

1953

Some studies on the diffusion of sodium in sodium tungsten bronze

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**SOME STUDIES ON THE DIFFUSION OF SODIUM IN
SODIUM TUNGSTEN BRONZE**

by

John Francis Smith

**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:

Signature was redacted for privacy.

In Charge of Major Work

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Dean of the Graduate College

Iowa State College

1953

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I. INTRODUCTION

An understanding of the process of diffusion in solids is fundamental to the understanding of many related phenomena. This is particularly true in the field of metallurgy. Diffusion is often the rate controlling factor in such diverse phenomena as sintering, phase change, corrosion, and precipitation. In addition it plays a part in grain growth, annealing, surface hardening, and other important metallurgical processes. Considering the wide range of applicability, it is not surprising that a great deal of interest and a large amount of time are currently being devoted to the subject. The object of the experiments described in this thesis was to collect reliable data with the hope that these data would contribute in some small way to the understanding of the general problem of lattice diffusion in the solid state.

Diffusion is the process of migration of atomic, ionic, or molecular species through a solid, liquid, or gaseous medium. Studies of lattice diffusion in the solid state involve the determination of the rate of migration of a given atomic species through a single phase region. The term lattice, or volume, diffusion is used in contrast to grain boundary diffusion and surface diffusion.

A large amount of research has been devoted to the study of solid state diffusion processes in the past sixty years, and a great deal of information is available in the literature. However, certain fundamental experimental conditions make the acquisition of good quantitative diffusion data difficult. A comparison of results between similar experiments by different investigators have shown wide discrepancies. This non-reproducibility of results has led to difficulty in interpreting the phenomenon of diffusion from a theoretical point of view. Only very recently has there been any indication that a method has been found which yields consistent results. This will be elaborated further in the next section.

It is certainly desirable that a method of obtaining reproducible results be available. However, an explanation of the discrepancies in previously obtained measurements is also desirable. The effect of variation in concentration gradients upon the diffusivity might shed some light on this problem.

The discovery of the Kirkendall effect^{1*} has shown one of the reasons for discrepancies. This effect shows

*Superscript numbers refer to references listed in Section VII.

definitely that the rate of diffusion of two independent species in the same solid solution is different. Stated in this way, this effect does not sound too surprising. The net result is, however, that more mass moves across a given cross section of a diffusion couple in one direction than in the opposite direction. It is not the purpose of this thesis to delve into the Kirkendall effect, but it is so important in the field of diffusion that it should be mentioned. The literature subsequent to the discovery of this effect adequately points out that when one studies diffusion one must define unequivocally what is meant by the diffusion coefficient. Often in the past what was measured was a net diffusion coefficient of two species rather than a diffusion coefficient of an individual species.

The mechanism of the process of diffusion is still not decided with any degree of certainty. Currently there are at least four prominent possibilities² to explain the mechanism of diffusion in solids. These are: (1) interstitial diffusion, (2) direct place-exchange, (3) Zener's ring mechanism, and (4) the vacancy mechanism. The first of these, interstitial diffusion, involves the migration of atoms through the interstices of a crystalline lattice. This seems to be a reasonable explanation for the diffusion

of small atoms such as hydrogen and carbon through lattices of larger atoms such as iron, and this mechanism is widely accepted as the explanation of the diffusion of small atoms through fairly open lattices of large atoms. However, size considerations seem to preclude its general applicability.

Direct place-exchange is merely the interchange of two atoms occupying neighboring sites in the lattice. Calculated activation energies³ for this mechanism are much larger than measured values. The calculations are based upon the energy necessary for an atom to move from an equilibrium position to an activated (or saddle) position midway between two equilibrium sites.

Zener's ring mechanism⁴ is a more elaborate hypothesis for having the atoms exchange places. In this instance several atoms move simultaneously. For example, in a four-membered ring composed of atoms A, B, C, and D, atom A moves to site B, B to C, C to D, and D to A, so that the cycle is completed. Activation energy calculations based upon this mechanism show that the number of atoms forming the ring which rotates with minimum lattice distortion is structure dependent. Energy calculations for this mechanism show considerably lower activation energies than for direct interchange, though still higher than measured values.

The vacancy mechanism hypothesizes the existence of vacant lattice sites. The atoms are free to move into the vacant position upon the accumulation of relatively small activation energies. Effectively, this causes a migration of the vacancy with an attendant redistribution of the positions of the atoms of the lattice. The activation energies⁵ calculated on the basis of this mechanism agree with measured values better than the other mechanisms although the values are still somewhat higher than measured activation energies. Inferentially the Kirkendall effect supports this mechanism, since a net mass transfer across a given cross section could be accounted for by the creation of vacancies on one side followed by annihilation on the other side. Much of the current interest in diffusion is due to the interest in the establishment of a relationship between diffusion and dislocations since dislocations are believed to be capable of serving as sources and sinks for vacancies. No direct method for proving the existence of vacancies has been devised; all of the evidence is circumstantial.

One additional aspect of the problem of diffusion upon which a considerable amount of work has been done is the treatment of the problem upon the basis of thermodynamic activities rather than upon the basis of concentrations. It has been hoped that substituting activity gradients for

concentration gradients would eliminate the dependence of the diffusion coefficient upon concentration. Two factors have worked against a satisfactory solution upon this basis. The first of these is that thermodynamic activities are usually equilibrium measurements while the diffusion process is a kinetic process. The second factor is that there is no way of evaluating the activity of the activated state. Re-stated, this means there is no way of measuring the activity of the atom in a position which is intermediate between two equilibrium positions.

The particular problem chosen for this investigation was the diffusion of sodium in the sodium tungsten bronzes. No activity data are available for bronzes of different sodium concentrations, but the data from this investigation may be re-examined should such information ever become available. In view of the difficulties encountered by previous investigators in applying activity values to diffusion calculations, it was not considered profitable in time expenditure to institute a program for activity measurement.

The sodium tungsten bronzes were chosen for this investigation because of their interesting properties, particularly their structure. The formula for the bronzes is Na_xWO_3 . The value of x varies from 0 to 1. A determination of the value of x thus determines the number of

sodium sites occupied and the number of sodium sites vacant in a continuous WO_3 lattice. With this interesting fact in mind, it was thought that a study of the rate of sodium diffusion in the bronzes might possibly be of some value in learning more about the phenomenon of solid state diffusion. Before any measurements were taken it was hypothesized that the diffusion rate would be relatively high with low activation energies. The concentration dependence expected was a decrease in sodium diffusivity with an increase in sodium concentration.

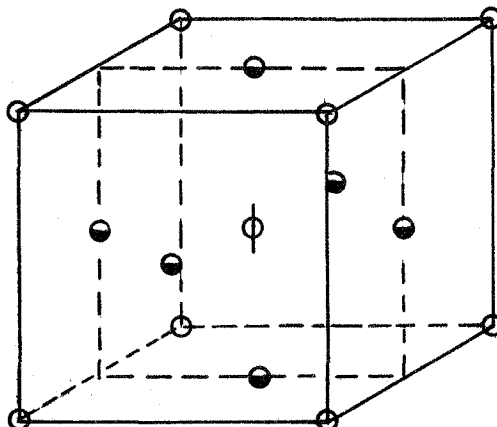
II. REVIEW OF PERTINENT LITERATURE

A. Sodium Tungsten Bronzes

The sodium tungsten bronzes⁶ were first reported by F. Wohler in 1824. The bronzes, Na_xWO_3 , exhibit typical metallic luster and exhibit good electrical conductivity. The bronzes crystallize in the cubic perovskite⁷ structure (Figure 1) when the value of x lies between 0.3 and 1.0. The bronzes become less metallic in appearance as the sodium concentration decreases. At high sodium concentrations with x near 1.0 the color is a golden yellow, and as the sodium content decreases the color shifts through orange, red, violet, to blue at low sodium concentrations.

The state in which sodium is present in the bronzes has been subject to some question. B. W. Brown and E. Banks⁸ on the basis of a minimum in electrical resistivity near $x = 0.7$ hypothesized that sodium is present in an equilibrium state, partly ionized and partly neutral atoms. F. Kupka and M. J. Sienko⁹, on the other hand, suggested that the sodium is almost completely dissociated into diamagnetic ions and free electrons. This suggestion is based upon magnetic susceptibility measurements.

UNIT CELL OF Na_xWO_3 PEROVSKITE
TYPE STRUCTURE



- ϕ TUNGSTEN
- \bullet OXYGEN
- \circ SODIUM

LATTICE PARAMETER

$$a_0 = 0.0820x + 3.7845$$

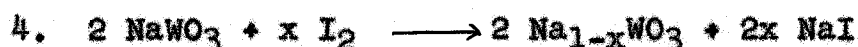
CUBIC SYMMETRY FOR RANGE

$$0.3 < x < 1.0$$

Figure 1. Structure of Cubic Phase of Na_xWO_3

W. Gardner¹⁰ has recently confirmed that the sodium is present as diamagnetic ions and free electrons. His data was obtained by measuring Hall coefficients in addition to electrical conductivity. The minimum in resistance according to Gardner's data is attributable to a maximum in electron mobility.

The following methods¹¹ have been used for the preparation of the sodium tungsten bronzes:



Only the first method was used for growing single crystals of the bronzes for the diffusion experiments. By varying the ratios of the reactants, bronzes of different sodium concentrations could be obtained. The stoichiometric equation as written is misleading because the bronze of composition $x = 1$ is extremely difficult to prepare. Crystalline cubes of the bronzes were obtained by this method which were up to one half centimeter on an edge. These crystals could be broken away from an intergrown matrix with the preservation of one or more well developed faces. Difficulty was encountered in growing large crystals below $x = 0.6$.

No phase diagram for the sodium tungsten bronzes is available. The nearest approach is the system $\text{Na}_2\text{WO}_4 - \text{WO}_3$ which was reported by F. Hoermann¹². It is known that for sodium concentrations below $x = 0.3$ there is a phase change to a tetragonal modification¹¹. Reduction of the sodium content to less than $x = 0.1$ leads to monoclinic tungstic oxide.

B. Historical Background of Diffusion

The study of the process of diffusion has been in progress for nearly a century. As early as 1855, Adolf Fick¹³ developed the basic equations describing the diffusion process. This is one of the instances in which the mathematical development preceded any experimental work. Early research was limited to gas and liquid systems. Later it was shown that the phenomenon also occurred in solid materials¹⁴. In 1868, Tchernoff placed two pieces of steel in contact and heated them above the A_3 point. This treatment caused the two pieces to unite. Spring, in 1882, pressed powdered solids under high pressures to form a compact mass. In 1896, this qualitative evidence was confirmed by

quantitative measurement. At that time Roberts-Austen of the British mint measured the diffusion rate of gold in lead.

Fick developed two equations¹⁴ describing the diffusion process. These are now referred to as Fick's laws. Fick's first law states that the mass transferred across a unit area perpendicular to the diffusion direction per unit time is proportional to the concentration gradient of the diffusing substance. In equation form this is

$$dm = D (\partial c / \partial z) dt . \quad (1)$$

The mass transferred per unit area at right angles to the concentration gradient is represented by the symbol m . The symbol D is the proportionality factor. It is called the diffusivity or, alternatively, the diffusion coefficient. Concentration is represented by c , while z is the direction of diffusion. The symbol t is time.

Fick's second law may be derived from the first in the following manner. Let the mass flux through a given area be represented by the symbol J :

$$J = dm/dt = D (\partial c / \partial z) . \quad (1a)$$

The flux through a second area which is a distance dz away will be

$$J + \left[\frac{\partial J}{\partial z} \right] dz = D \left(\frac{\partial c}{\partial z} \right) - \left[\frac{\partial (D \frac{\partial c}{\partial z})}{\partial z} \right] dz . \quad (1b)$$

By subtraction

$$\frac{\partial J}{\partial z} = \frac{\partial (D \frac{\partial c}{\partial z})}{\partial z} . \quad (2a)$$

However, the flux difference, $\partial J/\partial z$, equals the negative rate of concentration change. So that

$$\frac{\partial c}{\partial t} = - \frac{\partial (D \frac{\partial c}{\partial z})}{\partial z} . \quad (2b)$$

Originally D was considered independent of concentration and was taken outside of the differential. This step is valid for many examples of gaseous diffusion, but experiment has shown that this procedure is subject to error for most liquid and solid diffusion couples. An exception is the case of self-diffusion where the radioactive diffusing species is chemically identical with the matrix.

The solution of the second law equation is determined by the boundary conditions of a particular experiment. One method allowing a straight forward solution is to design an experiment yielding steady-state values. A second method of solution is that proposed by L. Boltzmann¹⁵ in 1894. Boltzmann proposed the substitution of a single variable, $u = z/t^{\frac{1}{2}}$, for the time and distance. This substitution transforms the equation to a solvable form. The substitution has been justified empirically.

The method used in analyzing the sodium tungsten bronze data was to take the first law as definitive for diffusivity. The complete details will be found in the experimental section.

Experimental approaches in diffusion studies have been diverse. Materials of different concentration are usually placed in proximity and a concentration gradient established by heating. The methods for obtaining close proximity have included welding, electrodeposition, sputtering, supplying the diffusing species as a vapor or liquid, and simple mechanical contact. The analyses of the gradients have also included a large number of methods: wet chemical, spectroscopic, x-ray lattice parameter, and a few less orthodox methods. At the present time the only common experimental techniques which allow the measurement of diffusivities in the absence of a chemical concentration gradient are (1) the radioactive tracer technique, (2) the internal friction method¹⁶, and (3) the method of G. C. Kuczynski¹⁷. Kuczynski's approach utilizes the measurement of the bond length between a metallic particle or wire sintered to a metallic block as a function of time. The principle of the internal friction method is that, in general, the application of a stress to a random solution will change the configuration to a non-random one. Atomic

redistribution must follow. A relaxation time may be obtained from internal friction measurements, and from this relaxation time diffusivities may be calculated. The only thing that need be said about radioactive tracer techniques is that the gradient analysis seems to be more reliable if the sample is sectioned and sections are counted than if the count is made of the face of the sample after each successive cut.

In choosing an experimental technique for the experiments with sodium tungsten bronze a large number of factors were considered. In order to measure the actual rate of atom movements which are continually occurring in all solids, it is certainly desirable to measure diffusion coefficients in the absence of any gradients. This is tantamount to defining Fick's first law as a limiting law with the value of the diffusivity being equal to the rate of atom movement when the concentration gradient approaches zero. Until very recently the diffusion measurements of different investigators have shown considerable variation in value. Now, however, the evaluation of self-diffusion in silver has been determined and checked by three different investigators¹⁸, all using the radioactive tracer technique. It seems, therefore, that a reproducible technique for self-diffusion has been worked out. One of the remaining problems then seems to be why have discrepancies occurred in

diffusion measurements made on binary couples. A. S. Nowick¹⁹ hypothesizes that one possible explanation for the variations was that different investigators made their measurements with a variety of concentration gradients. The presence of a steep concentration gradient might cause localized strains, distortions, or dislocations which would facilitate diffusion. He cites as evidence the fact that measured activation energies for the diffusion of a foreign solute ion are invariably lower than the activation energy for self-diffusion. The single exception noted was the experiment of W. A. Johnson²⁰ who measured the diffusion of gold in silver with a four per cent gradient. The activation energy calculated from these experimental data is within one kilogram calorie per mole of the activation energy of self-diffusion for silver. This is corroborative evidence that steep concentration gradients affect diffusivity values. The sodium tungsten bronze experiments were designed with the purpose of obtaining a considerable amount of data concerning time, concentration, and concentration gradient at a given temperature. It was hoped that some correlation between diffusivity and concentration gradient could be made. In addition data on the relationship between diffusivity and concentration were sought.

The actual experimental techniques should be designed to be as simple as possible. With this in mind it was decided to utilize the rather high volatility of sodium to establish the concentration gradient of sodium in the sodium tungsten bronzes. This effusion method can only be used where the diffusing element is of considerably greater volatility than the matrix. Using effusion to establish a concentration gradient is not new. It has been used frequently in the copper-zinc system²¹ since the volatility of zinc is considerably greater than copper.

The analysis of the concentration gradient was done by a determination of a precision lattice parameter. Copper x-ray radiation has a high absorption in the sodium tungsten bronzes, and it is possible to determine what is essentially a surface lattice parameter which in turn is a function of the surface sodium concentration. The method is similar to that used by A. H. Sully²² in his studies on nickel-chromium diffusion.

C. Theory

A straight forward development of the diffusivity as a function of the jumping frequency of sodium atoms is given for the sodium tungsten bronzes. This development is

patterned upon the treatment of A. G. Guy²³ of the problem of interstitial diffusion. Let N'' be the number of atoms moving from left to right per second; let f be the jumping frequency; and let n be the number of sodium atoms per square centimeter in a (100) plane. There are six possible positions into which a given sodium might jump. Therefore

$$N'' = (1/6) f n . \quad (3)$$

If the number of atoms making the reverse movement per second from the adjacent plane is N' , then

$$N' = (1/6) \left(f + \frac{\partial f}{\partial n} \frac{\partial n}{\partial z} dz \right) \left(n + \frac{\partial n}{\partial z} dz \right) \quad (4)$$

where z is the direction of diffusion. The increment of the jump, dz , in this case is equal to the lattice parameter a_0 . Making this substitution

$$N' = (1/6) \left(f + \frac{\partial f}{\partial n} \frac{\partial n}{\partial z} a_0 \right) \left(n + \frac{\partial n}{\partial z} a_0 \right) . \quad (5)$$

Subtracting equation 5 from equation 3 and neglecting the squared terms, the result is

$$\begin{aligned} N &= N'' - N' \\ &= - (1/6) \left(f + n \frac{\partial f}{\partial n} \right) \frac{\partial n}{\partial z} a_0 . \end{aligned} \quad (6)$$

N is the net number of sodium atoms which are transferred from left to right. If the concentration, c , is specified

in grams per cubic centimeter and the lattice parameter in centimeters, one may make the following substitution for n :

$$n = a_0 (N_A/A) c . \quad (7)$$

N_A is Avagadro's number, and A is the gram atomic weight of sodium. The resultant dimensions of n are grams per square centimeter. Then

$$(\partial n / \partial z) = a_0 (N_A/A) (\partial c / \partial z) . \quad (8)$$

Since N represents the net number of sodium atoms moving from left to right per second, the relation to the mass transfer will be

$$N = (N_A/A) (dm/dt) . \quad (9)$$

After rearranging equation 9 and substituting from the previous equations, the result is

$$\begin{aligned} (dm/dt) &= - (A/N_A) (1/6) (f + n \frac{\partial f}{\partial n}) (\partial n / \partial z) a_0 \\ &= - (1/6) (f + n \frac{\partial f}{\partial n}) (\partial c / \partial z) a_0^2 \\ &= - (1/6) (f + c \frac{\partial f}{\partial c}) (\partial c / \partial z) a_0^2 . \end{aligned} \quad (10)$$

When comparing this equation to Fick's first law, it is readily apparent that

$$D = (1/6) (f + c \frac{\partial f}{\partial c}) a_0^2 . \quad (11)$$

C. Wert and C. Zener²⁴ derive the following expression for the jumping frequency:

$$f = 6 f_0 \exp (-\Delta F/RT) . \quad (12)$$

The symbols are: R the gas constant, T the absolute temperature, ΔF the free energy of activation, and f_0 the frequency of vibration of the sodium atom. The partial derivative of f with respect to c is

$$(\partial f / \partial c) = - (f/RT) (\partial \Delta F / \partial c) . \quad (13)$$

Substituting equation 13 into equation 11, one obtains

$$D = f_0 a_0^2 \left(1 - \frac{c}{RT} \frac{\partial \Delta F}{\partial c} \right) \exp (-\Delta F/RT) . \quad (14)$$

This equation shows the dependence of measured diffusivities upon the concentration gradients. In the absence of a concentration gradient the equation simplifies to

$$\begin{aligned} D &= f_0 a_0^2 \exp (-\Delta F/RT) \\ &= f_0 a_0^2 \exp (\Delta S/R) \exp (-\Delta H/RT) . \end{aligned} \quad (15)$$

The entropy of activation, ΔS , is very nearly temperature independent so that it may be incorporated with the other constants. The equation then reduces to the ordinary form which is commonly used to describe the temperature dependence of the diffusivity:

$$D = D_0 \exp (-\Delta H/RT) . \quad (16)$$

Since this last equation has often been used to calculate activation energies from diffusion experiments, it is apparent that the variation of some of the reported activation energies between different investigators might be due to concentration gradients.

An independent evaluation of f_0 from Debye temperature measurements would be of value in trying to correlate diffusion theory with diffusion measurements. The Debye temperature could be obtained from the variation of the intensity of x-ray reflexions with temperature or from heat capacity measurements.

III. EXPERIMENTAL PROCEDURE

The principal objective in this investigation on the diffusivity of sodium in the sodium tungsten bronzes was the determination of the diffusion coefficients for sodium at various temperatures. From the temperature dependence of the diffusion coefficients, it should be possible to determine frequency factors and activation energies. In addition it was intended that the measurements be examined for dependence of diffusion coefficients upon concentration and upon concentration gradient.

A. Crystal Growth

Single crystals of sodium tungsten bronze were used in all experiments. The crystals were grown from a melt of sodium orthotungstate, tungstic oxide, and tungsten metal. These materials were combined in an approximate mole ratio of 6.5:4:1. Variations in this ratio were made to control the sodium content of the resultant bronze. The crystals were usually grown in one thousand gram batches which were heated to 1000° C. in porcelain crucibles. The mixtures

were held at this elevated temperature for two to eight hours in order to insure complete fusion. The temperature was then gradually lowered to about 600° C. at which temperature the power to the heating furnace was shut off. The size of the crystals grown depended upon the rate at which the temperature was decreased. The largest crystals were grown from melts that were cooled slowly for two to three days before the power was shut off. Using prolonged cooling times crystal faces were obtained which measured up to one-half centimeter on an edge. The normal habit of the crystals grown in this manner was an intergrown matrix of cubes. The cube faces were usually (100) planes, although occasionally a (110) plane would appear as a face.

After removal of the crucibles from the furnace, it was necessary to destroy the crucibles in order to remove the crystals. The excess sodium orthotungstate was dissolved away with hot water. Following the dissolution of the orthotungstate the fine particles of porcelain which adhered to the bronzes were removed with an aqueous solution of hydrofluoric acid. Single crystals were then broken away from the matrix manually.

Crystals whose sodium content in the formula Na_xWO_3 ranged between $x = 0.6$ and $x = 0.8$ were grown most easily. Large crystals for concentrations outside of this range were

not obtained. As a result of this limitation all measurements made in this investigation were made on crystals whose initial concentration was within this range.

B. Establishment of Concentration Gradient

Diffusion experiments of the ordinary type may be considered in three stages: (1) the establishment of a gradient, (2) the measurement of the gradient, and (3) calculation of desired information from the measurements. The establishment of a concentration gradient in the sodium tungsten bronzes was accomplished by sodium effusion under a vacuum at elevated temperatures. This procedure was chosen as the simplest method for establishing a concentration gradient. Several other methods were tried without much success.

It proved impossible to weld two crystals of different concentration together. Several methods were tried. Invariably one of two things happened. Either there was no fusion, or the crystals decomposed. As a result of this inability to secure a weld, an attempt was made to determine the melting point. No success was attained by heating in a resistance furnace or by arc melting. It was established that rapid decomposition occurred between 950° C. and

1000° C. A search of the literature also failed to disclose a successful measurement of the melting point. Mechanical joining of two crystals was not attempted since it was not considered a sufficiently reliable contact for reproducible diffusion.

Contact of a single crystal with liquid sodium resulted in chemical reduction of the sodium tungsten bronze by the sodium. An x-ray diffraction pattern of the water insoluble powder resulting from such a reduction was compared with the diffraction pattern for pure tungsten as shown in Table 1. These patterns showed that tungsten was one of the decomposition products. The other lines were probably due to one or more of the lower oxides of tungsten.

Since these methods for establishing regions of concentration difference had failed, an attempt was made to establish a gradient by diffusing sodium into the bronze when the sample was surrounded with a sodium vapor atmosphere. This approach appeared feasible but was not studied extensively since the method of effusion into a vacuum appeared to be a simpler technique.

The sodium effusion technique involved nothing more than heating the bronze crystals under reduced pressures of the order of 10^{-5} to 10^{-6} mm. of Hg. The apparatus used is pictured in Figure 2. The vacuum was obtained by using

Table 1
Interplanar Spacings and Intensities

Water insoluble reduction residue		Tungsten powder	
d (in Å)	Intensity*	d (in Å)	Intensity*
4.68	S		
2.88	S		
2.71	VVW		
2.47	S		
2.00	S	2.02	VVS
1.88	VVW		
1.79	VW		
1.68	W		
1.58	W		
1.46	VVW	1.44	W
1.40	VVW		
1.31	VVW		
1.27	VVVW		
1.17	M	1.18	M
1.11	W		
1.08	W		
1.02	VVW	1.02	W
0.986	VVVW		
0.922	M	0.924	S
0.865	VVW		
0.853	VVVW	0.854	W
0.837	W		
0.801	S	0.803	VS
0.794	VVW		
0.774	VVW	0.772	W

*The symbols used are as follows:

- S - strong
- M - medium
- W - weak
- V - very



Front View



Rear View

Figure 2. Heating Furnace and Vacuum System

a Welch Duo-Seal Model 1400 backing pump, a Distillation Products VMF 20 diffusion pump with Octoil-S, and a liquid air cold trap. The pressure in the high vacuum side of the system was measured with a National Research ionization gauge, while the forepressure was measured with a Hastings thermocouple gauge.

Prior to heating, the crystals were thoroughly cleaned in aqueous hydrofluoric acid to insure clean surfaces. A technique was developed which allowed crystals to be removed individually from the effusion furnace without disturbing the vacuum or cooling the furnace. It was thus possible to obtain data on several crystals at the same temperature with time as an adjustable parameter. A maximum of seven crystals could be placed in the furnace at one time.

The furnace was a 750 watt electrical resistance heater consisting of two halves which were hinged together. This construction made it possible to bring the furnace to temperature before being placed around the quartz tube containing the samples. The result was a very short time lapse in bringing the samples from room temperature to the equilibrium temperature for the run. The quartz tube was one and one-fourth inches in diameter and fitted snugly in the bore of the furnace. The quartz tube extended out

either end of the furnace for a distance of about one foot. Wound around the tube, immediately adjacent to the furnace on either end, were copper coils through which water was circulated to keep the system outside the furnace from rising above room temperature. At the extreme ends of the tube were soft rubber stoppers which were seated with apiezon grease. The tube was connected to the vacuum system through a ground glass seal.

The crystals were placed in the furnace in the following manner. The individual crystal was first placed in a short length of quartz tubing (Figure 3A) whose bore was just large enough to accommodate the crystal. On either side of the crystal were placed rings (Figure 3B) cut from smaller diameter quartz tubing. Niobium wire was wrapped around the whole (Figure 3C). Notches were ground in the outer tubing to prevent the wire from slipping. The quartz rings prevented the crystal from falling out of place or from making contact with the niobium wire while still leaving a large orifice through which the evaporated sodium might pass. The overall size of this assembly was approximately one inch long by three-eighths inch in diameter.

The crystals thus mounted were placed inside the quartz tube which was to be evacuated. The niobium wire had one end which was left sufficiently long so that it could be run

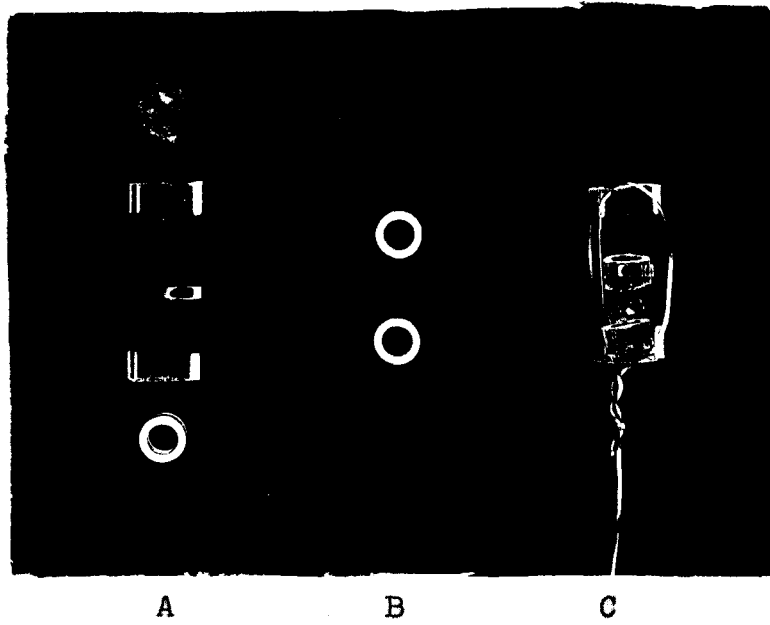


Figure 3. Quartz Container Assembly

through the rubber stopper at the end of the tube. A vacuum tight seal through the stopper was obtained by heating the wire to red heat and pushing it through the rubber. Wires from one-half of the crystals plus the thermocouple were run through the stopper at one end, while wires from the rest of the crystals were run through the stopper at the opposite end. Up to seven crystals could be packed in a length of less than three inches. By noting the order of packing and by numbering the wires accordingly, a given crystal was pulled from the furnace by pulling the appropriate wire. This was done without disturbing the vacuum or the temperature of the rest of the crystals.

Temperature control of the furnace was obtained through a Brown Elektronik Potentiometer controller-recorder. A chromel-alumel thermocouple was run from the sample area through a cold junction compensator to the potentiometer. The potentiometer governed a Modutrol motor which was connected mechanically to an autotransformer. The output of the autotransformer was fed to the furnace windings. The Brown Elektronik Potentiometer is a proportional controller whose corrective signal is proportional to the deviation of the input signal from the desired value. Since the Modutrol motor used on this equipment had an arc of rotation of ninety degrees, maximum control was obtained with the

Modutrol motor set at the forty-five degree position for the equilibrium temperature. This arrangement provided the proportional controller with adequate latitude for control in both directions. In order to achieve this control position for all temperatures, a second autotransformer was placed in the circuit to control the power input to the first autotransformer. The second autotransformer was set manually. With this system temperatures were easily controlled to $\pm 5^{\circ}$ C., and during some runs the temperatures were controlled to $\pm 3^{\circ}$ C. A block diagram is shown in Figure 4.

C. Measurement of the Gradient

After the samples were removed from the furnace they were mounted in bakelite cylinders one inch in diameter and approximately three-eighths inch thick. Other plastics were tried but bakelite appeared to be most satisfactory. The mounting procedure varied only slightly from the standard metallographic technique²⁵. When mounting the crystal it was necessary to exercise care in the positioning so that a (100) face would be flat against the base of the mounting die. This was to insure that the (100) face would be

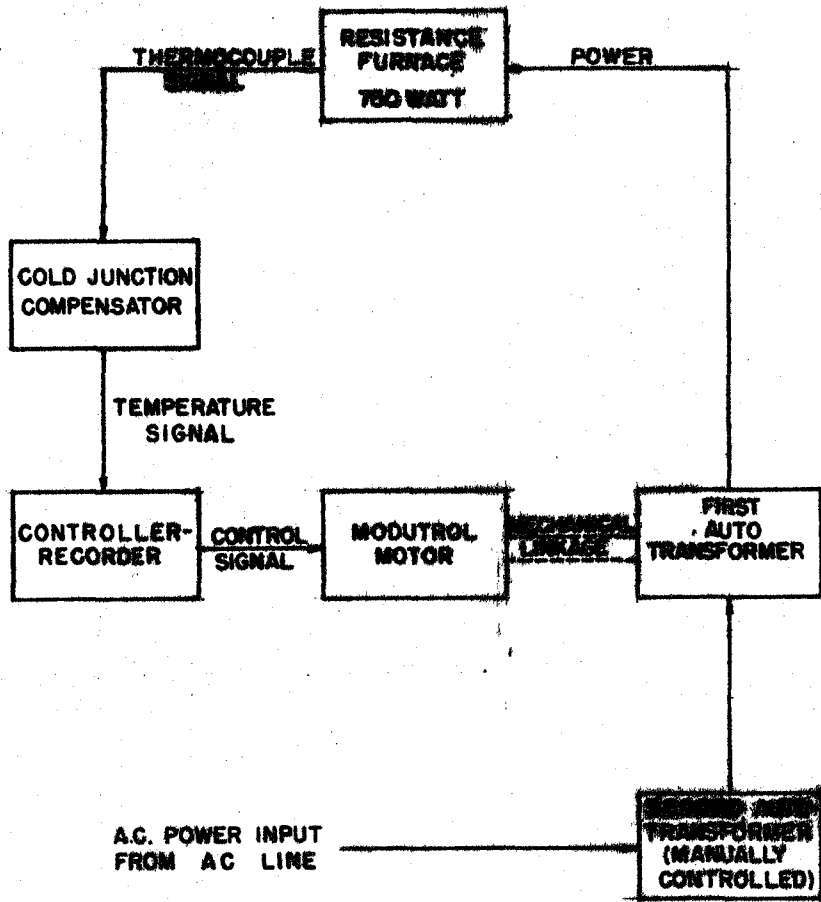


Figure 4. Block Diagram of Heating System

perpendicular to the axis of the cylinder. Pressures of the order of 6,000 p.s.i. were used in polymerizing the bakelite powder. These pressures were slightly higher than those normally used, but the increase resulted in a harder, more machinable mount.

Machining of the specimens in order to take off increments was a difficult problem. The sodium tungsten bronzes were extremely hard and brittle. The only hardness value that was obtained showed a Vickers hardness of 425. This measurement was made with a load of one kilogram. Increasing the load fractured the crystal. Attempts to obtain values from other crystals resulted in fracture even with one kilogram loads.

It proved possible to machine increments from tungsten bronze samples by using a cutting tool with a tungsten carbide tip. A smooth finish was retained using cuts up to 0.003 inch; heavier cuts led to pitting and crumbling of the sample. The cutting of a shoulder in the bakelite mounting (Figure 5) helped to position the sample in the lathe chuck. This shoulder was cut by mounting the plastic cylinder in a collet chuck. The axis of the cylinder was aligned with the axis of rotation of the lathe by butting the tailstock of the lathe against the base of the cylinder. This alignment procedure made certain that the plane of the

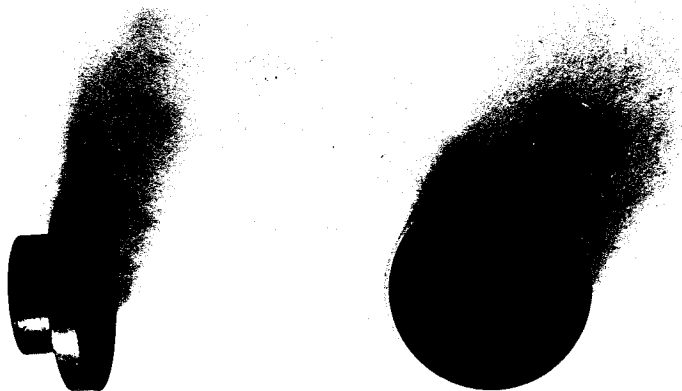


Figure 5. Bakelite Crystal Mount

shoulder was parallel to the plane of the surface. When the mounted crystal was subsequently placed in the lathe chuck, the shoulder fitted snugly against the chuck jaws. This fit allowed the sample to be put on the lathe with the knowledge that the (100) plane of the crystal would be perpendicular to the axis of rotation. Without this shoulder a tedious alignment was necessary for each turning.

Measurements to determine the amount which was machined from the crystals were made with a micrometer. This micrometer was equipped with a vernier scale which permitted the readings to be made to 0.0001 inch. The micrometer measurements were more reproducible and reliable than similar measurements made with a dial gauge.

Sodium concentration was measured by an x-ray determination of a precision lattice parameter. Vegard's law has been found to hold throughout the entire cubic range of the bronzes. The validity of the law for the bronzes has been established independently by three different investigators²⁶. The following equation for the Vegard relationship is the most recent, and it is considered to be the most accurate:

$$a_0 = 0.0820 x + 3.7845 \quad . \quad (17)$$

The precision lattice parameter, a_0 , was measured in true angstroms. The sodium content in the formula Na_xWO_3 was represented by the x in the equation. There was disagreement among the three investigators as to the value of the intercept in the equation. The magnitude of the variation in the intercept value was 0.006 \AA . However, all three investigators have agreed concerning the value of the slope. The disagreement in the value of the intercept arose from the difficulty in preparing stoichiometric sodium metatungstate.

The high absorption of the sodium tungsten bronzes for copper x-radiation was advantageous. Due to this high absorption, an x-ray diffraction pattern taken of a bronze crystal represented a diffraction pattern of the surface material. In Figure 6 were plotted the calculated absorption curves for two of the reflexions used in obtaining a precision lattice parameter. These two reflexions represented the extremes of absorption; the absorption curves for the other reflexions used in the parameter determination lay between the two plotted curves. These calculations were based upon the following relationships:

$$\begin{aligned} dI/I &= -\mu_b dp \\ &= -\mu_b (2/\sin \theta) dz . \end{aligned} \quad (18)$$

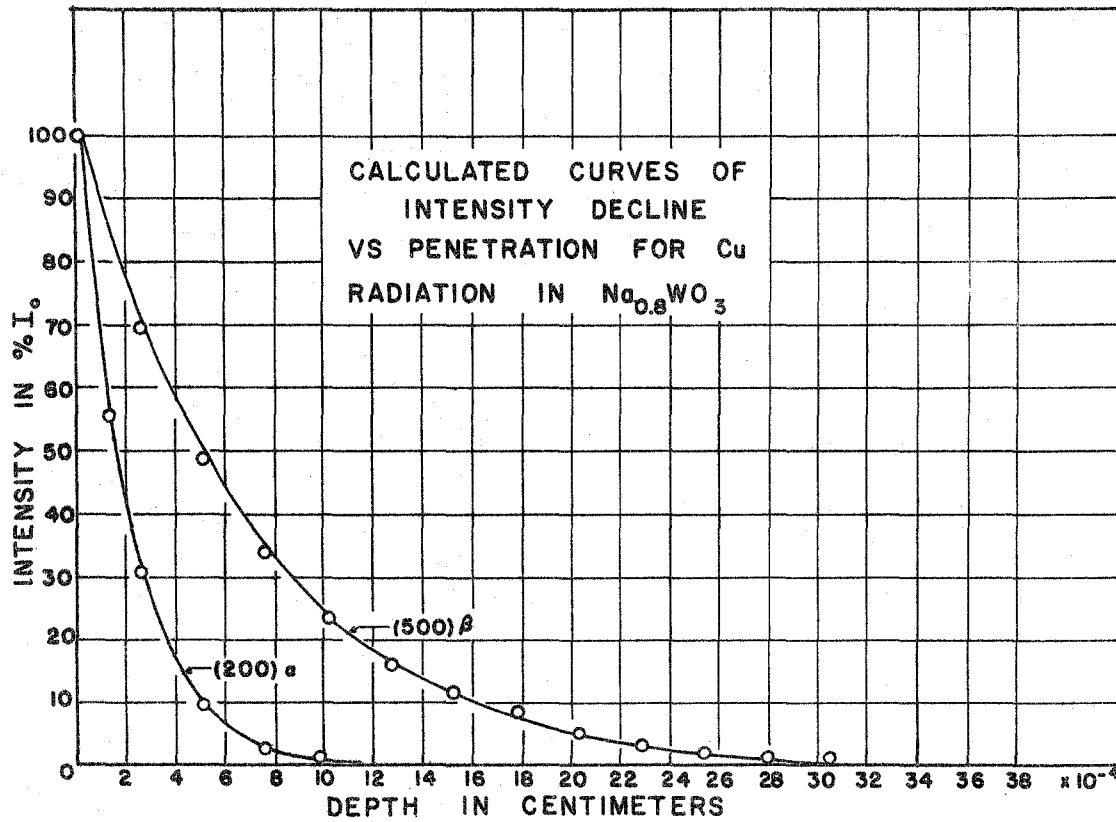


Figure 6. Intensity Decrease of Incident x-radiation as a Function of Depth

$$\mu_b = \left[(\mu/\rho)_{\text{Na}} x M_{\text{Na}} + (\mu/\rho)_{\text{W}} M_{\text{W}} + (\mu/\rho)_{\text{O}} 3M_{\text{O}} \right] \rho_b / M_b . \quad (19)$$

The intensity is designated by I, path length is p, θ is the Bragg angle, and z is the perpendicular depth from the crystal surface. The subscript b refers to the bronzes, while the other subscripts refer to the elemental components of the bronzes. The mass absorption coefficients²⁷ are μ/ρ , M represents the gram molecular weight, and x is the sodium concentration. The linear absorption coefficient, μ_b , calculated for a sodium tungsten bronze of $x = 0.8$ was 928.6 per cm. for Cu K α radiation and 642.2 per cm. for Cu K β radiation. The mass absorption coefficient of tungsten for Cu K β radiation used in these calculations was obtained by an interpolation²⁸ based on the following relationship:

$$\mu/\rho = c \lambda^3 Z^3 . \quad (20)$$

λ is wave length, Z is the atomic number, and c is a proportionality constant for a given spectral region.

A second calculation was made to determine the average depth of penetration of the radiation contributing to the various reflexion peaks. These values are tabulated in Table 2. The calculations were based upon the average value theorem:

$$\bar{z} = \frac{\int_0^{\infty} z \exp(-2\mu/\sin\theta) dz}{\int_0^{\infty} \exp(-2\mu/\sin\theta) dz} . \quad (21)$$

Table 2
Average Penetration of X-radiation Contributing
to Reflexions

Reflexion	θ in deg.	\bar{z} in centimeters
(500 β)	65.0	0.706×10^{-3}
(400 α)	53.5	0.434 "
(400 β)	46.5	0.564 "
(300 α)	37.0	0.325 "
(300 β)	33.0	0.424 "
(200 α)	23.5	0.216 "
(200 β)	21.3	0.282 "

The symbols represent the same values as in previous equations. These calculations verified the assumption that a diffraction pattern of a bronze crystal could be used to obtain a precision lattice parameter which represented, essentially, a surface concentration of sodium.

The concentration gradient was measured in the following manner. A crystal containing a concentration gradient was mounted in bakelite in the manner already described. An x-ray diffraction pattern was run using a Norelco X-ray Spectrometer Goniometer. The crystal was then removed from the spectrometer, a measured increment machined from the

specimen, and a diffraction pattern was then run on the new surface. The whole process was repeated until the region of uniform concentration in the crystal was reached. This procedure made it unnecessary to collect the turnings removed from the crystal.

The geometry of the Norelco unit is analagous to that of a Seeman-Bohlin camera. However, the radius of the circle of focus of the Norelco unit is a function of the diffraction angle while that of the Seeman-Bohlin camera is fixed. The Norelco unit utilizes a Geiger tube for the detection of the diffracted radiation. The Geiger tube is connected to an electronic panel which includes a counter circuit and a strip chart recorder. This method of detection eliminates film shrinkage errors in precision lattice determinations. The Geiger tube is mounted on the end of an arm which rotates at twice the speed at which the sample rotates. Thus the Geiger tube rotates through an angle 2θ while the crystal rotates through an angle θ . The physical construction is such that the x-ray source, the surface of the crystal, and the entrance slit to the Geiger tube determine the circle of focus.

Extrapolation is a conventional means of obtaining precision lattice parameters. Errors in lattice parameter approach zero as the Bragg angle approaches 90° . This is

apparent from the following relation which is derived from the Bragg equation:

$$\delta a/a = - \cot \theta \delta \theta . \quad (22)$$

In this equation a is the lattice parameter. The errors in angle determination, $\delta \theta$, arise from absorption and from geometrical errors. The evaluation of this function varies with the type of camera under consideration. A. J. C. Wilson²⁹ has considered this problem for the case of the Norelco unit. In his paper he has considered the following errors: absorption, angle setting of the crystalline sample, angle setting of the Geiger tube, and displacements of the crystal surface from tangency to the axis of rotation. His conclusions show that the shapes of the reflexion peaks are very sensitive to some of these errors but that the center of gravity of the reflexion intensity is considerably less sensitive. For this reason the measurements of 2θ in this investigation were done by using a planimeter to determine the coordinate which divided the reflexion into equal areas. After selecting this coordinate, its numerical value could be measured to $\pm 0.002^\circ$. Wilson has pointed out that while the precision of the spectrometer goniometer is as good or better than precision cameras the absolute accuracy may not be quite as good. This results

from the fact that the zero setting for the spectrometer goniometer is made by calibration with a standard such as silicon or quartz. The unit used in this investigation was calibrated with a silicon standard.

A blank was run to determine the reproducibility of the lattice parameter in a crystal. This was done by mounting a crystal with no concentration gradient and measuring the lattice parameter after each of several lathe turnings. The results are shown in Table 3. The extrapolations were made by plotting the lattice parameter calculated from a particular reflexion against the function $\frac{1}{2}\left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}\right)$ evaluated for the reflexion. It was found experimentally that plotting against this function gave a more linear plot than a simple $\cos^2 \theta$ extrapolation. The use of this function was originally proposed by J. B. Nelson and D. P. Riley³⁰, and tables of the function for various angles may be found in their paper. Figure 7 compares an extrapolation against this function with an extrapolation against $\cos^2 \theta$.

Unfiltered copper radiation was used when running these diffraction patterns. A total of nine (h 0 0) reflexions were obtained. These included both K α and K β reflexions. The seven reflexions of highest Bragg angle were used for extrapolation.

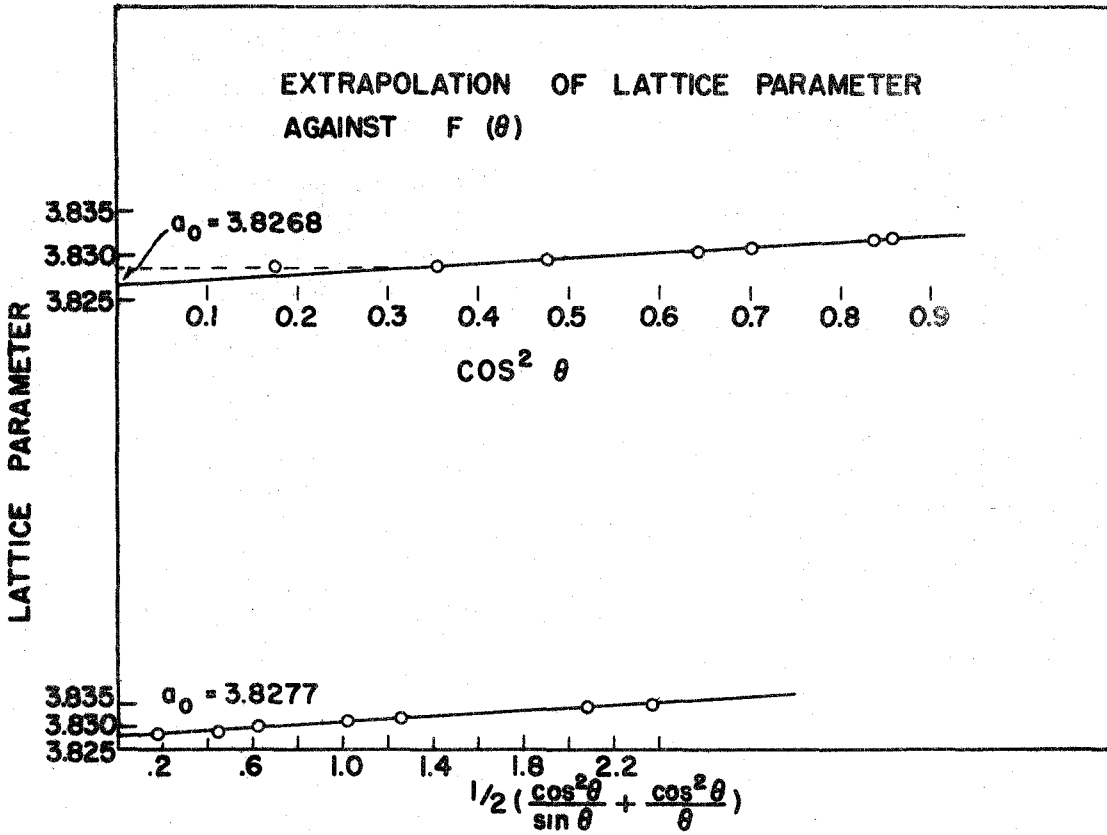


Figure 7. Extrapolation to Obtain Precision Lattice Parameter

Table 3

Reproducibility of Lattice Parameter Measurements

No.	Increment in centimeters	Lattice parameter	Deviation from average
A	0 x 10 ⁻³	3.8318	0 x 10 ⁻⁴
B	2.0 "	3.8314	-4 "
C	1.8 "	3.8319	+1 "
D	5.8 "	3.8319	+1 "
E	9.9 "	<u>3.8320</u>	+2 "
Average 3.8318 ± 0.0001 Å ^o			

D. Method of Treating Data

If the diffusivity was considered to be concentration dependent, the experimental conditions of this investigation presented a difficult set of boundary conditions for the solution of Fick's second law equation. In this effusion experiment there was a discontinuity in concentration at the crystal surface for all time values.

In order to avoid questionable assumptions, it was decided to seek diffusivity values from Fick's first law and to use the first law as the definitive expression for the diffusivity. The first step in the procedure was to plot a

family of curves of sodium concentration versus distance from the original crystal surface. This family of curves were plotted with time as the parameter. These curves represented values measured at a single temperature. The slope of any curve represented the concentration gradient at that point.

From the first family of curves, a second group of curves were plotted. These latter curves were of mass transfer against time with depth as a parameter. The mass transfer values were obtained from the first family of curves by measuring the area between the line representing the original concentration, ($t = 0$), and the line representing the final concentration at the time of interest, ($t = t_1$). This area was measured from infinite depth to the parametric depth. Infinite depth in this case represented the region of constant sodium concentration. The measured area represented the mass of sodium which had moved through unit cross-sectional area at the parametric depth during the period of the time parameter. The slopes of this second group of curves represented the rates of change of the mass transfer.

Pick's first law can be rewritten as

$$D(c) = - \frac{\left[(\partial m / \partial t)_{z = z_1} \right]_{t = t_1}}{\left[(\partial c / \partial z)_{t = t_1} \right]_{z = z_1}} \quad (23)$$

Thus diffusivity values are shown to be the ratio of two slopes. By measuring the slopes of the two families of curves discussed above, it was possible to calculate diffusivities. It was necessary that the measurements be made at corresponding coordinates. This correspondence in coordinates is shown by the subscripts in the equation. The subscripts inside of the brackets represent the parameter of the curve whose slope was measured. The subscripts outside of the brackets represent the abscissa at the point of measurement. Diffusivity values at different concentrations could be obtained since a particular combination of time and depth represented a single concentration.

IV. RESULTS

The diffusivity of sodium in $\text{Na}_{0.78}\text{WO}_3$ was measured at 832°C ., 752°C ., and 664°C .. The concentration-depth curves for these three temperatures are shown in Figures 8 to 10. The validity of the shape of the curves was inferred from additional measurements made on separate crystals when establishing the feasibility of effusion of sodium into a vacuum.

The mass transfer-time curves have been plotted in Figures 11 to 13. The points for the mass transfer-time curves were obtained by integrating the concentration-depth curves with a planimeter. The slopes of the two sets of curves were measured by the mirror technique³¹. The measured slopes and the calculated diffusivities are shown in Tables 4 to 6.

Since the measurements on the crystals were made at room temperature, the true diffusivity is found by correcting for the lattice expansion occurring between room temperature and the temperature of diffusion. The expansion coefficients were obtained from lattice parameter measurements made with a high temperature camera designed by P. Chiotti³². The data tabulated in Table 7 has been fit to the following formula by a least squares treatment:

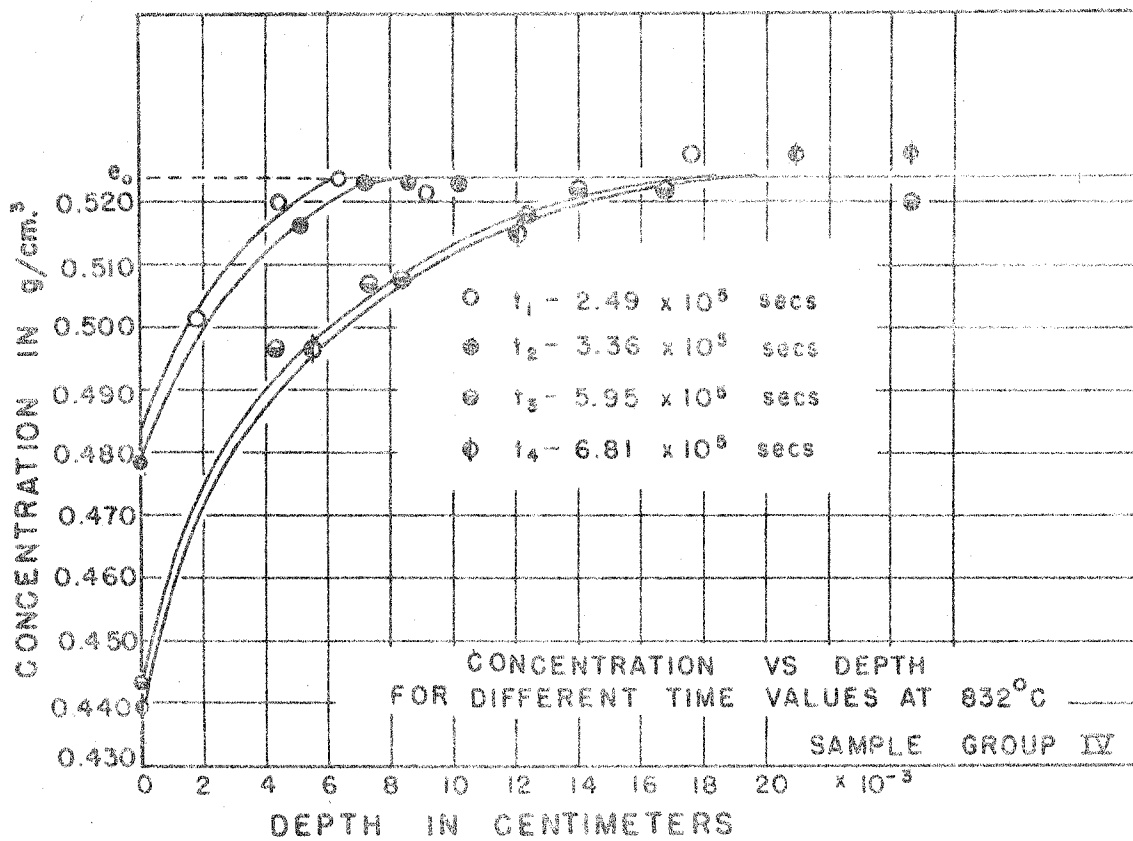


Figure 8. Concentration Versus Depth for Sample Group IV at 832° C.

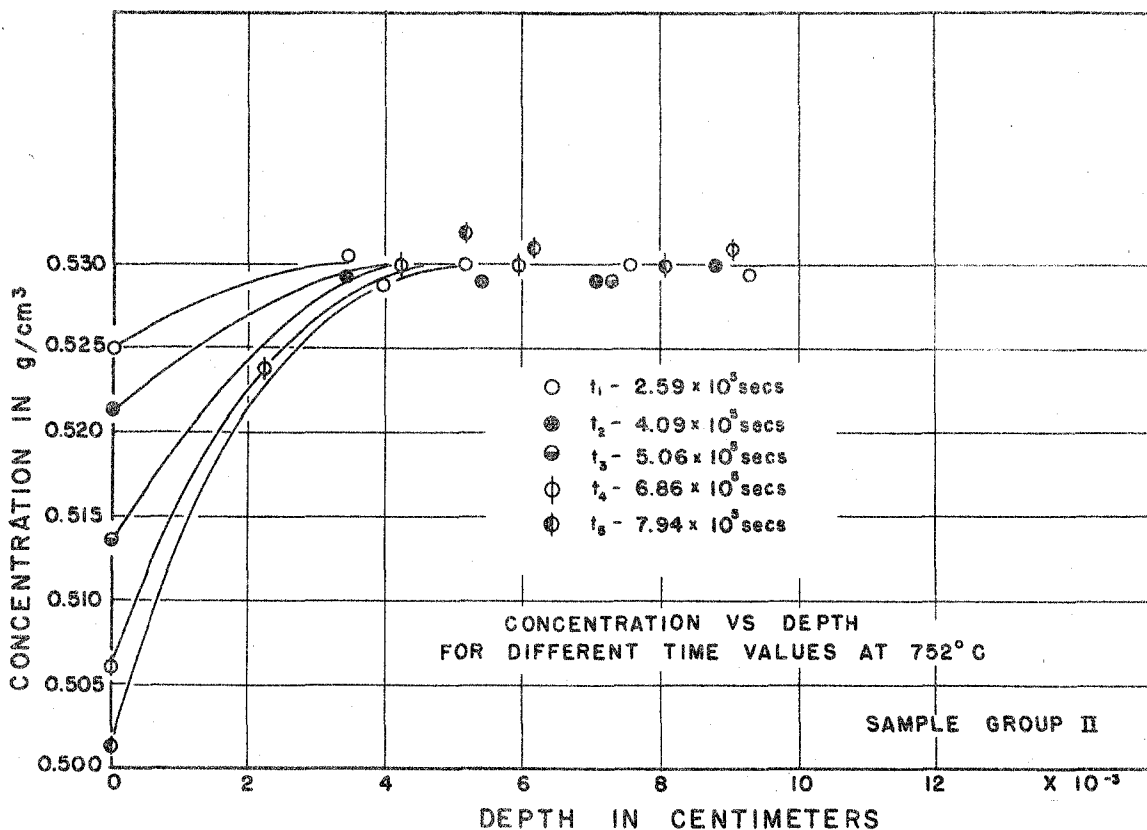


Figure 9. Concentration Versus Depth for Sample Group II at 752° C.

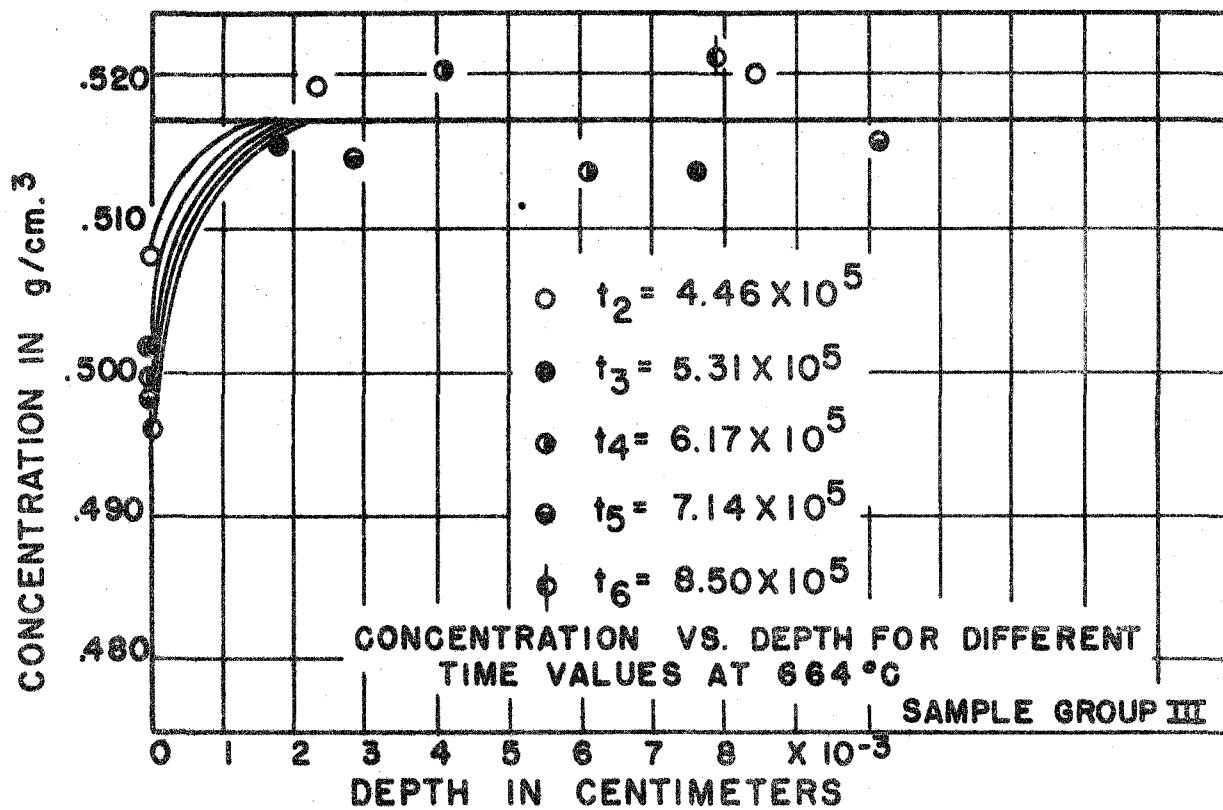


Figure 10. Concentration Versus Depth for Sample Group III at 664° C.

**MASS TRANSFER Vs TIME
AT VARIOUS DEPTHS.
(SAMPLE GROUP IV)**

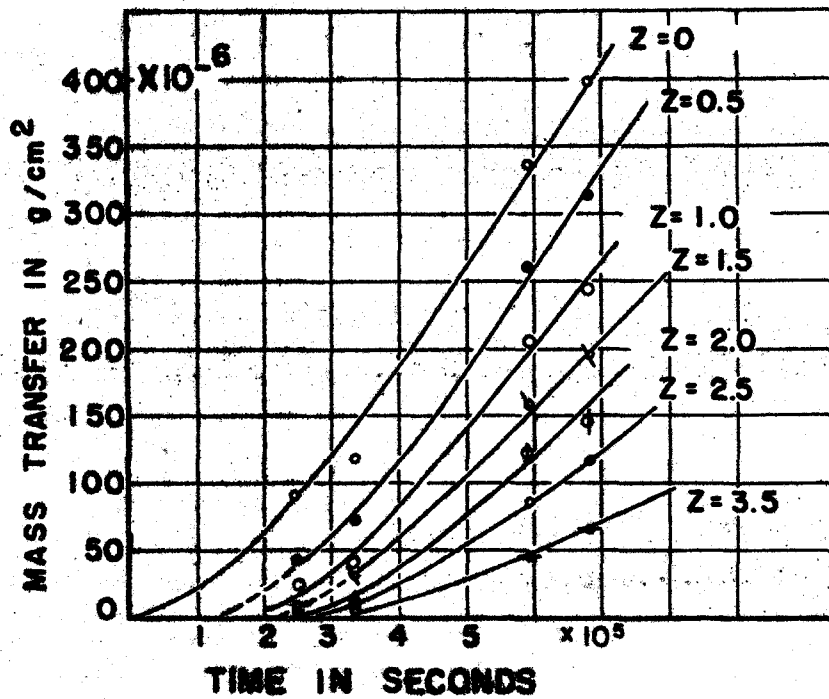


Figure 11. Mass Transfer Versus Time for Sample Group IV at $832^{\circ}C$.

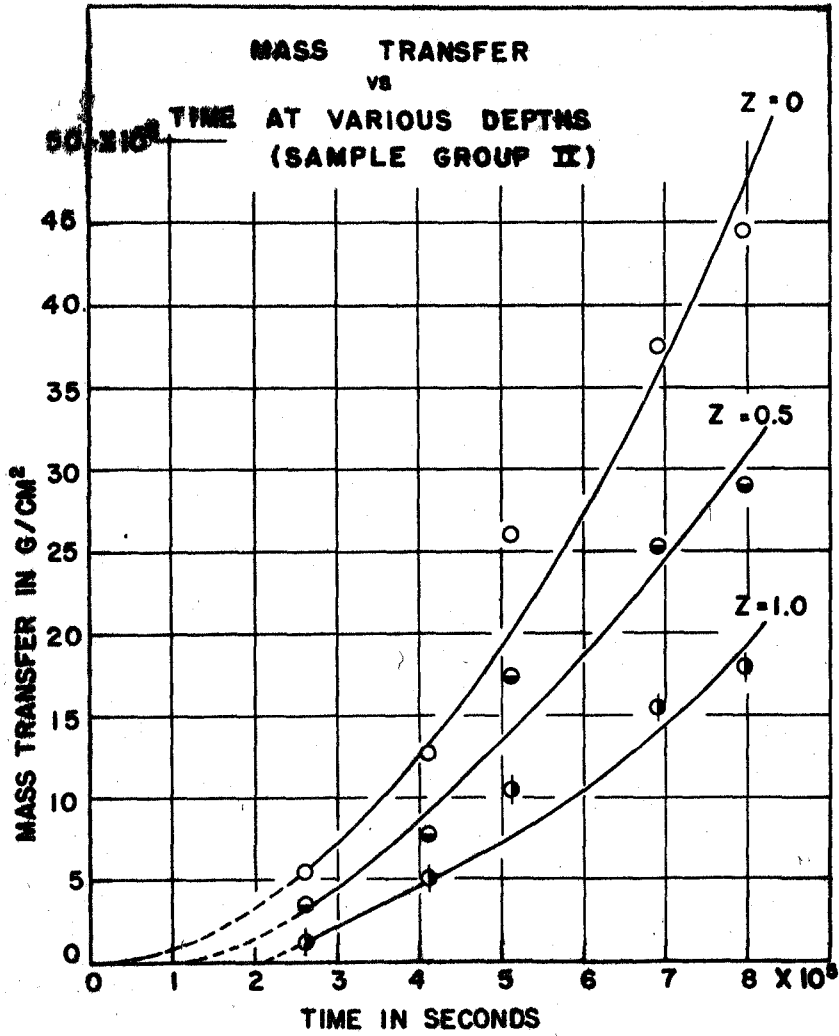


Figure 12. Mass Transfer Versus Time for Sample Group II at 752° C.

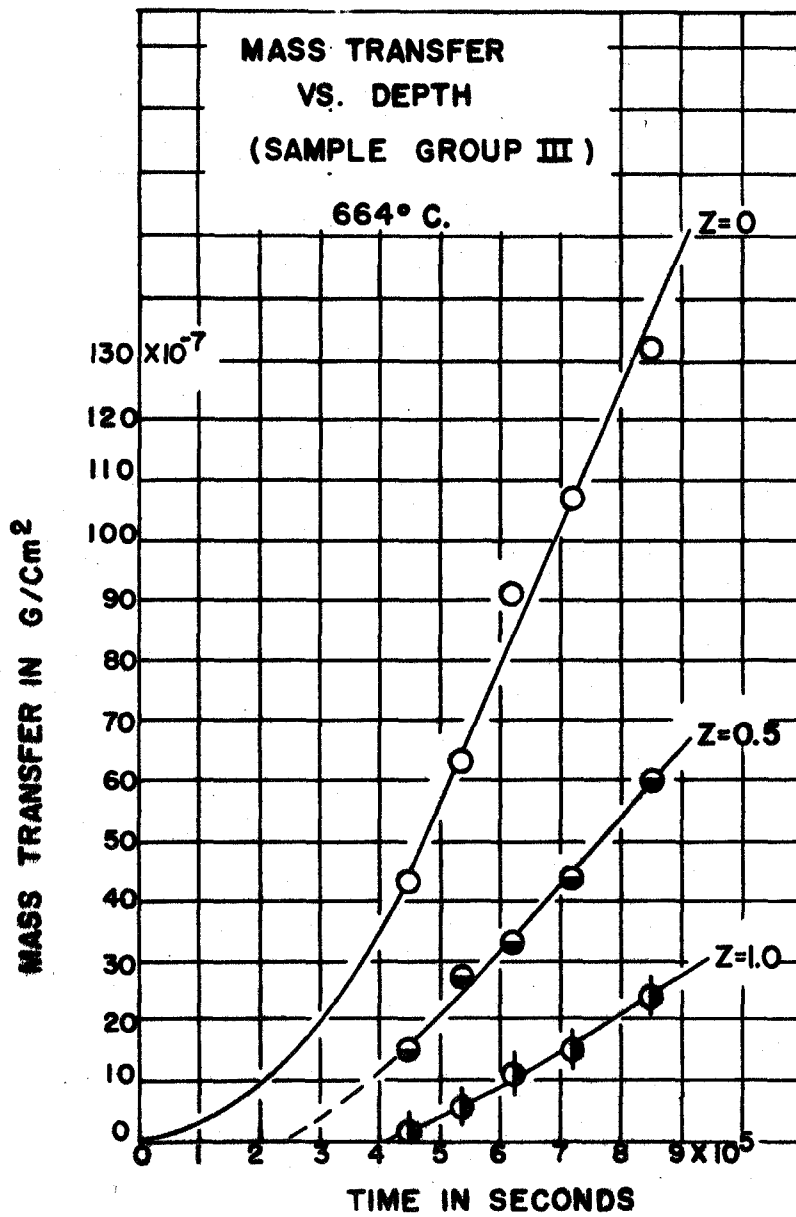


Figure 13. Mass Transfer Versus Time for Sample Group III at 664° C.

Table 4

Coordinates, Rate of Mass Transfer, Concentration Gradient, and Diffusivities for 832° C.

Depth in cm.	Time in sec.	$\frac{\partial m}{\partial t}$ in $\frac{g}{cm^2}$ sec.	$\frac{\partial c}{\partial z}$ in $\frac{g}{cm^4}$	D in $cm^2/sec.$
0	$x 10^{-3}$	6.81×10^5	75.6×10^{-11}	2.15×10^{-11}
0	"	5.95	74.6	1.67
0	"	3.36	62.1	4.81
0	"	2.49	53.7	4.71
1.3	"	6.81	74.9	5.72
1.3	"	5.95	75.5	6.19
1.3	"	3.36	50.9	6.36
1.3	"	2.49	38.7	4.45
2.5	"	6.81	64.5	7.93
2.5	"	5.95	65.4	8.05
2.5	"	3.36	46.2	8.64
2.5	"	2.49	29.8	4.79
3.8	"	6.81	54.9	8.47
3.8	"	5.95	50.5	9.10
3.8	"	3.36	35.5	7.54
3.8	"	2.49	24.1	5.15
5.1	"	6.81	51.1	9.94
5.1	"	5.95	44.8	9.91
5.1	"	3.36	24.5	7.68
5.1	"	2.49	11.3	4.81
6.4	"	6.81	37.0	7.89
6.4	"	5.95	34.4	8.49
6.4	"	3.36	18.1	7.90
8.9	"	6.81	22.8	9.05
8.9	"	5.95	22.4	9.11

Average Diffusivity: $6.8 \pm 0.5 \times 10^{-11} cm^2/sec.$

Table 5

Coordinates, Rate of Mass Transfer, Concentration Gradient, and Diffusivities for 752° C.

Depth in cm.	Time in sec.	$\frac{\partial m}{\partial t}$ in $\frac{g}{cm^2 \text{ sec.}}$	$\frac{\partial c}{\partial z}$ in $\frac{g}{cm^4}$	D in $cm^2/sec.$
0 x 10 ⁻³	7.94 x 10 ⁵	10.8 x 10 ⁻¹¹	14.4	7.5 x 10 ⁻¹²
0	6.86	9.1	10.2	8.9
1.3	7.94	6.5	10.3	6.3
1.3	6.86	5.9	8.56	6.9
2.5	7.94	4.6	8.80	5.2
2.5	6.86	4.2	6.89	6.1

Average Diffusivity: $6.8 \pm 0.7 \times 10^{-12} \text{ cm}^2/\text{sec.}$

Table 6

Coordinates, Rate of Mass Transfer, Concentration Gradient, and Diffusivities for 664° C.

Depth in cm.	Time in sec.	$\frac{\partial m}{\partial t}$ in g/cm ² sec.	$\frac{\partial c}{\partial z}$ in g/cm ⁴	D in cm ² /sec.
0 x 10 ⁻³	4.46 x 10 ⁵	23.0 x 10 ⁻¹²	19.7	11.7 x 10 ⁻¹³
0	5.31	23.0	36.3	6.34
0	6.17	23.0	44.4	5.18
0	7.14	23.0	48.3	4.76
0	8.50	23.0	34.4	3.04
0.5	4.46	9.24	5.54	16.7
0.5	5.31	10.1	8.99	11.2
0.5	6.17	10.4	10.7	9.72
0.5	7.14	11.0	12.0	9.17
0.5	8.50	11.3	13.9	8.13
1.0	4.46	4.52	3.08	14.7
1.0	5.31	5.06	4.59	11.0
1.0	6.17	5.74	5.15	11.1
1.0	7.14	5.96	5.89	10.1
1.0	8.50	6.71	7.23	9.28

Average Diffusivity: $9.7 \pm 0.8 \times 10^{-13}$ cm²/sec.

Table 7
Lattice Parameter Change with Temperature
for $\text{Na}_{0.8}\text{WO}_3$

	Temperature in °C.	Lattice parameter in Å
1st cycle	129	3.8450
	233	3.8469
	335	3.8518
2nd cycle	24	3.8423
	164	3.8453
	254	3.8495
	405	3.8547
	465	3.8557
	513	3.8571
	616	3.8589
680	3.8605	
3rd cycle	20	3.8422
	580	3.8579
	636	3.8595
	747	3.8620
Check	27	3.8424

Data used to calculate coefficients of linear expansion:

$$L = L_0 (1 + \alpha T + \beta T^2)$$

$$\alpha = 8.81 \times 10^{-6} \text{ per } ^\circ\text{C.}$$

$$\beta = -1.92 \times 10^{-9} \text{ per } ^\circ\text{C.}^2$$

Table 8

Temperature Corrected Diffusivities, Frequency Factor, and Activation Energy for $\text{Na}_{0.78}\text{WO}_3$

Temperature	Measured diffusivity	Correction factor for expansion	Corrected diffusivity
832° C.	6.8×10^{-11} cm ² /sec.	1.0116	6.9×10^{-11} cm ² /sec.
752° C.	6.8×10^{-12} "	1.0107	6.9×10^{-12} "
664° C.	9.7×10^{-13} "	1.0096	9.8×10^{-13} "

Calculated quantities:

(1) Frequency factor: $D_0 = 0.87 \pm 0.04$ cm²/sec.

(2) Activation energy: $\Delta H = 51.8 \pm 0.7$ kcal/mole

$$L = L_0 (1 + \alpha T + \beta T^2)$$

The calculated expansion coefficients were

$$\alpha = 8.81 \times 10^{-6} \text{ per } ^\circ\text{C.}$$

$$\beta = -1.92 \times 10^{-9} \text{ per } ^\circ\text{C.}^2$$

The uncorrected diffusivity, the correction factor, and the corrected diffusivity are listed in Table 8.

The temperature dependence of the diffusivities are shown in Figure 14. The graph shows that the data fit an equation of the Arrhenius type:

Temperatures: 832° C., 752° C., 664° C.

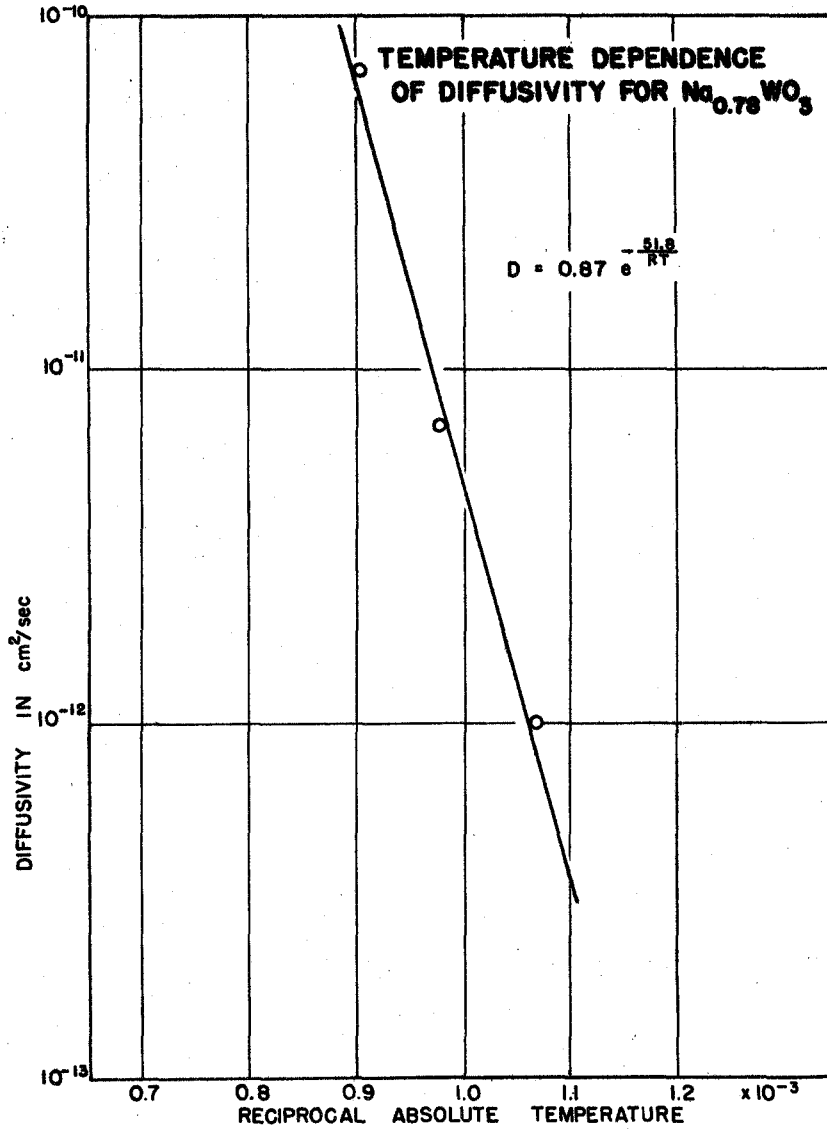


Figure 14. Temperature Dependence of Diffusivity for Na_{0.78}WO₃

$$D = D_0 \exp (-\Delta H/RT) . \quad (24)$$

The frequency factor, D_0 , was calculated to be 0.87 ± 0.04 cm²/sec. The activation energy, ΔH , was calculated to be 51.8 ± 0.7 kcal/mole. The frequency factor was of the correct order of magnitude predicted by current diffusion theory.

The errors involved in the determination were largely personal and not calculable. The depth measurements were made to ± 0.0001 cm. The standard deviation for the lattice parameter measurements shown in Table 3 was ± 0.0001 Å. This deviation represented a ± 0.001 g/cm³ deviation in the sodium concentration. The precision in these measurements was masked by the empirical fit of the concentration-depth curves to the measured points. The planimeter used in integrating the concentration-depth curves was read to two parts in ten thousand, but the significant error was the personal error in tracing the curve. The precision index listed for the average of the measured diffusivities is the standard deviation.

The magnitude of the sodium concentration change between initial and final value was intentionally kept small. This was done because diffusivity is a function of concentration, and it was desired to minimize the variation in the diffusivity. Justification of the averaging of

diffusivities measured at different concentrations was shown by plotting the measured diffusivities against sodium concentration. Nothing but random scatter was noted.

The magnitudes of the concentration gradients were not insignificant. An attempt was made to determine if Fick's first law was in this case a limiting law. Measured diffusivities were plotted against concentration gradient. An indefinite trend was noted in the direction of increasing diffusivity with decreasing concentration gradient. The magnitude of this trend was not considered significant.

V. DISCUSSION

A. This Investigation

Two conclusions may be made on the basis of this investigation. First, the existence of a large number of vacant sodium sites does not give rise to the rapid diffusion that was expected. Second, the experimental techniques used in this investigation combined with the data interpretation based upon Fick's first law provide a feasible approach to the study of diffusion.

Within the author's knowledge, the evaluation of diffusivities by taking the ratio of two slopes has not been done previously. The precision of this experimental method, taken as a whole, is not as good as that of the radioactive tracer technique. In addition the amount of time consumed in determining the diffusivity at a single temperature is greater than that consumed when using the tracer technique. The disadvantages are counterbalanced to some degree by the fact that several evaluations of the diffusivity at a given temperature can be made from one set of data. In general the method would not be recommended for studies in which the radioactive tracer technique could be used unless some particular advantage resulted. A specific example where the method might be used advantageously is the case in

which the effect of concentration gradient in diffusion is to be studied. The advantages in this latter case include a wide range of concentrations and concentration gradients plus the retention of steep gradients after very long periods of time. The discontinuity in concentration at the sample surface produces steep concentration gradients even after long periods of time whereas in the normal diffusion couple the gradients shallow with increasing time. It is evident that an effusion technique is limited to systems having one volatile component.

Before any measurements were made, it was expected that the rate of sodium diffusion through the sodium tungsten bronzes would be comparatively rapid. This expectation was based upon geometric considerations. If one assumes spherical packing and uses tabulated values³³ of the doubly charged oxygen ion, it is found that there is a hole 1.06 Å in diameter through which the sodium must pass when diffusing. This hole is centered in a square whose corners are occupied by four oxygens. Since the tabulated radius of the sodium kernel (singly charged sodium ion) was 0.98 Å, it was thought that the lattice distortion caused by passage of the sodium through the hole would be small. On this basis it was expected that the number of vacant sodium sites would govern the rate of diffusion. The number of

such vacant sites in the crystals used in the reported experiments was approximately one in five.

The actual measured activation energy was 51.8 kilogram calories per mole. Table 9 is included for a comparison of the measured activation energy for sodium diffusion in $\text{Na}_{0.78}\text{WO}_3$ with the activation energies found in other systems.

Table 9
Comparison of Some Reported Activation Energies

System	Reference	Activation energy
Ag in Ag	(34)	45.9 kcal/mol
Au in Cu	(34)	44.9
Co in Co	(35)	61.9
Co in Ni	(35)	68.3
Na in $\text{Na}_{0.78}\text{WO}_3$	(this report)	51.8

The measured activation energy was higher than expected. In a discussion of vacancy diffusion, C. Zener³⁶ has stated that the activation energy may be broken into two components: the energy necessary to form a vacancy of either the Frenkel or Schottky type, and the energy necessary for the diffusing atom to move from its equilibrium position to a position corresponding to the maximum of the potential barrier. Since the bronze crystals under consideration already had a considerable number of vacant sodium sites, the measured activation energy must represent the energy of lattice distortion caused by movement of the sodium from its equilibrium position to the jump site at the maximum of the potential energy barrier. Assumption of spherical packing and the use of tabulated radii is at best crude, but on the basis of the size considerations discussed above it would appear that the effective sodium radius is much greater than its tabulated ionic radius and that the valence electron which the sodium has contributed to the conduction band is still closely associated with the sodium kernel. Certainly, the presence of the sodium in the sodium tungsten bronzes as diamagnetic ions and free electrons does not mean that the sodium is ionic in the sense that sodium is ionic in sodium chloride.

An approximation of the entropy of activation may be made on the basis of an equation developed by C. Zener in

the paper cited above:

$$D_0 = \gamma a^2 \nu \exp (\Delta S/R) . \quad (25)$$

γ is a geometric factor which for the sodium tungsten bronzes is unity. The lattice parameter is a . ν is the Debye frequency for the diffusin species, and a reasonable order of magnitude for its value is 10^{13} per second. Using the measured value of the frequency factor and the appropriate values for the other terms, the entropy of activation, ΔS , is shown to be of the order of 0.01 kilocalorie per mole degree. Zener has also proposed in his paper an independent method of approximating this entropy. An independent evaluation of the entropy of activation would constitute a check on the measured frequency factor. However, this evaluation makes use of the temperature dependence of the elastic moduli and the melting point. Neither of these quantities is known for the bronzes.

An approximation of the frequency factor may be made on the basis of an equation proposed by S. Dushman and I. Langmuir³⁷. Their equation is

$$D_0 = a^2 \Delta H / N h . \quad (26)$$

N is Avagadro's number; h is Planck's constant; ΔH is the activation energy; and a is again the lattice parameter.

Substituting the appropriate values for the constants, the lattice parameter, and the measured activation energy shows the order of magnitude of the frequency factor to be $0.1 \text{ cm}^2/\text{sec}$. The measured value of the frequency factor was $0.87 \text{ cm}^2/\text{sec}$. This is considered satisfactory agreement since the Dushman-Langmuir equation is semi-empirical in nature and not as rigorous theoretically as Equation 19. In addition a relatively large error could be tolerated in the frequency factor without seriously affecting the accuracy of the activation energy since the activation energy is an exponential term.

The shape of the mass transfer-time curves is in agreement with what was expected. The rate of mass transfer is proportional to the product of the diffusivity times the concentration gradient. At any given depth, the sodium concentration will remain constant until some time ($t > 0$) when the concentration will begin to decrease and the mass transfer will become different from zero. An examination of the experiment will show that the concentration gradient at any depth other than the surface is a monotonically increasing function of time. The surface is excluded because it is the locus of discontinuity in the concentration gradient. For small concentration ranges, the diffusivity would be expected to remain nearly constant. Since the experiments

were carried out with the explicit purpose of keeping the concentration range small, the diffusivity would be only a proportionality constant, and the monotonic increase of the concentration gradient would reflect a proportional monotonic increase in the rate of mass transfer. This behavior is observed in the experimental plots.

B. Suggested Problems for Future Investigation

A list of problems for future investigation which might be suggested on the basis of the results obtained is:

1. Confirm the validity of the measured values by an independent experimental procedure, preferably the radioactive tracer technique.
2. Study both the activation energy and diffusivity as functions of concentration.
3. Repeat the experimental procedure used in this investigation using prolonged heating times to obtain very large concentration changes. It might then be possible to obtain some correlation between diffusivity and concentration or between diffusivity and concentration gradient.
4. Introduce impurities when growing the crystals to determine what effect the lattice strains, dislocations, and imperfections associated with the impurities have upon the diffusion rate.

A second determination of the activation energy and frequency factor by an independent method is desirable. The radioactive tracer method of determining diffusion values is

the most reputable. The major problem in applying that method to the study of sodium diffusivity in the sodium tungsten bronzes appears to be the problem of bonding a thin layer of radiosodium to the bronze surface. This layer should have a high specific activity and preferably be carrier free. One possibility that seems worthy of investigation is to bombard magnesium with neutrons. This produces the positron emitting Na^{22} . The Na^{22} could be separated from the magnesium matrix and plated onto a bronze crystal with a mass spectrograph. Experimentation would be necessary to determine the feasibility of this procedure.

The investigation of activation energy as a function of sodium concentration would provide information as to the relative roles of the number of vacant sodium sites and of the distortion energy accompanying a sodium jump. It seems inescapable that the number of vacant sodium sites must affect the rate of sodium diffusion. This would seem to be especially true at high sodium concentration because the probability of a particular sodium atom being adjacent to a vacancy decreases as the number of occupied sodium sites increases. Hence, the diffusivity would tend to decrease, and since on theoretical grounds the frequency factor is expected to remain between $1.0 \text{ cm}^2/\text{sec.}$ and $0.01 \text{ cm}^2/\text{sec.}$, the activation energy would be expected to increase. On

the other hand, it is conceivable that the activation energy might decrease with increasing sodium concentration since the lattice is expanded at higher sodium concentrations and less strain would be expected to accompany sodium diffusion.

Analogies between diffusion of sodium in the sodium tungsten bronzes and diffusion in systems involving substitutional solid solution should be made with caution. It is true that for high sodium concentrations the sodium tungsten bronzes may be considered as having a defect lattice. However, the situation differs from the ordinary defect lattice because the vacant sites in the bronzes are supposedly capable of being occupied only by sodium. In this sense the case of sodium diffusion in sodium tungsten bronze, even at high sodium concentration, should be considered more nearly analogous to interstitial diffusion. Even so, studies of diffusion rates in bronzes of high sodium concentration and with a relatively small number of vacant sites might provide some information relevant to the vacancy mechanism of diffusion. These studies would be even more interesting if they were enhanced by measurements made on crystals known to contain dislocations and imperfections since dislocations and imperfections are thought to be one source of lattice vacancies. The use of steep concentration gradients provides

one method of obtaining such dislocations and imperfections; a second method is to grow crystals containing introduced impurities. The sodium tungsten bronzes seem to be the unusual case of an interstitial solid solution which is capable of becoming saturated.

VI. SUMMARY

This investigation was undertaken to study the process of sodium diffusion in single crystals of the metallic sodium tungsten bronze. Concentration gradients were established by effusion of sodium from single crystals into a vacuum. The concentration gradients were measured by means of an x-ray determination of a precision lattice constant, subsequently making use of the Vegard's law relationship to evaluate the sodium concentration. Advantage was taken of the high absorption of copper x-radiation in the sodium tungsten bronze in order to measure the lattice parameter of an exposed crystal surface.

The diffusivity was evaluated by a method which to the author's knowledge has not been previously suggested or used. This method was based upon Fick's first law rather than his second. The data obtained from a series of crystals held at constant temperature for varying times gave a family of curves showing the concentration as a function of depth with time as a parameter. From these curves the mass of sodium transferred through a plane parallel to the surface and at any particular depth was plotted as a function of time. The slope of this curve divided by the

concentration gradient, both evaluated at the same time and depth, was the diffusivity for the corresponding concentration.

Three such series of crystals were run: one each at 664° C., 752° C., and 832° C. Diffusivities were evaluated for a bronze formula of $\text{Na}_{0.78}\text{WO}_3$. The evaluated diffusivities were fit to an Arrhenius type equation:

$$D = D_0 \exp(-\Delta H/RT) \quad (27)$$

$$D_0 = 0.87 \text{ cm}^2/\text{sec}$$

$$\Delta H = 51.8 \text{ kcal/mol} .$$

In conjunction with the diffusion studies it was necessary to determine the coefficients of linear expansion. For $\text{Na}_{0.8}\text{WO}_3$ the following expansion formula is valid:

$$L = L_0 (1 + 8.81 \times 10^{-6} T - 1.92 \times 10^{-9} T^2) . \quad (28)$$

In this equation L is any linear length and T is the temperature in °C.

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VIII. ACKNOWLEDGMENTS

The author wishes to express his gratitude to the Ames Laboratory for providing the facilities and equipment used in this investigation.

Sincere appreciation is tendered to Dr. G. C. Danielson for the constant advice, interpretation, and criticism without which this thesis could not have been prepared.

Especial thanks are due to Dr. H. A. Wilhelm for his encouragement and for his help in making the investigation possible.

For his suggestions, assistance, and for the use of his high temperature x-ray equipment, the author is deeply indebted to Dr. P. Chiotti.

For their perserverance, faith, and assistance, the author wishes to thank Mr. J. Anderson and Miss S. Shaw.

To all the members of the Ames Laboratory who so generously lent their time and talents to this investigation, the author wishes to express his sincere appreciation.