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THERMODYNAMICS OF THE SOLUTION OF MERCURY METAL

by

James Nelson Spencer

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

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Of Science and Technology
Ames, Iowa

1967

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INTRODUCTION

The solubility of mercury in various liquids is of interest to the photochemist in his efforts to understand mercury photosensitization of liquid hydrocarbons, the kineticist in the study of mercury-organo systems, and to the solution thermodynamicist for the study of solute-solvent interactions. The limited solubility of mercury metal in most liquids offers an excellent system for an appraisal of solute-solvent interactions. The solutions formed when mercury dissolves in a liquid are sufficiently dilute so that solute-solute interactions are negligible. Mercury, being a monatomic solute, offers no rotational or vibrational complications and further undergoes no chemical reaction with the solvent.

A determination of the solubility of mercury as a function of temperature permits the evaluation of thermodynamic properties of mixing. From these properties a comparison with theory may be made and an elucidation of the interaction between solute and solvent is possible. The theory of regular solutions as developed by J. H. Hildebrand is perhaps the most widely used for predictions of the properties of non-electrolyte solutions. The experimental data obtained in this work are used to present a severe test for this theory. The relationship between heats and entropies of vaporization found by Barclay and Butler is tested by calculating these thermodynamic properties from solubility data.

Solubility determinations permit the evaluation of the entropy change on mixing. The fundamental tenet of regular solution theory is that the entropy of mixing is ideal. Often in cases where there is a large disparity in molar volume between the solute and solvent a formulation designed to take into account these size differences is used in

place of ideal entropy. The solutions studied in this work offer a means of testing the relative merits of these two approaches to entropy changes since the ratio of the molar volumes is about ten to one for most cases studied.

The solubilities reported in this work were obtained by a tracer technique using radioactive mercury-203. Solubility measurements were made by a direct determination of the specific activity of the solution.

REVIEW OF THE LITERATURE

Solubility of Mercury Metal

Christoff (1), in 1908, observed that mercury dissolved in water to some extent. Christoff noted a loss in weight of a pycnometer which contained mercury after water had been allowed to pass over the mercury. Mercury, detected by the reduction of a solution of gold chloride, was qualitatively identified as a solute species in various liquids.

Bonhoeffer and Reichardt reported the absorption spectra of mercury dissolved in water in 1929. (2) Later these workers (3, 4) studied the absorption spectra of mercury dissolved in water, methanol, and n-hexane. Two absorption bands were found around 2537 Å. Bonhoeffer and Reichardt interpreted this splitting of the absorption band as a Stark effect since the splitting was found to increase in going from n-hexane to methanol to water. Recent work in this area seems to rule out the Stark effect as a cause for this splitting. While the splitting is found to vary with increasing polarity of the solvent, it does not vary within the same class of solvents (5). That is, the splitting seen in mercury saturated solutions of cyclic hydrocarbons does not vary from solvent to solvent even though the solvents have varying dielectric constants. Various theories (5) have been put forth to explain this splitting of the absorption band but the problem has not been resolved. Bonhoeffer and Reichardt also obtained values for the solubility of mercury in water, methanol, and n-hexane using a method involving the amalgamation of dissolved mercury on gold foil. Their results are given in Table 1.

In 1931 Stock and his co-workers (6, 7) proposed that the electro-deposition of dissolved mercury on a copper wire could be used to

determine mercury solubilities. Later (8) these same workers determined the solubility of mercury in air-free water, dilute aqueous potassium hydroxide, and potassium chloride, benzene, blood, and egg albumin. The values reported by them for water and benzene are recorded in Table 1. The solubility of mercury was found to be higher in water which had not had the air removed from it than in de-aerated water. They found that the solubility of mercury in organic solvents did not seem to be affected by the presence of air.

Pariaud and Archinard (9) measured the solubility of mercury in water using a colorimetric method. Their value for the mercury solubility is given in Table 1. Moser (10) has criticized this work on the grounds that no mention was made by these workers of oxidizing the mercury in solution. Their value for the mercury solubility then would not include the contribution due to the dissolved free mercury.

Moser and Voigt (11) used a tracer technique to determine mercury solubilities in several solvents. Their values are recorded in Table 1. These workers found solubility of mercury in water increased over a period of days. They attributed this solubility increase to irradiation of the water by the gamma rays and beta particles emitted by the radioactive mercury. This high energy radiation produces hydrogen peroxide and hydroxyl radicals which makes the irradiated water a good oxidant. The addition of hypophosphorous acid to this solution was found to eliminate this effect.

Klehr and Voigt (12) extended the work of Moser and Voigt by using a tracer technique to measure mercury solubilities in eight solvents. In three of these solvents the solubility was determined as a function of

Table 1. Reported values for the solubility of mercury metal

Solvent	T °C	Solubility $\left(\frac{\mu\text{-moles}}{1}\right)$	Investigators
n-pentane	25	5.8	Kuntz and Mains (13)
isopentane	25	5.5	Kuntz and Mains (13)
3-methylpentane	25	5.1	Kuntz and Mains (13)
2,2-dimethylbutane	25	5.0	Kuntz and Mains (13)
2,3-dimethylbutane	25	6.0	Kuntz and Mains (13)
perfluorodimethylcyclobutane	25	.34	Kuntz and Mains (13)
isooctane	25	4.6	Klehr and Voigt (12)
chlorobenzene	25	12.5	Klehr and Voigt (12)
bromobenzene	25	16.0	Klehr and Voigt (12)
cyclohexane	25	11.0	Moser and Voigt (11)
n-hexane	25	6.1-6.7	Moser and Voigt (11)
	40	13.5	Reichardt and Bonhoeffer (3)
	63	52	Reichardt and Bonhoeffer (3)
methanol	25	1.52	Kuntz and Mains (13)
	40	3.0	Reichardt and Bonhoeffer (3)
	63	1.8×10^3	Reichardt and Bonhoeffer (3)
benzene	25	12.0	Moser and Voigt (11)
	25	11.4	Klehr and Voigt (12)
	room	7.5-10.0	Stock et al. (8)
carbontetrachloride	25	7.5	Moser and Voigt (11)
	25	7.5	Klehr and Voigt (12)
toluene	25	12.5	Moser and Voigt (11)
	25	13.4	Klehr and Voigt (12)
nitrobenzene	25	9.3	Moser and Voigt (11)
	25	9.0	Klehr and Voigt (12)
n-decane	25	5.5	Kuntz and Mains (13)
	25	7.0	Klehr and Voigt (12)

Table 1. (Continued)

Solvent	T °C	Solubility $(\frac{\mu\text{-moles}}{1})$	Investigators
water	25-28	.15	Pariaud and Archinard (9)
	30	.1	Stock et al. (8)
	85	1.5	Stock et al. (8)
	100	3.0	Stock et al. (8)
	120	5.0	Reichardt and Bonhoeffer (3)
	25	.30	Moser and Voigt (11)
	25	.1	Kuntz and Mains (13)

temperature. They further compared the experimental solubilities with values predicted by the Hildebrand-Scatchard theory of solutions. The predictions of a modification of this theory due to Reed were also tabulated. Plots of the logarithmn of the mole fraction of mercury versus the logarithmn of the absolute temperature yielded entropies of solution. These entropies were found to be larger than ideal in two of the three cases tested. Their results at 25°C are given in Table 1.

More recent determinations of mercury solubilities have been made by Kuntz and Mains (13). They determined mercury solubilities using measurements of the optical density of a saturated solution of mercury in several solvents. Mercury absorption occurs at 2537 Å in the gas phase, however, as previously mentioned, in solution this absorption band is split into two components which appear on either side of 2537 Å. Combining the measurements of the solubility of mercury in n-hexane by Moser and Voigt with their optical density measurements, Kuntz and Mains obtained an extinction coefficient. This value for the coefficient coupled with optical density measurements was then used to calculated solubilities in other solvents. Their results at 25°C are given in Table 1. While their results agree with those of this work for three common solvents their method must be suspect. They reported saturation of the solutions was accomplished by vigorous shaking of mercury with the solvents for twenty minutes. Results of the present work indicate that it is doubtful that equilibrium could be attained in so short a time.

Pollard and Westwood, in their studies of exchange between metallic mercury and mercury compounds in solution, also determined the solubility of mercury in benzene (14).

Structure of Liquid Mercury

Mercury is taken as the classic example of a monatomic liquid and hence has been used as a standard in determining the hindrance to rotation and vibration in more complex liquids (15, 16).

Structural determinations on liquid mercury have shown that the repulsive potential for mercury increases less rapidly than that for the rare gases with their more tightly bound electrons (17). Liquid mercury has been shown to have about six atoms in the first coordination layer with the first maximum in the radial distribution function occuring at 3.00 Å (18). Fowkes (19) has shown that mercury atoms develop very strong dispersion forces. About 41% of the interatomic forces in mercury are dispersion forces while the metallic bonds make up about 59%.

Regular Solutions

It is necessary to clarify the term 'regular solution' as used in this work. The regular solution concept as originally conceived and defined by J. H. Hildebrand has been subject to many interpretations. It is unfortunate that several authors, particularly the British ones, have adopted the term 'regular solution' but not the original definition. Hildebrand first proposed this term in 1929 in these words (20): "A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged."

According to Hildebrand's hypothesis many non-ideal solutions have sufficient thermal energy to overcome the tendency to segregation due to different molecular fields and therefore possess nearly ideal entropy of mixing. We shall consider in this work an ideal solution to be one in

which the heat of mixing is zero, the entropy of mixing is ideal, and the activity of a component is equal to its mole fraction over the entrie composition range, the pure component being selected as the standard state for both solvent and solute. Briefly an ideal solution is one for which Raoult's law holds for both components. A regular solution is one in which there may be a heat of mixing and in which there is sufficient thermal energy to give maximum randomness of the components i.e., ideal entropy. The activity of a component in a regular solution is generally greater than the mole fraction of that component.

Hildebrand has gently scolded the authors who have redefined the term 'regular solution': "I cite these differences not for the purpose of asserting my rights as the inventor of the term, but to urge that so useful a concept, to which a simple, definite measuring was originally attached should not be robbed of its significance by different writers redefining it, each in his own way. I have no objection to a redefinition that may appear desirable in the light of present knowledge, but it should be made by general consent." (21)

Hildebrand was led to this concept by a study of iodine solubilities in various solvents. He noted that the slopes of the lines obtained by plotting the logarithm of the mole fraction of iodine versus the reciprocal of the absolute temperature exhibited a similarity in all cases examined except for benzene. It has subsequently been shown that iodine and benzene form a 1:1 complex accounting for deviations from regularity (22, p. 82).

Hildebrand has cited evidence for nearly ideal entropy of mixing in many cases (22, chpt. 3). He has found that when a component is added

to a solution at constant pressure and the solution expands by the
partial molar volume, $\overline{V}_2$, of that component, the partial molar entropy is
approximately given by:

$$-R\ln x_2 + (\overline{V}_2 - V_2{}^o)\ \frac{\partial P}{\partial T})_{V,1},$$

where x_2 is the mole fraction of the added component, $V_2{}^o$ is the molar
volume of the pure component and $\frac{\partial P}{\partial T})_{V,1}$ is the thermal pressure (22, p. 153).

Scatchard (23) and later Hildebrand and Wood (24) derived an equation
for the heat of mixing. This term when coupled with ideal entropy affords
a means of calculating solubilities from the properties of the pure com-
ponents. This formulation has been found to have a wider range of applica-
bility to solution of non-electrolytes than any other theory. This
theory will be further discussed in the section entitled Hildebrand-
Scatchard Equations.

Barclay-Butler Rule

Early workers found that there were many substances, pure liquids
or solutes in dilute solution, which, when compared at a common temperature
and between the same standard states, gave values of heats and entropies
of vaporization which varied linearly with each other. Bell (25) found
a linear relation between heats and entropies of solution for gases for
five different solutes in each of five solvents. Evans and Polanyi (26)
found a straight line relationship held for the heats and entropies of
vaporization for the same solute in different solvents. It remained for
Barclay and Butler (27) to show that there was a universal relationship
which fit the entropies of vaporization of pure liquids and of solutes
from dilute solutions. They found that the values of the heat and entropy
of vaporization at a given temperature could be fairly accurately repre-

sented by an equation of the form:

$$\Delta S^V = A + B\Delta H^V.$$

They determined the values of A and B by plotting experimental heats and entropies of vaporization. The relation they found, from which no normal substance, pure liquid or dilute solution deviates very greatly, is at 25°C:

$$\Delta S^V = .001\Delta H^V + 27.7,$$

where the entropy change is given in the usual units. The standard states chosen were a hypothetical mole fraction of unity for the solute and a pressure of one torr for the gas. The pure liquid is the standard state for the pure substances. A wide variety of cases was covered in the original Barclay-Butler curve. These include the vaporization of pure liquids, vaporization of several gases from their solution in benzene, various vaporizable solutes in acetone, and the four lower alcohols from benzene. Frank (28) has reexamined the Barclay-Butler relationship and in light of better experimental information has found that the best fit to experimental data is given by:

$$\Delta S^V = .00124\Delta H^V + 25.94.$$

The units and standard states here are as before. Frank originally used one atmosphere as the standard state for the gas and the expression Rln 760 = 13.19 has been subtracted from his equation in order to employ the same standard state as before.

In papers by Frank (28, 29) and Frank and Evans (30) an interpretation of the relation between heat and entropy of vaporization is given. The interpretation is in terms of a free volume. The free volume used by these authors is that volume accessible to the center of a molecule.

This is an extension of the 'cage' concept of solution and liquid structure. Frank writes for this free volume, V_f,

$$V_f = \beta \left[\frac{RT}{\Delta E^V}\right]^3 ,$$

where ΔE^V is the energy of vaporization and

$$\beta = \frac{\gamma f b^3 g^3}{h_3 n_3} .$$

Here γ measures the interference in the liquid with the internal motions of the molecule, and f, b, g, h, and n are quantities which depend on the geometry of the liquid and the energetic and dynamic interaction of the molecules. Frank points out that the chief burden of a variation in β falls on γ. The Barclay-Butler rule is then shown to imply a general tendency for a liquid to have a smaller β the larger its heat of vaporization. In many cases then a smaller value for β means γ is smaller, resulting from increased interference with rotation of the molecules in the liquid. Using these ideas and empirically determined relations between β and the heat of vaporization Frank and Evans derived equations for the entropy of mixing and the partial entropies of vaporization. While these equations fit experimental data fairly well they have been justifiably criticized by Rice (31) who points out that certain relations used in the discussion of pure liquids entered into the theory of solutions modified only slightly, if at all.

Free Volume Theory

The free volume concept is an extension of the idea that each molecule is enclosed by its neighbors in a sort of cage. These ideas were first developed by Lennard-Jones and Devonshire (32) and by Eyring and Hirschfelder (33). According to this theory the entropy of vaporization may be given by:

$$\Delta S^V = R\ln \frac{V_g}{V_f} , \qquad\qquad (1)$$

where V_g is the volume of the gas and V_f is a free volume. This free volume is not the whole cell volume, but is the average volume in which the movement of the center of the molecule inside the cell is restricted due to the repulsion by the surrounding molecules. Equation 1 also assumes that the internal motions of the molecule are as free in the condensed phase as in the gas.

These ideas have been extended to a general theorem by Frank (29). Since $S = k\ln\Omega$, where Ω is the total number of possible states of the system compatible with the prescribed total energy, we may write:

$$\Delta S = S_B - S_A = k\ln\frac{\Omega_B}{\Omega_A} ,$$

where Ω is given by:

$$\Omega = \prod_{j=1}^{j=s} \frac{(2\pi m_j kTe)^{3N_j/2}}{N_j!\, h^{3N_j}} V_{f_j}^{N_j} .$$

Here N_j is the number of different kinds of molecules and S is the number of kinds of atoms present and $V_{f_1} = \int dx_1 dy_1 dz_1$ over all configurations compatible with the energy, etc. Then

$$\Delta S = n_1 R\ln \left(\frac{V_{f_B}}{V_{f_A}}\right)_1 + n_2 R\ln \left(\frac{V_{f_B}}{V_{f_A}}\right)_2 + \ldots ,$$

where the n_i are numbers of moles.

In most real liquids the internal motions are not as free as in their vapors. Therefore equations of the type developed will not correctly give the entropy of vaporization. As pointed out by Frank (28), the most significant interference with internal motions concerns only rotation. This follows from the fact that the positions of Raman and infrared lines are not greatly shifted in passing from vapor to liquid which means the vibrational motions are not greatly perturbed. Broadening of the lines or bands on condensation is caused by rotational energy differences,

which may add to or subtract from the changes in vibrational energies. Frank introduces a factor, γ, to measure the interference with the internal motions in the condensed phase. Since it measures the fraction of rotation the molecule is able to execute after condensation γ is ≤ 1. Then the entropy of vaporization is given by:

$$\Delta S^V = R\ln \frac{V_g}{\gamma V_f} \, , \tag{2}$$

since the free volume in the vapor is essentially the same as the volume of the vapor. Equation 2 is applicable as long as the internal vibrational motions are actually separable from the translation and rotation of the molecule, the internal vibrational motions of the molecules are not changed by the presence of neighbors, and oscillations which have replaced rotations in the liquid are essentially classical.

The application of (2) to solutions often leads to values of the free volume of the solute as large as or even larger than the volumes of the pure solvent. Rice (31) and Frank and Evans (30) have pointed out that this can only be explained as an effect of the solute on the solvent. When a solute replaces a solvent molecule the forces on the neighboring solvent molecules may be weaker than before and the solvent molecules are able to vibrate and rotate more freely. This results in a gain in entropy.

MATERIALS AND PROCEDURES

Apparatus

The solutions were brought to equilibrium in constant temperature water baths, controlled to within $\pm$ 0.1°C by an E. H. Sargent company heating pump operating with a mercury thermoregulator. An ice bath was used for making measurements at 0°C. The thermometers were obtained from Scientific Glass Apparatus Co. and covered the temperature range -1 to +51°C. They were calibrated against thermometers which had been calibrated against NBS standards. The solutions were constantly shaken by a Burrell wrist action shaker. The experimental solutions were equilibrated in glass stoppered 25 ml volumetric flasks.

Aliquots of the equilibrated solutions were counted using a conventional single channel scintillation spectrometer, manufactured by the Nuclear-Chicago Corporation. Initially a 2"x2" well type NaI crystal was employed, which was later changed to a 4"x4" well type crystal. The window with of the spectrometer was adjusted to count only the photo-peak at .279 mev.

Materials

The mercury-203 used in this work was obtained from Oak Ridge Laboratories and from Nuclear Science and Engineering, Pittsburgh. The radioactive mercury was shipped as mercuric nitrate. Standard solutions were prepared by adding the desired amount of mercury-203 to mercuric nitrate carrier. Baker analyzed mecuric nitrate (99.7%) was used as carrier. Reduction to elemental mercury was accomplished by addition of hypophosphorous acid to the mercuric nitrate solution. The mercury

was coagulated into a globule by addition of hydrochloric acid, washed, and dried over phosphorous pentoxide. A weighed amount of this mercury was transferred to a volumetric flask, dissolved in

nitric acid, and diluted with water. Three milliliter aliquots of the
standards were counted and compared to the same volumes of the mercury-
saturated solvents.

Previous results obtained in this laboratory (12) indicated that
the gamma radiation (.279 mev) absorbed in the liquid samples would be
only a small fraction of the total. It was also shown that the change
in density from water to the organic solutions would lead to differences
of less than 1% in the counting rate.

Mercury-203 decays by emission of a beta particle of maximum energy
.21 mev accompanied by a single gamma ray of .279 mev energy. It has
a half life of 47 days (34).

The following solvents were obtained from Phillips Petroleum
Company and were Phillips 'Research Grade' solvents. These solvents were
used without further purification. The purities in mole percent are
indicated after each solvent.

n-hexane	99.99
n-heptane	99.92
n-octane	99.82
2,2-dimethylbutane	99.97
isooctane	99.97
cyclohexane	99.99
methylcyclohexane	99.91
benzene	99.91
toluene	99.96
t-butylbenzene	99.74

The cyclohexene used was obtained from Phillips (99.94 mole percent) and Matheson, Coleman, and Bell (99.9 mole percent). The cyclohexene from both companies was found to cause a black deposit to appear on the mercury, presumably mercuric oxide formed by action of peroxides present in the solvents (35, pp. 791-85). The cyclohexene was washed with aqueous sodium hydroxide, dried over drierite, refluxed over sodium, and distilled through a Vigreaux type column. This treatment was adequate to remove the impurities causing the blackening in the solvent obtained from Matheson, Coleman, and Bell. The Phillips solvent was further washed with an acidified solution of ferrous sulfate, dried, and redistilled. It was found necessary to add a small amount of hydroquinone to these solvents to prevent further peroxide formation. Experiments using this solvent with and without addition of hydroquinone gave similar results (Table 2).

The n-butyl ether (99^+ mole percent) obtained from Matheson, Coleman, and Bell was also found to cause a black deposit on the mercury. It was washed with an acidified solution of ferrous sulfate, dried over drierite, and distilled. A small amount (10 ppm) of hydroquinone was added to inhibit further peroxide formation.

The isopropyl ether (99^+ mole percent) obtained from Matheson, Coleman, and Bell did not give reproducible values for the solubility of mercury. Degassing the solvent gave concentrations of dissolved mercury larger than expected and results which were not reproducible. Addition of hypophosphorous acid to this solvent eliminated the solubility increase and gave reproducible values for the mercury concentration which remained constant over a period of days. Varying the amount of the acid added to this ether did not affect the measured solubilities as indicated in

Table 2. Effect on mercury solubility of the addition of hypophosphorous acid and hydroquinone to solvents

Solvent	T °C	Additive	Mercury Solubility ($\frac{moles}{l}$)
cyclohexene	30	hydroquinone	18.0×10^{-6}
		none	17.9×10^{-6}
isopropyl ether[a]	25	50 μl hypophosphorous acid	4.6×10^{-6}
		200 μl hypophosphorous acid	4.8×10^{-6}
		500 μl hypophosphorous acid	4.6×10^{-6}
n-butyl ether[a]	20	5 μl hypophosphorous acid	5.5×10^{-6}
		none	5.6×10^{-6}

[a]Addition made to 10 ml of solvent.

Table 2. The solutions analyzed contained 10 μl of hypophosphorous acid added to 10 ml of solvent. It is felt that since degassing the iso-propyl ether had little or no effect on the solubility, radiation damage is partially to blame for the observed solubility increase. The hypophosphorous acid would then serve as a scavenger. Since the solubility of mercury remained constant with time in the iso-propyl ether to which hypophosphorous acid was added, no effect of varying the acid concentration in the solvent was found, and also since the presence of the acid did not affect the solubility in n-butyl ether (Table 2), the solubilities were taken to be that of dissolved free mercury.

The perfluorodimethylcyclobutane was obtained from DuPont. The solvent was a mixture of the 1,2 and 1,3 isomers and was used without further purification.

The hypophosphorous acid used was Baker and Adamson U.S.P. Grade containing 30-32% acid.

Conductivity water doubly distilled from alkaline permanganate was used for solubility determinations in water. Previous work in this laboratory had shown that the solubility of mercury in water undergoes an increase over a period of days (11), but that this effect could be eliminated by the addition of hypophosphorous acid. It was further shown that varying the amount of the acid added to the water had no effect on the measured solubility. The role of the hypophosphorous acid is not known with certainty. In this work a sample of water was degassed, but still gave a concentration of dissolved mercury as large as those samples which had not been degassed or had the acid added to them. It has been estimated that water, when exposed to radiation, develops an

oxidation potential of about +.95 volts due to decomposition of the water molecules to form hydrogen peroxide and radicals (36). The solubility increase is probably due to oxidation of the mercury by the agents which cause this increase in potential. It is also possible that the presence of dissolved oxygen, as reported by Stock (8), may have an effect. It would seem that the hypophosphorous acid may serve as a reducing medium for the oxidized mercury, as well as serving as a scavenger for the radicals produced by the action of radiation on water. Since the solubility measurements were found to be independent of the hypophosphorous acid content of the water, this can be taken to indicate that the solubility measured is the concentration of free mercury in solution and not that of an oxy-phosphorous salt of mercury. Moser and Voigt (11) also found good agreement between the solubilities experimentally measured in water and those inferred from solubilities in n-hexane and cyclohexane as obtained indirectly by combining the solubility in n-hexane and cyclohexane with distribution ratios between these solvents and water.

Experimental Procedure

In order to be assured that the solutions were at equilibrium and that radiation was not affecting the results, the solubility of mercury in n-heptane and benzene was followed over a period of days. The results are given in Table 3 and Figures 1 and 2. These results indicate that equilibrium is attained after about 24 hours. The solubility is also seen to remain constant over a period of several days. If radiation damage had occurred in these systems to an extent that the solubilities were affected, the solubility would not have remained constant. The

Table 3. Solubility of mercury as a function of time

Solvent	T °C	Time (hours)	Mercury Concentration[a] $(\frac{\mu\text{-moles}}{1})$
benzene	15.5	26	7.1
		40	7.0
		78	7.6
		103	7.2
		125	7.3
		159	7.1
n-heptane	22.5	27	5.2
		60	5.6
		100	5.8
		123	5.7
		172	5.8

[a]Each reported solubility is the average of two samples.

measurements reported for all samples were obtained after a period of 24 hours of shaking the mercury with the solvent of interest and were continued over a period of three days. If the mercury concentration remained constant over the three days this was taken as the equilibrium concentration of the dissolved mercury.

In practice, two samples of the solvent of interest of ten milliliters each were placed in stoppered twenty five milliliter volumetric flasks, each flask containing a globule of radioactive mercury, the specific
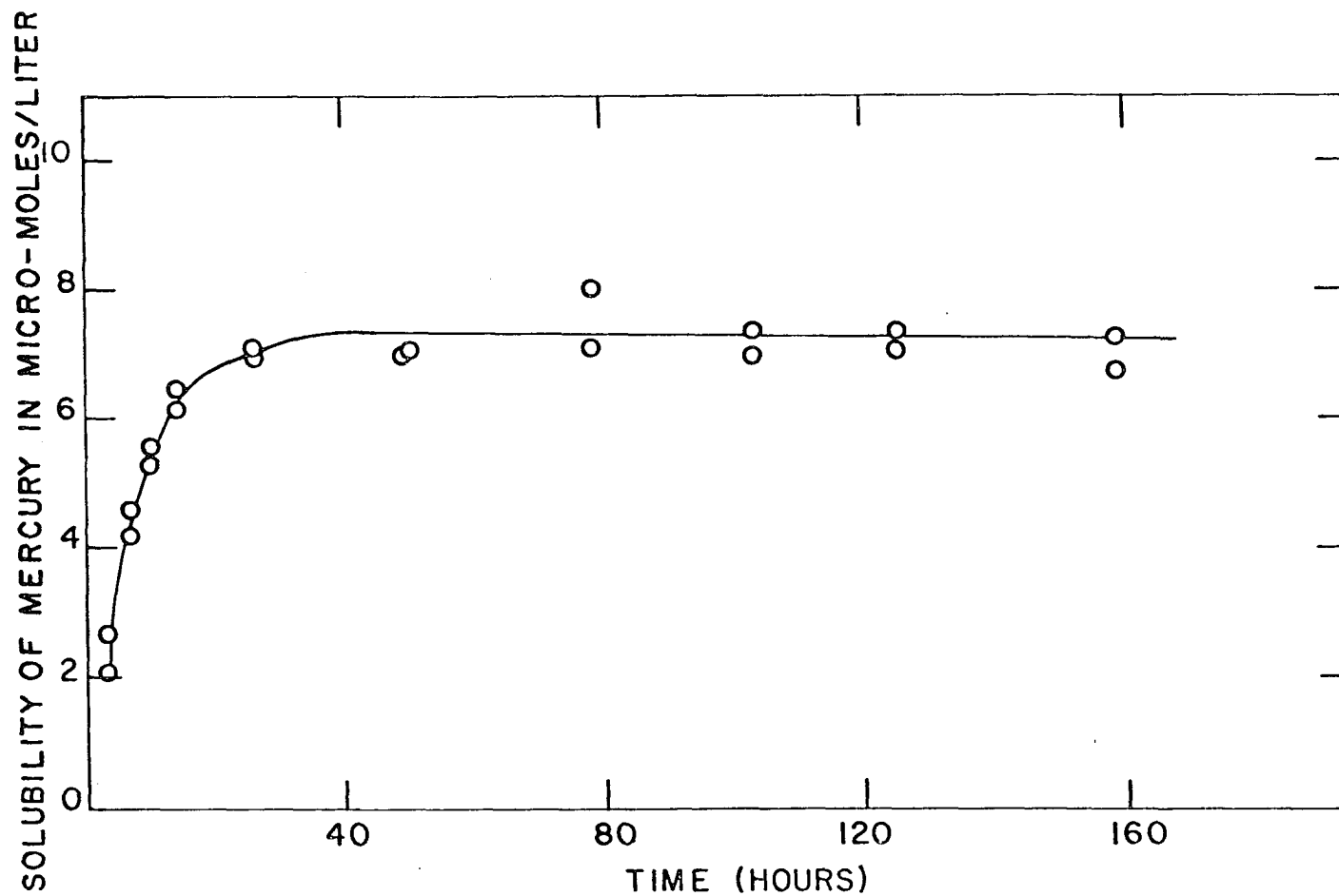
Figure 1. Solubility of mercury in benzene as a function of time
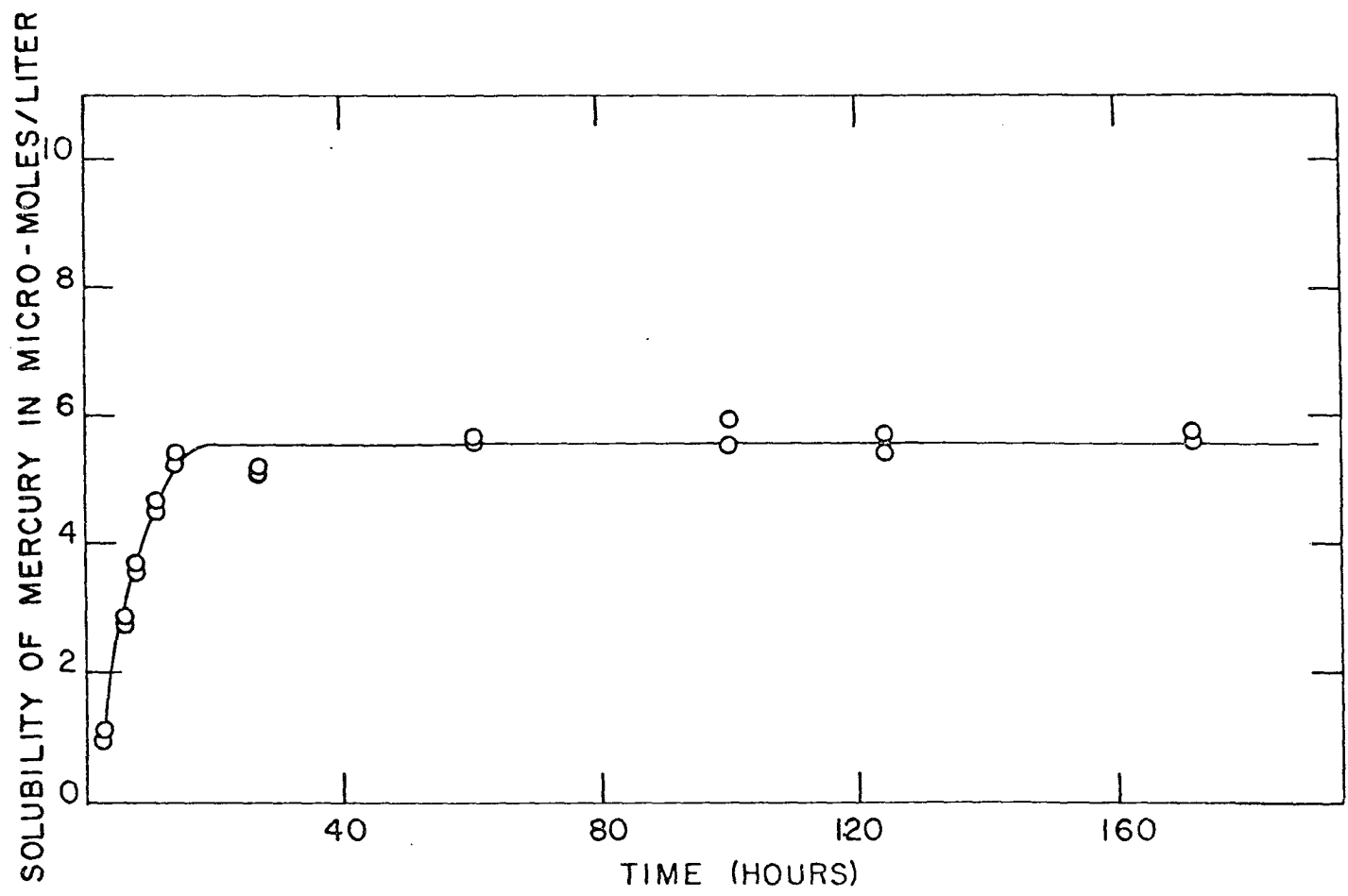
Figure 2. Solubility of mercury in n-heptane as a function of time

activity of which was known. Twenty four hours after the samples were placed in the constant temperature bath, a three milliliter aliquot of each solution was taken and counted. The activity was compared to that of the standards counted at the same time. This procedure was repeated each day for a period of at least three days.

METHOD OF INTERPRETING DATA

Experimental Measurements

In order to calculate the solubility of mercury in these solvents from radiochemical data, we assume that the counting efficiency for any two samples is the same. Then we may write: Efficiency of counting sample = Efficiency of counting standard or

where

$$\frac{R_{spl}}{\lambda N_{spl}} = \frac{R_{std}}{\lambda N_{std}} \quad,$$

R = counts/minute

spl = sample

std = standard

λN = true disintegration rate

N = total number of mercury atoms

= concentration of mercury atoms in an aliquot

= C moles/liter.

Since identical volumes of standard and sample were counted:

$$\frac{R_{spl}}{\lambda C_{spl}} = \frac{R_{std}}{\lambda C_{std}} \quad,$$

then

$$C_{spl} = \frac{R_{spl} \, C_{std}}{R_{std}} \quad.$$

Statistics and Experimental Error

The error reported for a solubility measurement for all solvents except water is the standard deviation of a single measurement.

Reported solubility $= A \pm B$; where

$$A = \frac{\Sigma x_i}{n}$$

$$B = \sqrt{\frac{\Sigma (\Delta x_i)^2}{n-1}}$$

$$\Delta x_i = A - x_i$$

n = number of measurements

x_i = individual measurements.

The error reported for the solubilities in water is the standard deviation of the mean. Reported solubility in water $= A \pm \frac{B}{\sqrt{n}}$; where the symbols are as previously defined.

In all cases sufficient counts were recorded so that the statistical counting error was less than 2%.

The errors reported for the entropy of solution are the errors in the slopes of the lines obtained by plotting the logarithmn of the mole fraction of mercury versus the logarithmn of the absolute temperature. The slopes and errors were calculated by the method of least squares. The errors reported for the entropies of vaporization of mercury from these solutions are the errors in the slopes of the lines obtained by plotting the free energy change against the temperature. The slopes and errors were calculated as before. The errors in the vapor pressures of mercury and the solvents used in this work are not known. Likewise the errors involved in the heats of vaporization of the pure substances are not known but it is unlikely that these errors amount to more than 2 e.u. for entropy calculations.

EXPERIMENTAL RESULTS

The solubilities of mercury in the various solvents studied are given

in Table 4 as a function of temperature. Plots of the logarithm of the

Table 4. The solubility of mercury as a function of temperature.

Solvent	T °C	Solubility $\left(\frac{\text{x-moles}}{1}\right)$	-log x	log T
n-octane	0	1.6 ± .1	6.606	2.436
	15	3.8 ± .1	6.212	2.460
	20	6.7 ± .1	6.090	2.467
	25	8.7 ± .3	5.959	2.475
	30	10.8 ± .3	5.845	2.482
	35	12.6 ± 1.0	5.747	2.489
n-hexane	0	1.4 ± .1	6.750	2.436
	15	3.7 ± .1	6.319	2.460
	20	4.8 ± .1	6.203	2.467
	25	6.3 ± .3	6.081	2.475
	30	8.2 ± .3	5.963	2.482
	35	10.4 ± .2	5.857	2.489
n-heptane	0	1.4 ± .1	6.699	2.436
	15	3.7 ± .1	6.268	2.460
	20	4.8 ± .1	6.152	2.467
	25	6.6 ± .2	6.012	2.475
	30	8.5 ± .4	5.900	2.482
	35	10.9 ± .8	5.788	2.489
isooctane	0	1.0 ± .1	6.793	2.436
	13.5	2.1 ± .1	6.463	2.457
	15	2.2 ± .1	6.441	2.460
	20	3.3 ± .1	6.264	2.467
	25	4.2 ± .2	6.157	2.475
	30	5.3 ± .1	6.053	2.482
	35	6.6 ± .3	5.955	2.489
2,2-dimethylbutane	0	1.3 ± .1	6.775	2.436
	15	2.8 ± .2	6.433	2.460
	20	3.7 ± .1	6.309	2.467
	25	4.7 ± .3	6.201	2.475

Table 4. (Continued)

Solvent	T °C	Solubility $\left(\frac{\mu\text{-moles}}{1}\right)$	-log x	log T
	30	6.0 ± .1	6.093	2.482
	35	7.3 ± .7	6.004	2.489
cyclohexane	15	7.6 ± .2	6.088	2.460
	20	9.4 ± .2	5.991	2.467
	25	12.1 ± .3	5.879	2.475
	30	14.8 ± .4	5.790	2.482
	35	17.4 ± .2	5.717	2.489
	40	22.3 ± 1.5	5.607	2.496
cyclohexene	0	3.1 ± .1	6.513	2.436
	15	7.5 ± .1	6.122	2.460
	20	10.4 ± .3	5.978	2.467
	25	13.3 ± .3	5.868	2.475
	30	17.9 ± 1.0	5.736	2.482
methylcyclohexane	0	2.2 ± .1	6.561	2.436
	15	5.2 ± .1	6.180	2.460
	20	6.9 ± .2	6.055	2.467
	25	9.1 ± .1	5.932	2.475
	30	11.3 ± .2	5.836	2.482
	35	14.5 ± .4	5.726	2.489
benzene	15	6.6 ± .1	6.234	2.460
	20	8.9 ± .1	6.102	2.467
	22.5	10.4 ± .2	6.033	2.471
	25	11.9 ± .6	5.969	2.475
	30	15.2 ± .2	5.864	2.482
	35	21.1 ± 1.3	5.719	2.489
toluene	0	3.1 ± .3	6.492	2.436
	15	6.5 ± .1	6.163	2.460
	20	9.7 ± .6	5.987	2.467
	25	12.0 ± .1	5.893	2.475
	30	16.1 ± .3	5.762	2.482
	35	19.8 ± .9	5.670	2.489
o-xylene	0	2.6 ± .3	6.512	2.436
	20	9.3 ± .1	5.950	2.467
	25	12.0 ± .3	5.837	2.475
	30	15.5 ± .5	5.724	2.482
	35	21.4 ± 1.7	5.582	2.489

Table 4. (Continued)

Solvent	T °C	Solubility ($\frac{\mu\text{-moles}}{1}$)	-log x	log T
isopropylbenzene	0	2.7 ± .1	6.433	2.436
	20	8.5 ± .2	5.926	2.467
	25	10.6 ± .3	5.828	2.475
	30	13.7 ± .3	5.714	2.482
	35	18.0 ± 1.3	5.594	2.489
t-butylbenzene	0	2.1 ± .1	6.496	2.436
	15	5.5 ± .2	6.072	2.460
	25	9.6 ± .3	5.827	2.475
	30	12.3 ± .9	5.717	2.482
	35	15.1 ± .5	5.625	2.489
	40	18.6 ± 1.0	5.496	2.496
isopropyl ether	0	1.2 ± .1	6.783	2.436
	15.5	2.9 ± .1	6.390	2.460
	20	4.0 ± .2	6.249	2.467
	25	4.8 ± .1	6.167	2.475
	30	6.1 ± .1	6.060	2.482
	35	7.4 ± .1	5.973	2.489
n-butyl ether	0	1.7 ± .1	6.550	2.436
	15.5	4.4 ± .3	6.128	2.460
	20	5.6 ± .1	6.023	2.467
	25	7.1 ± .2	5.927	2.475
	30	9.1 ± .5	5.807	2.482
	35	10.5 ± .2	5.742	2.489
perfluorodimethylcyclobutane	0	.04 ± .01	8.169	2.436
	16.5	.21 ± .03	7.432	2.462
	18	.22 ± .02	7.410	2.464
	21	.30 ± .01	7.273	2.469
	25	.38 ± .01	7.166	2.475
water	0	.12 ± .02	8.665	2.436
	15.5	.21 ± .01	8.422	2.460
	20	.24 ± .02	8.363	2.467
	25	.28 ± .01	8.296	2.475
	30	.29 ± .01	8.280	2.482
	35	.34 ± .01	8.210	2.489

mole fraction of mercury versus the logarithm of the absolute temperature are given in Figures 3-13. The densities used in the calculations of the mole fractions were taken from ACS publications (37, 38), the Handbook of Chemistry and Physics (39), Timmermans (40), an Fife and Reid (41). The density of perfluorodimethylcyclobutane was estimated from an empirical rule given by Reed (42).

The equation of the straight line obtained by plotting as above is given in Table 5.
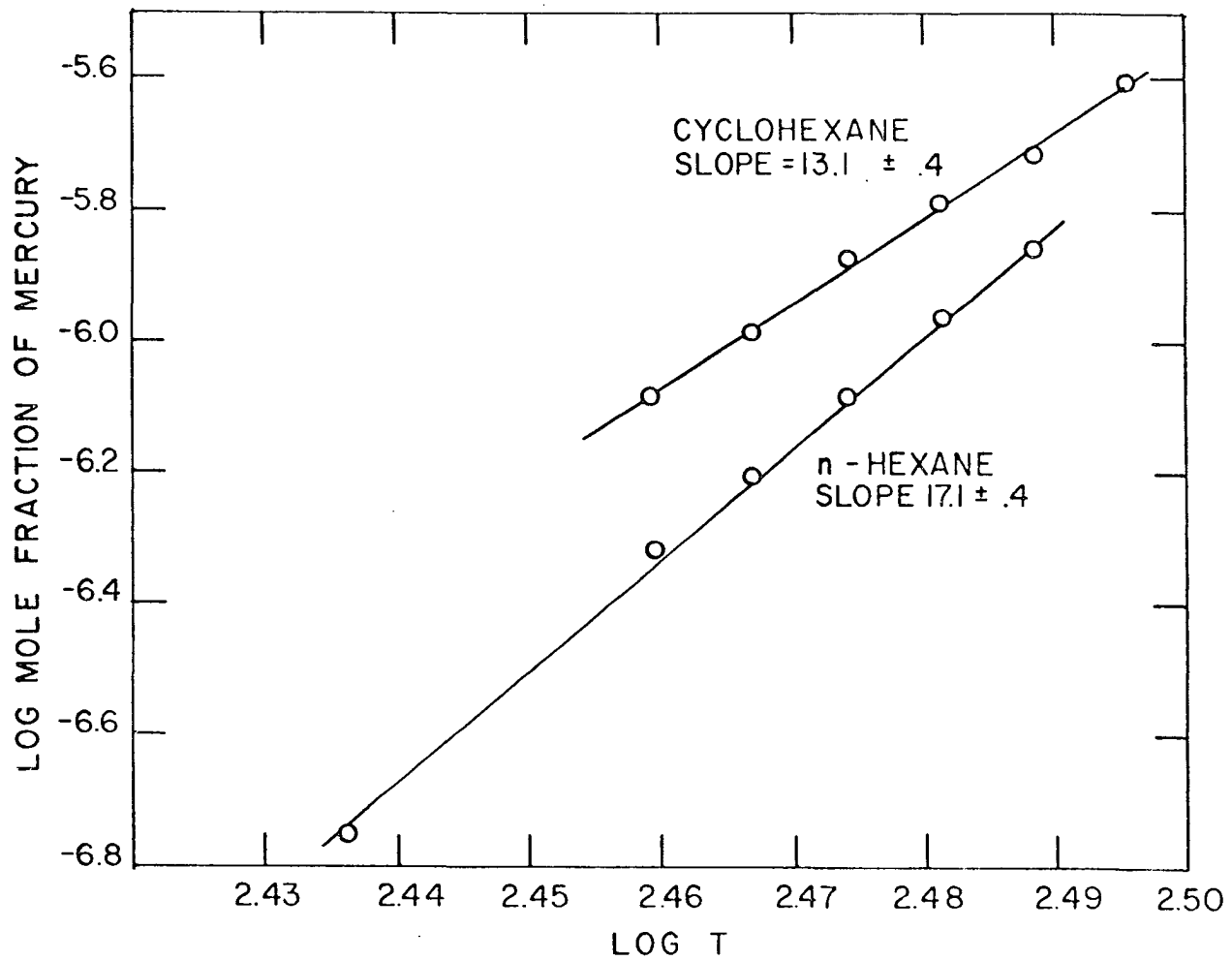
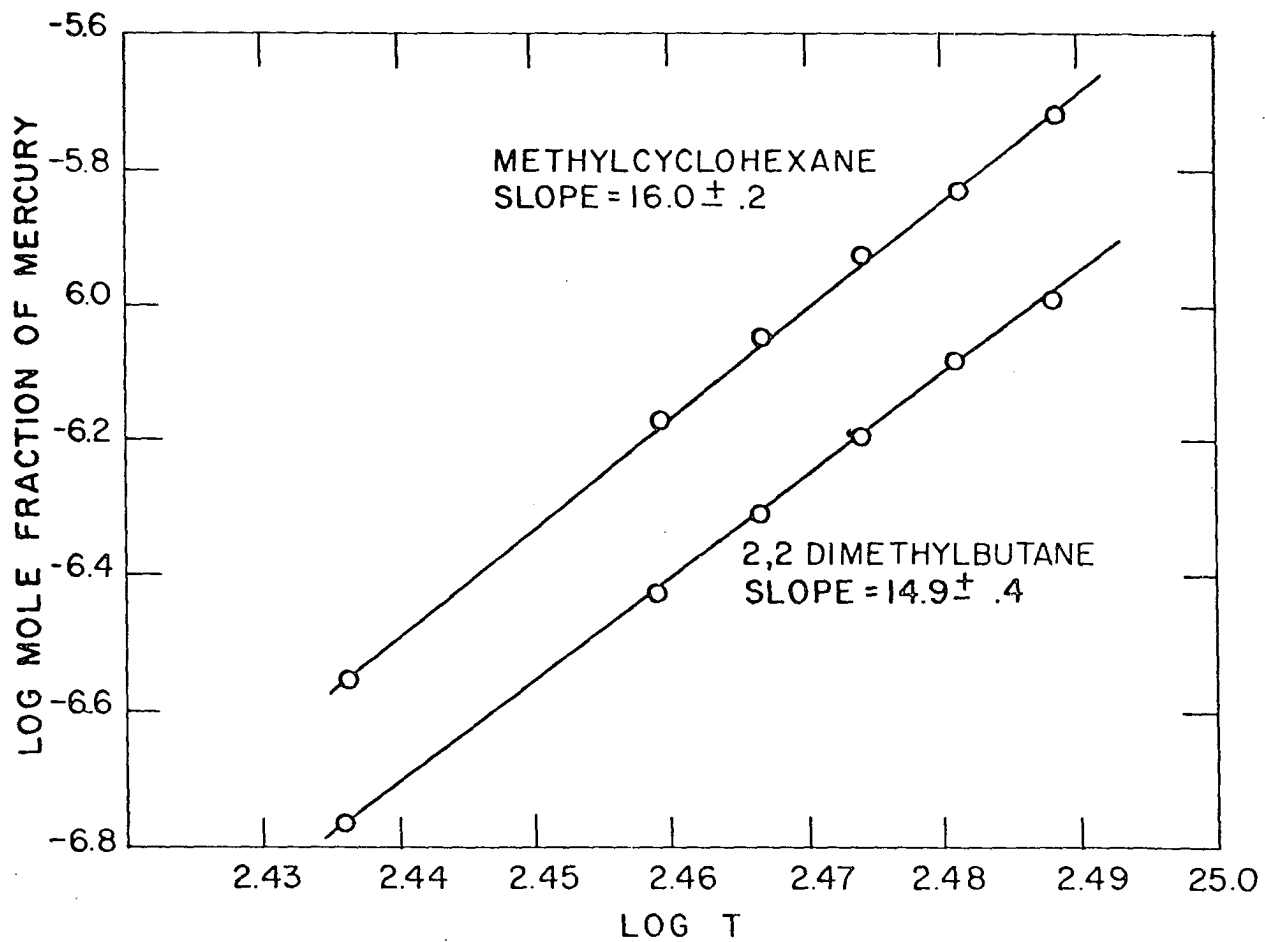Figure 3. Solubility of mercury in n-hexane and cyclohexane

Figure 4. Solubility of mercury in methylcyclohexane and 2,2-dimethylbutane
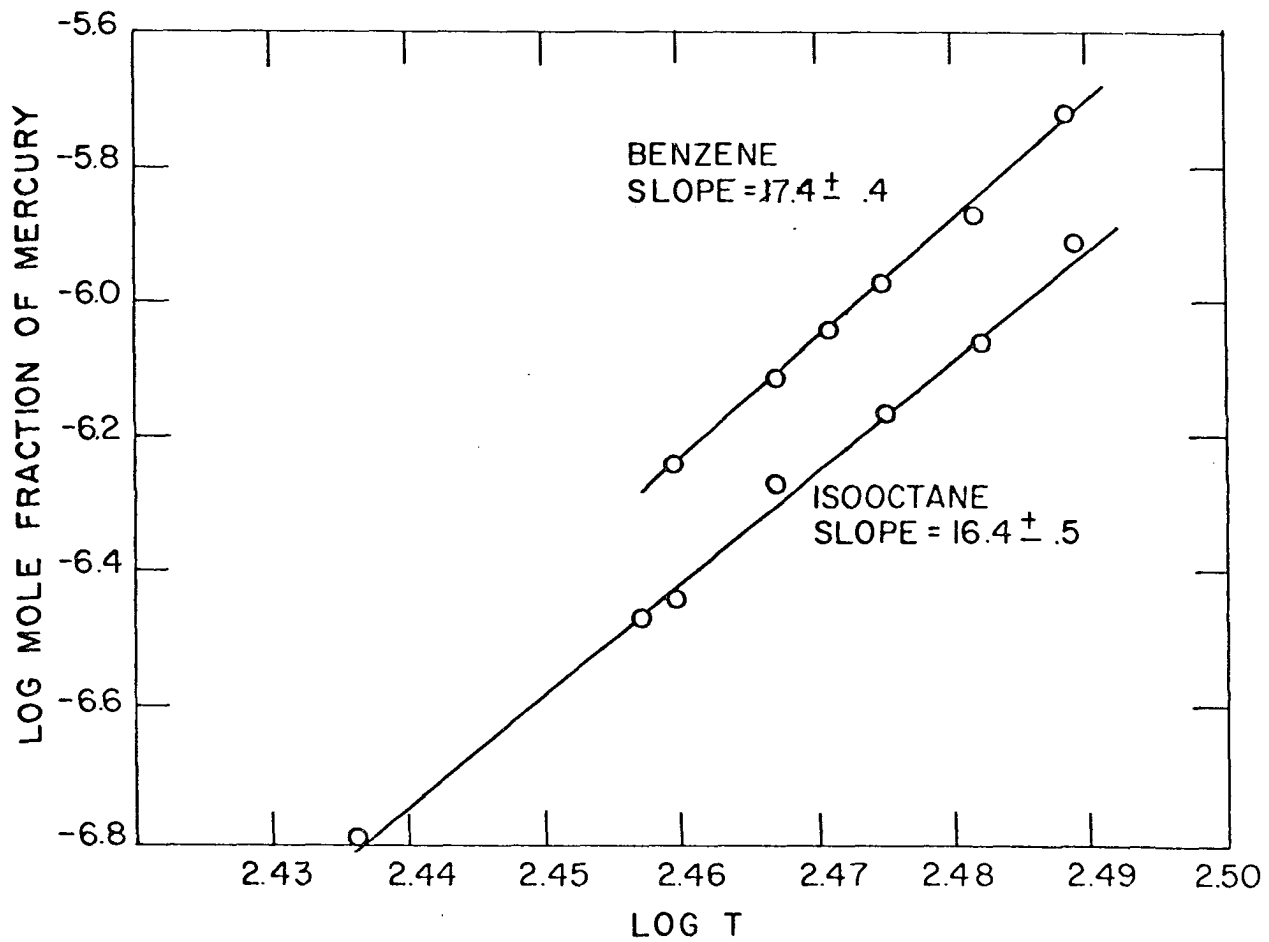
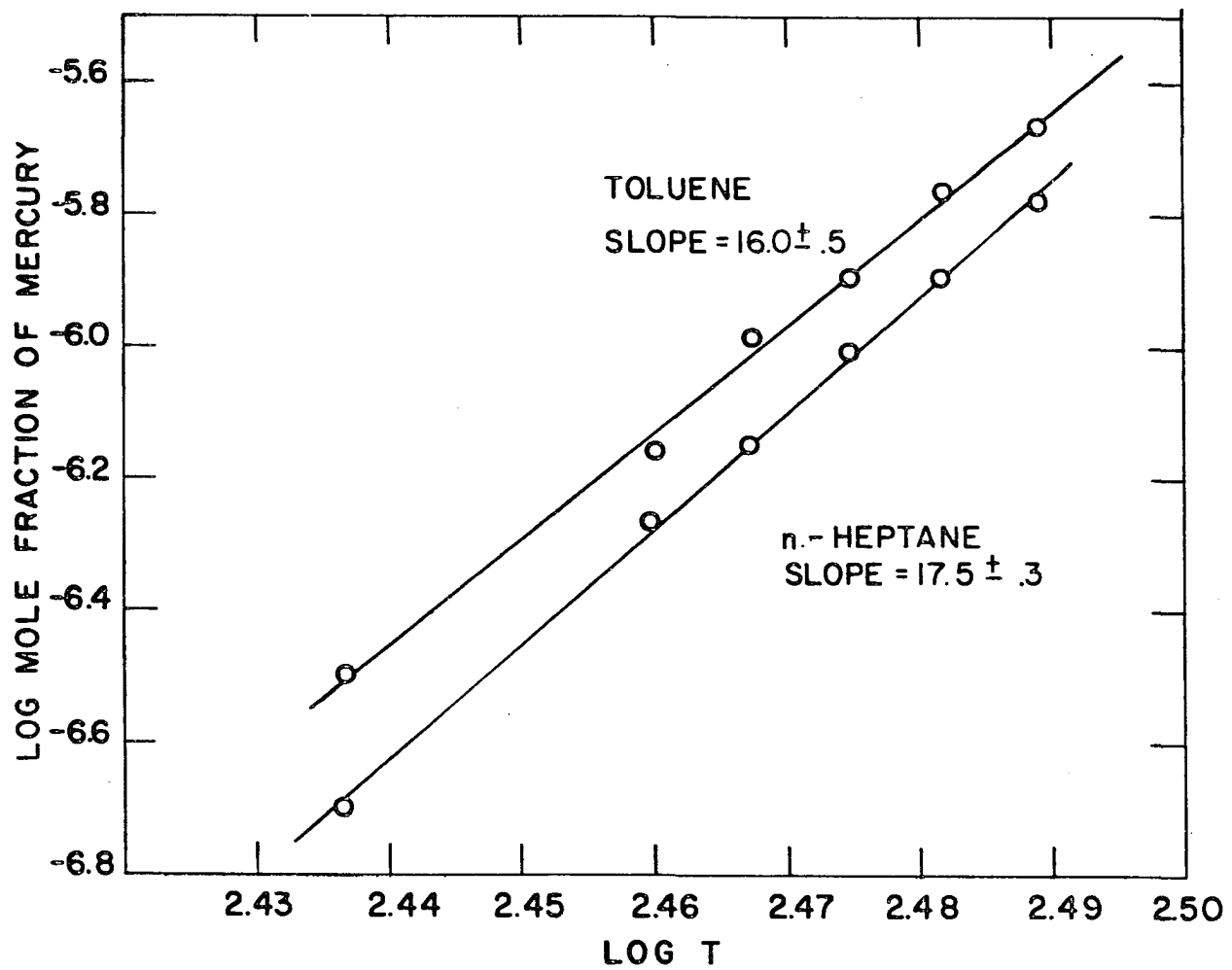Figure 5. Solubility of mercury in isooctane and benzene

Figure 6. Solubility of mercury in toluene and n-heptane
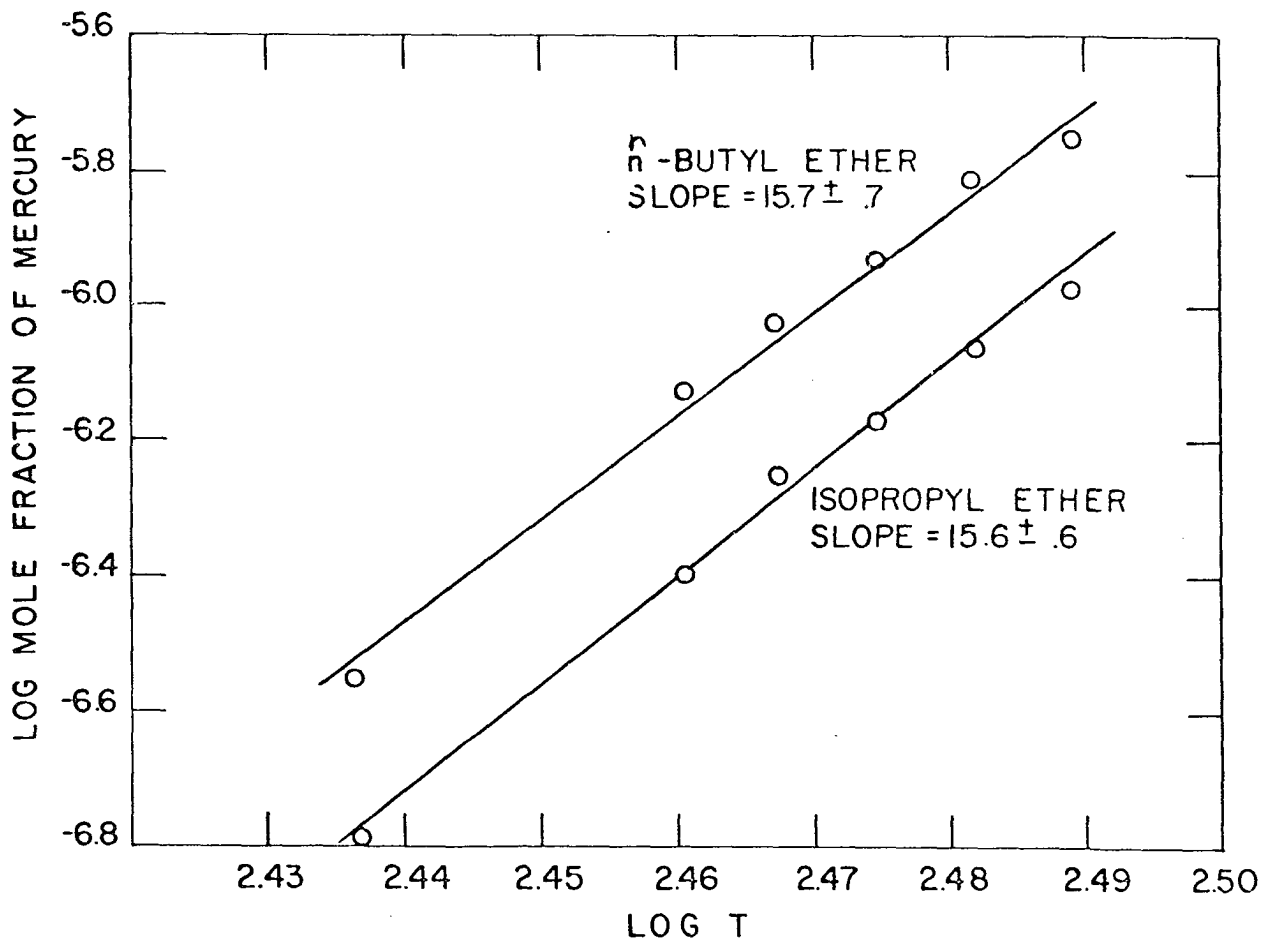
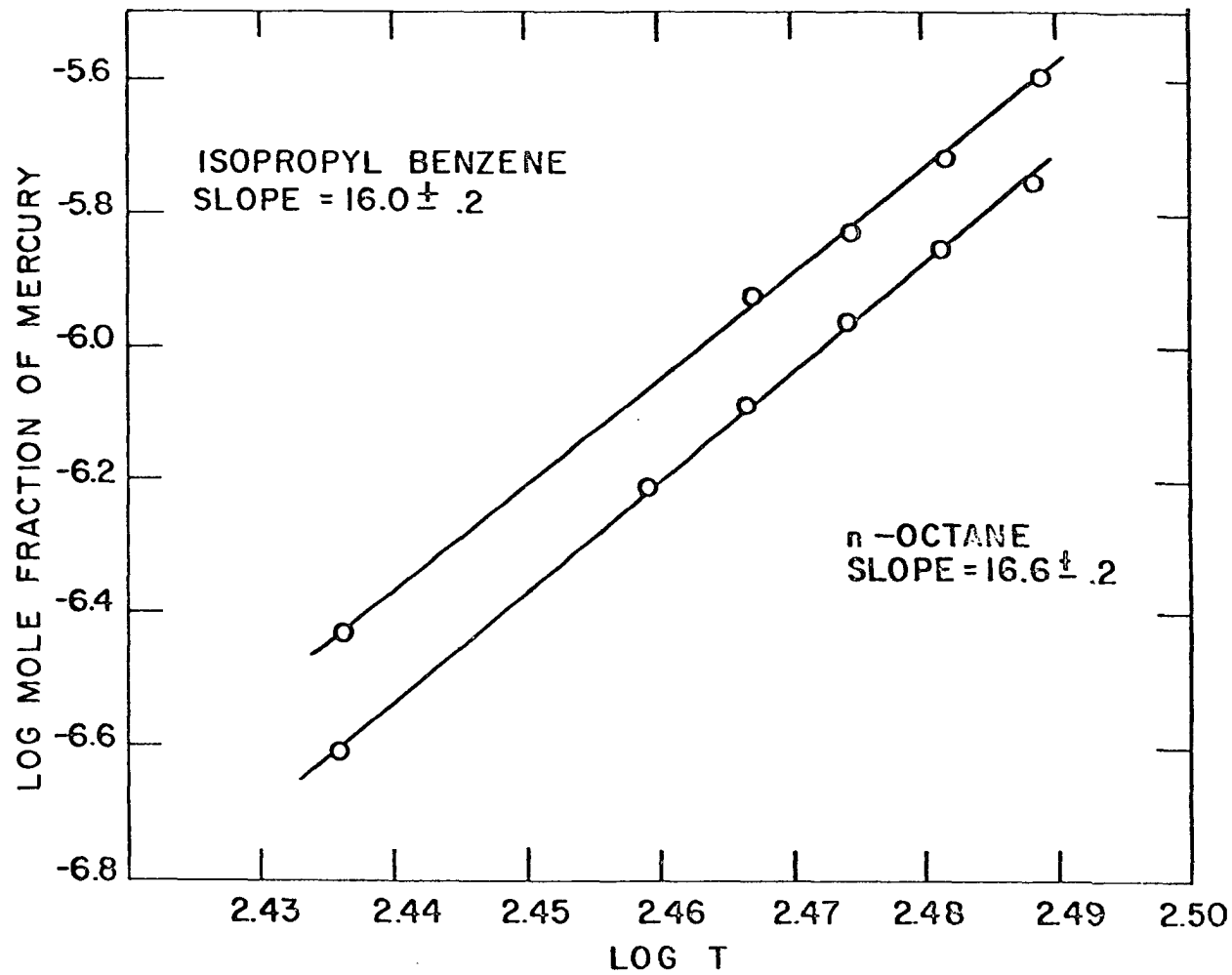Figure 7. Solubility of mercury in n-butyl ether and isopropyl ether

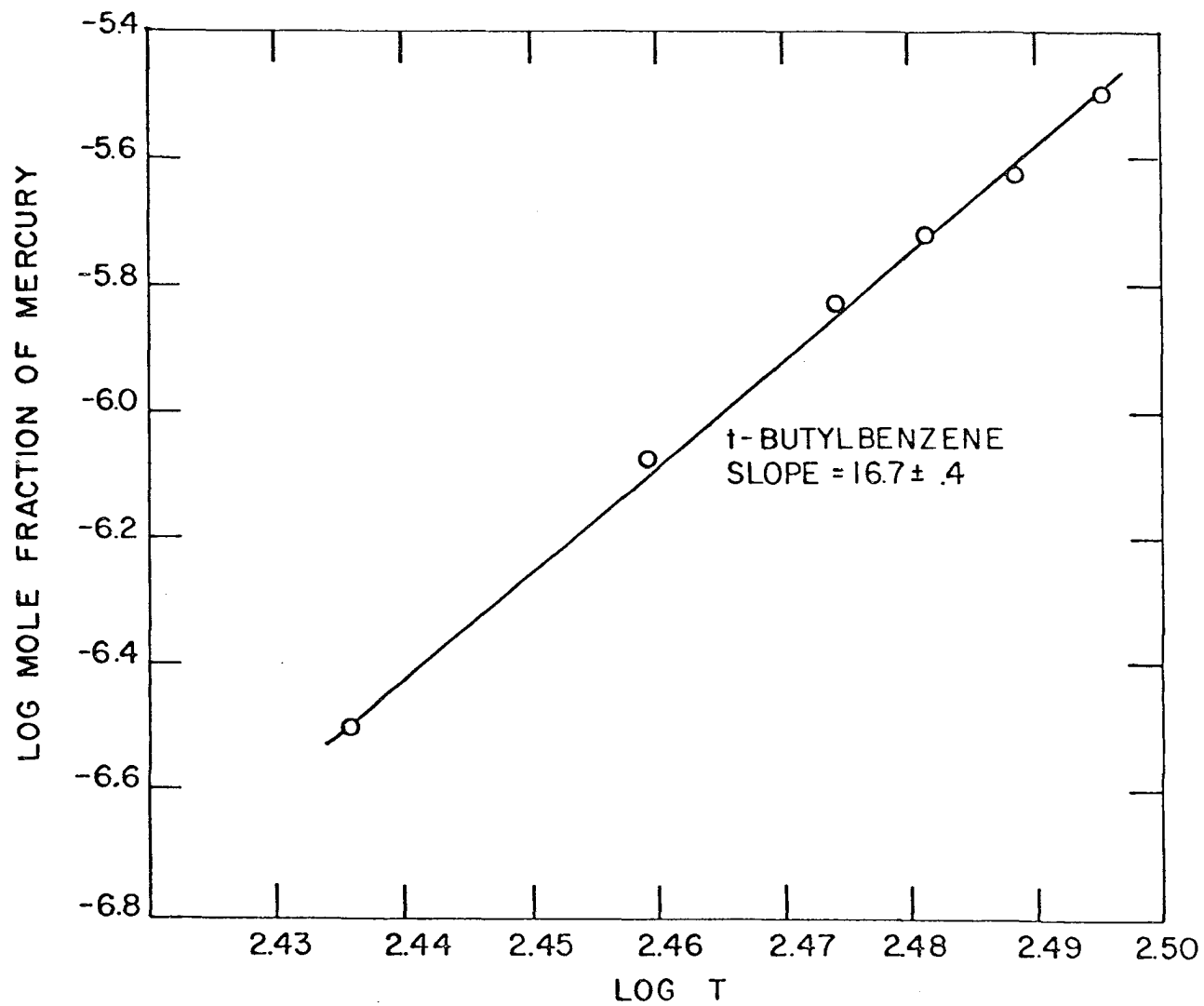Figure 8. Solubility of mercury in n-octane and isopropylbenzene

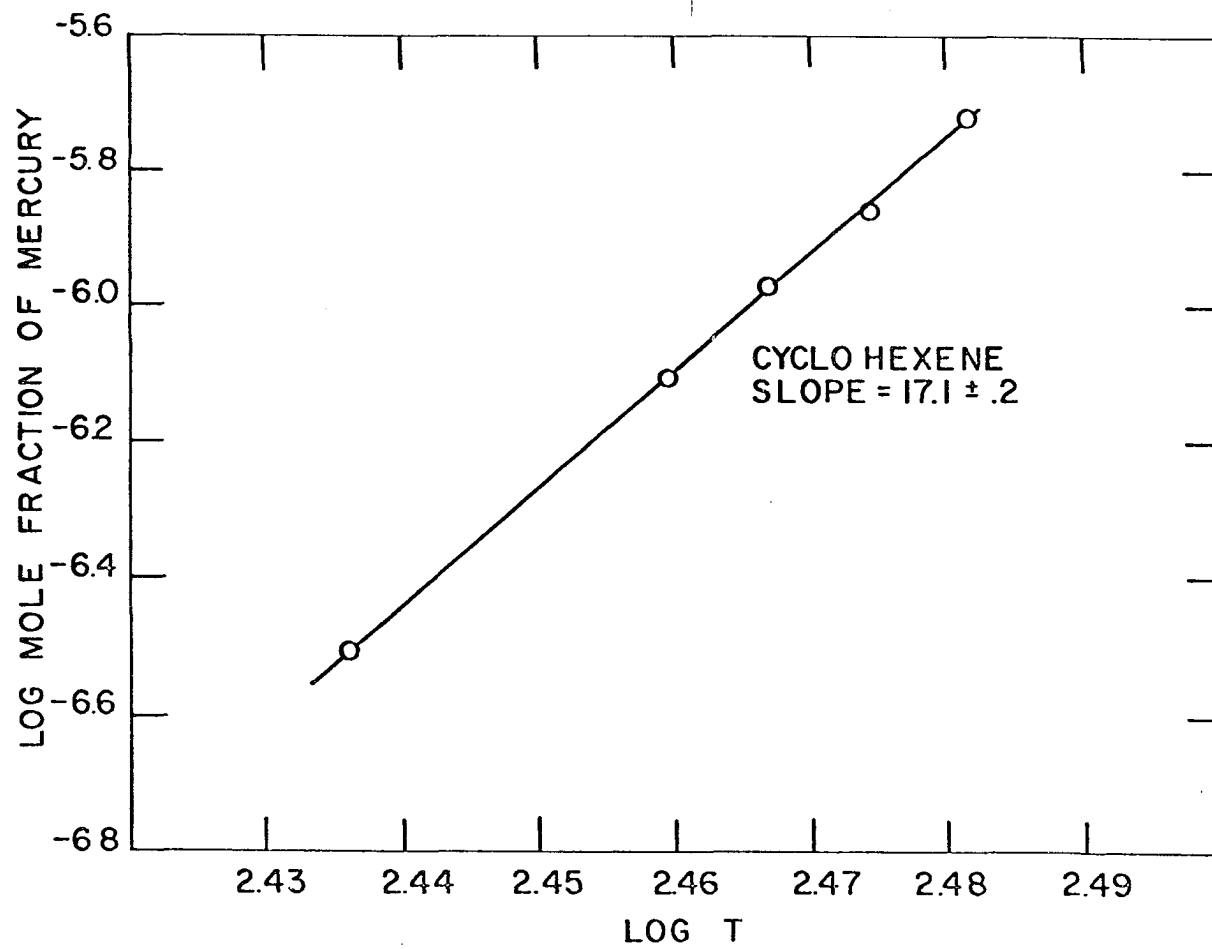Figure 9. Solubility of mercury in t-butylbenzene

Figure 10. Solubility of mercury in cyclohexene
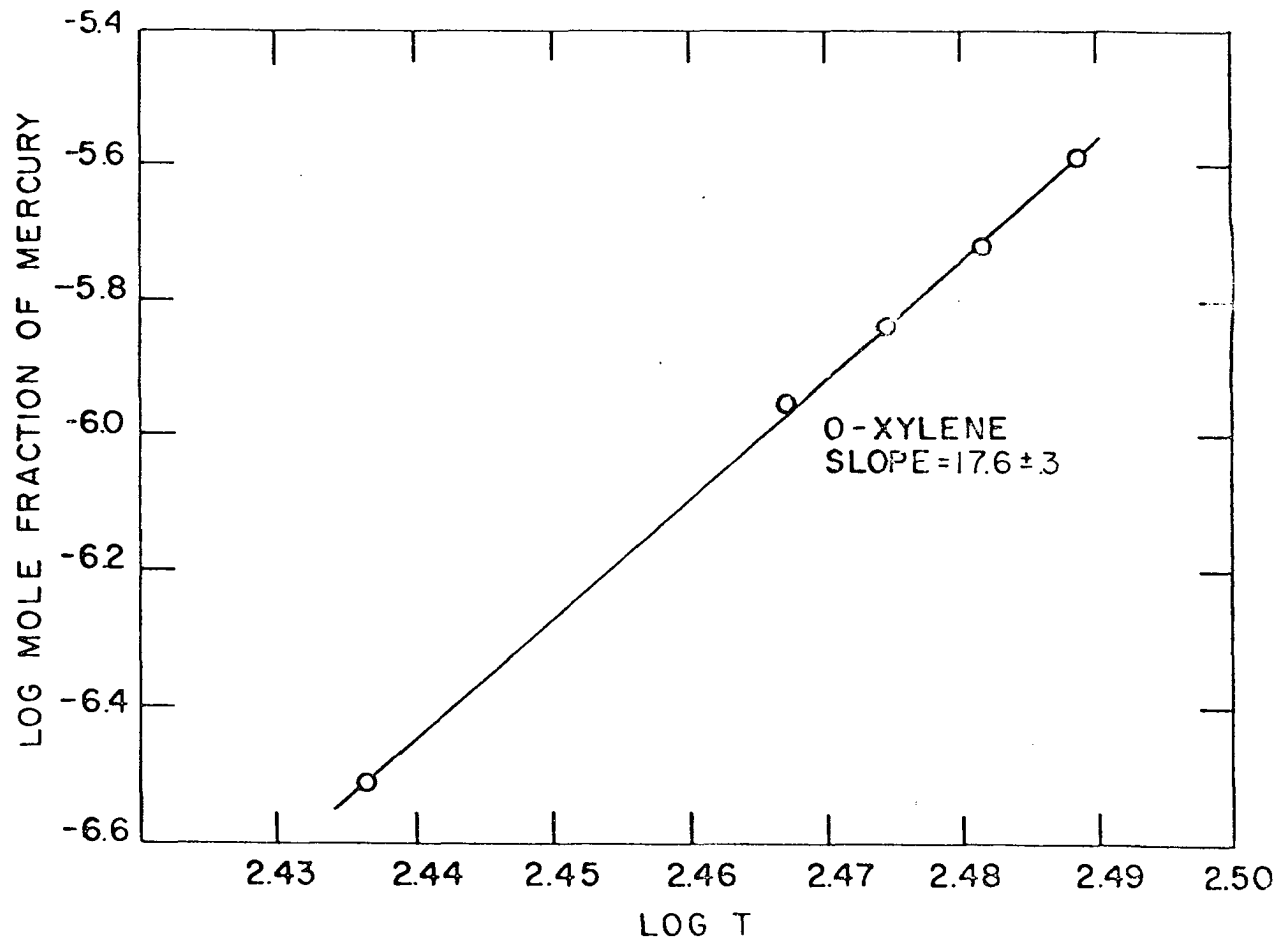
Figure 11.   Solubility of mercury in o-xylene
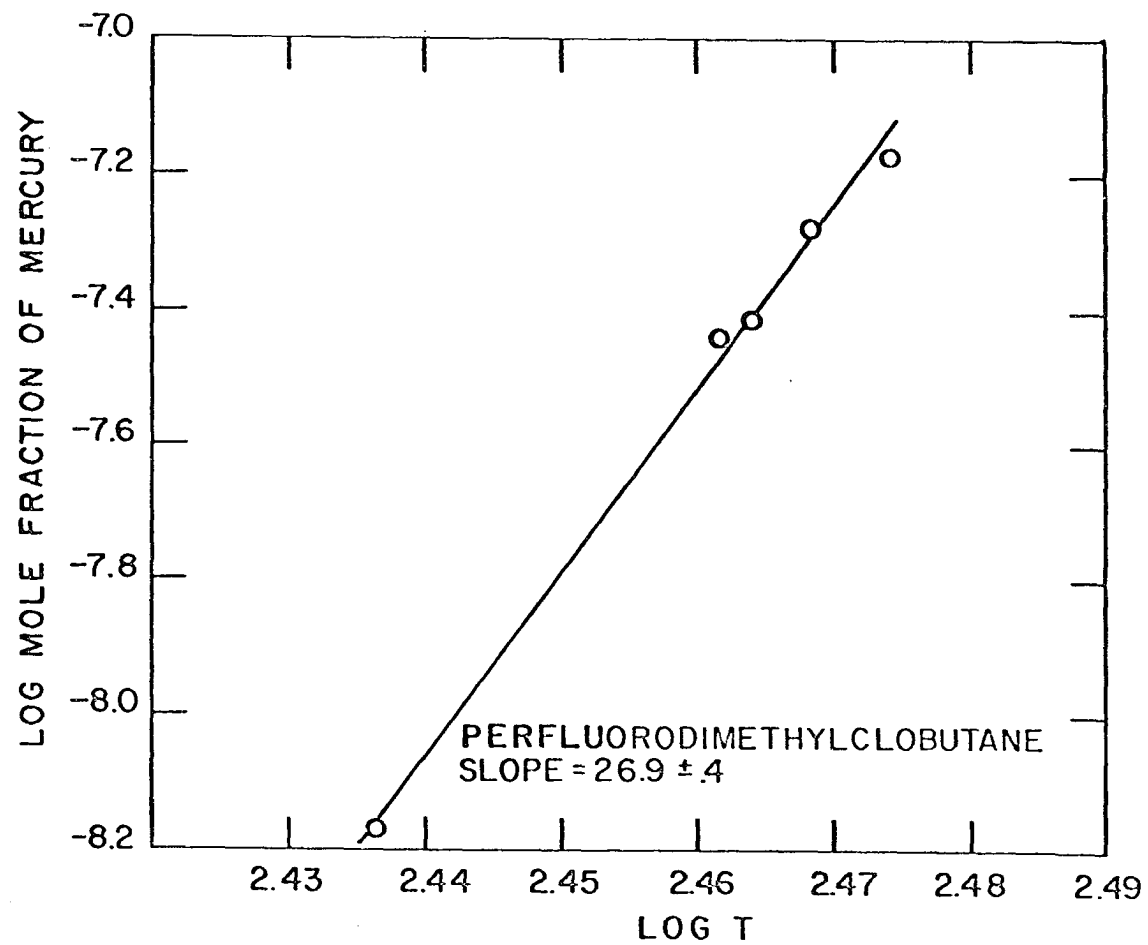
Figure 12. Solubility of mercury in perfluorodimethylcyclobutane
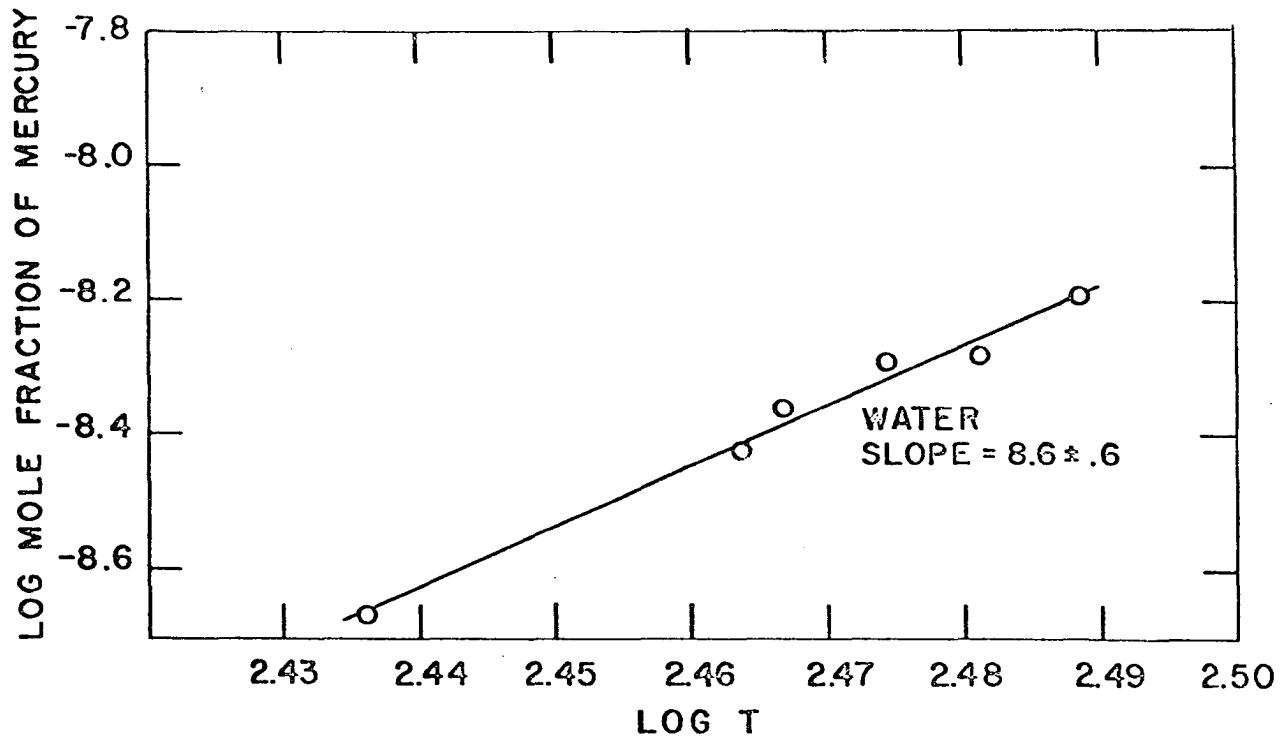
Figure 13.   Solubility of mercury in water

Table 5. Least squares equations giving the temperature dependence of the solubility of mercury[a]

Solvent	A	B
n-hexane	17.084 ± 0.420	-43.366
n-heptane	17.462 ± 0.301	-49.234
n-octane	16.583 ± 0.228	-47.003
isooctane	16.377 ± 0.451	-46.698
2,2-dimethylbutane	14.905 ± 0.380	-43.089
cyclohexane	13.140 ± 0.359	-38.405
cyclohexene	17.148 ± 0.230	-48.294
methylcyclohexane	16.011 ± 0.226	-45.563
benzene	17.407 ± 0.360	-49.047
toluene	16.034 ± 0.538	-45.567
o-xylene	17.635 ± 0.316	-49.473
isopropylbenzene	15.957 ± 0.235	-45.307
n-butyl ether	15.666 ± 0.650	-44.696
isopropyl ether	15.633 ± 0.578	-44.855
t-butylbenzene	16.689 ± 0.388	-47.140
perfluorodimethylcyclobutane	26.921 ± 0.347	-73.746
water	8.600 ± 0.575	-29.597

[a] $\log x = A \log T + B$.

DISCUSSION OF EXPERIMENTAL RESULTS

Hildebrand-Scatchard Equations

Scatchard (23), in 1931, using Hildebrand's ideas, developed an expression for the energy change on mixing. In this derivation Scatchard assumes: 1. the mutual energy of two molecules depends only upon the distance between them and their relative orientation, and not at all on the nature of the other molecules between or around them or on the temperature; 2. the distribution of the molecules in position and in orientation is random, i.e., it is independent of the temperature and of the nature of other molecules present; 3. the change of volume on mixing at constant pressure is zero.

With these assumptions Scatchard wrote for the "cohesive energy" of a mole of liquid mixture:

$$-E^m = \frac{C_{11}V_1^2x_1^2 + 2C_{12}V_1V_2x_1x_2 + C_{22}V_2^2x_2^2}{x_1V_1 + x_2V_2} ,$$

where for the pure components $-E = C_{11}V_1$ etc., x refers to the mole fraction and the V's are volumes. Then

$$C_{11} = \frac{-E_1}{V_1} .$$

in which C_{11} is called the cohesive energy density. The quantity $-E$, may be identified with the energy of vaporization, ΔE^V, and then C_{11} becomes:

$$C_{11} = \frac{\Delta E^{V_1}}{V_1} .$$

Transforming the above equation to volume fractions ϕ_1 and ϕ_2 where

$$\phi_1 = \frac{x_1V_1}{x_1V_1 + x_2V_2} \quad \text{and} \quad \phi_2 = \frac{x_2V_2}{x_2V_2 + x_2V_2} ,$$

we find

$$\Delta E^m = E^m - E_1x_1 - E_2x_2 = (x_1V_1 + x_2V_2)(C_{11} + C_{22} - 2C_{12})\phi_1\phi_2 .$$

Scatchard further assumed that the interaction term C_{12} may be taken as the geometric mean of the terms for the pure components, i.e.,

$$C_{12} = (C_{11}C_{22})^{\frac{1}{2}}.$$

Then

$$(C_{11} + C_{22} - 2C_{12}) = (C_{11}^{\frac{1}{2}} - C_{22}^{\frac{1}{2}})^2 .$$

The square roots of the cohesive energy densities are called solubility parameters and given the symbol δ. Rewritting we find

$$\Delta \bar{E}^m = (x_1 V_1 + x_2 V_2)\left[(\frac{\Delta E^V_1}{V_1})^{\frac{1}{2}} - (\frac{\Delta E^V_2}{V_2})^{\frac{1}{2}}\right]^2 \phi_1 \phi_2$$

$$= (x_1 V_1 + x_2 V_2)(\delta_1 - \delta_2)^2 \phi_1 \phi_2 . \qquad (3)$$

Hildebrand and Wood (24), in 1933, derived the same equation by integrating the inter-molecular potential energies between pairs throughout the liquid by aid of radial distribution functions.

Differentiation of Equation 3 yields partial molar energies of mixing:

$$\Delta \bar{E}^m_1 = V_1 \phi_2^2 (\delta_1 - \delta_2)^2$$

$$\Delta \bar{E}^m_2 = V_2 \phi_1^2 (\delta_1 - \delta_2)^2 ,$$

where the bars denote partial molar quantities and the other symbols are as previously defined.

Because of the essential identity of the Helmholtz free energy of mixing at constant volume and the Gibbs free energy of mixing at constant pressure (43, chpt. 8), we may write for the Gibbs excess free energy:

$$G_P^E \approx A_V^E = E_V^E - TS_V^E ,$$

where the superscript E refers to the excess functions and the subscripts indicate the quantity to be held constant. By the regular solution hypothesis $S^E = o$ and we have:

$$G_P^E = E_V^E = \Delta E_V^m .$$

Using the solubility parameter equation we find:

$$G^E = (x_1 V_1 + x_2 V_2)(\delta_1 - \delta_2)^2 \phi_1 \phi_2 ,$$

or the free energy change on mixing is:

$$\Delta G^m = RT(x_1 \ln x_1 + x_2 \ln x_2) + (x_1 V_1 + x_2 V_2)(\delta_1 - \delta_2)^2 \phi_1 \phi_2 .$$

The partial molar free energies for the solute then are:

$$\bar{G}^E_2 = RT \ln \gamma_2 = V_2 \phi_1^2 (\delta_2 - \delta_1)^2$$

$$\Delta \bar{G}_2 = RT \ln a_2 = RT \ln x_2 + V_2 \phi_1^2 (\delta_2 - \delta_1)^2 . \qquad (4)$$

These equations apply to the constant pressure process. The two terms on the right of Equation 4 are not separately the entropy and heat of mixing for the constant pressure process. Because of the near identity of G_p and A_V, the excess entropy of solution at constant pressure, due to expansion, is balanced in a regular solution by a corresponding enthalphy of expansion. Then these corrections can be neglected with little or no error in calculating isothermal excess free energies or isothermal solubilities. In other words the calculated values of excess free energies and solubilities should agree more nearly with experimental values than either the heat or entropy terms separately. This is so because the minimization of Gibbs free energy translates any errors in the model into second order terms. Consequently free energies and solubilities are not affected as strongly by volume changes as are the heat and entropy separately.

We may write then for the partial molar free energy change for the solute:

$$\Delta \bar{G}_2 = RT \ln x_2 + V_2 \phi_1^2 (\delta_2 - \delta_1)^2 .$$

For the solutions here considered $\phi \approx 1$ and for the saturated solution $\Delta \bar{G}_2 = 0$. Then we have,

$$-R \ln x_2 = \frac{V_2(\delta_2 - \delta_1)^2}{T} , \tag{5}$$

so that an estimation of the solubility is possible if the δ values are

known.

Values for δ may be obtained from various sources (43, chpt. 23).

Since

$$\Delta H^V - P \Delta V = \Delta H^V - RT = \Delta E^V ,$$

where ΔH^V and ΔE^V are the heats and energies of vaporization respectively,

we may calculate δ from:

$$\delta = (\frac{\Delta H^V - RT}{V})^{\frac{1}{2}} . \tag{6}$$

Heats of vaporization may be obtained from vapor pressure measurements

using the Clausius-Clapeyron equation, estimation from an empirical

relation given by Hildebrand and Scott (43, pp. 426-427), or from

calorimetric data. Values of δ may also be estimated from surface tensions,

internal pressure, equations of state, critical constants, and optical

data. Direct determination of the heat of vaporization by calorimetric

means is to be preferred in arriving at a value for δ.

It is futile to try to calculate δ values for the exact temperature

and pressure of the experimental measurement. In Hildebrand's words

(22, p. 169): "Not only are temperature and pressure corrections for δ

difficult and frequently unreliable; they are virtually worthless even

if done correctly." The solubility parameter equations are intended

only to be "zero" approximations. Since one can expect only approximate

agreement with experimental data, generally it is sufficient to have

self-consistent values of δ at one temperature, 25°C is usually taken

for convenience. The δ values, however, should be calculated from

data on the liquid below its normal boiling point since the δ so obtained

bears a truer relation to the properties of the liquid.

The δ values used in this work were obtained whenever possible from

heats of vaporization at 25°C (37, 38). The heats of vaporization at

25°C of isopropyl ether, n-butyl ether, and perfluorodimethylcyclobutane

were estimated from Hildebrand and Scott's empirical rule (43, pp. 426-427).

No attempt has been made to calculate the temperature dependence of the δ

values.

The solubilities calculated according to the simple Hildebrand

equation (5) are given in Table 6 along with the experimental solubilities

at 25°C. For the ethers and the straight and branched chain aliphatics

the calculated solubility in moles per liter agrees quite satisfactorily

with the experimental values. The cyclic hydrocarbons show somewhat

poorer agreement and the aromatics disagree by the largest amount. Con-

sidering that the metallic nature of mercury has not been taken into

account in these equations it would not be expected that calculated and

experimental values for the solubility would agree closely. It is

somewhat surprising that as simple a theory as this would give the

agreement with experiment that it does. It is interesting that the

calculated solubilities for the aromatic systems differ from the

experimental by a greater factor than is found in the non-aromatic systems.

It is also noted that through the ethers and the non-aromatic hydro-

carbons that the mole fraction of mercury shows a general increase with

increasing δ value, while for the aromatics no such trend is seen.

Since this theory rests on the assumption that only dispersion

forces are available, it is surprising that the calculated solubility

Table 6. Experimental and calculated solubilities at 25°C

Solvent	δ	Experimental	Eqn. (5)	Eqn. (11)	Eqn. (13)	Exptl. mole fraction x 10^7
			Solubility (μ-moles$/l$) Calculated			
2,2-dimethylbutane	6.7	4.7	3.3	12.3	3.3	6.3
isooctane	6.9	4.2	3.4	15.3	4.0	7.0
n-hexane	7.3	6.3	6.9	21.7	6.1	8.3
n-heptane	7.4	6.6	6.9	23.0	6.6	9.7
n-octane	7.6	6.7	7.0	31.1	7.2	11.0
methylcyclohexane	7.8	9.1	12.6	45.2	9.9	11.7
cyclohexane	8.3	12.1	23.6	73.0	14.8	13.2
cyclohexene	8.5	13.3	35.2	105.6	20.2	13.6
t-butylbenzene	8.4	9.6	20.7	87.6	17.1	14.9
isopropylbenzene	8.5	10.6	25.7	94.9	19.0	17.3
toluene	8.9	12.0	52.5	160.0	23.4	12.8
o-xylene	9.0	12.0	51.6	174.9	14.4	14.5
benzene	9.2	11.9	87.2	223.1	33.0	10.6

Table 6. (Continued)

Solvent	δ	Solubility ($\frac{\mu\text{-moles}}{1}$) Calculated [1]				Exptl. mole fraction x 10^7
		Experimental	Eqn. (5)	Eqn. (11)	Eqn. (13)	
isopropyl ether	7.0	4.8	4.5	17.5	4.5	6.8
n-butyl ether	7.6	7.1	7.6	34.6	7.9	12.1
water	23.4	.28	13.6×10^6	13.6×10^6	---	.05
perfluorodimethylcyclobutane	5.8	.38	.81	4.0	1.27	.7
mercury	30.9	----	----	----	----	----

in the ethers agrees favorably with the observed solubility. This and the fact that the solubility does not differ greatly from what would be expected on the basis of δ values indicates that the dipole is sufficiently well buried and specific directional forces are unimportant. The parameters C_{11}, C_{22}, and C_{12} are proportional to the intermolecular attractive forces, but where dipoles are present, depend not only upon dispersion forces, but also upon electrostatic induction and dipole interactions. Induction forces are smaller than dipole forces and will not be treated here. For a given position of two dipoles the force varies with the inverse cube of their distance. The effect of attraction will be to tend to bring the dipoles into an orientation with respect to each other which has the lowest energy. The average energy of two like dipoles may be given by

$$\epsilon = \frac{2\mu^4}{3r^6 kT} .$$

Here μ is the dipole moment and r the distance between dipoles. Correspondingly then writing for the C's (43, chpt. 9):

$$C_{11} = \delta_1{}^2 + w_1{}^2$$

$$C_{12} = \delta_1\delta_2 + w_1 w_2$$

$$C_{22} = \delta_2{}^2 + w_2{}^2 .$$

The δ's now signify the contribution of the dispersion forces and the w's the orientation or dipole forces. The w's are given by:

$$w_1 = \mu_1{}^2 \sqrt{\frac{2}{3V_1 r^6 kT}} ,$$

where the volume V_1 is incorporated for dimensional consistency, and r is the distance between dipole centers.

If we assume the heat of mixing may be represented as before, that is by:

$$\Delta H^m = (x_1 V_1 + x_2 V_2)(C_{11} + C_{12} - 2C_{12})\phi_1\phi_2 ,$$

and substitute for the C's the new expressions we find,

$$\Delta H^m = (x_1 V_1 + x_2 V_2) \left[(\delta_1 - \delta_2)^2 + (w_1 - w_2)^2 \right] \phi_1 \phi_2 ,$$

and for the partial heat of the solute,

$$\Delta \bar{H}_2 = V_2 \left[(\delta_1 - \delta_2)^2 + (w_1 - w_2)^2 \right] \phi_1 .$$

It is important to remember here that the δ's no longer are defined as $\left(\frac{\Delta E^V}{V} \right)^{\frac{1}{2}}$ but rather as

$$\frac{\Delta E^V}{V} = \delta^2 + w^2.$$

The quantity, $(w_1 - w_2)^2$ may be shown to be (44):

$$(w_1 - w_2)^2 = \frac{3.25 \times 10^7}{V_1^2 RT} \left(\frac{\mu_1^2}{\sqrt{V_1}} - \frac{\mu_2^2}{\sqrt{V_2}} \right),$$

where the μ's are dipole moments expressed in Debyes. Since μ_2 for mercury is zero we have:

$$(w_1)^2 = \frac{3.25 \times 10^7}{V_1^2 RT} \left(\frac{\mu_1^2}{\sqrt{V_1}} \right).$$

Taking 1.3 Debyes as the dipole moment for isopropyl ether (45) at 25°C we find $(w_1)^2 \approx .05$, which is neglible. Similarily for n-butyl ether with a dipole of 1.2 Debyes (37) and a larger volume than isopropyl ether an even smaller correction for the contribution of dipole forces to the heat of mixing is found. This contribution is neglible so that we may take for the ethers $\frac{\Delta E^V}{V} \approx \delta^2$. The dipole forces depend on μ^4 however and increasing the dipole moment quickly increases the significance of the orientation effect. Water has a dipole of 1.85 Debyes (39) and a small molar volume. For water then w amounts to about 10 $(cal/ml)^{\frac{1}{2}}$, so that orientation forces play an important part for this solvent. The abnormalty of water as a solvent will be seen to depend on its hydrogen bonding properties rather than on its dipole. For the ethers then and the other solvents which have a small dipole we may neglect the orientational contribution to the heat of mixing.

As previously discussed solubilities and free energies are less affected by volume changes and inadequacies in a particular model than are heat and entropy separately. According to the simple solubility parameter theory the excess free energy should be given by:

$$\overline{G}_2^E = V_2(\delta_1 - \delta_2)^2 . \tag{7}$$

The experimental excess free energy is calculated from:

$$\overline{G}_2^E = \Delta\overline{H}_{exptl}^m - T(\Delta\overline{S}_{exptl} - \Delta\overline{S}_{ideal}) ,$$

where $\Delta\overline{S}_{ideal}$ is the ideal entropy of mixing. The calculated and experimental results are compared in Table 7. The calculated excess free energies agree quite satisfactorily for all except the aromatics and water.

Table 7. Calculated excess free energies at 25°C

Solvent	Experimental[a]	$\overline{G}_2^E(\frac{cal}{mole})$ Calculated Eqn. (7)	Eqn. (14)
n-hexane	8288.8	8254.7	8328.5
n-heptane	8199.4	8185.1	8210.2
n-octane	8139.8	8115.4	8098.5
isooctane	8378.3	8536.3	8440.3
2,2-dimethylbutane	8467.7	8678.6	8675.9
cyclohexane	8020.5	7636.7	7914.3
cyclohexene	7990.6	7436.7	7768.2
methylcyclohexane	8080.1	7908.0	8053.1

[a]Calculated from $\overline{G}_2^E = \Delta\overline{H}_2 - T(\Delta\overline{S}_2 - \Delta\overline{S}_{2ideal})$.

Table 7. (Continued)

| Solvent | Experimental[a] | $\bar{G}_2^E(\frac{cal}{mole})$ Calculated | |
		Eqn. (7)	Eqn. (14)
benzene	8139.7	6978.7	7469.6
toluene	8050.3	7172.9	7539.7
o-xylene	7960.9	7107.7	7868.1
isopropylbenzene	7931.1	7436.7	7617.1
t-butylbenzene	7960.9	7503.4	7617.5
isopropyl ether	8408.2	8465.2	8465.1
n-butyl ether	8080.1	8045.8	8023.0
water	11300.2	834.4	------
perfluorodimethylcyclobutane	10703.9	9336.8	9077.0

Mixed Solvents

According to solubility parameter theory the solubility of mercury in mixed solvents may be calculated by (43, chpt. 12):

$$-Rlnx_2 = V_2(\delta_2 - \delta_m)^2 \frac{1}{T} \tag{8}$$

where

$$\delta_m = \frac{\phi_1\delta_1 + \phi_3\delta_3}{\phi_1 + \phi_3} ,$$

and the subscript 2 refers to mercury, the subscripts 1 and 3 to the solvents.

The increase in the solubility of mercury in n-octane due to the addition of t-butylbenzene and the solubility increase in n-hexane due to addition of cyclohexane is given in Table 8. The solubility at zero

Table 8. Solubility of mercury in mixed solvents at 25°C

Mixture	Volume fraction t-butylbenzene	Solubility (μ-moles/l)	log mole fraction Exptl.	log mole fraction Calc. Eqn. (8)
n-octane + t-butylbenzene	0	6.7 ± .1	-5.959	-5.941
	.3	7.7 ± .2	-5.906	-5.790
	.5	8.3 ± .1	-5.878	-5.690
	.7	8.7 ± .1	-5.862	-5.591
	1	9.6 ± .3	-5.827	-5.493
	Volume fraction cyclohexane			
n-hexane + cyclohexane	0	6.3 ± .3	-6.081	-6.043
	.2	7.3 ± .1	-6.035	-5.941
	.8	10.9 ± .2	-5.911	-5.640
	1	12.1 ± .3	-5.879	-5.591

volume fraction for t-butylbenzene and cyclohexane may be calculated with good agreement with the experimental. As the volume fraction of these two solvents is increased the calculated value is somewhat farther from the experimental.

Entropy of Solution

Entropy is the thermodynamic quantity most related to the structure of solutions. Correspondingly it is of interest to compare experimental entropies of solution with those calculated from theoretical considerations. The partial entropy of solution may be calculated from solubility data by plotting the logarithm of the mole fraction of solute versus the logarithm of the absolute temperature. This method of calculation requires that the pure solute be chosen as a standard state. This choice has the advantage of offering a convenient means of interpreting data, since with this choice of a standard state we are measuring non-ideality as referred to Raoult's law, however this choice of a standard state has been criticized (46) for the cases in which the pure solute exhibits some structure. This criticism is just since there are often molecular interactions, such as hydrogen bonding, in the pure liquid which are difficult to define and evaluate. It has also been pointed out by Wood (47) that when a structured solute dissolves to an infinitely dilute solution the solute distribution may become random leading to an excess positive entropy. In the case of mercury this choice of a standard state is acceptable since mercury is a monatomic liquid containing no anomalous structural factors.

The method employed in this work to obtain entropies of mixing from

solubility data is due to Hildebrand (48). We may write for the partial entropy of mixing:

$$\bar{S}_2 - S_2^o = -\left[\frac{\partial(\bar{G}_2 - G_2^o)}{\partial T}\right]_{P,x}$$

$$= \left[\frac{\partial(\bar{G}_2 - G_2^o)}{\partial \ln x_2}\right]_{P,T}\left[\frac{\partial \ln x_2}{\partial T}\right]_{\bar{G}_2 - G_2^o, P},$$

where the superscript o refers to the pure liquid and the subscript 2 refers to the solute. Further

$$\bar{G}_2 - G_2^o = RT\ln\frac{f_2}{f_2^o},$$

where f_2 is the fugacity of the solute in the solution and f_2^o is that of the pure solute, in this case liquid mercury. If the solvents used in this work are not soluble in the mercury f_2^o is not a function of x_2 and we write

$$\left[\frac{\partial(\bar{G}_2 - G_2^o)}{\partial \ln x_2}\right]_{P,T} = RT\left(\frac{\partial \ln f_2}{\partial \ln x_2}\right)_{P,T} = RT\left(\frac{\partial \ln a_2}{\partial \ln x_2}\right)_{P,T}$$

thus

$$\bar{S}_2 - S_2^o = R\left(\frac{\partial \ln x_2}{\partial \ln T}\right)_{sat,P}\left(\frac{\partial \ln a_2}{\partial \ln x_2}\right)_{P,T}.$$

In the dilute region of these solutions, Henry's law holds, and $a_2 = kx_2$ so that

$$\left(\frac{\partial \ln a_2}{\partial \ln x_2}\right)_{P,T} = 1$$

and the entropy is given by

$$\bar{S}_2 - S_2^o = R\left(\frac{\partial \ln x_2}{\partial \ln T}\right)_{sat,P}. \tag{9}$$

The slopes of the straight lines, found by plotting the logarithm of the mole fraction of mercury versus the logarith m of the absolute temperature, when multiplied by R give directly the partial entropy of solution. The slopes of these lines were obtained by the method of least

squares and the entropies so calculated are given in Table 9.

Since $\Delta \bar{F} = 0$, $T\Delta \bar{S} = \Delta \bar{H}$, and the corresponding enthalpies may be obtained. The enthalpies at 25°C are also listed in Table 9.

It is seen that in the majority of cases studied the entropy change is larger than $-R \ln x_2$, the ideal entropy of mixing. This excess of entropy over ideal may arise from several sources and is discussed in the following section. The anomalous case of water is discussed in a later section.

Excess Entropy

There are several factors at constant pressure which may contribute to the excess entropy of mixing (47). These factors include differences in the relative sizes of the molecules, the spatial distribution of the molecules about a reference molecule, the lack of randomness of the orientational distribution about a reference molecule, and the contribution due to volume changes.

The spatial distribution is the smallest of these effects. This lack of randomness in the position of the centers of molecules depends on the energy of mixing and has been shown to contribute a negative excess entropy (47). This negative contribution, which is probably more important for polar molecules, disappears at infinite dilution and will not contribute significantly to the solutions studied here.

The orientational distribution may produce a large positive excess entropy. As already pointed out the dissolution of a structured solute to an infinitely dilute solution where the solute may become random leads to an excess positive entropy. Further the orientational distribution of

Table 9. Heats and entropies of mixing at 25°C

Solvent	$\Delta \bar{S}_2$ (ideal)[a]	$\Delta \bar{S}_2$ (Flory-Huggins)	$\Delta \bar{S}_2$ (Exptl.)	$\Delta \bar{H}_2$ (Exptl.)[b]
n-hexane	27.8	30.4	34.0 ± .8	10137.4
n-heptane	27.5	30.3	34.8 ± .6	10376.0
n-octane	27.3	30.3	33.0 ± .4	9339.3
isooctane	28.1	31.1	32.6 ± 1.0	9720.0
2,2-dimethylbutane	28.4	31.0	29.6 ± .8	8825.5
cyclohexane	26.9	29.1	26.0 ± .8	7752.2
cyclohexene	26.8	28.9	34.0 ± .4	10137.4
methylcyclohexane	27.1	29.6	31.8 ± .4	9481.5
benzene	27.3	29.2	34.6 ± .8	10316.3
toluene	27.0	29.2	31.8 ± 1.0	9481.5
o-xylene	26.7	29.1	35.0 ± .6	10435.6
isopropylbenzene	26.6	29.3	31.8 ± .4	9481.5
t-butylbenzene	26.7	29.6	33.2 ± .8	9898.9

[a]Entropy units are cal/deg mole.

[b]Heat units are cal/mole.

Table 9. (Continued)

Solvent	$\Delta \bar{S}_2$ (ideal)[a]	$\Delta \bar{S}_2$ (Flory-Huggins)	$\Delta \bar{S}_2$ (Exptl.)	$\Delta \bar{H}_2$ (Exptl.)[b]
isopropyl ether	28.2	30.9	31.0 ± 1.2	9243.0
n-butyl ether	27.1	30.1	31.2 ± 1.4	9302.6
water	37.9	37.9	17.1 ± 1.2	5098.5
perfluorodimethylcyclobutane	32.7	35.9	53.4 ± .8	15921.7

the solvent may be changed by the substitution of a solute for a solvent molecule. Since mercury is a structureless monatomic liquid no structural entropy can be gained by dissolution to an infinitely dilute solution. What effect the substitution of a mercury solute for a solvent molecule has on the entropy of the solvent can best be dealt with in terms of free volumes and further discussion is given in the section entitled Free Volume.

The question of the contribution to the entropy of mixing due to differences in sizes of the components is much debated. The correction as generally applied leads to excess positive entropies. The most commonly applied correction for size differences is the Flory-Huggins expression. This expression for the entropy of mixing is:

$$\Delta \bar{S}_2 = -R[\ln \phi_2 + \phi_1(1 - \frac{V_2}{V_1})] , \tag{10}$$

where the symbols are as previously defined. It was originally developed for polymer solutions and amounts to letting the coordination number about a molecule go to infinity. Guggenheim (49, chpt. 10) has shown that this formulation gives better agreement with more exact statistical treatment than does ideal entropy for mixtures of trimers and tetramers, either open chain or cyclic, with monomers. Hildebrand (50) in 1947 derived an equation for entropy of mixing of unequal size molecules which unlike the statistical treatments did not require assumption of a particular solution model. The equation he derived for the partial molar entropy change is given by:

$$\Delta \bar{S}_2 = R \left[\ln \frac{n_2(V_2 - b_2) + n_1(V_1 - b_1)}{n_2(V_2 - b_2)} + \frac{n_1[(V_2 - b_2) - (V_1 - b_1)]}{n_2(V_2 - b_2) + n_1(V_1 - b_1)} \right],$$

in which V_1 and V_2 are molar volumes and b_1 and b_2 intrinsic Van der Waals volumes. This expression assumes that the Van der Waals free volume is

available to both components. If the free volumes, (V-b), for the two components are equal the formulation reduces to ideal entropy. If the free volumes are set proportional to their molar volumes, the expression for athermal mixtures reduces to:

$$\Delta \bar{S}_2 = -R[\ln\phi_2 + \phi_1(1 - \frac{V_2}{V_1})] \, ,$$

which is Flory-Huggins entropy. So it would seem that the assumption involved in invoking Flory-Huggins entropy is that the Van der Waals free volumes are proportional to the molar volumes. Since the intro-duction of this equation, Hildebrand has come to feel that it should apply to gaseous systems but that its applicability to condensed systems is dubious (51).

Hildebrand later showed that disparity in molar volumes in the case of compact molecules has virtually no effect on the entropy of mixing (22, p. 33). He found that when

$$R \frac{\partial \ln x_2}{\partial \ln T}$$

is plotted against ideal entropy for iodine in various solvents of widely different volumes the points fall on a straight line. According to Flory-Huggins entropy, the solvents with volumes much larger than that of iodine should fall above the line drawn through the points for solvents with volumes close to that of iodine.

Flory-Huggins entropy has been and continues to be a popular expres-sion for the entropy due to components of differing volume. The values of the entropy change calculated according to this formulation are given in Table 9. This expression leads to an excess positive entropy and is seen to be in closer agreement with experiment than ideal entropy in almost all systems considered here.

Flory-Huggins entropy is often substituted into the solubility

parameter equations for ideal entropy. The equation then takes on the

form:

$$\Delta \bar{G} = V_2 \phi_1^2 (\delta_2 - \delta_1)^2 + RT[\ln\phi_2 + \phi_1(1 - \frac{V_2}{V_1})] . \qquad (11)$$

In many cases calculations of the solubility from this equation have led

to better results than those which employ ideal entropy. The solubilities

of mercury as calculated by the above, listed in Table 6, are larger than

the experimental and better agreement with the observed solubilities

is obtained using ideal entropy.

The entropies reported in this work are those at constant pressure

and not at constant volume. Hildebrand (22, chpt. 3) has shown that when

the volume change is taken into account the entropy of mixing is nearly

ideal. He has further shown that the difference between the entropy change

at constant volume and that at constant pressure is approximately given by:

$$(\Delta \bar{S}_2)_P - (\Delta \bar{S}_2)_V = \frac{\partial P}{\partial T})_{V,1} \bar{V}_2^E ,$$

where $\frac{\partial P}{\partial T})_{V,1}$ is the thermal pressure of the solvent and $\bar{V}_2^E$ is the excess

volume. According to the regular solution hypothesis that there is

sufficient thermal agitation to give maximum randomness in the mixture, the

entropy change at constant pressure should be given by:

$$-R\ln x_2 + \frac{\partial P}{\partial T})_{V,1} \bar{V}_2^E .$$

Owing to the extreme diluteness of the solutions studied, it was not

possible to make a determination of the volume change on mixing. It is

interesting, however, to use the experimental result and the above equation

to calculate a volume change if all of the difference was due to this

effect. The value of the thermal pressure for n-heptane is 8.41 atm/deg

(52). The entropy change observed for this system is 34.8 e.u. and the

corresponding ideal entropy is 27.5 e.u. Then

$$34.3 - 27.5 = \frac{\partial P}{\partial T})_{V,1} \overline{V}_2^E$$

and $\overline{V}_2^E = 35.8$ ml/mole. Since the molar volume of mercury is 14.8 ml/mole this would mean that the partial molar volume of mercury in this solution is 50.6 ml/mole. This is an expansion of some 300% over that of pure mercury. If Flory-Huggins entropy is employed so that the entropy of mixing at constant pressure is given by:

$$\Delta \overline{S}_2 = -R[\ln\phi_2 + (1 - \frac{V_2}{V_1})] + \frac{\partial P}{\partial T})_{V,1} \overline{V}_2^E$$

we find for n-heptane, $\overline{V}_2^E = 22$ ml/mole or a partial molar volume of mercury of 36.8 ml/mole. If these calculations are accepted at face value an interpretation of the solute-solvent interaction may be made. Since the mercury solute would occupy nothing like the partial volume here calculated for n-heptane, a considerable amount of this volume would have to be interpreted as a local expansion of the solvent. It is well known that the partial volumes of permanent gases in non-polar solvents are very large, the partial volume of H_2 in CCl_4 is about 40 ml/mole (43, chpt. 15). But it is also known that the replacement of a solvent molecule by a permanent gas solute results in weaker forces acting on the neighboring solvent molecules (22, p. 45). This allows the solvent to expand increasing its rotational and vibrational freedom and results in an entropy gain by the solvent. If the expansions calculated above are real, the solvent could possibly undergo a reduction so as to increase its entropy. In view of mercury's strong dispersion forces it would not seem that this is likely. No doubt there is a volume change but it does not seem that the volume change would be this large. There is also a possibility that the solvent reacts in some manner to these strong

dispersion forces of mercury. This again comes under the heading of the

orientational contribution to the entropy and further discussion is given

in the section entitled Free Volume.

Reed's Modification

Reed (53) has modified the original solubility parameter equations

in an attempt to account for the large excess free energies of hydrocarbon-

fluorocarbon systems. He has written the interaction term at constant

volume as:

$$C_{12} = (C_{11}C_{12})^{\frac{1}{2}} f_I f_d \, ,$$

where f_I is given by

$$\frac{2(I_1 I_2)^{\frac{1}{2}}}{I_1 + I_2}$$

and f_d is given by

$$\left[\frac{2(d_{11}{}^o d_{22}{}^o)^{\frac{1}{2}}}{d_{11}{}^o + d_{22}{}^o} \right]^3 \, .$$

The I's are the ionization potentials of the molecules and the d^o's are

the distances between molecule centers when the potential energy is at a

minimum. Under this assumption it is strictly correct to regard C_{12} as

the geometric mean of C_{11} and C_{22} only when f_I and f_d are unity. Reed

is then able to write for the partial molar energy of mixing at constant

volume:

$$\Delta \bar{E}_2^m = V_2 \phi_1^2 \left[(\delta_1 - \delta_2)^2 + 2\delta_1 \delta_2 (1 - f_I f_d) \right]$$

This expression for the energy of mixing has been combined with ideal

entropy to obtain a predicted value of the solubility of mercury in these

solvents provided f_I and f_d are known. Ionization potentials taken

from various sources (54, 55, 56, 57, 58) have been used to calculate f_I.

In all cases for which data were available f_I was found to be essentially

unity. In order to evaluate f_d recourse was taken to an approximation given by Hirschfelder, Bird, and Spotz (59):

$$d^{\circ} \approx A(V_c)^{1/3} ,$$

where A is a constant and V_c is the critical volume. This approximation should not be too bad for nearly spherical molecules but is only a rough estimate for non-spherical ones. Values for the critical volumes of the solvents were taken from ACS publications (37, 38) and the mercury critical volume from Klehr (12). The mercury solubilities may then be calculated from:

$$-Rlnx_2 = V_2[(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_If_d)]\frac{1}{T} . \qquad (12)$$

The solubilities so calculated are given in Table 10. We may also substitute Flory-Huggins entropy for the left hand side of Equation 12. The solubilities calculated according to the Flory-Huggins term are also given in Table 10.

Table 10. Calculation of mercury solubilities at 25°C using Reed's modification

Solvent	Experimental	Solubility (μ-moles) Eqn. (12)	Flory-Huggins entropy[a]
n-hexane	6.3	1.5	5.4
n-heptane	6.6	.7	3.0
n-octane	6.7	1.0	4.4
isooctane	4.2	.6	2.5
cyclohexane	12.1	5.7	17.8

[a]Calculated from $-R[ln\phi_2 + (1 - \frac{V_2}{V_1})] = \frac{V_2}{T}[(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_If_d)]$

Table 10. (Continued)

Solvent	Experimental	Solubility (μ-moles) Eqn. (12)	Flory-Huggins entropy[a]
cyclohexene	13.3	8.8	24.9
methylcyclohexane	9.1	2.8	10.0
benzene	11.9	24.2	63.4
toluene	12.0	10.9	32.9
o-xylene	12.0	7.7	26.2
isopropylbenzene	10.6	3.5	13.7
t-butylbenzene	9.6	2.1	9.1
2,2-dimethylbutane	4.7	.9	3.2

Reed's modification has given a reasonably satisfactory explanation for the heats and excess free energies of hydrocarbon-fluorocarbon systems. This modification would, however, predict for other solutions similar anomalies which are not observed (22, pp. 98-99). Reed later pointed out that the discrepancy could be explained by incorporation of another factor, f_α, designed to account for polarizability in solution so that C_{12} would be given by (60):

$$C_{12} = (C_{11}C_{22})^{\frac{1}{2}} f_I f_d f_\alpha .$$

Unfortunately there appears to be no good way to evaluate f_α and Reed has used solubility data to evaluate f_α.

Reed's modification coupled with Flory-Huggins entropy gives calculated solubilities which in general are not too much better than the

original solubility parameter equations. These equations suffer from the fact that the metallic nature of mercury is not taken into account. Nevertheless this modification serves to point out the over simplification of the original Hildebrand-Scatchard equations.

Modification of the Hildebrand Equations

It has been mentioned that the Hildebrand equations as applied in the preceding sections do not take into account the metallic nature of mercury. Pure mercury has in addition to dispersion forces, a metallic bond, while the pure hydrocarbons have only dispersion force interactions. We have seen that the dipole moments of some of the solvents studied have a negligible effect on the solubility calculations. The metallic bond would not be expected to interact with the hydrocarbons. In using the properties of the pure components to predict the interaction of mercury with these hydrocarbons only the dispersion force contribution of mercury should be considered. That is, instead of the interaction term being taken as $C_{12} = (C_{11}C_{22})^{\frac{1}{2}} = \delta_1\delta_2$, an effective δ, that due only to dispersion forces should be used, so that C_{12} should be written as $C_{12} = \delta_1\delta_2^d$, where δ_2^d is the δ value of mercury that is due only to dispersion forces. When the δ value for mercury is calculated from energies of vaporization the energy measured is not only that required to overcome the dispersion forces, but also that to overcome the metallic bond. Since the latter will contribute nothing in the way of an interaction with the hydrocarbons, we are ascribing to the mercury additional forces which will not come into play in the mixture. These observations are particularly important in systems like water which have available a hydrogen bond. If the hydrogen bond contributes nothing in the way of solubility any solubility

parameter obtained from energies of vaporization will include also the

energy of breaking the hydrogen bonds and hence incorporate into

a force that will not be effective in terms of interactions with other

molecules.

Using this reasoning we may write for the partial molar heat of

mixing:

$$\Delta \bar{H}_2 = V_2[\delta_1^2 + \delta_2^2 - 2\delta_1\delta_2^d] \ .$$

An estimate of δ_2^d for mercury may be obtained from the work of

Fowkes (19). Using measurements of the interfacial tension between

mercury and organic solvents Fowkes has shown that of the 484 dynes/cm

surface tension of mercury at 20°C about 200 dynes/cm are due to disper-

sion forces. This amounts to better than 41% of the total interatomic

forces in mercury. The other 59% of these forces are attributed to the

metallic bond operating in liquid mercury. Hildebrand (43, p. 431) has

further shown that a plot of $\frac{\Delta \bar{E}^V}{V}$ versus $\frac{\gamma}{V^{1/3}}$ at 25°C, where γ is the

surface tension, yields a curve which may be fitted by:

$$\delta = k(\frac{\gamma}{V^{1/3}})^{.43} \ ,$$

where $k = 4.1$ and is temperature dependent. If we use Fowkes' value for

the surface tension that is due only to dispersion forces we find that

if mercury behaved as a liquid with only dispersion forces operating

the δ as given by this equation would be about 27 cal$^{\frac{1}{2}}$/ml$^{\frac{1}{2}}$.

The findings by Fowkes would also indicate that about 6 kcal (61)

of the heat of vaporization of mercury would be due to dispersion forces.

Fowkes' results are at 20°C but due to the small change in the surface

tension of mercury in going from 20 to 25°C (62) we may as an approxima-

tion assume his values to be true at 25°C. If the δ value is calculated

from:

$$\delta = (\frac{\Delta H^V - RT}{V})^{\frac{1}{2}} \, ,$$

where the ΔH^V is the part of the heat of vaporization due to dispersion

forces we find $\delta^d = 19.1$, a considerable difference from that as found

by use of the surface tension equation. At any rate the interaction term

will be less than the geometric mean of the cohesive energy densities

of the pure components. In order to apply the Hildebrand equations then,

a larger entropy term than ideal will have to be used with the heat term

just proposed if we are to have any success at calculating solubilities

or excess free energies. Flory-Huggins entropy may be taken as an

approximation since as we have seen it is a better approximation to the

entropy than ideal. Coupled with the heat term then we have:

$$V_2[\delta_1^2 + \delta_2^2 - 2\delta_1\delta_2^d] = -RT[\ln\phi_2 + (1 - \frac{V_2}{V_1})] . \qquad (13)$$

Substituting first the value of 27 for δ_2^d we find the results

given in Table 6. We see that the calculated solubilities agree on the

whole with the observed solubilities more closely than those calculated

by the original Hildebrand equation. Since it would seem that value

of δ_2^d as calculated by the heat of vaporization should be more appro-

priate for use here it must be conceded that either the interaction term

is much larger than would be expected on the basis of the dispersion

forces or that the surface tension calculation gives a truer interpre-

tation of the magnitude of the interactions. It is easily seen that

substitution of the value 19.1 for δ_2^d would lead to calculated solu-

bilities much smaller than those observed. It is also noted that the

value of δ_2^d of 27 fits all but the aromatics to a good approximation

and even in the case of the aromatics gives better values than the

original Hildebrand equation. In the case of o-xylene the calculated

solubility is as close to the observed as should be expected. It seems

best to regard the value of $\delta_2{}^d = 27$ as an empirical number, the sort of

number that might have been obtained by substituting all the known

quantities including the solubilities into Equation 13 and calculating

a value for $\delta_2{}^d$. If this had been done the value of 27 would of course

been a good average for all but the aromatics. Applying this procedure

to the aromatics and calculating a value for $\delta_2{}^d$ from the observed

solubilities we find $\delta_2{}^d = 25.1$, a number still larger than the 19.1

found using the heat of vaporization.

The excess free energies as calculated by this procedure are also

in good agreement except for the aromatics as seen in Table 7. The excess

free energy may be thought of for the purpose of this calculation as

arising from a thermal and an athermal contribution. The thermal contri-

bution is the heat of mixing as calculated from:

$$\Delta \bar{H}_2 = V_2[\delta_1{}^2 + \delta_2{}^2 - 2\delta_1\delta_2{}^d] \ .$$

The athermal contribution comes from the excess of Flory-Huggins over the

ideal and is given by:

$$\bar{S}^E = -R[\ln\phi_2 + (1 - \frac{V_2}{V_1})] - [-R\ln x_2]$$
$$= -R\ln \frac{V_2}{V_1} - R(1 - \frac{V_2}{V_1}) \ .$$

combining the thermal and athermal contributions then we obtain for the

excess free energy:

$$\bar{G}^E = V_2[\delta_1{}^2 + \delta_2{}^2 - 2\delta_1\delta_2{}^d] + RT[\ln\frac{V_2}{V_1} + (1 - \frac{V_2}{V_1})]. \qquad (14)$$

Barclay-Butler Rule

The effect the orientational change of the solvent has on the entropy of mixing may be interpreted in terms of the free volume concept. Since this concept has been used to offer an explanation for the Barclay-Butler rule the discussion will deal with this rule initially.

We may write for the partial molar free energy of the vapor for the solute:

$$\mu_g = \mu^o_g + R\ln p,$$

where p is the partial pressure due to mercury. We have assumed that the vapor behaves ideally and have taken the standard state to be the vapor at unit pressure, here one torr will be employed. Similarily we may write for the solute's partial free energy in the dilute solution:

$$\mu = \mu^o + R\ln x.$$

Here we have taken the standard state to be one of a hypotehtical mole fraction of unity. We assume that Henry's law is obeyed as a limiting law and that the solutions here considered are dilute enough for this to be true.

Now for an equilibrium process:

$$\mu = \mu^o + RT\ln x = \mu_g = \mu^o_g + RT\ln p,$$

so that

$$\mu^o - \mu^o_g = RT\ln p/x.$$

The corresponding entropy changes may be obtained by differentiating the free energy with respect to temperature. The entropy of vaporization is then given by:

$$-S^o + S^o_g = \frac{d[RT\ln p/x]}{dT} = S^o_g - S^o = \Delta S^V.$$

This entropy change is the difference between the standard state in solution and the standard state of the vapor.

The heat of vaporization from infinitely dilute solution may then be calculated from:

$$\Delta H^V = -RT\ln p/x + T \frac{d[RT\ln p/x]}{dT} \, .$$

The mercury vapor pressures are taken from the Handbook of Chemistry and Physics (39). The assumption of ideal gas behavior for the mercury vapor is not a serious error. Giauque (63) has shown that gas imperfections for mercury are negligible below its boiling point. The heats and entropies calculated as formulated above are listed in Table 11

Table 11. Heats and entropies of vaporization of the mercury solute and entropies of vaporization of the pure substances at 25°C

Solvent	ΔS_2^V [a]	ΔH_2^V [b]	ΔS^{Vo}
n-hexane	32.2 ± .4	5040.2	35.3
n-heptane	31.2 ± .5	4836.0	36.9
n-octane	32.6 ± .5	5325.7	38.6
isooctane	34.2 ± 1.0	5532.9	35.9
2,2-dimethylbutane	36.9 ± .5	6278.0	33.6
cyclohexane	37.5 ± .8	6895.7	35.6
cyclohexene	31.3 ± .6	5062.1	35.6
methylcyclohexane	33.6 ± .4	5660.6	35.9

[a] Entropy units are cal/deg mole.

[b] Heat units are cal/mole.

Table 11. (Continued)

Solvent —	ΔS_2^{Va}	ΔH_2^{Vb}	ΔS^{Vo}
benzene	29.7 ± .9	4447.4	36.2
toluene	33.2 ± 1.2	5594.5	37.1
t-butylbenzene	31.5 ± .5	5177.6	39.8
o-xylene	30.0 ± .5	4716.7	38.4
isopropylbenzene	33.2 ± .4	5683.1	39.2
n-butyl ether	34.2 ± .9	5846.3	39.7
isopropyl ether	35.4 ± .8	5877.1	35.1
water	58.8 ± .9	9953.1	41.5
perfluorodimethylcyclobutane	19.0 ± 2.6	-374.0	34.0
mercury	----------	------	36.4

and a plot of ΔS^V v. ΔH^V is given in Figure 14. Figure 14 also reproduces the curve of Barclay and Butler (27) as well as that of Frank (28).

The slope of the line relating the heats and entropies of vaporization of mercury from these solvents is quite different from the curve expected for normal solutes given by Barclay and Butler or Frank. That the behavior of mercury in the solutions does not follow the normal curve is not surprising in view of its relatively small size and metallic nature. Since these solutions are very dilute in mercury, the anomalous behavior may be attributed to peculiarities in individual mercury atoms, that is the abnormality is due to differences in the force field of a single mercury atom rather than to the bulk properties of mercury. With its large
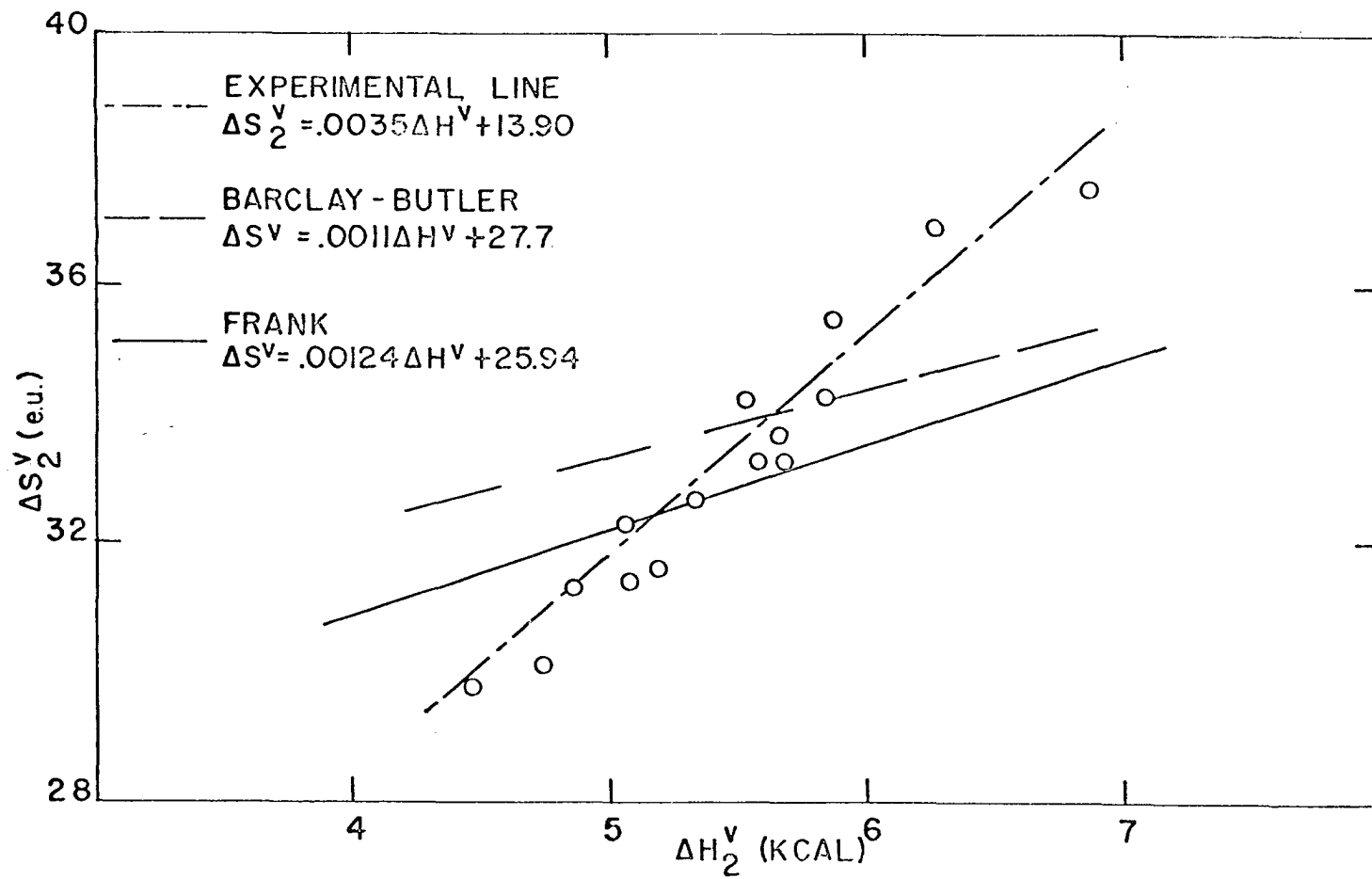
Figure 14. Comparison of experiment with the Barclay-Butler rule

number of electrons mercury should develop strong dispersion forces. It would seem that in these dilute solutions only mercury dispersion forces would come into play and since these are known to be strong forces they would be sufficient to account for the different behavior of these systems.

It is seen here that the entropy of vaporization of the pure solvent, which is given to within a small error by the Frank line, does not fall on the line which represents the entropy of vaporization of the mercury solute from it. It is expected that the entropy of vaporization of pure mercury would not fall on the same line as the entropy of vaporization of the mercury solute, since in these solutions only dispersion forces are in operation while in the pure mercury metallic bonds are in contention. Frank and Evans (30) have derived an equation for the entropy of vaporization of solutes from dilute solution which indicates that the entropy of vaporization of the pure solvent should fall on the same line as the entropy of vaporization of the solute from it. An exception however was reported in their paper. It was found that when sulfur dioxide dissolves in non-polar solvents a considerable deviation from the Barclay-Butler line was observed. The magnitude of this deviation was nearly the same as that of the mercury solutions. This deviation was attributed to the small size and high dipole moment of sulfur dioxide.

As seen in Table 11 the entropies of vaporization of mercury from the organic solvents are within a few e.u. of each other. The behavior of mercury in water, which has an entropy of vaporization some 20 e.u. higher than that of the other solvents will be discussed in the section entitled Mercury Solubility in Water.

Free Volume

The entropies of vaporization of the pure solvents at 25°C may be calculated from:

$$\Delta S^{Vo} = \frac{\Delta H^{Vo}}{T} + Rlnp,$$

where p is the vapor pressure at 25°C and ΔH^{Vo} is the corresponding heat of vaporization. Here the standard state of the vapor is as before, one torr and the pure liquid is the standard state for the condensed phase. We have assumed that the vapor behaves ideally. The entropies so calculated for the pure solvents and mercury are listed in Table 11.

The heats of vaporization of the pure solvents were taken from sources previously indicated. The vapor pressures were taken from various sources (37, 38, 39, 64, 65, 66). The vapor pressure of perfluorodimethylcyclobutane was estimated using the Clausius-Clapeyron equation and the heat of vaporization at 25°C as calculated from Hildebrand and Scott's empirical rule. There is likely to be considerable error in the data on this solvent and consequently the equation of the line connecting the heats and entropies of vaporization of the solute does not include the data on perfluorodimethylcyclobutane.

The entropy change on vaporization of the mercury may be written:

$$\Delta S_2^{V} = Rln \frac{V_g}{\gamma V_{f_2}} ,$$

where γ is unity for the mercury solute. If there was no solvent reaction and the mercury solute occupied the same free volume in solution as in the pure mercury, the entropy of vaporization of the solute would be the same as that of the pure mercury. Since the mercury solute is smaller than the solvent molecules it would be expected to fill in the crevices in the solution and increase the size of its free volume box over that in

the pure mercury. This would lead to a lower entropy of vaporization for the solute than for the pure mercury. In general this is what is observed as can be seen by reference to Table 11. In the absence of a solvent effect a free volume change for the mercury of about ten would lead to an entropy difference of about 4.6 e.u., which is nearly what is observed on the average.

The solvent, however, is not expected to act as an inert diluant. Due to the strong dispersion forces developed by mercury the replacement of a solvent molecule by a mercury solute could result in an increased attraction on the neighboring solvent molecules. These attractive forces are operative over a longer range than repulsions, and we may regard repulsive forces as coming into play only in the event of actual collision of the molecules. This could lead to restriction of rotation of the solvent molecules and thus lower the entropy of the solvent. This effect would be in the opposite direction from that of an increased free volume box for mercury and the solvent reaction would be in competition with the free volume change. If this effect occurs, mercury would have to occupy a larger free volume than previously assigned to it in order to compensate for restricted motion of the solvent molecules.

The entropy of vaporization of the pure solvent may be given by:

$$\Delta S_1^{Vo} = R\ln \frac{V_g}{\gamma_1^o V_{f_1}^o} \, .$$

In comparing the entropy of vaporization of the mercury solute to that of the pure solvent we see that in general the entropy of vaporization of the solute is less than that of the pure solvent. If there was no solvent reaction and the mercury solute occupied the same free volume as the solvent itself, the entropy of vaporization of the mercury would

be less than that of the pure solvent by the amount:

$$\Delta S_1{}^{Vo} - \Delta S_2{}^{V} = R\ln \frac{V_g}{\gamma_1{}^o V_{f_1}{}^o} - R\ln \frac{V_g}{V_{f_2}} = R\ln \frac{1}{\gamma_1{}^o} ,$$

where the superscript o refers to the pure substance and the subscript 2
to the mercury in solution. We may estimate $\gamma_1{}^o$ from an empirical relation
given by Frank (28). Values of $R\ln \frac{1}{\gamma_1{}^o}$ are recorded in Table 12. As seen
by reference to Table 12 $R\ln \frac{1}{\gamma_1{}^o}$ is generally less than the difference
between the entropy of vaporization of the pure solvent and that of the
mercury solute. This would indicate that in the absence of a solvent
reaction the free volume occupied by the mercury solute is somewhat larger
than that of the pure solvent. This is not unexpected in view of the
relatively small size of mercury. It is seen by reference to Table 12 that
a free volume box for mercury in solution of about five times that of the
pure solvent would be adequate to account for the largest differences
between the entropy of vaporization of the pure solvent and that of the
solute. This choice of a free volume box for mercury in solution can be
valid only if the solvent undergoes no reaction.

If the solvent reacts to a mercury solute in the manner previously
described, i.e., the solvent molecules about the solute find themselves
under greater constraint due to the large attractive field presented
by the mercury solute, its entropy will be lowered and in order to com-
pensate for this effect the free volume box assigned to mercury must be
even larger than that just assigned. Therefore it would seem reasonable
to set a volume ten times that occupied by the pure solvent as an upper
limit for a free volume box for the mercury solute.

We have arrived at a size for the free volume box of mercury in

Table 12. Comparison of entropy differences and $R\ln\frac{1}{\gamma_1^o}$ at 25°C

Solvent	$\Delta S_1^{V_o} - \Delta S_2^{V_a}$ [a]	$\Delta S_2^{V_o} - \Delta S_2^{V_a}$ [a]	$R\ln\frac{1}{\gamma_1^o}$ [a]
n-hexane	3.1	4.2	2.3
n-heptane	5.7	5.2	2.9
n-octane	6.0	3.8	3.5
isooctane	1.7	2.2	2.7
2,2-dimethylbutane	-3.3	-.5	1.8
cyclohexane	-1.9	-1.1	2.5
cyclohexene	4.3	5.1	2.5
methylcyclohexane	2.3	2.8	2.7
benzene	6.5	6.7	2.6
toluene	3.9	3.2	3.1
t-butylbenzene	8.3	4.9	4.4
n-butyl ether	5.5	2.2	3.8
isopropyl ether	-.3	1.0	2.3
o-xylene	8.4	6.4	3.8

[a]Units are cal/deg mole.

Table 12. (Continued)

Solvent	$\Delta S_1^{V_o} - \Delta S_2^{V_a}$ [a]	$\Delta S_2^{V_o} - \Delta S_2^{V_a}$ [a]	$R\ln\dfrac{1}{\gamma_1^o}$ [a]
isopropylbenzene	6.0	3.2	4.1
perfluorodimethylcyclobutane	15.0	15.4	1.8
water	-17.3	-22.4	3.9

solution by examination of the experimental data with the assumption of some solvent reaction. Eyring, Hirschfelder, and Stevenson (67) have derived an equation showing that the free volume of a molecule at a given temperature and pressure depends only on the internal pressure of the liquid in which it is immersed. They have shown that the ratio of the free volume in solution to that of the pure component is inversely proportional to the cube of the internal pressures, i.e.,

$$\frac{V_{f_1}}{V_{f_1}^{~o}} = \frac{(P_{i_1}^{~o} + P_{ex_1})^3}{(P_{i_1} + P_{ex_1})^3} ,$$

where V_{f_1} is the free volume in solution, $V_{f_1}^{~o}$ is the free volume of the pure component, P_{i_1} is the internal pressure of the liquid in which the solute is immersed and $P_{i_1}^{~o}$ the internal pressure of the pure component. P_{ex} is the external pressure which is negligible in comparison with the internal pressure which for the solvents studied here is on the order of a few thousand atmospheres. Then we may write:

$$\frac{V_{f_1}}{V_{f_1}^{~o}} = \left(\frac{P_{i_1}^{~o}}{P_{i_1}}\right)^3 .$$

Hildebrand (41, chpt. 5) has shown that the internal pressure, $(\frac{\partial E}{\partial V})_T$, may be given by:

$$\left(\frac{\partial E}{\partial V}\right)_T = n\frac{\Delta E^V}{V} = n\delta^2 ,$$

where n is generally unity and ΔE^V is the energy of vaporization. Changing the subscript we may calculate the free volume occupied by the mercury solute from:

$$\frac{V_{f_2}}{V_{f_2}^{~o}} = \left[\frac{.33(30.9)^2}{\delta_1^{~2}}\right]^3 = \left[\frac{315.1}{\delta_1^{~2}}\right]^3 ,$$

where δ_1 is the solubility parameter of the solvent. The solubility parameters for the solvents of this work range from 7-9. Using $\delta_1 = 9$ in the above equation we obtain for the minimum size of the mercury free volume box in these solvents:

$$\frac{V_{f_2}}{V_{f_2}^0} = [3.89]^3 = 58.9,$$

so that the free volume available to the mercury in solution is nearly 60 times as large as the free volume in the pure mercury. Using Bondi's (68) value of .13 ml/mole as the free volume for pure mercury we see that the mercury in solution should occupy a free volume of about 7.7 ml/mole. By reference to Table 13 it is seen that this represents a factor of about

Table 13. Free volumes

Substance	T °K	V_f ($\frac{ml}{mole}$) [a]	V_{f_s} ($\frac{ml}{mole}$) [b]
n-hexane	293	.733	.517
2,2-dimethylbutane	293	.726	.567
cyclohexane	293	.48	.27
n-heptane	293	.53	.38
methylcyclohexane	293	.55	.28
n-octane	293	.53	.31
mercury	300	.13	.014

[a]Calculated by Bondi (68).

[b]From velocity of sound measurements (68).

ten increase over the free volume of pure hexane and 2,2-dimethylbutane

which show the largest free volume and a factor somewhat larger for the

remaining solvents for which Bondi gives data. Since we do not have the

necessary data to carry through detailed calculations only a qualitative

description will be attempted. To this end we take as an average free

volume box for the mercury a box some ten times larger than that occupied

by the solvent.

Cyclohexane shows, according to the preceding discussion, one of the

largest degrees of restriction of motion due to the presence of a mercury

solute. The entropy of fusion of cyclohexane at its melting point is

2.2 e.u. (69, p. 202). This relatively small value is taken to indicate

that cyclohexane is able to rotate somewhat freely in the solid (69,

chpt. 14 and 70, pp. 313-314). This not only lowers the entropy of fusion

but also prolongs the range of stability of the solid. The addition of a

methyl group to form methylcyclohexane reduces the ability of the compound

to rotate in the solid and results in a striking difference in the melting

points of cyclohexane and methylcyclohexane, 6.5°C and -126.4°C respec-

tively. If each mercury solute were able to 'freeze' its nearest

neighboring solvent molecules completely the loss in entropy of the solvent

corresponding to cubic packing about the solute would be six times the

2.2 or about 13 e.u. An individual cyclohexane molecule would not be

expected to 'freeze' completely. It is more likely that several molecules

would partially 'freeze'. Since the forces causing the restriction of

cyclohexane would not extend for more than a couple of molecular diameters

it would seem that perhaps two dozen or so cyclohexane molecules would

actually be involved in the 'freezing'. If the net effect of this

'freezing' was such that the six nearest neighbors lost about half as much entropy as they would on complete freezing the entropy loss of the solvent would be on the order of 6 or 7 e.u. and probably would not exceed 13 e.u.

As seen from Table 13 a factor of ten increase over the free volume available to cyclohexane would amount to an increase of some 37 times the free volume of pure liquid mercury. Then the entropy of vaporization of the mercury from solution should be less than that of the pure mercury by $R\ln$ 37 or 7.2 e.u. The experimental difference is -1.1 e.u., so that 8.3 e.u. must be lost to restriction of solvent motion in agreement with what we might expect from the preceding discussion. The entropy of vaporization of the solute should be less than the entropy of vaporization of the pure cyclohexane by the amounts $R\ln \frac{1}{\gamma_1^{\,0}}$ and $R\ln 10$. Estimating $\gamma_1^{\,0}$ from Frank's empirical relation to be .29 we find $R\ln \frac{1}{\gamma_1^{\,0}}$ amounts to 2.5 e.u. This plus the free volume change of 4.6 e.u. amounts to an entropy of vaporization of 7.1 e.u. less than that of the pure solvent providing the solvent does not react to the mercury solute. But by our previous findings about 8.3 e.u. is lost to the solvent reaction. Subtracting this from 7.1 e.u., we find the entropy difference to be -1.2 e.u., the experimental difference being -1.9 e.u.

The values of the entropy difference, $\Delta S_1^{\,Vo} - \Delta S_2^{\,V}$, calculated as above are given in Table 14 for those solvents on which data were available. We have used the free volumes as calculated by Bondi. Free volumes obtained by velocity of sound measurements could also have been used. The conclusions are the same in both cases despite the discrepancy in the two free volumes.

Table 14. Experimental and calculated values for the difference $\Delta S_1^{V_o}$ - ΔS_2^V at 25°C

Solvent	$\Delta S_1^{V_o} - \Delta S_2^V$	
	Calculated	Experimental
cyclohexane	-1.2	-1.9
n-hexane	3.1	3.1
2,2-dimethylbutane	-2.1	-3.3
methylcyclohexane	1.7	2.3
n-heptane	5.3	5.7
n-octane	4.5	6.0

Since we have used the properties of the mercury saturated solution to obtain the amount of entropy lost to restriction the calculated and experimental entropy difference should agree if Frank's γ_1^o is close to the true degree of restriction. The agreement between this calculated and experimental entropy difference is good and so this is taken as an indication of the consistency of this approach with respect to the properties of the solution and the pure liquids as well. If an assumption of no solvent reaction to a mercury solute or an entropy gain by the solvent is employed no consistent explanation of the observed data is possible. The factor of ten chosen here for the size of the free volume box is quite artificial. The important point is that whatever size is assigned to the mercury free volume box it must be larger than that occupied by the pure solvent if the data interpretation is to be consistent.

It is perhaps no coincidence that the entropies of fusion of

2,2-dimethylbutane, .6 e.u. (69, p. 202), and of cyclohexane, 2.2 e.u.,

are somewhat less than those of the other solvents studied and at the same

time these solvents appear to react more strongly to the presence of a

mercury solute. An entropy of fusion this low, as already pointed out,

means that there is some rotation in the solid. There could be then

less objection from these two solvents to being 'frozen' by a mercury

solute than from the other solvents.

The effect that the interactions just discussed have on the entropy

of mixing of liquid mercury with the various solvents may now be inter-

preted. Looking first at cyclohexane it is seen that the entropy of

mixing is less than ideal. Complex formation between solvent and solute

or solute-solute association could produce an entropy of mixing less

than ideal. However NMR evidence (5) indicates that no stable complex

is formed in mercury saturated solutions of alkanes or chloroalkanes so

that complex formation here seems unlikely. In addition the spectra

of mercury-cyclohexane solutions show no abnormalities. Solutions of

mercury in methylcyclohexane as well as in other cyclic systems give a

spectral splitting of the mercury absorption band that agrees with the

splitting observed in mercury-cyclohexane solutions. The possibility

of the formation of Hg_2 molecules in solution has also been ruled out

by Vinogradov and Gunning (5) on the basis of the validity of Beer's

law for these solutions. Then it would seem that the reasoning previously

applied would be applicable here. That is the introduction of a mercury

solute brings about changes in the solvent so as to lower the entropy.

In the other solvents this effect is not so pronounced. We may consider

then that the entropy change in these systems stems from the following factors: 1. the configurational entropy change, 2. the free volume change that mercury undergoes, and 3. the change in the solvent's orientational distribution that the introduction of a mercury solute may bring about.

We may then write for the partial entropy change on mixing:

$$\Delta \bar{S}_2 = -R \ln x_2 + R \ln \frac{V_{f_2}}{V_{f_2}^o} - \Delta S^S \,, \tag{15}$$

where we have taken the configurational entropy change to be ideal, V_{f_2} is the free volume of mercury in solution, $V_{f_2}^o$ is the free volume of pure mercury and ΔS^S is taken to be the entropy loss due to the solvent reaction and is given by:

$$\Delta S^S = \Delta S_2^V - \Delta S_2^{V_o} + R \ln \frac{V_{f_2}}{V_{f_2}^o} \,.$$

Substituting this into Equation 15 gives:

$$\Delta \bar{S}_2 = -R \ln x_2 + (\Delta S_2^{V^o} - \Delta S_2^V). \tag{16}$$

The entropy changes calculated according to Equation 16 are given in Table 15.

Since the free volume is certainly a function of the volume, Equation 16 previously derived to calculate the entropy change on mixing would take into account any volume changes incurred on mixing and would correspondingly lead to a calculated entropy of mixing at constant pressure. An exact form of the functional relationship between the free volume and volume is not known, consequently the magnitude of the volume change still cannot be properly assessed. However, by using Equation 16 the volume changes may be taken into account without actually knowing

Table 15. Calculated entropies of mixing at 25°C

Solvent	$\Delta \bar{S}_2$ (Eqn. 16)	$\Delta \bar{S}_2$ (Flory-Huggins)[a]	$\Delta \bar{S}_2$ (Eqn. 9)
n-hexane	32.0	34.6	34.0 ± .8
n-heptane	32.7	35.5	34.8 ± .6
n-octane	31.1	34.1	33.0 ± .4
isooctane	30.3	33.3	32.6 ± 1.0
2,2-dimethylbutane	27.9	30.5	29.6 ± .8
cyclohexane	25.8	28.0	26.0 ± .8
cyclohexene	31.9	34.0	34.0 ± .4
methylcyclohexane	29.9	33.4	31.8 ± .4
benzene	34.0	36.9	34.6 ± .8
toluene	30.2	32.4	31.8 ± 1.0
o-xylene	33.1	35.5	35.0 ± .6
isopropylbenzene	29.8	32.5	31.8 ± .4
t-butylbenzene	31.6	34.5	33.2 ± .8
isopropyl ether	29.2	31.9	31.0 ± 1.2

[a]Calculated from $\Delta \bar{S}_2 = -R[\ln \phi_2 + (1 - \frac{V_2}{V_1})] + (\Delta S_2^{Vo} - \Delta S_2^{V})$.

Table 15. (Continued)

Solvent	$\Delta \bar{s}_2$ (Eqn. 16)	$\Delta \bar{s}_2$ (Flory-Huggins)[a]	$\Delta \bar{s}_2$ (Eqn. 9)
n-butyl ether	29.3	32.3	31.2 ± 1.4
perfluorodimethylcyclobutane	48.1	51.3	$53.4 \pm .8$
water	15.5	15.5	17.1 ± 1.2

their magnitude. The other significant contributions to the entropy are the orientational distribution change of the solvent and possible size differences between solute and solvent.

Although we have previously used arguments based on the size differences between the solute and solvent to obtain a free volume in solutions for mercury we see that according to Eyring's approach the internal pressure solely determines the size of the free volume box. We have also used ideal entropy of mixing in Equation 15. The effect of substituting Flory-Huggins entropy for this term would be to raise the entropies calculated by about 2 e.u. (Table 15). This would make the agreement with experiment closer in most cases. In general the entropies calculated using Equation 16 with Flory-Huggins entropy substituted for ideal are higher than the experimental and those calculated using ideal entropy are less. This is in agreement with current thinking. It is now felt that for molecules of different sizes the Flory-Huggins term is an over correction but still more nearly correct than ideal entropy. While the magnitude of the errors involved in this work do not permit an unequivocal proof for this thinking, it is seen that the trend certainly implies that Flory-Huggins is a better approach to the entropy than ideal and does amount to an over correction.

Mercury Solubility in Water

That the dissolution of mercury in water should be different from its dissolution in organic solvents is not surprising in view of the hydrogen bonding tendencies of water. It is well known that in ice the water molecules are arranged in a tetrahedral structure. Liquid water has been described as a broken down ice structure in which the water

molecules attempt to maintain the tetrahedral symmetry but due to thermal agitation are always breaking the hydrogen bonds so that tetrahedral symmetry is never quite achieved. The accepted structure of water seems to be that there are regions in which water has a crystalline character and regions in which it does not. Each region of course is rapidly changing its personnel (71).

Looking first at the heats and entropies of hydration, i.e., the negative of the heats and entropies of vaporization (Table 11), we see that although mercury dissolves in water with an evolution of more heat than that of the organic solvents, it is less soluble in water. This behavior is attributed to the entropy of vaporization being higher in water. It has already been shown that there exists a linear relationship between the entropy and heat of vaporization in non-polar organic solvents. Butler (72, chpt. 17) has shown a similar relation applies to water systems in which the solute does not form hydrogen bonds with the water. He finds that the entropy of vaporization of gases from water is about 12 e.u. greater than from non-associated solvents for the same heat of vaporization.

Since the entropy of vaporization of these gases and in our case of mercury from water is greater than that from organic solvents, the entropy in aqueous solution must be abnormally low. The partial molar entropy of a substance in solution includes not only the entropy of the solute molecules, but also any changes of entropy which the solute molecules bring about in their action on the solvent. Thus if the presence of a solute molecule diminishes the entropy of the solvent molecules about it, the partial entropy of the solute will be abnormally low. In

the case of water this may occur if the solute restricts the number of configurations open to water, or reduces the ability of the water molecules to rotate. The explanation suggested by Frank and Evans (30) and seemingly now well confirmed is that when a rare gas atom or non-polar solute dissolves in water, the water structure is changed in the direction of greater crystallinity. The water molecules form a structure about the solute, thus reducing the solvent's entropy. This structured arrangement has been called 'icebergs' by various writers. This psuedo-freezing of water causes it to lose heat and entropy. This heat adds on to the heat of solution giving a large heat of vaporization. This loss in entropy is what causes the entropy of vaporization to be so large. When mercury is the solute the entropy of vaporization from water is some 20 e.u. higher than that from the organic solutions. Contrary to earlier findings that it is the property of an individual mercury atom to which deviation from the Barclay-Butler rule is ascribed, it is clear here that the anomalous behavior of solutes in water must be attributed to the properties of water in bulk. Correspondingly it is interesting to note that the entropy and heat of vaporization of mercury from water falls on the same line as for vaporization of non-polar gaseous solutes (Figure 15).

It is not difficult to understand why the partial entropy of mixing is lower for the mercury-water system than for the mercury saturated organic solutions. We have seen that introduction of a mercury solute modifies the water structure giving a lower entropy in solution. This means that the predominant factor in the temperature dependence of the solubility of mercury in water, and hence the lower entropy of this
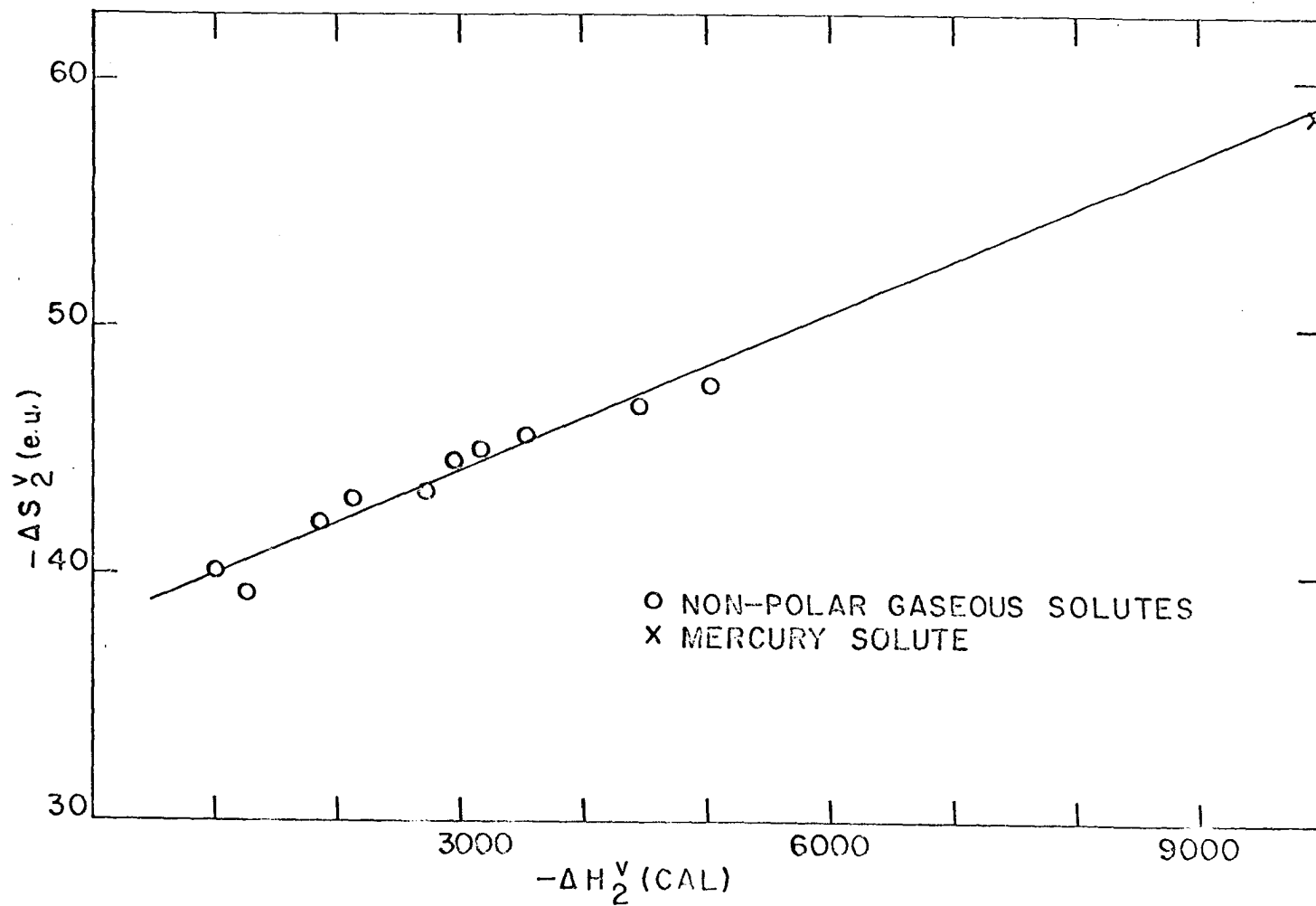
Figure 15. Heat and entropy of hydration for mercury and non-polar gaseous solutes

solution, is an orientational change of the solvent molecules as they react to the exchange of a solute molecule for one of their own kind.

SUMMARY AND CONCLUSIONS

The simple solubility parameter equations give calculated values of
mercury solubilities which agree well with the experimental in most cases
studied. That this is so is no doubt due to a fortuitous cancellation of
several factors. This is clearly seen by reference to Fowkes' value for
the magnitude of the dispersion forces of mercury. It seems clear that
the interaction term must be smaller than that predicted by the Hildebrand-
Scatchard equations. Correspondingly the entropy term coupled with the
energy of mixing must be larger than ideal if the calculated values are
to agree with experiment. Since the hypothesis of regular solution
theory is that the entropy is ideal it would seen that either this
hypothesis must be modified or the energy term is not adequate.

The entropy change on mixing is between ideal and Flory-Huggins
entropy, but Flory-Huggins entropy is more nearly correct. The difference
between Flory-Huggins and ideal entropy amounts to only about 2 e.u. for
the cases studied and since Flory-Huggins entropy amounts to a slight
overcorrection for unequal sizes, the difference between the two terms
would be small for most solutions. For compact molecules whose sizes do
not differ as much as those of this work, ideal entropy is an adequate
representation of the entropy change at constant volume. The molecules
must, however, be compact. According to the formulation adopted here, if
the molecules have different packing factors or if the molecules are
sufficiently different in structure, it is possible to lose or gain degrees
of internal freedom. If the entropy of mixing is to be given only by the
configurational change, the entropy of vaporization of the solute from the

solution must be the same as the entropy of vaporization of the pure liquid solute. This is equivalent to requiring that the environment in the mixture be the same as in the pure liquid. If the free volume is not the same in the mixture as in the pure liquid or if the internal degrees of freedom are affected by the environment of the mixture, the entropy of mixing cannot be ideal. It is possible that the entropy of mixing at constant pressure could reduce to ideal at constant volume since the volume changes would certainly affect the free volume as well as the internal degrees of freedom. This is true even if the mixture partners have unequal internal pressures as long as there is sufficient thermal energy to overcome the tendency to segragation and there are no packing or structural factors to affect the rotational or vibrational freedom. Likewise, even if the internal pressures are the same the shapes of the molecules must be taken into account.

Since the entropy of vaporization of mercury from these solutions is different from that of pure mercury and since mercury has no internal degrees of freedom, it is necessary to explain this difference as being due to free volume changes and to the influence of the mercury solute on the solvent. When these factors are taken into account the use of Flory-Huggins entropy gives closer agreement with experimental entropies than does ideal. This is in accord with the use of an interaction term of the type calculated using Fowkes' value for the dispersion forces of mercury. The use of Flory-Huggins entropy coupled with the new interaction term can be made to give better agreement with experiment than the original Hildebrand-Scatchard equations. The interaction term still is larger than would be expected on the basis of the interaction term as calculated

from Fowkes' data. It must be concluded that there are other factors contributing to the interaction which are not included in these equations.

Reed has attempted to incorporate additional factors into the interaction term, but the solubilities calculated from his equations do not agree with experiment as well as those calculated from the original equations. The ratio of the ionization potentials in all cases calculated was found to be essentially unity and therefore does not contribute to the interaction term. The same criticism must be made of Reed as of Hildebrand, that is, Reed's modification does not allow for the metallic nature of mercury and should be applied only when the mixture partners are capable of exhibiting only dispersion forces.

The deviation of mercury-water solutions from regularity was seen to be the result of a solvent rearrangement about the solute so as to cause the entropy of the solution to be lower than ideal. This behavior of water is not unique to mercury-water solutions but is observed in all water solutions involving non-polar solutes. The mercury-water solution is actually more normal than the mercury-organic solutions, as evidenced by the fact that the heat and entropy of vaporization of mercury from water fall on the same line given by Butler for the vaporization of non-polar gases. This would indicate that the tendency for water molecules to structure themselves about the mercury solute is more important to the properties of the solution than is the peculiarity in the force field of mercury which causes its solution in organic solvents to deviate from the normal behavior as given by the Barclay-Butler rule.

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ACKNOWLEDGMENTS

The author wishes to express his appreciation for the suggestions and criticisms received from Professor A. F. Voigt during the course of this work. Also much appreciated is the advice and assistance given by Wayne Stensland, Ken Malaby, John Gonser and Harold Olson.