12})/2.$$

We can collect all of these results in the following form:

$$C_{ij} = \begin{pmatrix} B+4\mu/3 & B-2\mu/3 & B-2\mu/3 & 0 & 0 & 0 \\ B-2\mu/3 & B+4\mu/3 & B-2\mu/3 & 0 & 0 & 0 \\ B-2\mu/3 & B-2\mu/3 & B+4\mu/3 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{pmatrix}.$$

There is also another, more elegant method to derive the expression for C_{ijkl}. First, we note that in an isotropic solid, the components of C_{ijkl} cannot change upon rotation of the coordinate system. The only second-rank tensor that does not change upon rotation of the coordinate axes is the tensor $A\delta_{ij}$, where A is a scalar and δ_{ij} is the Kronecker delta (see Appendix III). Second, examination of Eq. (7.23) shows that the symmetry condition is only satisfied by the tensors $\delta_{ij}\delta_{kl}$ and $(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$. Therefore, C_{ijkl} must have the following form:

$$C_{ijkl} = a\delta_{ij}\delta_{kl} + b(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}),$$

where a and b are scalars. Inserting this expression into Hooke's law (Eq. (7.24)), we find:

$$\begin{aligned} \sigma_{ij} &= a\delta_{ij}\delta_{kl}\varepsilon_{kl} + b(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\varepsilon_{kl} = a\delta_{ij}\varepsilon_{kk} + 2b\varepsilon_{ij} \\ &= (a + 2b/3)\delta_{ij}\varepsilon_{kk} + 2b(\varepsilon_{ij} - \delta_{ij}\varepsilon_{kk}/3). \end{aligned}$$

Comparing this equation with Hooke's law for isotropic solids (Eq. (7.28)) we find:

$$a = B - 2\mu/3; \qquad b = \mu$$

and

$$C_{ijkl} = (B - 2\mu/3)\delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}).$$

You should demonstrate to yourself that this expression is consistent with that found above, where we explicitly wrote the C_{ij} tensor.

7.3.2.2. We can rewrite the new expression for Hooke's law as

$$\sigma_{ij} = \frac{E}{1+\nu}\left(\varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij}\right) + \frac{E}{1+\nu}\left(\frac{1}{3} + \frac{\nu}{1-2\nu}\right)\varepsilon_{kk}\delta_{ij}.$$

Comparing this with Eq. (7.28), we find:

$$2\mu = \frac{E}{1+\nu}; \qquad B = \frac{E}{3(1-2\nu)};$$

Solving these equations for μ and B, we find:

$$E = \frac{9B\mu}{3B+\mu}; \qquad \nu = \frac{3B-2\mu}{2(3B+\mu)}.$$

Chapter 8

8.1.2.1. Equation (8.12) implies:

$$k = \frac{1}{t}\ln\frac{c^0}{c} = \frac{1}{t}\ln\frac{c^0}{c^0/4} = \frac{1}{t}\ln 4 = 0.14\ \text{min}^{-1}.$$

8.1.2.2. Equation (8.11) implies:

$$\frac{1}{c_\text{A}} = \frac{1}{c_\text{A}^0} + kt; \qquad c_\text{A} = \frac{c_\text{A}^0}{1+ktc_\text{A}^0}.$$

The fraction of A which will react during time t is

$$100\%\left(1-\frac{c_\text{A}}{c_\text{A}^0}\right) = 100\%\left(1-\frac{1}{1+ktc_\text{A}^0}\right) - 100\%\frac{ktc_\text{A}^0}{1+ktc_\text{A}^0}$$
$$= 86.6\%.$$

8.1.2.3. Since the reactants were taken in the stoichiometric ratio, the kinetic equation takes the following form:

$$\frac{\mathrm{d}p_\text{A}}{\mathrm{d}t} = -kp_\text{A}^n$$

(an analogous equation can be written for B). Therefore, in order to determine the order of the reaction, we should calculate the pressure of A as a function of time. We notice that the pressures of A and B will be the same during the reaction. Therefore, the total pressure is $p = 2p_\text{A} + p_\text{C}$. On the other hand, at $t = 0$, the total pressure was $p^0 = 2p_\text{A}^0$. From the stoichiometry of the reaction, we find $p_\text{C} = p_\text{A}^0 - p_\text{A}$. Using these relations, we obtain:

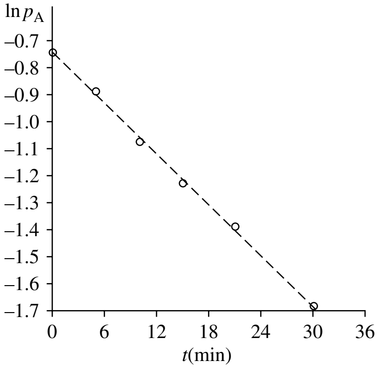
$$p = 2p_\text{A} + p_\text{C} = 2p_\text{A} + p_\text{A}^0 - p_\text{A} = p_\text{A} + p_\text{A}^0 = p_\text{A} + p^0/2$$

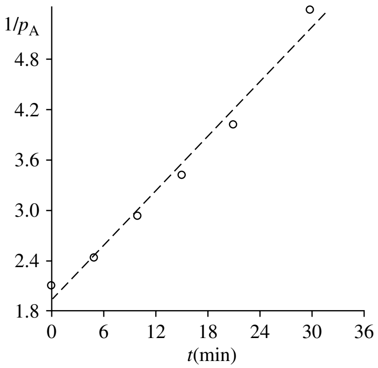
$$p_\text{A} = p - p^0/2.$$

The corresponding numerical results are given in the table:

t(min)	0	5	10	15	21	30
p_A(atm)	0.477	0.412	0.342	0.293	0.250	0.186

The figures show these data in coordinates appropriate for first- and second-order reactions. On the basis of these plots, we conclude that the reaction is first-order.





8.1.4.1. The half-life of a first order reaction (see Eq. (8.14)) is:

$$t_{1/2} = \frac{\ln 2}{k}.$$

Using this equation, we find that at $T = 260$ K, $k_{260} = 0.0010$/min. Using the Arrhenius equation:

$$\ln k_2 = \ln k_1 + \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

we find that $k_{350} = 0.64$/min. Finally, using the kinetic equation for a first-order reaction

$$\ln c = \ln c^0 - kt,$$

we obtain $t = (1/k)\ln[c^0/(c^0/3)] = 1.7$ min.

8.2.2.1. The concentration of N_2 can be described using the following kinetic equation:

$$2\frac{dc_{N_2}}{dt} = k_1 c_{NO}.$$

The kinetic equation describing the evolution of the concentration of nitric oxide is:

$$\frac{dc_{NO}}{dt} = -k_1 c_{NO} - k_2 c_{NO}$$

or

$$c_{NO} = c_{NO}^2 e^{-(k_1+k_2)t}.$$

Inserting this expression into the kinetic equation for N_2, we find:

$$\frac{dc_{N_2}}{dt} = \frac{1}{2} k_1 c_{NO}^0 e^{-(k_1+k_2)t}$$

$$c_{N_2} = A - \frac{1}{2}\frac{k_1}{k_1 + k_2} c_{NO}^0 e^{-(k_1+k_2)t},$$

where A is a constant. At $t = 0$, $c_{N_2} = 0$. Therefore,

$$A = \frac{1}{2}\frac{k_1}{k_1 + k_2}c^0_{NO}$$

and

$$c_{N_2} = \frac{1}{2}\frac{k_1}{k_1 + k_2}c^0_{NO}(1 - e^{-(k_1+k_2)t}) = 1.04 \text{ mole/l}.$$

Analogously, we find

$$c_{N_2O} = \frac{1}{2}\frac{k_2}{k_1 + k_2}c^0_{NO}(1 - e^{-(k_1+k_2)t}) = 0.74 \text{ mole/l}.$$

8.2.2.2. If this reaction was elementary, the kinetic equation would take the following form:

$$\frac{1}{2}\frac{dc_{HI}}{dt} = kc_{H_2}c_{I_2}.$$

For the second mechanism, we obtain:

$$\frac{1}{2}\frac{dc_{HI}}{dt} = k_3c_I^2c_{H_2}$$

$$\frac{1}{2}\frac{dc_I}{dt} = k_1c_{I_2} - k_2c_I^2 - k_3c_I^2c_{H_2} = 0$$

$$c_I = \left(\frac{k_1c_{I_2}}{k_2 + k_3c_{H_2}}\right)^{1/2}$$

$$\frac{dc_{HI}}{dt} = \frac{2k_3k_1}{k_2 + k_3c_{H_2}}c_{I_2}c_{H_2}.$$

If $k_3c_{H_2} \ll k_2$, the last equation reduces to:

$$\frac{1}{2}\frac{dc_{HI}}{dt} = \frac{k_3k_1}{k_2}c_{I_2}c_{H_2}.$$

This equation coincides with the kinetic equation describing the first mechanism.

8.2.3.1. The kinetic equation for the formation of C_2Cl_6 takes the following form:

$$\frac{dc_{C_2Cl_6}}{dt} = k_2c_{C_2Cl_5}c_{Cl_2} + k_3c^2_{C_2Cl_5}.$$

Since the chain length (i.e. number of reactions in a chain) is large, we can neglect the rate of chain termination (the second term on the right-hand side of the kinetic equation) and the equation reduces to:

$$\frac{dc_{C_2Cl_6}}{dt} = k_2c_{C_2Cl_5}c_{Cl_2}.$$

At steady-state, the rate at which we form new chains is equal to the rate of chain termination, therefore,

$$k_0 c_{\mathrm{Cl_2}} = k_3 c^2_{\mathrm{C_2Cl_5}}.$$

Inserting this result into the previous equation, we find:

$$\frac{\mathrm{d}c_{\mathrm{C_2Cl_6}}}{\mathrm{d}t} = k_2\sqrt{\frac{k_0}{k_3}}c^{3/2}_{\mathrm{Cl_2}}.$$

8.2.3.2. It was established in Section 8.2.3 that:

$$\frac{n_{\mathrm{st}}}{n_0} = \frac{\tau}{\beta}; \qquad \frac{\omega}{\omega_{\mathrm{st}}} = \frac{n}{n_{\mathrm{st}}} = 1 - \mathrm{e}^{-\beta t/\tau}.$$

Combining these equations, we obtain:

$$\frac{n_{\mathrm{st}}}{n_0} = -\frac{\mathrm{t}}{\ln(1-(\omega/\omega_{\mathrm{st}}))} = 0.1.$$

Chapter 10

10.1.1.1. The pressure of the gas inside the shell is equal to:

$$p = \frac{RT}{V}n.$$

Differentiating this equation we find:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{RT}{V}\frac{\mathrm{d}n}{\mathrm{d}t}.$$

In order for the gas to pass through the metallic shell, it must first dissolve into it and then diffuse through it. The loss of the gas inside the shell is determined by its flux through the shell:

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = Sj.$$

According to Fick's first law:

$$j = -D\frac{\partial c}{\partial r}.$$

The concentrations of the gas on the inner and outer surfaces of the shell are equal to its solubilities in the metal corresponding to the gas pressures inside and outside of the shell, respectively. Since the shell is thin, we can replace the derivative $\partial c/\partial r$ in Fick's law with its finite difference approximation $-(c_{\mathrm{in}} - c_{\mathrm{out}})/d$ (the minus sign takes into account the fact that the concentration decreases from the inner to outside surfaces), where d is the thickness of the shell. The gas solubility obeys Henry's law $c = p/h$. Thus,

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{RT}{V}\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{RT}{V}Sj = \frac{RT}{V}SD\frac{\partial c}{\partial r} = -\frac{RT}{V}SD\frac{p_{\mathrm{in}} - p_{\mathrm{out}}}{hd}$$
$$= -A(p_{\mathrm{in}} - p_{\mathrm{out}}),$$

where A is a constant which does not depend on pressure. The solution of this equation takes the following form:

$$p_{\text{in}} = p_{\text{out}} + (p_0 - p_{\text{out}})\mathrm{e}^{-At}.$$

Using this formula we find:

$$A = -\frac{1}{t_1}\ln\frac{p_1 - p_{\text{out}}}{p_0 - p_{\text{out}}} = 0.00057\ 1/\text{h}$$

$$t_2 = -\frac{1}{A}\ln\frac{p_2 - p_{\text{out}}}{p_0 - p_{\text{out}}} = 440\ \text{h}.$$

10.1.1.2. The solution of this example problem is analogous to the previous one with the exception that instead of Henry's law we must use Sieverts's law $c = \sqrt{p/s}$:

$$\sqrt{p_{\text{in}}} - \sqrt{p_0} + \sqrt{p_{\text{out}}}\ln\frac{\sqrt{p_{\text{in}}} - \sqrt{p_{\text{out}}}}{\sqrt{p_0} - \sqrt{p_{\text{out}}}} = -\frac{1}{2}Bt$$

$$B = -\frac{2}{t_1}\left\{\sqrt{p_1} - \sqrt{p_0} + \sqrt{p_{\text{out}}}\ln\frac{\sqrt{p_1} - \sqrt{p_{\text{out}}}}{\sqrt{p_0} - \sqrt{p_{\text{out}}}}\right\}$$
$$= 0.00235\ \text{atm}^{1/2}/\text{h}$$

$$t_2 = -\frac{2}{B}\left\{\sqrt{p_2} - \sqrt{p_0} + \sqrt{p_{\text{out}}}\ln\frac{\sqrt{p_2} - \sqrt{p_{\text{out}}}}{\sqrt{p_0} - \sqrt{p_{\text{out}}}}\right\} = 426\ \text{h}.$$

10.1.3.1. The solution of the diffusion equation in this case takes the following form:

$$c(x,t) = \frac{q}{\sqrt{\pi Dt}}\mathrm{e}^{-x^2/4Dt} = a\mathrm{e}^{-bx^2}.$$

Using this expression, we find:

$$\frac{d^2c}{\mathrm{d}x^2} = -2ab(1 - 2bx_0^2)\mathrm{e}^{-bx_0^2} = 0$$

$$x_0 = \sqrt{\frac{1}{2b}} = \sqrt{2Dt}.$$

10.1.3.2. The solution of the diffusion equation in this case takes the following form:

$$c(x,t) = \frac{q}{\sqrt{\pi Dt}}\mathrm{e}^{-x^2/4Dt}.$$

Using this expression, we find:

$$D = \frac{x_2^2 - x_1^2}{4t\ln(I_1/I_2)} = 10^{-12}\ \text{m}^2/\text{s}.$$

10.1.3.3. Since $c_0 = c(x, 0) = 0.1\%$ and $c_s = c(0, t) = 1\%$, the solution of the diffusion equation takes the following form:

$$c - 0.1 = (c_s - 1)\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

and we find:

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.61; \qquad \frac{x}{2\sqrt{Dt}} = 0.61,$$

(see Appendix IV). At the temperature of the experiment $D = 2.2 \cdot 10^{-7}\,\mathrm{cm}^2/\mathrm{s}$, therefore,

$$t = \frac{25 \cdot 10^{-4}}{4 \cdot (0.61)^2 2.2 \cdot 10^{-7}} = 7.6 \cdot 10^3\ \mathrm{s} = 2.1\ \mathrm{h}.$$

10.1.3.4. If we assume that D does not depend on concentration and, therefore, on position, the solution of the diffusion equation takes the following form:

$$c(x, t) = \frac{c_0}{2}\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right].$$

Since $c = 0.3c_0$, we obtain $\operatorname{erf}\left(x/(2\sqrt{Dt})\right) = 0.4$, $x/(2\sqrt{Dt}) = 0.38$ (see Appendix IV) and $D_1 = 4.7 \cdot 10^{-13}\,\mathrm{m}^2/\mathrm{s}$.

10.1.3.5. Since 90% of the hydrogen which was originally in the plate came out, we conclude that the diffusion path has the same order as the plate thickness L. Assuming that $t \geq 0.05(L^2/D) = 125\,\mathrm{s}$, we find that the amount of hydrogen remaining is $q = 0.1q_0 = (8/\pi^2)q_0 e^{-\pi^2 Dt/L^2}$ and, therefore, $t = 527\,\mathrm{s}$. This is consistent with our assumption that $t > 125\,\mathrm{s}$.

10.1.3.6. The solution of the diffusion equation takes the following form:

$$c(x, t) - c_0 = (c_s - c_0)\operatorname{erf}c\left(\frac{x}{2\sqrt{Dt}}\right).$$

In order to apply this solution, we need to know the carbon concentration on the surface of the steel. It is controlled by equilibrium of the following reaction:

$$[\mathrm{C}] + 2\mathrm{H}_2 = \mathrm{CH}_4.$$

Since the standard state for carbon is graphite, the value of ΔG^0_{T} for this reaction coincides with that for reaction

$$\mathrm{C}_{(\mathrm{graphite})} + 2\mathrm{H}_2 = \mathrm{CH}_4.$$

At $T = 1173\,\mathrm{K}$, we obtain

$$K_p = e^{-\Delta G^0_{1173}/1173R} = 0.022.$$

On the other hand, we can express the equilibrium constant in terms of equilibrium concentrations:

$$K_p = \frac{1}{p}\frac{x_{\mathrm{CH}_4}}{a_c x^2_{\mathrm{H}_2}}.$$

We find $a_c = 0.113$. Using the plot of the carbon activity versus its atomic fraction, we determine that the carbon atomic fraction is 0.010. The weight fraction of carbon can be obtained as follows:

$$c_s = \frac{M_C x_C}{M_C x_C + M_{Fe} x_{Fe}} 100\% = 0.22\%.$$

Finally, using the solution of the diffusion equation and the value of the carbon diffusivity at $T = 1173$ K ($D_C = 1.63 \cdot 10^{-7}$ cm^2/s), we find that $c = 0.45\%$ at a depth of 600 µm.

10.2.1. The distance between nearest neighbor sites in an fcc lattice is $\Delta = a/\sqrt{2}$. If the hop frequency is $\Gamma = 1$ s, $D = (1/6)\Delta^2\Gamma = (a^2/12)\Gamma = 2 \cdot 10^{-16}$ cm^2/s. Using the temperature dependence of the diffusivity specified in the example problem, we find $T = 675$ K.

10.2.2. Using $x_{dif} = \sqrt{2Dt}$, we obtain the following estimations:

(1) at $T = 300$ K $x_{dif} = 2.6 \cdot 10^{-16}$ cm
(2) at $T = 1200$ K $x_{dif} = 1.9 \cdot 10^{-3}$ cm
(3) at $T_{melt} = 1355$ K $x_{dif} = 6.0 \cdot 10^{-3}$ cm.

10.3.2.1. The vacancy formation enthalpy can be estimated as $\Delta H_v^f \approx 10RT_{melt} = 113$ kJ/mole. The diffusivity can be expressed in term of the hop frequency as $D = a^2\Gamma/12$ (see Example problem 10.2.1). At T_{melt} $\Gamma = 2.5 \cdot 10^7$ s^{-1} and at $T = 300$ K, $\Gamma = 10^{-19}$ s.

10.6.1. Equation (10.36) implies

$$\xi = 2b\sqrt{D_\beta t}.$$

Using the following equation:

$$F(b) = \frac{c_s - c_{\beta\alpha}}{c_{\beta\alpha} - c_{\alpha\beta}} = \frac{50 - 40}{40 - 35} = 2$$

and Appendix IV, we find $b = 0.8$ and $\xi = 81.6$ µm.

10.7.1. Inserting Eq. (10.43) into the second expression in Eq. (10.42), we find:

$$j_{Q_{steady-state}} = L_{QC}\frac{L_{CQ}}{L_{CC}}\frac{\nabla T}{T} - L_{QQ}\frac{\nabla T}{T} = \left(\frac{L_{CQ}^2}{L_{CC}} - L_{QQ}\right)\frac{\nabla T}{T}.$$

Taking into account that:

$$\frac{L_{QC}}{L_{CC}} = Q^*, \qquad L_{CC} = \frac{D_C c_C}{RT} \quad \text{and} \quad L_{QQ} = \lambda_0 T,$$

we can rewrite this equation as:

$$j_{Q_{steady-state}} = \left(\frac{Q^{*2} D_C c_C}{RT} - \lambda_0 T\right)\frac{\nabla T}{T} = -\left(\lambda_0 - \frac{Q^{*2} D_C c_C}{RT^2}\right)\nabla T.$$

Therefore,

$$\lambda_{steady-state} = \lambda_0 - \frac{Q^{*2} D_C c_C}{RT^2} > \kappa.$$

10.7.2. Combining the first expression in Eq. (10.42) and the following relations:

$$\frac{L_{QH}}{L_{HH}} = Q^* \quad \text{and} \quad L_{HH} = \frac{D_H c_H}{RT},$$

we obtain:

$$j_H = -L_{HH}\nabla_T \mu_H - L_{HQ}\frac{\nabla T}{T} = -D_H c_H \left(\nabla(\ln\, c_H) + \frac{Q^*}{RT}\nabla(\ln\, T) \right).$$

The concentration should be expressed in atom/cm^3 (in accordance with the dimensionality of the flux):

$$c_H = \frac{N_H}{V} = \frac{N_A n_H}{V} \approx \frac{x_H N_A n_{Fe}}{V} = \frac{x_H N_A m_{Fe}}{M_{Fe} V} \approx \frac{x_H \rho N_A}{M_{Fe}}$$
$$= 8.5 \cdot 10^{18} \ \text{atom/cm}^3.$$

Now, using the previous equation, we obtain $Q^* = 210$ kJ/mole.

Chapter 12

12.2.4.1. The number of molecules with an energy corresponding to the Jth level is

$$N_J = N \frac{(2J+1)e^{-(T_c/T)J(J+1)}}{\sum_{J=0}^{\infty}(2J+1)e^{-(T_c/T)J(J+1)}}.$$

At $T \gg T_c$, this equation reduces to (see the derivation of Eq. (12.55))

$$N_J = N\frac{T_c}{T}(2J+1)e^{-(T_c/T)J(J+1)}.$$

The most populated level is the value of J for which N_J is a maximum with respect to J:

$$\frac{dN_J}{dJ} = N\frac{T_c}{T}\left[2e^{-(T_c/T)J(J+1)} - (2J+1)\frac{T_c}{T}(2J+1)e^{-(T_c/T)J(J+1)} \right]$$
$$= 0$$

or

$$J_{max} = \frac{1}{2}\left(\sqrt{\frac{2T_c}{T}} - 1 \right).$$

12.2.5.1. The partition function of the anharmonic oscillator takes the following form:

$$Z = \int_{-\infty}^{+\infty} e^{-\left((\beta x^2/2) - \gamma x^3 - \delta x^4\right)/k_B T} dx$$
$$= \int_{-\infty}^{+\infty} e^{-\beta x^2/2k_B T} e^{\left(\gamma x^3 + \delta x^4\right)/k_B T} dx.$$

Expanding the second exponent in the last integral and performing the integration, we find:

$$Z \approx \int_{-\infty}^{+\infty} \mathrm{e}^{-\beta x^2/2k_\mathrm{B}T}\left(1+\frac{\gamma x^3}{k_\mathrm{B}T}+\frac{\delta x^4}{k_\mathrm{B}T}+\frac{\gamma^2 x^6}{2(k_\mathrm{B}T)^2}\right)\mathrm{d}x$$
$$=\sqrt{\frac{2\pi k_\mathrm{B}T}{\beta}}+\frac{\delta}{k_\mathrm{B}T}\frac{3}{4}\sqrt{\frac{\pi(2k_\mathrm{B}T)^5}{\beta^5}}+\frac{\gamma^2}{2(k_\mathrm{B}T)^2}\frac{15}{8}\sqrt{\frac{\pi(2k_\mathrm{B}T)^7}{\beta^7}}$$
$$=\sqrt{\frac{2\pi k_\mathrm{B}T}{\beta}}\left(1+\frac{15\gamma^2 k_\mathrm{B}T}{2\beta^3}+\frac{3\delta k_\mathrm{B}T}{\beta^2}\right).$$

The average potential energy of the anharmonic oscillator can be found using Eq. (12.34), which in this case takes the following form:

$$U = k_\mathrm{B}T^2\frac{\partial \ln Z}{\partial T}.$$

Expanding the logarithm of the partition function, we find:

$$\ln Z = \frac{1}{2}\ln\frac{2\pi k_\mathrm{B}T}{\beta}+\ln\left(1+\frac{15\gamma^2 k_\mathrm{B}T}{2\beta^3}+\frac{3\delta k_\mathrm{B}T}{\beta^2}\right)$$
$$\approx \frac{1}{2}\ln\frac{2\pi k_\mathrm{B}}{\beta}+\frac{1}{2}\ln T+\frac{15\gamma^2 k_\mathrm{B}T}{2\beta^3}+\frac{3\delta k_\mathrm{B}T}{\beta^2}.$$

Inserting this result into the expression for the internal energy yields:

$$U = \frac{k_\mathrm{B}T}{2}+\frac{15\gamma^2(k_\mathrm{B}T)^2}{2\beta^3}+\frac{3\delta(k_\mathrm{B}T)^2}{\beta^2}.$$

Finally, the heat capacity is:

$$c=\frac{\partial U}{\partial T}=\frac{k_\mathrm{B}}{2}+k_\mathrm{B}^2\left(\frac{15\gamma^2}{\beta^3}+\frac{6\delta}{\beta^2}\right)T.$$

The first term on the right side of this equation is similar to the high temperature limit of the heat capacity of the quantum-mechanical oscillator. In fact, this term is one half that found in Eq. (12.73) because the present derivation only includes the contribution from the potential energy (the kinetic energy gives an equal contribution). Note that this first term does not depend on temperature. The second term is a linear function of temperature and is the correction associated with anharmonicity.

12.2.5.2. The average deviation of the interatomic distance from its $T=0$ equilibrium value is:

$$\bar{x}=\frac{\int_{-\infty}^{+\infty} x\mathrm{e}^{-\left((\beta x^2/2)-\gamma x^3-\delta x^4\right)/k_\mathrm{B}T}\mathrm{d}x}{\int_{-\infty}^{+\infty} \mathrm{e}^{-((\beta x^2/2)-\gamma x^3-\delta x^4)/k_\mathrm{B}T}\mathrm{d}x}$$
$$=\frac{\int_{-\infty}^{+\infty} x\mathrm{e}^{-\beta x^2/2k_\mathrm{B}T}\mathrm{e}^{\left(\gamma x^3+\delta x^4\right)/k_\mathrm{B}T}\mathrm{d}x}{\int_{-\infty}^{+\infty} \mathrm{e}^{-\beta x^2/2k_\mathrm{B}T}\mathrm{e}^{(\gamma x^3+\delta x^4)/k_\mathrm{B}T}\mathrm{d}x}.$$

Expanding the second exponential in both integrals on the right side, we obtain

$$\bar{x} \approx \frac{\int_{-\infty}^{+\infty} x\mathrm{e}^{-\beta x^2/2k_\mathrm{B}T}(1+(\gamma x^3/k_\mathrm{B}T)+(\delta x^4/k_\mathrm{B}T))\mathrm{d}x}{\int_{-\infty}^{+\infty} \mathrm{e}^{-\beta x^2/2k_\mathrm{B}T}(1+(\gamma x^3/k_\mathrm{B}T)+(\delta x^4/k_\mathrm{B}T))\mathrm{d}x}$$

$$= \frac{(3/4)(\gamma/k_\mathrm{B}T)\sqrt{\pi(2k_\mathrm{B}T/\beta)^5}}{\sqrt{(2\pi k_\mathrm{B}T/\beta)}(1+(15\gamma^2 k_\mathrm{B}T/2\beta^3)+(3\delta k_\mathrm{B}T/\beta^2))} \approx \frac{3\gamma k_\mathrm{B}T}{4\beta^2}.$$

The linear coefficient of thermal expansion is:

$$\alpha = \frac{1}{a_0}\frac{\partial \bar{x}}{\partial T} = \frac{3\gamma k_\mathrm{B}}{4a_0\beta^2}.$$

Note that the linear coefficient of thermal expansion is zero in the case of an harmonic oscillator ($\gamma = 0$). Therefore, we must conclude that thermal expansion is associated with anharmonicity.

12.2.5.3. The contributions of the translational and rotational degrees of freedom to the molar heat capacities are (see Eqs (12.41) and (12.59))

$$c_{\mathrm{Vtran}} = \frac{3}{2}R$$

and

$$c_{\mathrm{Vrot}} = R.$$

The characteristic temperature for the vibrational degree of freedom (see Eq. (12.66)) is:

$$\theta = \frac{hc\tilde{\nu}}{k_\mathrm{B}} = \frac{6.63 \cdot 10^{-34} \cdot 3 \cdot 10^8 \cdot 2215 \cdot 10^2}{1.38 \cdot 10^{-23}} = 3187\ \mathrm{K}.$$

The vibrational contributions to the molar heat capacity (see Eq. (12.72)) are $c_{\mathrm{Vvib}} = 0.03$ J/(K mole) at $T = 298$ K and $c_{\mathrm{Vvib}} = 2.57$ J/(K mole) at $T = 800$ K. Summing all three contributions, we obtain the molar isochoric heat capacity of CO is $c_\mathrm{V} = 20.82$ J/(K mole) at $T = 298$ K and $c_\mathrm{V} = 23.36$ J/(K mole) at $T = 800$ K. The isobaric heat capacities can be obtained by adding R to these values: $c_\mathrm{p} = 29.13$ J/(K mole) at $T = 298$ K and $c_\mathrm{p} = 31.67$ J/(K mole) at $T = 800$ K. Experiment yields $c_\mathrm{p} = 29.11$ J/(K mole) at $T = 298$ K and $c_\mathrm{p} = 31.62$ J/(K mole) at $T = 800$ K. This is excellent agreement between experiment and theory.

12.2.5.4. The contribution to the entropy associated with translational motion of molecules can be calculated as (see Eqs (12.37) and (12.40))

$$S_{\mathrm{tran}} = \frac{3}{2}R + R\ln Z_{\mathrm{tran}} + R\ln\frac{e}{N}.$$

Using Eq. (12.37), we find:

$$\begin{aligned}\ln Z_{\text{tran}} &= \frac{3}{2}\ln M + \frac{5}{2}\ln T - \ln p + \ln\frac{(2\pi)^{3/2}k_{\text{B}}^{5/2}}{h^3 N_{\text{A}}^{1/2}}\\ &= \frac{3}{2}\ln(28\cdot 10^{-3}) + \frac{5}{2}\ln 298 - \ln(1.013\cdot 10^{5})\\ &\quad + \ln\frac{(2\pi)^{3/2}(1.38\cdot 10^{-23})^{5/2}}{(6.63\cdot 10^{-34})^{3}(6.02\cdot 10^{23})^{1/2}}\\ &= 70.33,\end{aligned}$$

and $S_{\text{tran}} = 150.3$ J/(K mole). The rotational part of the entropy can be calculated as (see Eqs (12.55), (12.57), and (12.58))

$$S_{\text{rot}} = \frac{U_{\text{rot}}}{T} + R\ln Z_{\text{rot}}$$

where

$$U_{\text{rot}} = RT,$$

$$\ln Z_{\text{rot}} = \ln J + \ln T - \ln\sigma + \ln\frac{8\pi^2 k_{\text{B}}}{h^2}$$

and

$$J = \frac{m_1\cdot m_2}{m_1+m_2}r_{12}^2 = \frac{M_1\cdot M_2}{N_{\text{A}}(M_1+M_2)}r_{12}^2.$$

Inserting the handbook data in these equations yields $J = 1.450\cdot 10^{-46}$ kg m^2, $\ln Z_{\text{rot}} = 4.674$, and $S_{\text{rot}} = 47.2$ J/(K mole). Equation (12.69) implies that the contribution of the vibrational degree of freedom to the molar entropy is less than 0.01 J/(K mole). Therefore, we find that $S = 197.4$ J/(K mole) at $T = 298$ K. Experiment yields $S = 197.5$ J/(K mole). This is in excellent agreement with this theoretical prediction.

12.2.7.1. Equation (12.83) implies:

$$S_{\text{el}} = \frac{\partial A_{\text{el}}}{\partial T} = Nk_{\text{B}}\ln\left[g_0 + g_1 \mathrm{e}^{-\Delta/k_{\text{B}}T}\right] + \frac{Ng_1(\Delta/T)\mathrm{e}^{-\Delta/k_{\text{B}}T}}{g_0 + g_1\mathrm{e}^{-\Delta/k_{\text{B}}T}}.$$

The electronic contribution to the molar heat capacity is:

$$c_{\text{el}} = T\frac{\partial S_{\text{el}}}{\partial T} = Nk_{\text{B}}\left(\frac{\Delta}{k_{\text{B}}T}\right)^2 \frac{g_0 g_1}{(g_0 + g_1\mathrm{e}^{-\Delta/k_{\text{B}}T})(g_1 + g_0\mathrm{e}^{-\Delta/k_{\text{B}}T})}.$$

Since, $g_0 = g_1 = 2$ for NO, this equation yields $c_{\text{el}} = 2.82$ J/(K mole) at $T = 50$ K and $c_{\text{el}} = 0.26$ J/(K mole) at $T = 500$ K.

12.2.9.1. The mass of the Cs sample changes during the annealing process because some of the Cs vapor escapes through the hole and more Cs evaporates to keep the vapor saturated; hence,

$$\Delta w = m \wedge St,$$

where m is the mass of the Cs atom, S is the area of the hole in the chamber wall, and $\wedge$ is the number of Cs atoms which cross through a unit area of the hole in a unit time (i.e. the Cs flux). The flux can be determined from Eq. (12.98), such that the change in mass is:

$$\Delta w = \frac{m p_{\mathrm{s}} \pi (d/2)^2 t}{\sqrt{2\pi m k_{\mathrm{B}} T}}.$$

Therefore, the pressure of the saturated vapor is:

$$p_{\mathrm{s}} = \frac{4\Delta w \sqrt{2\pi k_{\mathrm{B}} T}}{t d^2 \sqrt{\pi m}} = \frac{4 \cdot 604 \cdot 10^{-6} \sqrt{2 \cdot 1.38 \cdot 10^{-23} \cdot 773 \cdot 6.02 \cdot 10^{23}}}{80 \cdot (0.7 \cdot 10^{-3})^2 \cdot \sqrt{\pi \cdot 132.9 \cdot 10^{-3}}}$$
$$= 1.08 \cdot 10^4\,\mathrm{Pa} = 0.107\,\mathrm{atm}.$$

Note that this type of experiment is commonly used to determine the saturated vapor pressure (the Knudsen method).

12.2.11.1. Using Eq. (12.103), we obtain:

$$z = 4\sigma n \left(\frac{k_{\mathrm{B}} T}{\pi m}\right)^{1/2} = 4\pi d^2 \frac{p}{k_{\mathrm{B}} T} \left(\frac{k_{\mathrm{B}} T}{\pi m}\right)^{1/2} = 4 d^2 p \left(\frac{\pi}{m k_{\mathrm{B}} T}\right)^{1/2}$$
$$= 4 \cdot (2.04 \cdot 10^{-10})^2 \cdot 1.013 \cdot 10^5 \sqrt{\frac{\pi \cdot 6.02 \cdot 10^{23}}{20.18 \cdot 10^{-3} \cdot 1.38 \cdot 10^{-23} \cdot 600}}$$
$$= 1.44 \cdot 10^9.$$

12.2.11.2. Using Eq. (12.106), we obtain:

$$\lambda = \frac{1}{\sqrt{2}\sigma n} = \frac{k_{\mathrm{B}} T}{\sqrt{2}\pi d^2 p}.$$

Therefore,

$$d = \sqrt{\frac{k_{\mathrm{B}} T}{\sqrt{2}\pi \lambda p}} = \sqrt{\frac{1.38 \cdot 10^{-23} \cdot 273}{\sqrt{2}\pi \cdot 1.28 \cdot 10^{-9} \cdot 1.013 \cdot 10^5}}$$
$$= 2.5 \cdot 10^{-10}\ \mathrm{m} = 2.5\ \text{Å}$$

12.2.11.3. The process cross-section in this case is:

$$\sigma_{ij} = \begin{cases} \sigma_{0ij} & \text{at} \quad v \geq v_0 \\ 0 & \text{at} \quad v < v_0 \end{cases}.$$

Analogously to the derivation of Eq. (12.103), we obtain:

$$z_{ij} = n_j \sigma_{0ij} \left(\frac{m_{ij}}{2\pi k_{\mathrm{B}} T}\right)^{3/2} 4\pi \int_{v_0}^{\infty} \mathrm{e}^{-m_{ij} v_{ij}^2 / 2 k_{\mathrm{B}} T} v_{ij}^3 \mathrm{d} v_{ij}$$
$$= 4 n_j \sigma_{0ij} \left(\frac{m_{ij}}{2\pi k_{\mathrm{B}} T}\right)^{1/2} \left(1 + \frac{m_{ij} v_0^2}{2 k_{\mathrm{B}} T}\right) \mathrm{e}^{-m_{ij} v_0^2 / 2 k_{\mathrm{B}} T}.$$

Combining this result with Eq. (12.104) gives us the number of such collisions per unit volume and time with relative velocity greater than v_0 as:

$$Z_{ij}(v_0) = Z_{0ij}\left(1 + \frac{m_{ij}v_0^2}{2k_\mathrm{B}T}\right)\mathrm{e}^{-m_{ij}v_0^2/2k_\mathrm{B}T},$$

where Z_{0ij} can be found from Eq. (12.104).

12.3.1.1. Consider the dissociation of the dimers via the following simple reaction:

$$\mathrm{Na}_2 = 2\mathrm{Na}.$$

Its equilibrium constant is

$$K_p = \frac{p_\mathrm{Na}^2}{p_{\mathrm{Na}_2}} = p\frac{(1 - x_{\mathrm{Na}_2})^2}{x_{\mathrm{Na}_2}} \approx p\frac{1 - 2x_{\mathrm{Na}_2}}{x_{\mathrm{Na}_2}},$$

and, therefore,

$$x_{\mathrm{Na}_2} = \frac{1}{K_p/p + 2}.$$

At the normal boiling temperature of any substance, the pressure of its saturated vapor is $p = 1$ atm. Therefore, the problem of finding the molar fraction of the dimer is reduced to finding the equilibrium constant K_p.

The partition function for Na is

$$P(\mathrm{Na}) = P_\mathrm{tran}(\mathrm{Na})P_\mathrm{el}(\mathrm{Na}).$$

The translational partition function can be calculated as (see Eqs (12.118) and (12.37)

$$\begin{aligned} P_\mathrm{tran}(\mathrm{Na}) &= \left(\frac{mk_\mathrm{B}T}{2\pi\hbar^2}\right)^{3/2} \\ &= \left(\frac{23.0\cdot 10^{-3}\cdot 1.38\cdot 10^{-23}\cdot 1163}{2\pi\cdot 6.022\cdot 10^{23}\cdot(1.055\cdot 10^{-34})^2}\right)^{3/2} = 8.21\cdot 10^{32} \end{aligned}$$

and $P_\mathrm{el}(\mathrm{Na}) = 2$ (see Section 12.2.7).

The partition function for Na_2 is

$$P(\mathrm{Na}_2) = P_\mathrm{tran}(\mathrm{Na}_2)P_\mathrm{rot}(\mathrm{Na}_2)P_\mathrm{vib}(\mathrm{Na}_2).$$

The translational partition function can be calculated as (see Eqs (12.118) and (12.37))

$$P_\mathrm{tran}(\mathrm{Na}_2) = \left(\frac{mk_\mathrm{B}T}{\pi\hbar^2}\right)^{3/2}.$$

The rotational partition function can be calculated as (see Eqs (12.54) and (12.55))

$$P_{\mathrm{rot}}(\mathrm{Na}_2)=\frac{1}{\sigma}\frac{T}{T_{\mathrm{c}}}=\frac{2Ik_{\mathrm{B}}T}{2\hbar^2}$$
$$=\frac{0.5\cdot 23.0\cdot 10^{-3}\cdot(2.18\cdot 10^{-10})^2\cdot 1.38\cdot 10^{-23}\cdot 1163}{6.022\cdot 10^{23}\cdot(1.055\cdot 10^{-34})^2}$$
$$=1308.$$

The characteristic vibrational temperature for Na_2 is

$$\theta=\frac{h\tilde{\nu}c}{k_{\mathrm{B}}}=\frac{6.63\cdot 10^{-34}\cdot 159.2\cdot 10^2\cdot 3\cdot 10^8}{1.38\cdot 10^{-23}}=229.5\ \mathrm{K}$$

and the vibrational partition function is (see Eq. (12.67))

$$P_{\mathrm{vib}}(\mathrm{Na}_2)=\frac{1}{1-\mathrm{e}^{-\theta/T}}=5.58.$$

The equilibrium constant for the dissociation reaction is

$$K_c=\frac{P(\mathrm{Na})^2}{P(\mathrm{Na}_2)}\mathrm{e}^{-\Delta E_{\mathrm{d}}/k_{\mathrm{B}}T}$$
$$=\frac{4(mk_{\mathrm{B}}T/2\pi\hbar^2)^{3/2}P_{\mathrm{tran}}(\mathrm{Na})}{(mk_{\mathrm{B}}T/\pi\hbar^2)^{3/2}P_{\mathrm{rot}}(\mathrm{Na}_2)P_{\mathrm{vib}}(\mathrm{Na}_2)}\mathrm{e}^{-\Delta E_{\mathrm{d}}/k_{\mathrm{B}}T}$$
$$=\frac{\sqrt{2}P_{\mathrm{tran}}(\mathrm{Na})}{P_{\mathrm{rot}}(\mathrm{Na}_2)P_{\mathrm{vib}}(\mathrm{Na}_2)}\mathrm{e}^{-\Delta E_{\mathrm{d}}/k_{\mathrm{B}}T}=1.1\cdot 10^{26}.$$

This expression was written for the special case in which concentrations are expressed in molecules/m^3. The value of K_{c} corresponding to the concentrations expressed in mole/l can be obtained as follows

$$K_c=\frac{1.1\cdot 10^{26}}{6.022\cdot 10^{23}\cdot 10^3}=0.182.$$

The equilibrium constant K_p can be now calculated as

$$K_p=RT\cdot K_{\mathrm{c}}=0.0821\cdot 1163\cdot 0.182=17.4$$

and the molar fraction of dimers is

$$x_{\mathrm{Na}_2}=\frac{1}{17.4/1+2}=0.051.$$

12.3.2.1. Equations (12.128) and (12.129) can be combined to write the steric factor as

$$\sigma=\frac{A_{\mathrm{exp}}}{\pi(r_{\mathrm{A}}+r_{\mathrm{B}})^2((1/m_{\mathrm{A}})+(1/m_{\mathrm{B}}))^{1/2}((8k_{\mathrm{B}}T/\pi))^{1/2}}.$$

A_{exp} can be determined from the temperature dependence of the rate constant (see Eq. 8.21):

$$\begin{aligned} A_{\mathrm{exp}} &= k_1 \left(\frac{k_2}{k_1}\right)^{T_2/(T_2-T_1)} = 0.713 \cdot 10^{-2} \cdot \left(\frac{5.89}{0.713}\right)^{323.2/(323.2-293.1)} \\ &= 5.01 \cdot 10^{7}\ 1/(\text{mole min}) \\ &= 5.01 \cdot 10^{7} \cdot 10^{-3}/(60 \cdot 6.022 \cdot 10^{23})\ \mathrm{m}^3/(\text{molecules s}) \\ &= 1.39 \cdot 10^{-21}\ \mathrm{m}^3/(\text{molecules s}). \end{aligned}$$

The diameter of a molecule can be estimated from the liquid density. If we assume that the molecules are hard spheres which form a dense packing then the volume per molecule is $8r^3/\sqrt{2}$.[1] This implies that:

$$N_{\mathrm{a}} \frac{8r^3}{\sqrt{2}} = \frac{M}{\rho}$$

and

$$r = 6.65 \cdot 10^{-2} \left(\frac{M}{\rho}\right)^{1/3}.$$

Using the data provided in the example problem, we find:

$$r_{\mathrm{C_5H_5N}} = 2.87 \cdot 10^{-10}\ \mathrm{m} \quad \text{and} \quad r_{\mathrm{CH_3I}} = 2.64 \cdot 10^{-10}\ \mathrm{m}.$$

Combining these results and the first equation, we obtain:

$$\begin{aligned} \sigma &= \frac{1.39 \cdot 10^{-21}}{\pi \cdot (2.87+2.64)^2 \cdot 10^{-20} \left[((1/79)+(1/142))6.02 \cdot 10^{23}/10^{-3}\right]^{1/2} \times ((8 \cdot 1.38 \cdot 10^{-23} \cdot 293.1)/\pi)^{1/2}} \\ &= 4.2 \cdot 10^{-6}. \end{aligned}$$

Chapter 13

13.2.1.1. The expression for the Gibbs free energy consists of two parts: a term corresponding to the ideal gas and a correction associated with deviations from ideality, that is,

$$G = G_{\mathrm{ideal}} + \Delta G_{\mathrm{vd}W}.$$

The first term is (see Eq. (12.19))

$$G = -RT \ln(Z/N_{\mathrm{a}}) = -RT(\ln Z_{\mathrm{tran}} + \ln Z_{\mathrm{rot}} + \ln Z_{\mathrm{el}} - \ln N_{\mathrm{a}}),$$

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[1] This result was obtained by assuming the molecules are on a face-centered cubic lattice. If we assume a different packing, the constants in this expression will be only slightly different.

excluding the vibrational contribution (see Table 12.1 in Section 12.2.4). As discussed above (see Example problem 12.2.5.4), we can write the individual contributions as:

$$\ln Z_{\mathrm{tran}} = \frac{3}{2}\ln M + \frac{5}{2}\ln T - \ln p + \ln\frac{(2\pi)^{3/2}k_{\mathrm{B}}^{5/2}}{h^3 N_{\mathrm{A}}^{1/2}} = \frac{5}{2}\ln T - \ln p + 67.81$$

$$\ln Z_{\mathrm{rot}} = \ln J + \ln T - \ln\sigma + \ln\frac{8\pi^2 k_{\mathrm{B}}}{h^2} = \ln T - 1.42$$

$$\ln Z_{\mathrm{el}} = \ln 3,$$

(the ground state of oxygen is a triplet—see Section 12.2.7). Using these results, we obtain the following expression for the Gibbs free energy of O_2 in the ideal gas model approximation:

$$G_{\mathrm{ideal}} = -\frac{7}{2}RT\ln T - RT\ln p - 12.73RT.$$

In order to calculate the correction associated with deviations from ideality, we start from the following general thermodynamic relation:

$$\left(\frac{\partial G}{\partial p}\right)_T = V.$$

Writing the same relation for the ideal gas and subtracting it from this relation, we find:

$$\left(\frac{\partial (G - G_{\mathrm{ideal}})}{\partial p}\right)_T = V - V_{\mathrm{ideal}}.$$

If we use the van der Waals equation (Eq. (13.36)) of state, this equation can be rewritten as:

$$\left(\frac{\partial \Delta G_{\mathrm{vd}W}}{\partial p}\right)_T = \frac{N^2 k_{\mathrm{B}} T}{V\mathrm{p}} b - \frac{N^2}{V\mathrm{p}} a.$$

Since this is a small correction, we can (with the same accuracy as the van der Waals equation of state itself) replace the volume in this equation with Nk_BT/p:

$$\left(\frac{\partial \Delta G_{\mathrm{vd}W}}{\partial p}\right)_T = Nb - \frac{N}{k_{\mathrm{B}}T} a.$$

Integration of this equation yields:

$$\int_0^{\Delta G_{\mathrm{vd}W}} \mathrm{d}\Delta G_{\mathrm{vd}W} = \int_0^p \left(Nb - \frac{N}{k_{\mathrm{B}}T} a\right) \mathrm{d}p$$

$$\Delta G_{\mathrm{vd}W} = Nbp - \frac{Nap}{k_{\mathrm{B}}T}.$$

Thus, the Gibbs free energy for O_2, in the van der Waals approximation, takes the following form:

$$G = -\frac{7}{2}RT\ln T - RT\ln p - 12.73RT + Nbp - \frac{Nap}{k_{\mathrm{B}}T}.$$

Recall that we already used this expression to describe deviations from ideality in Example problem 1.4.2.1 without proof.

13.2.2.1. Using Eqs (13.40) and (13.39), we find that $b = 3.258 \cdot 10^{-2}$ l/mole and $a = 1.393$ atm l^2/mole^2. Inserting these values into Eq. (13.41), we obtain $p_c = 48.6$ atm. The experimental value is 49.7 atm. Note, that use of the equation of state for ideal gases predicts $p = 129.6$ atm under the same conditions.

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