

SELF-DIFFUSION IN ALPHA BRASS

by

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ABSTRACT

The diffusivity of Zn^{65} in an alloy of 17 atomic per cent Zn and 83 atomic per cent Cu has been measured over the temperature range 730-950 °C, using radioactive tracer techniques. The temperature dependence of the diffusion coefficient is given by:

$$D_{Zn} = 0.44 \exp -(42,800/RT) \text{ cm}^2/\text{sec}.$$

Corrections of the diffusion coefficients for small differences in specimen composition have been made using the theory of Hoffman, Turnbull, and Hart. The temperature dependence of the b correction factor has been measured as:

$$b_{Zn} = 228.9 \exp (9560/RT) \text{ cal/mole}.$$

Comparison of results with other tracer measurements and with chemical diffusion measurements has been made. A semi-quantitative comparison of theory and experimental data is presented.

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1. INTRODUCTION

Problems dealing with the rate of diffusion of zinc and copper in brass alloys have been investigated by several workers. Most of these investigations have been performed by a technique involving sectioning and chemical analysis. Activation energies obtained by different investigators have shown little agreement. This activation energy is a measure of the thermal energy required to form vacancies in a crystal, and to cause atoms to jump from their lattice sites into these vacancies. The activation energy, Q , for a brass alloy containing 17 atomic per cent zinc will be used as a comparison feature of the following experimental studies.

The earliest precise work, that of Rhines and Mehl (1), was done on polycrystalline brass bars which were electroplated with copper. Plated specimens were placed in diffusion furnaces and annealed at various temperatures for periods up to three months. Following the annealing operation, the outside copper plate was machined off in a precision lathe. An even number of cuts were taken on both

sides of the brass-copper interface. Distances from the original interface for each cut were measured with micrometers. Sections cut from the bars were chemically analyzed for copper content, and the zinc content was obtained by difference. From these data, a plot of composition versus distance from the original interface was made.

Analysis of data was done by the Matano equation which is:

$$D = \frac{1}{2t} \frac{dx}{dc} \int_0^c x \, dc. \quad (1-1)$$

In this equation D is the diffusion coefficient in cm^2/sec , t is the time in seconds, dx/dc is the slope of the penetration curve at the concentration c , and $\int_0^c x \, dc$ is the area enclosed by the curve, the interface and the limits of concentration 0 and c . The interface in this case is not the original interface, but is defined as that point where equal numbers of atoms have passed in opposite directions. This interface, known as the Matano interface, is at the penetration distance, x , such that areas on either side of x enclosed by the penetration curve are equal.

Using a graphical solution of the Matano equation, Rhines and Mehl (1) obtained an activation energy of 32,000 calories per mole.

Corrections for the chemical activity of the components in the alloys used by Rhines and Mehl were applied to the respective diffusion coefficients by Birchenall and Mehl (2). These corrections were applied using the assumption that chemical activity, not chemical concentration is the driving force in the diffusion process. The individual diffusion coefficients were corrected using the following equation:

$$D = \frac{D(\text{exp.})}{\left| V_1 + c_1 \frac{dV_1}{dc_1} \right| \left| V_2 + c_2 \frac{dV_2}{dc_2} \right|} \quad (1-2)$$

D is the corrected diffusion coefficient, $D(\text{exp.})$ is the experimental diffusion coefficient, V_1 and V_2 are the activity coefficients of the components whose compositions are c_1 and c_2 respectively, dV_1/dc_1 and dV_2/dc_2 are the slopes of the activity coefficient-composition curves at compositions c_1 and c_2 .

The activation energy obtained by this method was a questionable 30,000 \pm 50 per cent calories/mole.

Experiments done by da Silva and Mehl (3) repeated the work of Rhines and Mehl. The only difference was that inert wire and foil markers were also used to measure the diffusion coefficient using the Kirkendall effect (4). The activation energy measured by this technique was approximately 40,000 calories per mole.

Further work by Horne and Mehl(5) using the sectioning-and-chemical-analysis technique in addition to marker-movement measurements yielded an activation energy of approximately 37,000 calories per mole.

It is apparent that the technique of sectioning and chemical analysis has not produced consistent results. LeClaire (6) has expressed doubt concerning the precision of the diffusion coefficients obtained by this method because of the large composition gradient present in the specimens, and the Matano analysis of the data.

Some of the failings of this technique are that only an average diffusion coefficient is measured, that is, only some average activation energy for both components in the alloy is measured, and the individual activation energies of the separate components are not determined.

Recent availability of high specific activity radioisotopes has allowed a more refined method of measuring diffusion coefficients and determining activation energies. This method, described by Tomizuka (7), has been the basis of the more recent diffusion measurements.

2. OBJECTIVE

The purpose of this investigation was to determine the activation energy and frequency factor for volume diffusion of zinc in a brass alloy containing 17 atomic per cent zinc. It was intended that this investigation would furnish diffusion data of higher precision than those available from earlier studies employing other techniques. It was also intended that the results of this study, in conjunction with those of recent works using radioactive tracers would provide additional information on the relation between diffusion coefficients and solute concentration in alpha brass.

3. THEORETICAL BACKGROUND

3.1 Fick's Laws

The diffusion of atoms in a homogeneous alloy system is described by Fick's first and second laws (8). If the diffusion is unidirectional, Fick's first law states:

$$J = -D \frac{dc}{dx} \quad (3.1-1)$$

where J is the flow of atoms across a unit area, c is the concentration of the tracer atom, x is the depth of penetration, and D is the diffusion coefficient. In the radioactive-tracer technique, the concentration c is assumed to be negligible and does not affect the composition of the alloy. As a result of these conditions, D is a constant independent of the depth of penetration x , and the surface concentration of the isotope c_0 . Assuming continuity of mass and volume across the diffusion area, the second form of Fick's law is:

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (3.1-2)$$

Imposing the boundary conditions of a semi-infinite

crystal on whose face is plated an infinitely thin layer of diffusion atoms, the solution(9) for equation (3.1-2) is:

$$c(x, t) = \frac{c(0, 0) \exp(-x^2/4Dt)}{\sqrt{(\pi Dt)}} \quad (3.1-3)$$

Substituting specific activity A for the concentration:

$$A(x, t) = \frac{A(0, 0) \exp(-x^2/4Dt)}{\sqrt{(\pi Dt)}} \quad (3.1-4)$$

Taking the natural logarithm of equation (3.1-4):

$$\ln [A(x, t)] = \ln \left[\frac{A(0, 0)}{\sqrt{(\pi Dt)}} \right] - (x^2/4Dt) \quad (3.1-5)$$

Differentiating with respect to x^2 :

$$\frac{d[\ln A(x, t)]}{d(x^2)} = \frac{-1}{4Dt} \quad (3.1-6)$$

Transposing equation (3.1-6):

$$D = \frac{-1}{4Dt \, d(\ln A)/d(x^2)} \quad (3.1-7)$$

Thus if the common logarithm of the activity is plotted versus the square of the penetration distance, the diffusion coefficient may be determined from:

$$D = \frac{-1}{(2.3025)(4)(t)(\text{slope})} \quad (3.1-8)$$

It has been found that diffusion coefficients are related to temperature by an Arrhenius equation:

$$D = D_0 \exp -(Q/RT) \quad (3.1-9)$$

Taking the natural logarithm of equation (3.1-9):

$$\ln D = \ln D_0 - Q/RT \quad (3.1-10)$$

Differentiating with respect to $1/T$:

$$\frac{d(\ln D)}{d(1/T)} = -Q/R. \quad (3.1-11)$$

Transposing:

$$Q = -R \frac{d(\ln D)}{d(1/T)}$$

If the common logarithm of each diffusion coefficient is plotted versus the reciprocal of the absolute diffusion temperature, the activation energy, Q , may be determined from:

$$Q = (2.3025)(R)(\text{slope}). \quad (3.1-13)$$

3.2 Theory of Hoffman, Turnbull, and Hart

A theory explaining the enhancement of solute diffusion in an alloy as the solute concentration is increased has been proposed by Hoffman, et al. (10), and Hart, et al. (11). Although a theory describing both solvent and solute diffusion enhancement has been presented by these authors, only the effect of solute enhancement is of interest in this paper.

Figure 1 is present in the interest of clarity and will aid in the explanation of the theory.

Let:

- v_1^0 = The exchange frequency of a lattice vacancy with a solvent atom outside the first coordination shell of the solute.
- v_1^1 = The exchange frequency of a lattice vacancy with a solvent atom in the first coordination shell of the solute.
- v_2 = The exchange frequency of a solute and a lattice vacancy.
- X_v^0 = The fraction of vacant lattice sites outside the first coordination shell of the solute.
- X_v^1 = The fraction of vacant lattice sites in the first coordination shell of the solute.

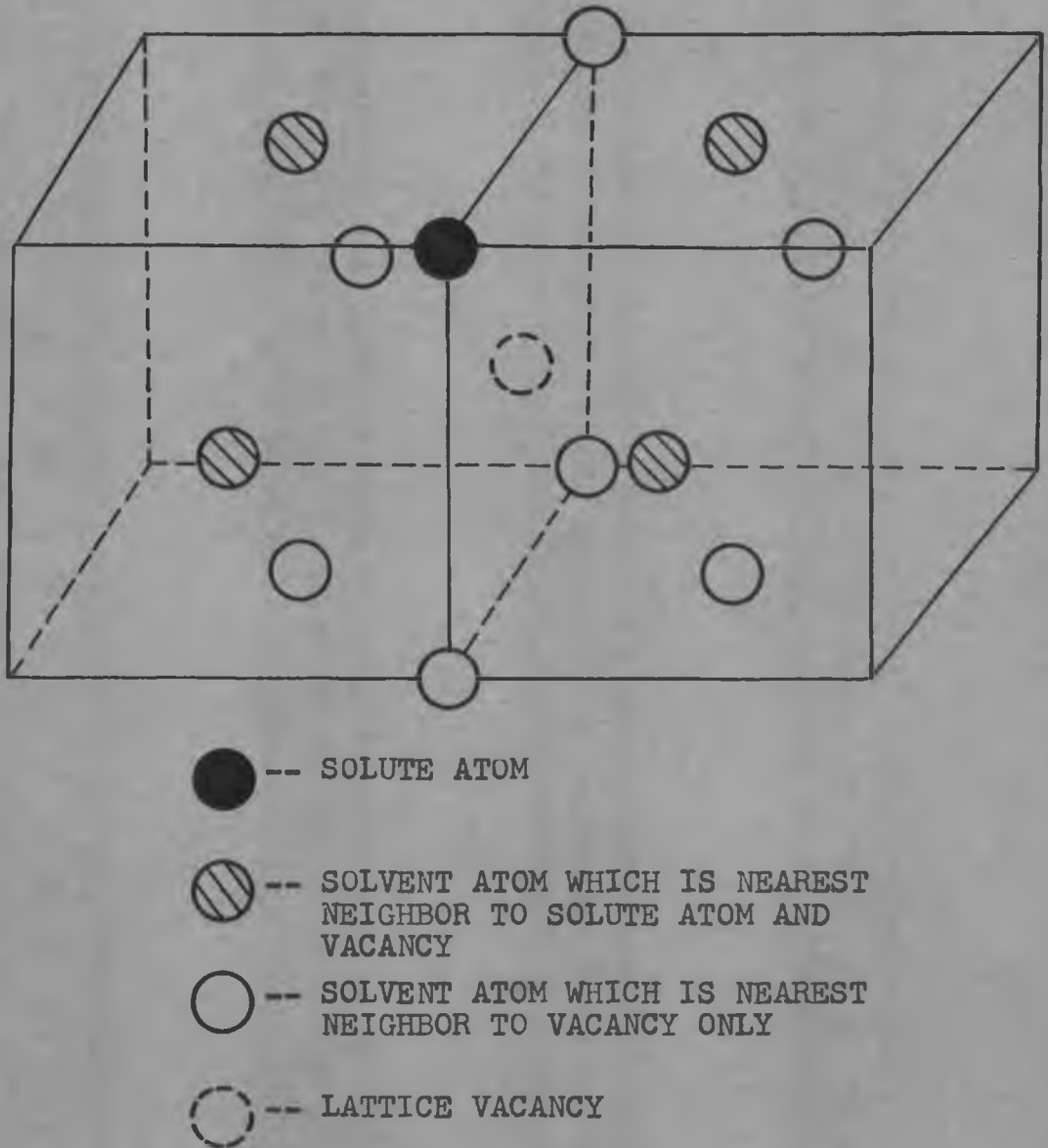


Fig. 1. Face-centered-cubic structure exhibiting a solute atom, a vacancy, and nearest neighbor solvent atoms.

It is assumed that the disturbed region immediately surrounding the solute atom is only one coordination shell in radius.

Diffusion is considered to be a two-step process, first a solute atom will exchange with the vacancy, secondly a solvent atom will exchange with the same vacancy. Thus the frequency, f_2 , of a solute diffusion jump is the product of the solute-vacancy exchange frequency v_2 , the vacancy concentration near the solute, X_v' , and the probability p_1 that the vacancy in the first coordination shell of the solute will exchange with a solvent atom.

Since:

$$p_1 = \frac{(4v_1' + 7v_1^0)}{(4v_1' + 7v_1^0 + v_2)} \quad (3.2-1)$$

$$\text{then: } f_2 = (v_2)(X_v')(p_1). \quad (3.2-2)$$

It has been shown (12) that the solute self-diffusion coefficient would reduce to:

$$D_2 = 1/6 \lambda^2 f_2 \quad (3.2-3)$$

where λ is the migration distance of the solute in the vicinity of the solvent and the vacancy.

If the rate of solute diffusion is primarily governed by the solute-vacancy exchange mechanism, then, $(4v_1' + 7v_1^0) \gg v_2$ and equation (3.2-3) reduces to:

$$D_2 = (1/6) v_2 \lambda^2 X_v^{-1}. \quad (3.2-4)$$

If the rate of solute diffusion is primarily governed by the solvent-vacancy exchange while in the first coordination shell of the solute, then $v_2 \gg v_1' \gg v_1^0$ and:

$$D_2 = (2/3) v_1' \lambda^2 X_v^{-1}. \quad (3.2-5)$$

If the rate of solute diffusion is primarily governed by the solvent-vacancy exchange outside the first coordination shell of the solute, then $v_2 \gg v_1^0 \gg v_1'$ and;

$$D_2 = (7/6) v_1^0 \lambda^2 X_v^{-1}. \quad (3.2-6)$$

The above explicit theoretical treatment is difficult to evaluate since much of the necessary data are not available. Since this is the case, Hoffman, et al. (10) have proposed empirical equations of the form:

$$D(X) = D(0) \exp (1+bX) \quad (3.2-7)$$

and,

$$D(X) = D(0) \exp (bX) \quad (3.2-8)$$

where $D(X)$ is the diffusion coefficient of the solute in an alloy of composition X , $D(0)$ is the diffusion coefficient of the solute in the pure solvent, and b is a measure of the increased diffusivity of the solute

caused by an increase of the solute concentration X. Since b is related to temperature by an Arrhenius equation, it is a measure of the increase in the number of vacancies and the increase of the appropriate exchange frequencies.

4. EXPERIMENTAL PROCEDURE

4.1 Specimen Preparation

A large polycrystalline ingot of alpha brass containing approximately 17 atomic per cent zinc was prepared by melting together weighed amounts of spectrographically pure materials. The metals were placed in a graphite crucible and melted under a nitrogen atmosphere in a high frequency induction furnace in an effort to obtain a homogeneous alloy. The ingot was sent to Dr. C. M. Glass of the Ballistics Research Laboratories, Aberdeen Proving Grounds, Maryland, where several attempts were made to grow a single crystal using a modified Bridgman technique. The best product of these attempts was a polycrystal, 1.25 cm in diameter by 11 cm in length consisting of four to five columnar grains. It was observed that a concentration gradient of zinc in the alloy resulted from the passage of the melt through the Bridgman furnace. Because of this gradient, specimens for the diffusion experiment were chosen over the center section of the ingot.

The polycrystal was axially mounted in a two-inch

diameter plexiglass tube. Plaster of Paris was poured around the ingot in order to prevent any undue stressing during the subsequent cutting operation.

A high-speed, water-cooled, Alundum cutting wheel was used to cut the ingot into nine right cylindrical sections. Following the cutting operations, the specimens were ground flat on graded emery papers, and heavily electropolished to remove the worked metal. The polished sections were sealed in a quartz tube under one atmosphere of argon, and annealed for eight hours at 550 °C. A visual examination of each specimen was made for evidence of recrystallization. One of the specimens did show some recrystallization and was not used in the experiment. A Laue back-reflection photograph of one of the sections was taken to determine if any residual stress remained in the material. The sharpness of the Laue spots confirmed that the specimens were stress free. The faces of the specimens were photographed and are shown in Fig. 2.

A high-purity radioisotope of Zn^{65} was obtained from the Oak Ridge National Laboratory. Approximately 2 millicuries were received in the chemical form of $ZnCl_2$ dissolved in HCl. The plating solution was made by diluting approximately two drops of solution in 50 milliliters of distilled water.

Fig. 2 Photographs of diffusion specimen surfaces. Enlarged 2X in reproduction.



SPECIMEN NO. 8



SPECIMEN NO. 7



SPECIMEN NO. 6



SPECIMEN NO. 5



SPECIMEN NO. 4

A platinum wire was used as the anode and the diffusion specimen as the cathode in the plating procedure. The current density varied from 1.3 to 2.0 milliamperes per square centimeter during the 20 minute plating period. The plating on the specimen was very light, and was estimated as 50 to 1000 Å thick.

Each diffusion specimen was individually sealed in a Vycor capsule under one atmosphere of argon. The purpose of the argon atmosphere was to minimize the loss of zinc from the surface of the alloy.

4.2 Diffusion Anneals

Diffusion anneals were carried out in a linear resistance furnace. Temperatures were controlled to $\pm 1/2$ °C through the use of a control system utilizing a platinum resistance thermometer as one leg of an ac-resistance-bridge balancing circuit. This control system has been described in detail by Tomizuka and Zimmerman(13). Temperatures were measured with a Leeds and Northrup millivolt potentiometer using a calibrated Pt-10%Pt-Rh thermocouple.

The diffusion anneal was carried out in the following manner. The furnace was heated to the desired temperature and allowed to stabilize for 24 to 48 hours. The encapsulated specimen was then placed in the furnace and a heat-up curve was determined by

measuring the temperature at time intervals following the insertion of the capsule. The furnace normally returned to a temperature 5 °C below the equilibrium temperature approximately 10 minutes after the sample was inserted. The time at which the furnace reached this temperature was recorded as the start of the diffusion anneal. After the specimen had remained in the furnace the desired length of time, from 6 to 27 hours, the capsule was quickly removed and quenched in a beaker of water. Running water was poured into the beaker to cool the specimen as quickly as possible. The time at which the specimen was quenched was recorded as the finish of the anneal.

4.3 Sectioning

After quenching, the specimen was removed from the capsule and placed in a Rivett precision lathe. The lathe is equipped with an adjustable chuck which allows the face of the diffusion specimen to be aligned perpendicular to the lathe axis. During the cutting operation the specimen was entirely enclosed in a plexiglass box in order to prevent loss of chips. After the face of the specimen had been adjusted to perpendicularity, a side cut of 40 to 50 mils was taken to eliminate the effects of radial and surface

diffusion. The amount of material removed was determined from the relation, $x = 10(D't)^{1/2}$, where x is the depth in cm to be removed, t is the length of the anneal in seconds, and D' is an overestimated value of the diffusion coefficient. The surface of the specimen was then rechecked for perpendicularity, and the cutting tool was zeroed by using a Simpson ohm-meter, and an electrically insulated cutting tool. Cuts ranging from 0.7 to 1.8 mils in thickness were taken off the face of the specimen. The thickness was measured with a dial indicator calibrated in 0.1 mil increments. Total number of cuts varied from 12 to 18 and total cut thickness varied from 8 mils to 28 mils. Individual cuts were placed in small glass vials, and the chips were pressed to the bottom of the vial to maintain consistent counting geometry.

4.4 Counting and Weighing

Counting was done in a scintillation gamma-ray counter using a well-shaped, thallium-doped, sodium iodide crystal. The equipment consisted of a Baird-Atomic model 312. A super-stable high voltage power supply, a Baird-Atomic non-overloading amplifier, a Radiation Instrument Development model 32-2 pulse height analyzer, and a Radiation Instrument Development Laboratory model 49-22 scalar.

Counting was done on the 112 mev gamma peak of the Zn⁶⁵ isotope. A two-volt channel width was used to bracket the peak. Background radiation was measured before and after counting and an average background correction was made to the data. Because of the 247 day half-life of this isotope, no correction was necessary for decay during counting.

Each cut was weighed on a Mettler semi-micro balance to a precision of 0.02 milligrams.

A plot of the specific activity (counts/min/mg) versus distance squared (cm^2) was made from the measured data for each of the five diffusion anneals. In each case a straight line was obtained when these data were plotted on semi-logarithmic paper. The diffusion coefficient for each annealing temperature was determined from the slope of each line.

4.5 Chemical Analysis

As was stated previously, a concentration gradient was present in the ingot. It was necessary to know the precise composition of each specimen in order to correct the diffusion coefficient to a uniform composition value.

A 250 milligram section for chemical analysis was taken from each specimen immediately following the sectioning procedure. The section was taken

from an area adjacent to the diffusion surface.

An electrolytic plating procedure described by Low(14) was used to determine the composition of each specimen. The sample was dissolved in 8 ml HNO_3 , 8 ml H_2O , and 1 ml H_2SO_4 . The solution was diluted to approximately 100 ml and placed in the plating apparatus. This apparatus consisted of a 6-volt battery, an ammeter, a voltmeter, a platinum-gauze cathode, and a platinum-wire anode. A direct current supply of 2.5 volts and 0.2 amps was maintained during the 4-hour plating process. No zinc was plated from solution since the electrode potential was far below the 6.5 volts required to plate zinc. Continuous stirring of the solution was used to obtain a strong, uniform plate. All weighings were done on a Mettler semi-micro balance to a precision of 0.02 mg. A precision of $\pm 0.01\%$ was obtained with method of chemical analysis. The above precision was checked by determining the recovery of a pure copper sample.

Since only the copper content was determined chemically, the zinc content was determined by difference.

5. EXPERIMENTAL DATA

Tables I through V contain the pertinent data gathered in this investigation. When these data are plotted, Figs. 3 through 7 result, showing the relation of the square of the penetration distance to the log of the specific activity. Fig. 8 is a graphical representation of the zinc concentration gradient in the ingot used in this experiment.

TABLE I
ACTIVITY-PENETRATION DATA FOR SPECIMEN NO. 4

CUT NO.	WEIGHT OF CUT (mg)	THICKNESS OF CUT (cm x 10 ⁴)	SPECIFIC ACTIVITY (Counts/min mg)	PENETRATION DIST. \bar{x}^2 (cm ² x 10 ⁴)
4-1	13.94	23.03	303.9	0.01
4-2	12.55	20.73	300.8	0.11
4-3	15.01	24.79	299.3	0.31
4-4	14.30	23.62	291.7	0.65
4-5 *	17.29	28.56	281.6	1.13
4-6 *	18.27	30.18	248.9	1.85
4-7 *	25.86	42.71	224.0	2.97
4-8 *	28.81	47.59	180.0	4.73
4-9 *	22.64	37.40	147.1	6.76
4-10 *	29.85	49.31	103.8	9.19
4-11 *	27.82	45.95	74.0	12.31
4-12 *	27.53	45.47	48.5	15.73
4-13 *	29.45	48.64	29.1	19.68
4-14 *	29.84	49.29	16.3	24.27
4-15 *	24.20	39.97	9.6	28.86
4-16	26.09	43.09	4.4	33.49
4-17	26.99	44.58	2.3	38.77
4-18	24.08	39.77	1.2	44.19

TEMPERATURE = 950.3 °C

TIME = 21,990 sec

COMPOSITION = 14.88 a/o Zn

* POINTS USED IN LEAST SQUARES SOLUTION.

TABLE II
ACTIVITY-PENETRATION DATA FOR SPECIMEN NO. 5

CUT NO.	WEIGHT OF CUT (mg)	THICKNESS OF CUT (cm $\times 10^4$)	SPECIFIC ACTIVITY (Counts/min mg)	PENETRATION DIST. x^2 (cm ² $\times 10^4$)
5-1	42.24	63.32	364.2	0.10
5-2 *	11.85	17.76	364.6	0.52
5-3 *	12.17	18.24	332.5	0.81
5-4 *	15.02	22.52	299.1	1.22
5-5 *	15.26	22.88	275.7	1.78
5-6 *	19.15	28.71	240.1	2.53
5-7 *	19.10	28.63	195.6	3.54
5-8 *	19.05	28.56	151.7	4.68
5-9 *	17.23	25.83	118.0	5.93
5-10 *	18.22	27.31	90.6	7.29
5-11 *	18.85	28.26	65.1	8.87
5-12 *	17.76	26.62	47.1	10.58
5-13 *	17.82	26.71	30.4	12.39
5-14 *	29.27	43.88	18.4	14.99
5-15 *	20.46	30.67	10.3	18.03
5-16 *	22.86	34.27	5.8	20.89
5-17	31.24	46.83	2.7	24.76
5-18	22.37	33.53	1.3	28.92

TEMPERATURE = 879.2 °C TIME = 40,590 sec COMPOSITION = 16.19 a/o Zn

* POINTS USED IN LEAST SQUARES SOLUTION.

TABLE III
ACTIVITY-PENETRATION DATA FOR SPECIMEN NO. 6

CUT NO.	WEIGHT OF CUT (mg)	THICKNESS OF CUT (cm x 10 ⁴)	SPECIFIC ACTIVITY (Counts/min mg)	PENETRATION DIST. \bar{x}^2 (cm ² x 10 ⁴)
6-1	50.83	71.37	631.3	0.18
6-2 *	10.04	14.10	541.8	0.87
6-3 *	10.78	15.14	453.6	1.23
6-4 *	10.96	15.39	360.0	1.67
6-5 *	16.55	23.24	252.9	2.32
6-6 *	14.90	20.92	154.9	3.19
6-7 *	14.27	20.04	89.8	4.12
6-8 *	8.79	12.34	59.9	4.94
6-9 *	11.05	15.51	36.6	5.70
6-10 *	11.40	16.00	21.8	6.64
6-11 *	9.79	13.75	12.6	7.58
6-12 *	12.29	17.26	7.4	8.63
6-13	9.58	13.45	4.1	9.74
6-14	9.87	13.86	2.4	10.78
6-15	10.56	14.83	1.6	11.94

TEMPERATURE = 809.9 °C TIME = 43,530 sec COMPOSITION = 17.26 a/o Zn

* POINTS USED IN LEAST SQUARES SOLUTION.

TABLE IV
ACTIVITY-PENETRATION DATA FOR SPECIMEN NO. 7

CUT NO.	WEIGHT OF CUT (mg)	THICKNESS OF CUT (cm x 10 ⁴)	SPECIFIC ACTIVITY (Counts/min mg)	PENETRATION DIST. $\frac{x^2}{2}$ (cm ² x 10 ⁴)
7-1	12.72	19.77	187.8	0.01
7-2 *	8.25	12.82	203.7	0.07
7-3 *	15.60	24.24	185.2	0.19
7-4 *	13.55	21.06	151.8	0.45
7-5 *	12.55	19.50	117.0	0.77
7-6 *	15.92	24.74	86.9	1.20
7-7 *	12.47	19.38	56.3	1.74
7-8 *	10.45	16.24	38.5	2.24
7-9 *	12.39	19.26	25.2	2.80
7-10 *	16.67	25.91	13.3	3.61
7-11 *	12.76	19.83	6.6	4.53
7-12	14.69	22.83	2.4	5.48
7-13 *	13.23	20.56	1.4	6.55
7-14	17.98	22.94	0.5	7.85

TEMPERATURE = 764.9 °C TIME = 69,660 sec COMPOSITION = 18.18 a/o Zn

* POINTS USED IN LEAST SQUARES SOLUTION.

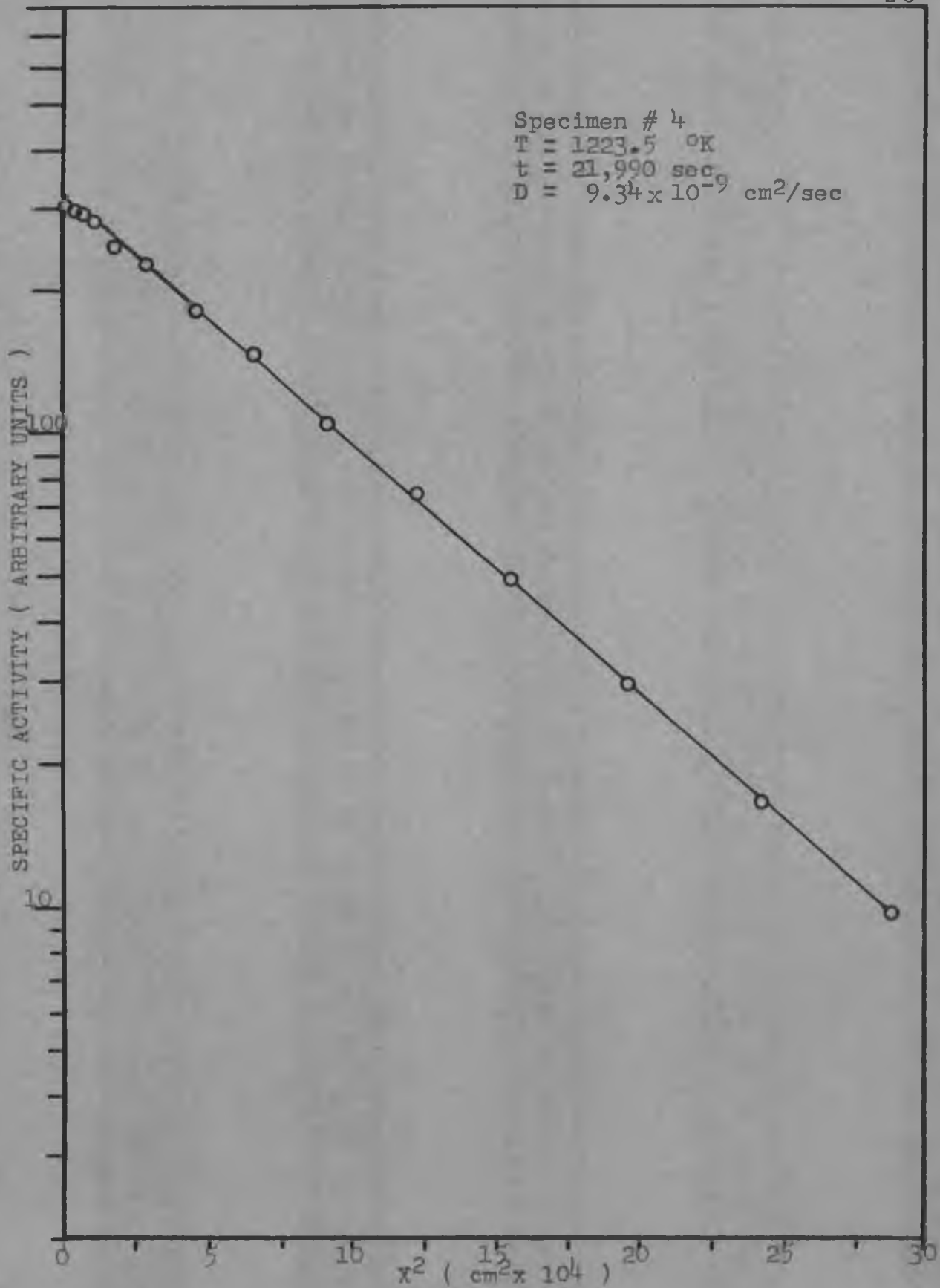
TABLE V
ACTIVITY-PENETRATION DATA FOR SPECIMEN NO. 8

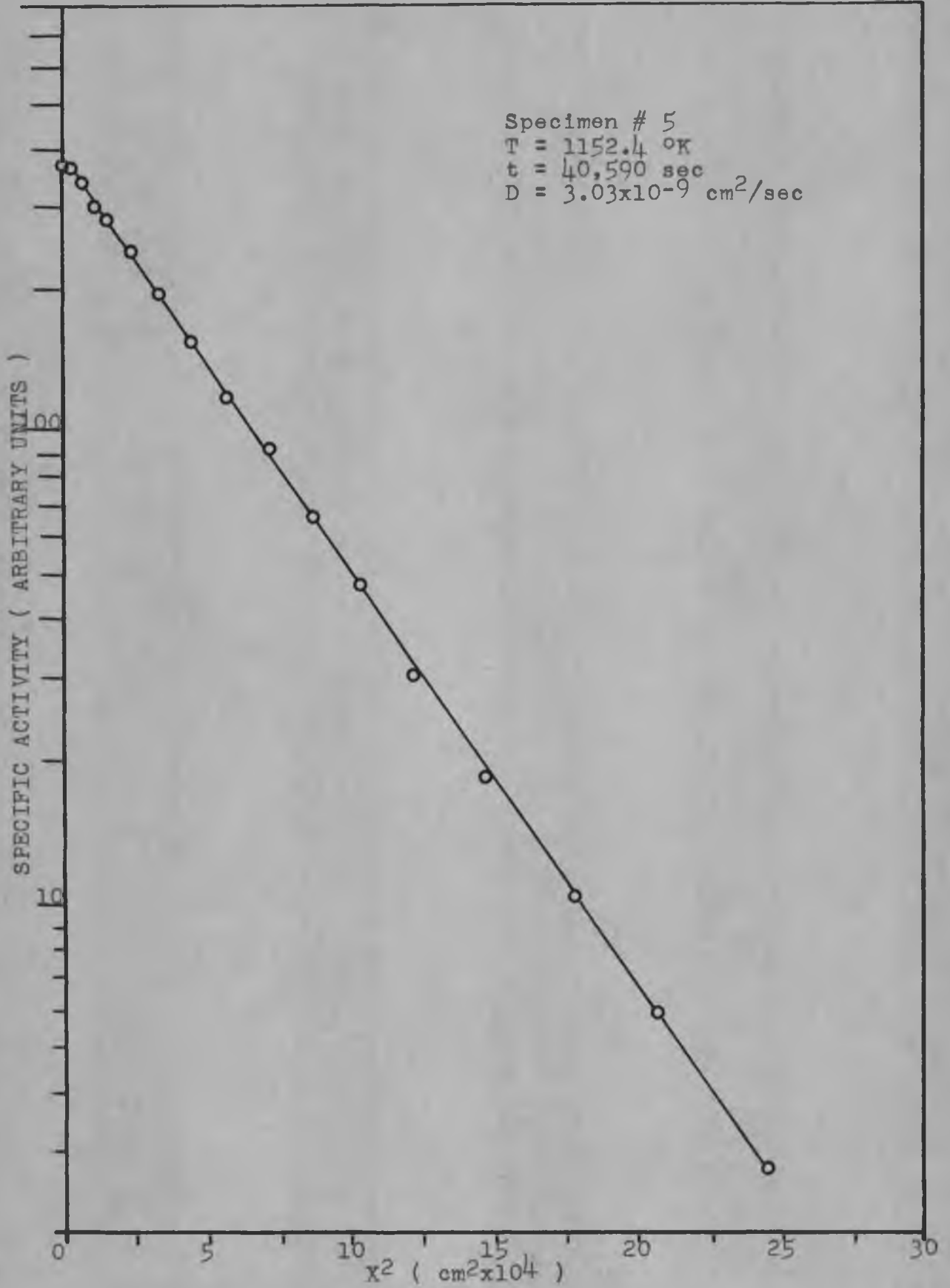
CUT NO.	WEIGHT OF CUT (mg)	THICKNESS OF CUT (cm $\times 10^4$)	SPECIFIC ACTIVITY (Counts/min mg)	PENETRATION DIST. x^2 (cm ² $\times 10^4$)
8-1	24.74	57.55	1967.0	0.08
8-2 *	9.79	22.77	244.5	0.47
8-3 *	7.40	17.21	185.0	0.79
8-4 *	9.20	21.40	127.1	1.17
8-5 *	7.24	16.84	88.77	1.62
8-6 *	8.33	19.38	56.9	2.12
8-7 *	7.81	18.17	30.7	2.69
8-8 *	8.61	20.03	16.3	3.36
8-9 *	8.71	20.26	7.9	4.14
8-10 *	10.18	23.68	2.8	5.08
8-11	8.99	20.19	0.4	6.13
8-12	5.89	13.70	0.1	7.03

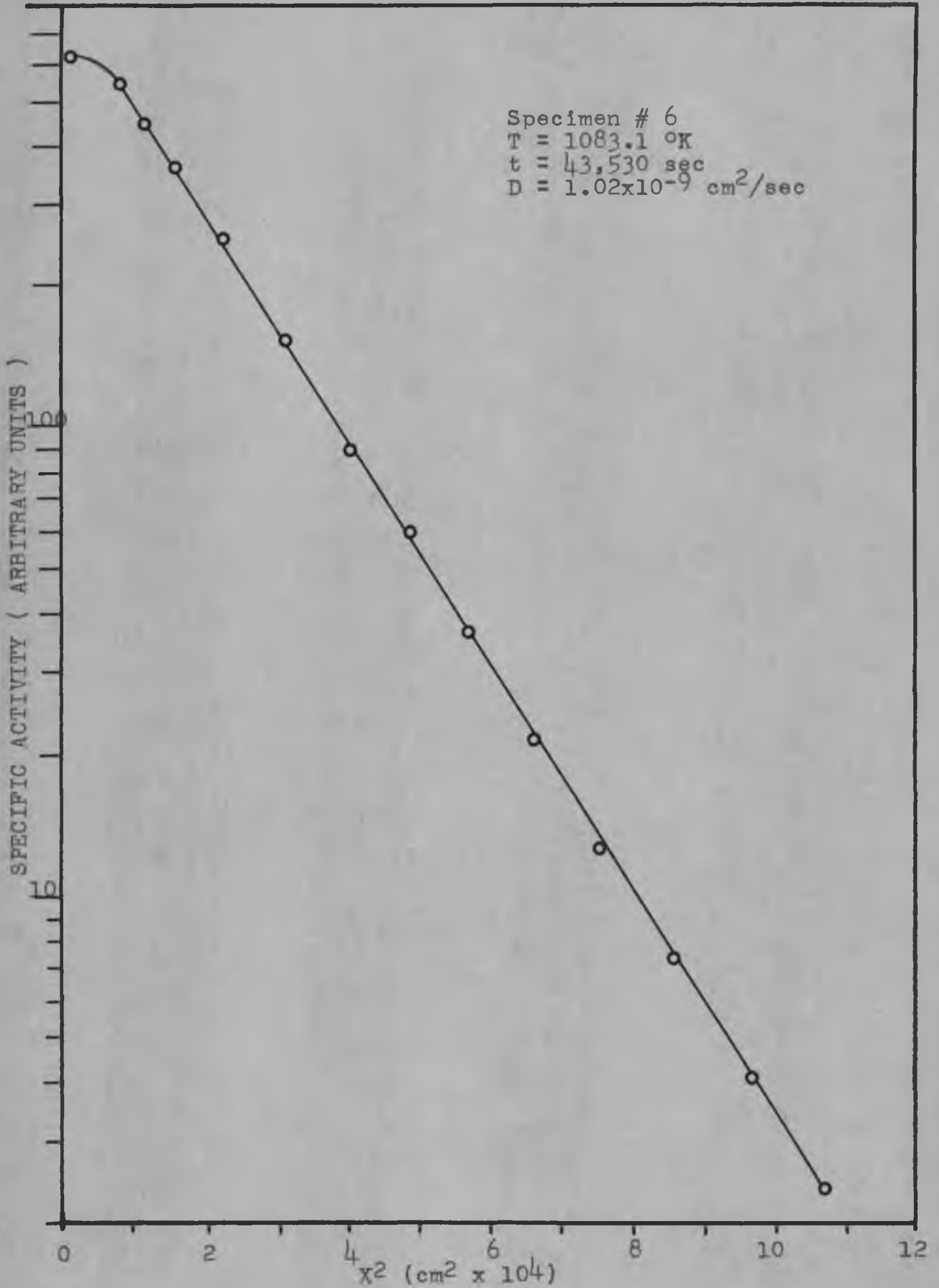
TEMPERATURE = 723.9 °C TIME = 98,540 sec COMPOSITION = 18.54 a/o Zn

* POINTS USED IN LEAST SQUARES SOLUTION.

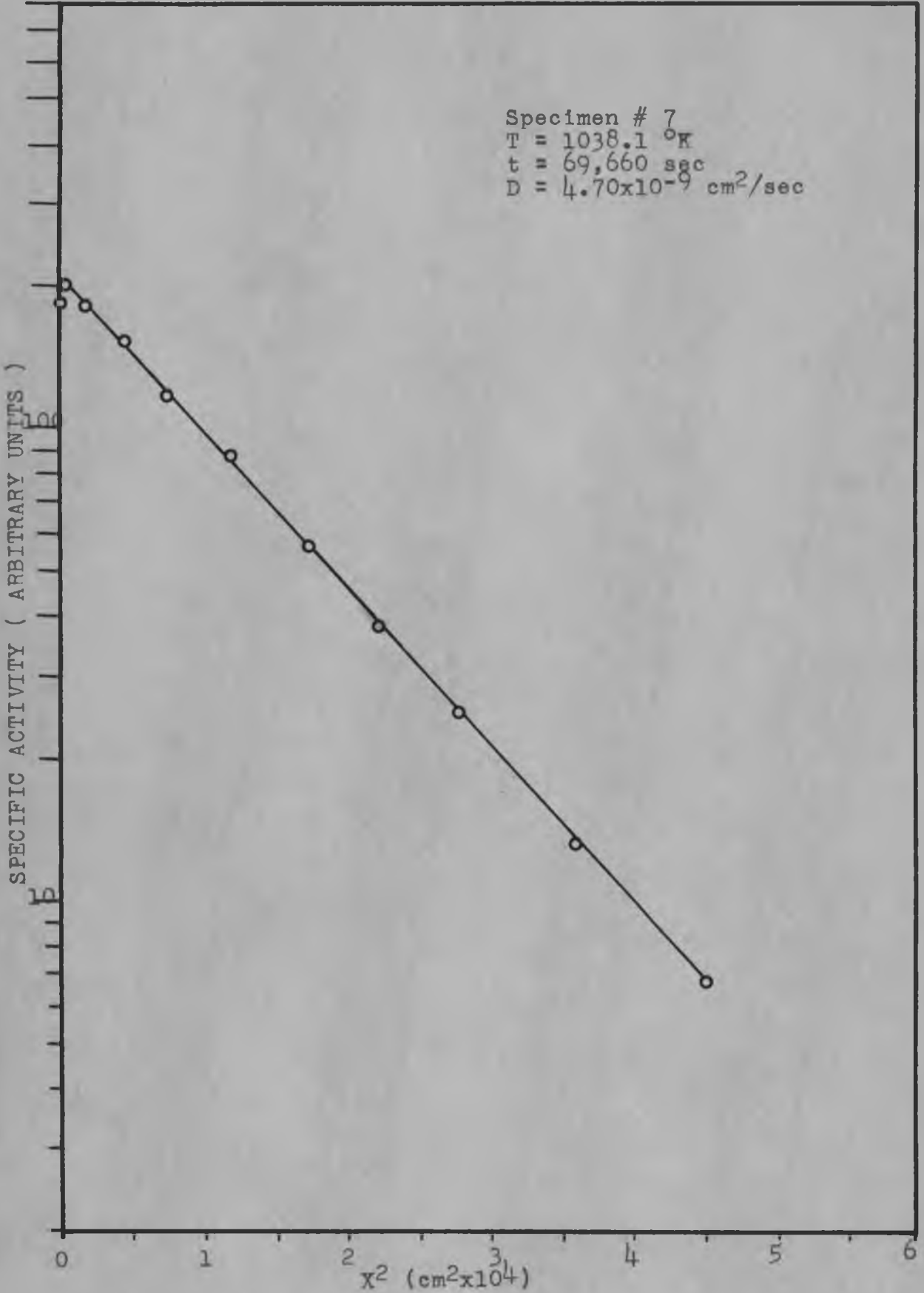
Figs. 3--7 Plots of specific activity versus distance squared for the five diffusion anneals.





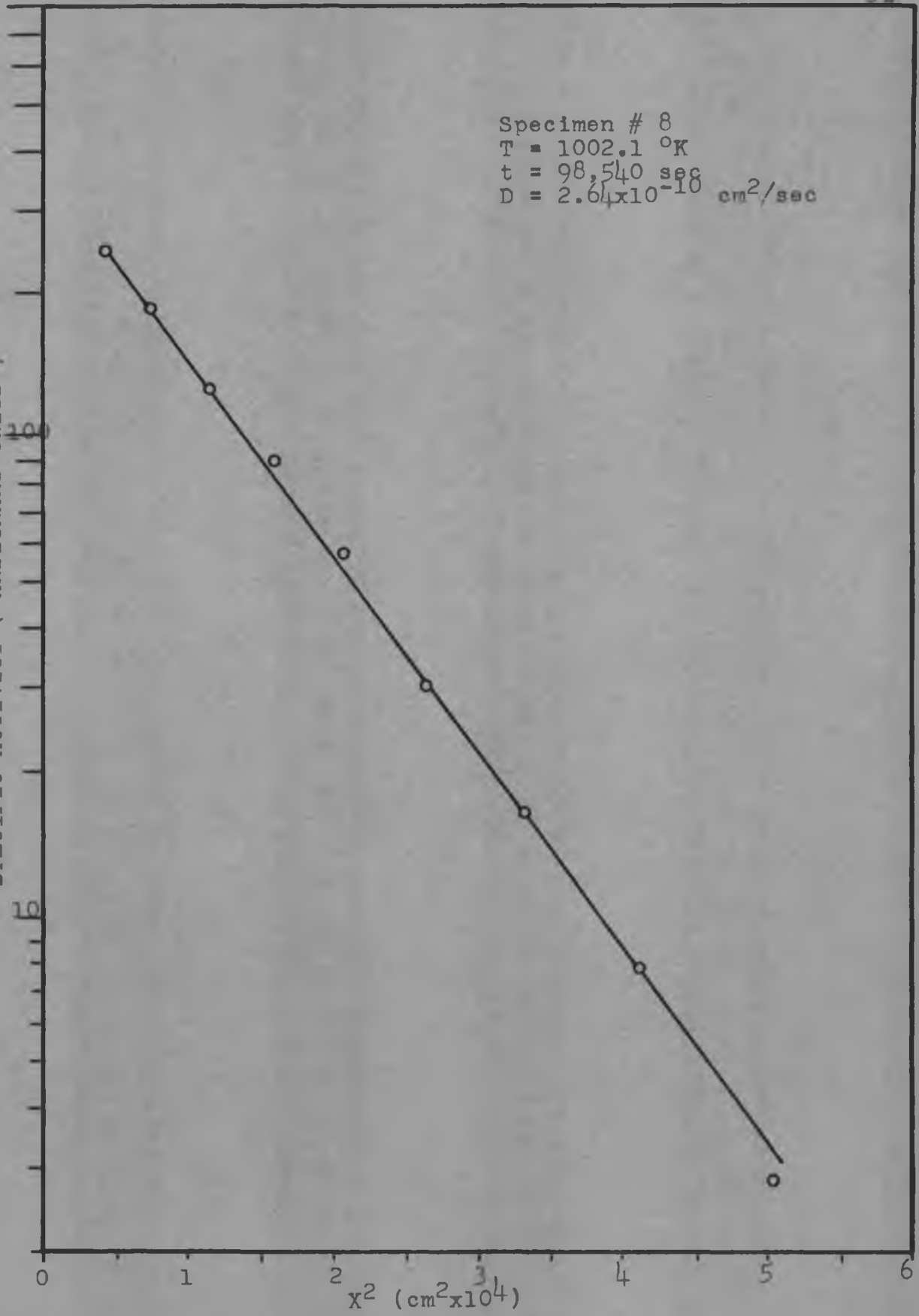


Specimen # 7
T = 1038.1 °K
t = 69,660 sec
D = 4.70x10⁻⁹ cm²/sec



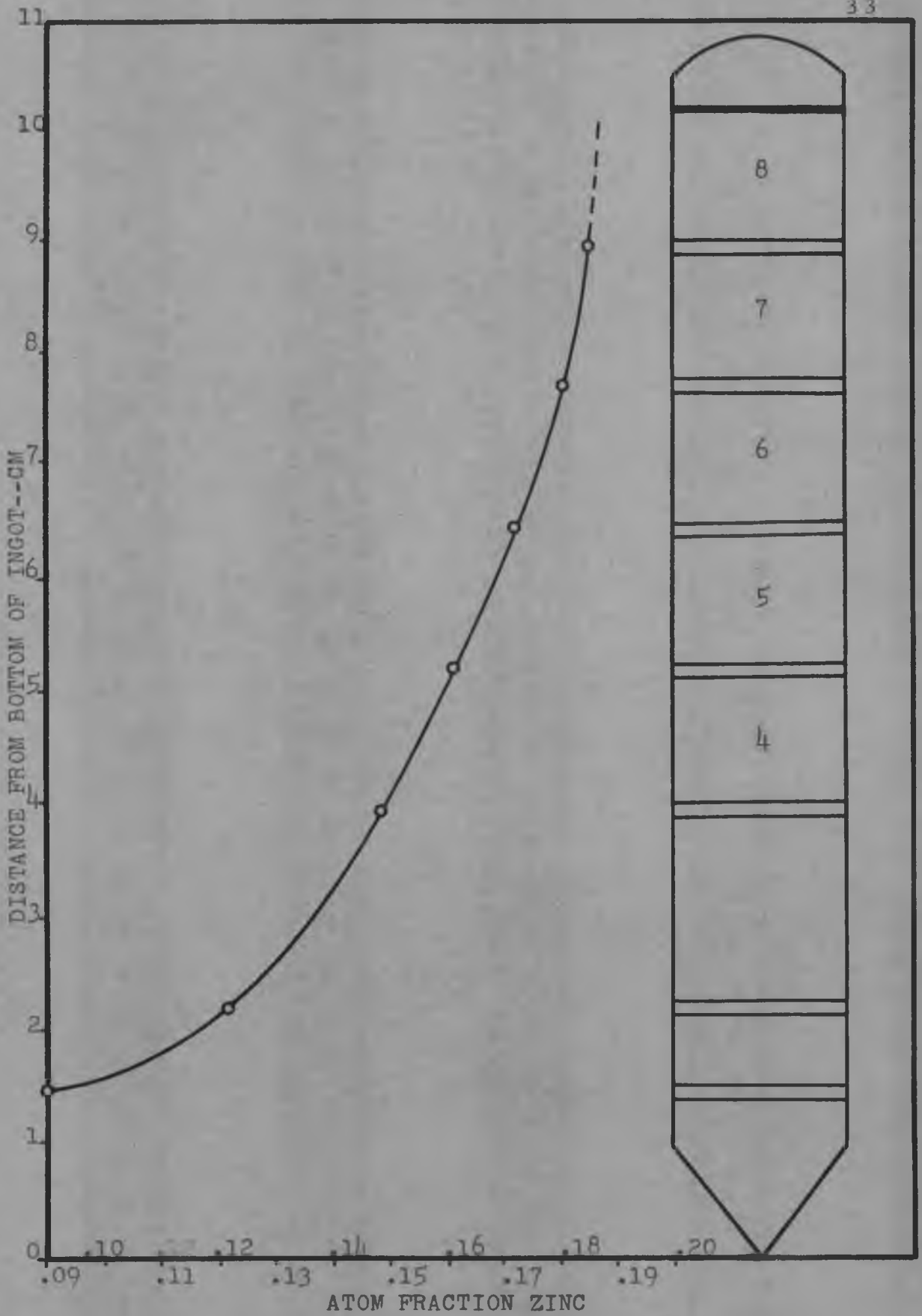
Specimen # 8
T = 1002.1 °K
t = 98,540 sec
D = 2.64×10^{-10} cm²/sec

SPECIFIC ACTIVITY (ARBITRARY UNITS)



X² (cm² x 10⁴)

Fig. 8 Variation of chemical composition along length of brass ingot. Sections removed for chemical analysis are immediately adjacent to the diffusion surfaces.



6. TREATMENT OF DATA

The experimental diffusion coefficients obtained directly from the slopes of the activity-penetration plots, Figs. 3--7, could not be used directly to determine the activation energy and frequency factor. This was due to the chemical concentration gradient, Fig. 8, present in the ingot. Because of this gradient, it was necessary to correct the experimental diffusion coefficients to a single composition value.

To introduce a minimum change in the value for each diffusion coefficient, corrections were made about a mean composition of 17 atomic per cent zinc. Corrections were made using the analysis of Hoffman, et al. (10), by assuming an exponential change in the diffusion coefficient with solute concentration. The equation derived from the above analysis by Lazarus and Tomizuka (15) is:

$$D(X)_T = D(0)_T \frac{D_o(X)}{D_o(0)} \exp (bX/RT) \quad (6-1)$$

where $D(X)$ is the measured diffusion coefficient at

a composition X and temperature T , $D(0)$ is the diffusion coefficient of zinc in pure copper at T obtained from the equation:

$$D(0)_{Zn} = 0.34 \exp -(45,600/RT) \quad (6-2)$$

determined by Hino, et al. (16). $D_o(X)$ and $D_o(0)$ are the respective frequency factors for the compositions X and 0 , and b is the correction factor.

Data for each diffusion specimen were put into the form of equation (6-1). This procedure resulted in five simultaneous equations in which the factor $D_o(X)/D_o(0)$ varies with composition, b varies with temperature, and $D(0)$ and $D(X)$ vary with both composition and temperature. In order to obtain b values, simultaneous equations were solved which resulted in the form:

$$\frac{D(X_1)_{T_1}}{D(X_2)_{T_2}} = \frac{D(0)_{T_1}}{D(0)_{T_2}} \left[\frac{D_o(X_1)}{D_o(0)} \right] \exp \frac{b}{R} \left[\frac{X_1}{T_1} - \frac{X_2}{T_2} \right] \quad (6-3)$$

Over the composition range X_1 to X_2 the ratio of frequency factors was considered to be unity, and a value of b was determined. Values of b were determined for each of the ten combinations of the five equations. From these values, a mean b value was obtained for each diffusion temperature.

A plot of the b values versus the reciprocal of the absolute diffusion temperature was made, Fig. 9, and a least-squares solution was used to determine the equation of the line.

The measured diffusion coefficients were corrected to a single composition by substituting the calculated b values and experimental data into the following equation determined by Lazarus and Tomizuka (15):

$$D(.17)_T = D(X)_T \exp b(.17 - X/RT). \quad (6-4)$$

The corrected diffusion coefficients were plotted versus the reciprocal of the absolute diffusion temperature, and the activation energy and frequency factor were determined from a least-squares solution of the data.

7. RESULTS OF ANALYSIS

The preceding treatment of the experimental data yielded a composition correction factor, b , which is related to the absolute temperature according to the equation:

$$b_{Zn} = 228.9 \exp(9560/RT).$$

Application of the correction factor to the diffusion coefficients resulted in corrected diffusion coefficients presented in Table VI.

The equation relating the corrected diffusion coefficients to the reciprocal of the absolute diffusion temperatures was determined from Fig. 10 to be:

$$D_{Zn} = 0.44 \exp -(42,800/RT).$$

Fig. 9 Relation between chemical composition correction factor and the reciprocal absolute temperature.

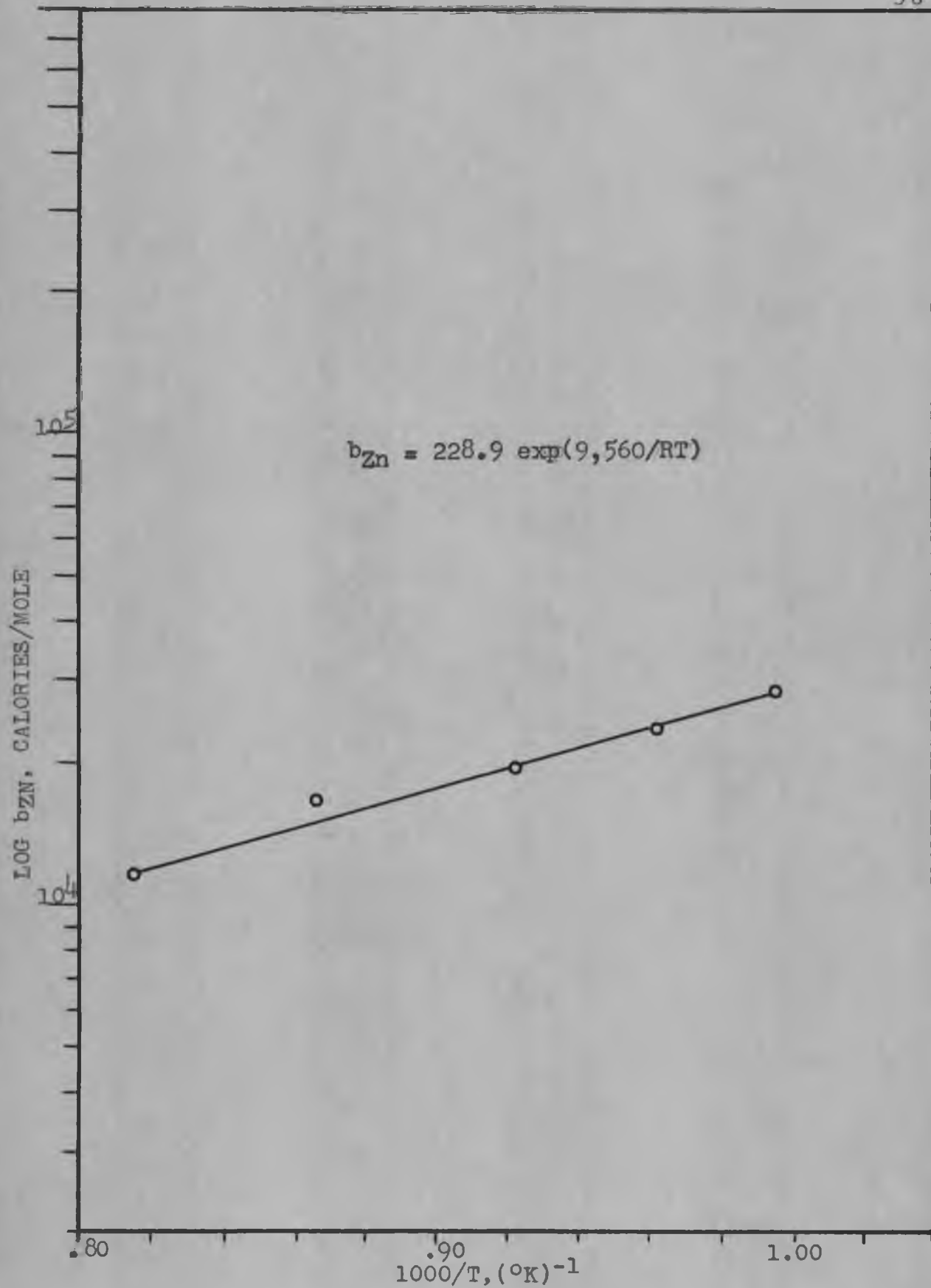


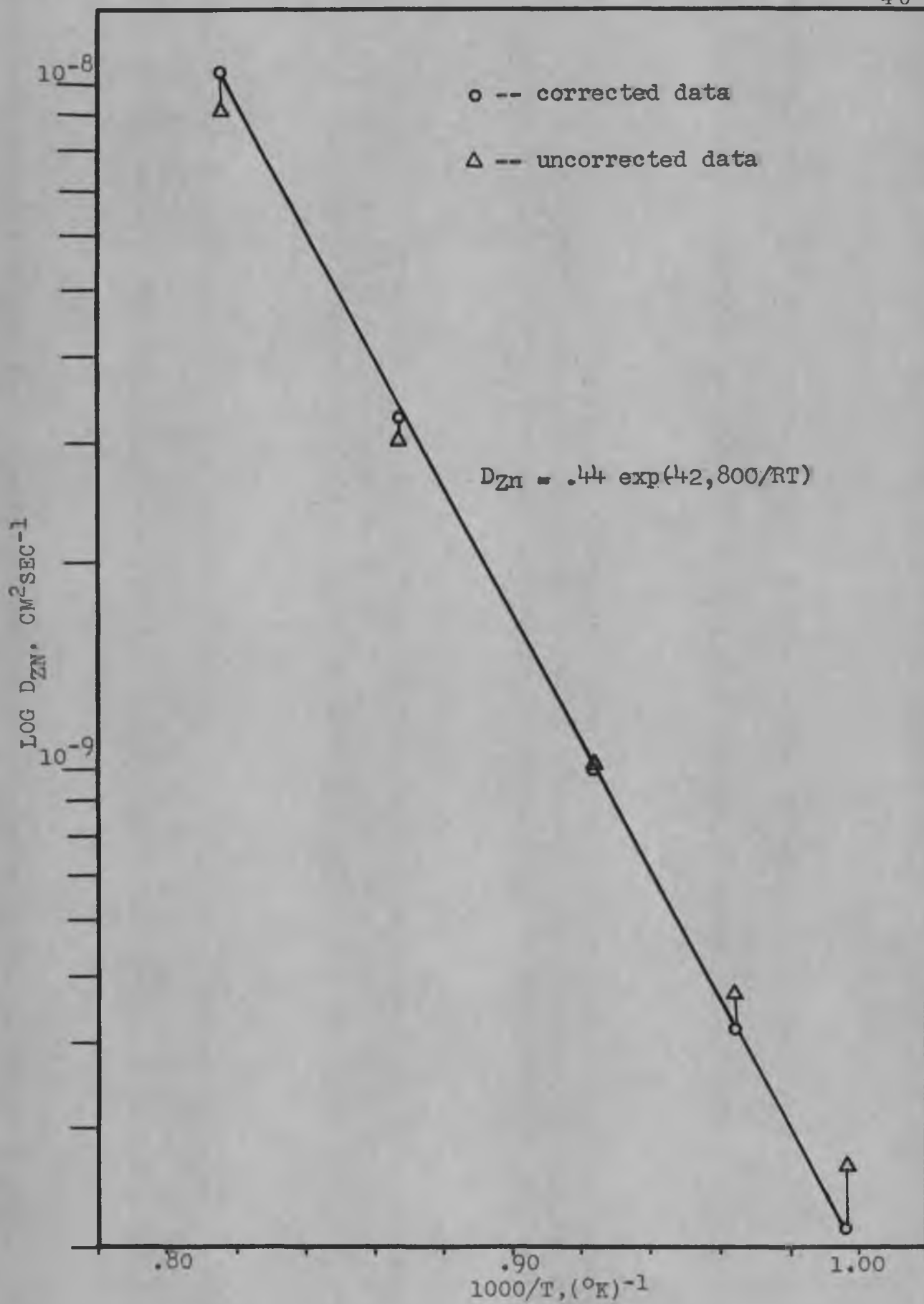
TABLE VI
EXPERIMENTAL RESULTS

SPECIMEN NO.	DIFF. TEMP °K	COMPOSITION Ata/o Zn	D (EXPERIMENTAL) (cm ² /sec)	CORRECTION FACTOR b (cal/mole)	D (CORRECTED) (cm ² /sec)
4	1223.5	14.88	9.34×10^{-9}	11,626	1.03×10^{-8}
5	1152.4	16.19	3.03×10^{-9}	16,554	3.22×10^{-9}
6	1083.1	17.26	1.02×10^{-9}	19,240	9.98×10^{-10}
7	1038.1	18.18	4.70×10^{-10}	23,419	4.12×10^{-10}
8	1002.1	18.54	2.64×10^{-10}	28,337	2.12×10^{-10}

$$b = (228.9) \exp(9,560/RT)$$

$$D = (0.44) \exp(-42,800/RT)$$

Fig. 10 Comparison of corrected and uncorrected diffusion coefficients as a function of the reciprocal absolute temperature.



8. DISCUSSION OF RESULTS

8.1. General

From Figs. 3--7 it is evident that the polycrystalline specimens were suitable for the diffusion measurement, that is, the few grain boundaries present in the specimens did not play an important part in the diffusion process. Had grain boundary diffusion played a predominant role in the diffusion, the log of the specific activity would be linearly related to x the penetration distance. Since a linear relation to x^2 was evident, it is felt that volume diffusion was the dominant mechanism(7).

It can be seen from Fig. 9, that the composition correction factor, b , is exponentially related to the reciprocal of the absolute temperature in agreement with the experience of Hoffman, et al.(10). Only one experimentally-determined point did not fall on the line. No explanation is offered for this discrepancy since an effort was made to duplicate conditions for each diffusion run.

The application of the b correction factor to the

experimentally-determined diffusion coefficients yielded corrected diffusion coefficients which are exponentially related to the reciprocal of the absolute temperature. From Fig.10 it is evident that the correction procedure produced consistent changes in the measured diffusion coefficients. It is felt that a minimum error was introduced into the experimentally-determined diffusion coefficients by making corrections about the mean composition value.

8.2 Comparison of Present Tracer Measurements With Previous Chemical Measurements.

The activation energy for diffusion in this alloy obtained by the author does not agree with the values determined by workers using the sectioning-and-chemical-analysis technique. Differences in activation energy values reported by the author and those of Rhines and Mehl; Birchenall and Mehl; da Silva and Mehl; and Horne and Mehl, are 10.8, 12.8, 2.8, and 5.8 kilocalories per mole respectively. These differences are considerable, ranging from a 30 per cent difference (Birchenall and Mehl) to a 6.5 per cent difference (da Silva and Mehl).

It is felt that the following factors contributed to this difference in the measurements: the author used essentially boundary-free specimens, those of Mehl's school used fine-grained polycrystalline

specimens; the author used a single composition alloy, while Mehl, et al. used large composition gradient specimens. These factors would contribute to the lower activation energy values observed by workers using the sectioning-and-chemical-analysis technique. As mentioned before, the Boltzman-Matano analysis of the data is subject to question. The scatter in the measurements obtained by workers using the chemical technique is sufficient to justify the above statement.

8.3 Comparison of Present Tracer Measurements With Other Tracer Measurements.

The activation energy for diffusion determined in this investigation compares favorably with values determined by other workers, (17, 18) for different compositions of brass. These results are tabulated in Table VII, and are plotted in Figs. 11 and 12.

TABLE VII
Activation Equations For the Alpha Brass System
Determined by Radioactive Tracer Measurements

Atom Fraction Zinc	D_0 (cm^2/sec)	Q (cal/mole)	Reference
0.0001	0.20	45,600	Hino, et al. (17)
0.1700	0.44	42,800	Present Study
0.2700	0.62	41,160	Inman, et al. (18)
0.3100	0.73	40,700	Hino, et al. (17)

Fig. 11. Relation of the activation energy for diffusion to the zinc concentration in the alpha brass system.

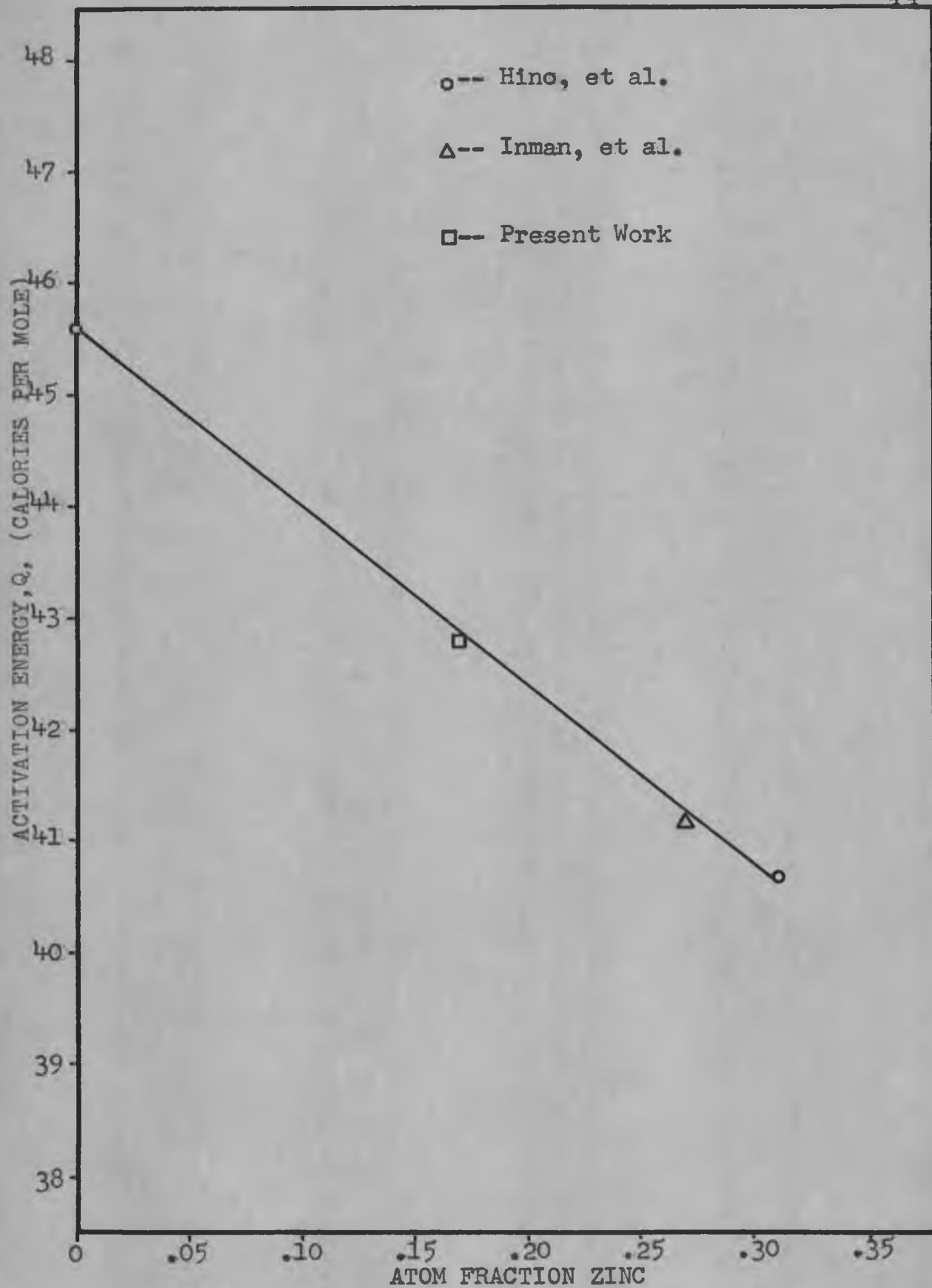
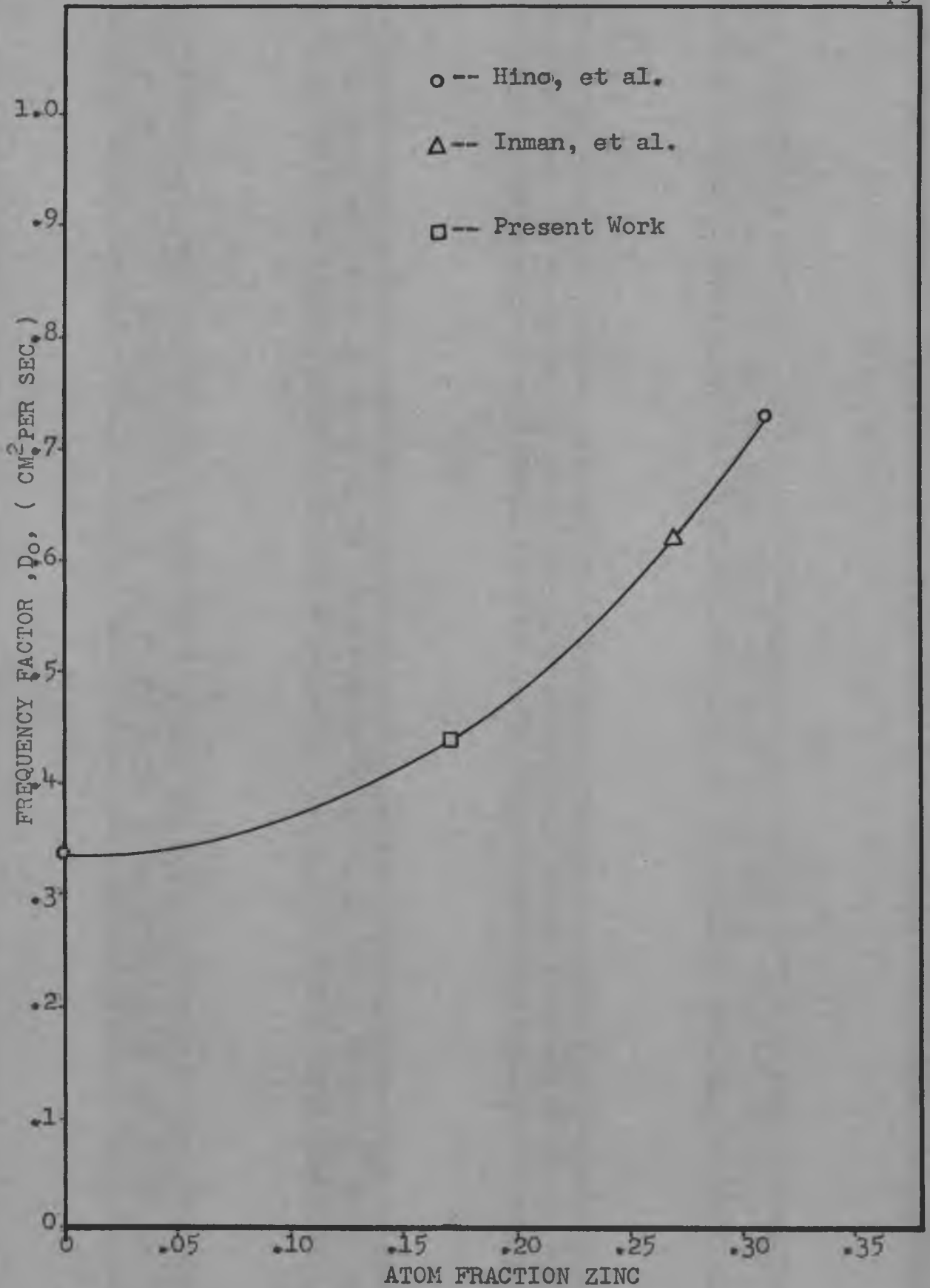


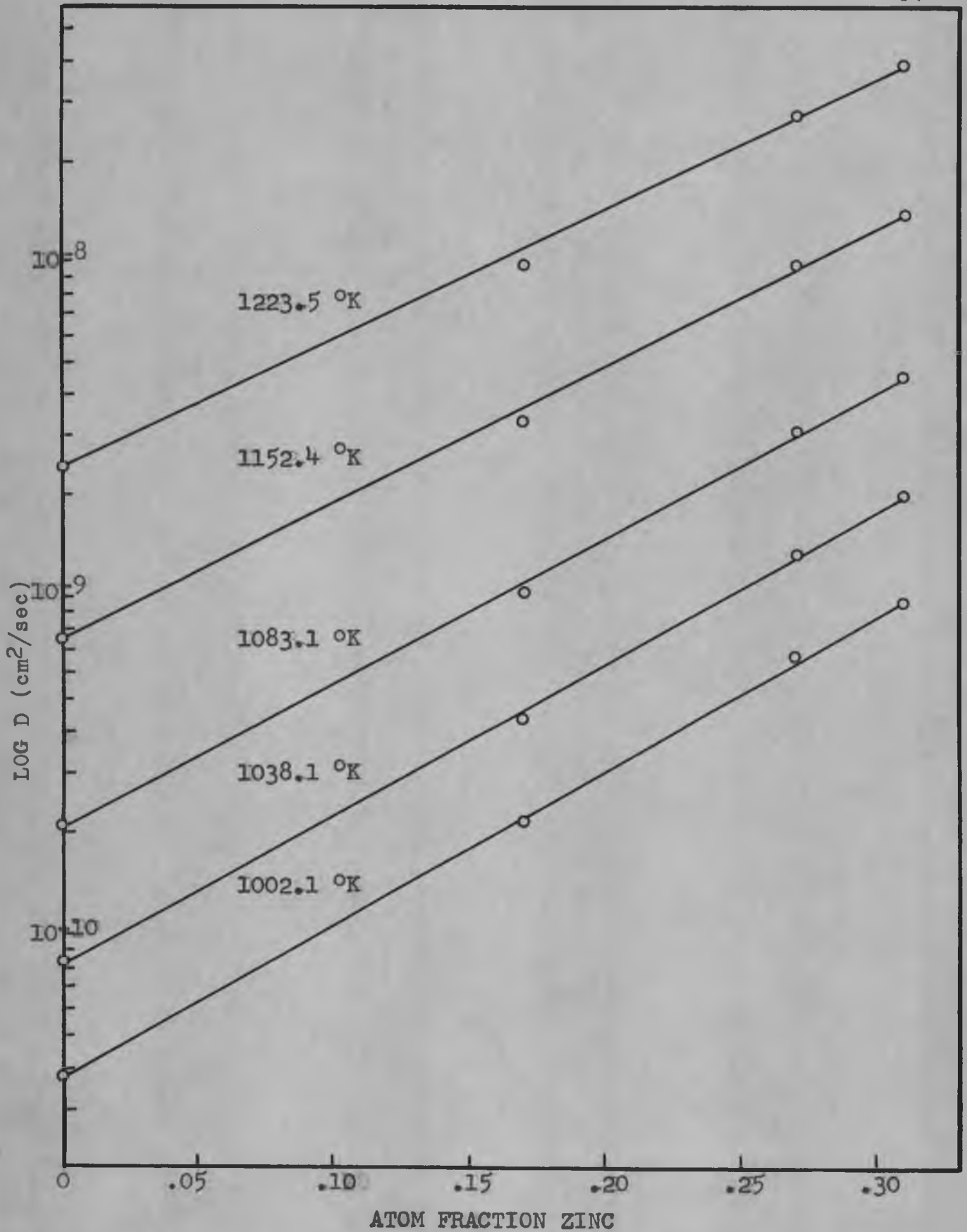
Fig. 12 Relation of the frequency factor, D , to the zinc concentration in the alpha brass^o system.



As shown in Fig. 11, the activation energies obtained by different workers using the tracer technique are linearly related to the solute concentration. From Fig. 12, it may be seen that the values of the frequency factor also show a regular increase with solute concentration.

To determine the agreement of the diffusion coefficients for the different composition values, the activation equations in Table VII were evaluated at various temperatures. The log of the diffusion coefficients was plotted versus the zinc concentration in the alloys. This procedure resulted in a family of lines in which the log of the diffusion coefficients increases linearly with the solute concentration. A good agreement is evident for these independent measurements, as shown in Fig. 13. It may be seen that the diffusion coefficients determined by the author are consistently lower than those of Hino or Inman. An evaluation of this difference revealed that the major discrepancy could be corrected by a 10 per cent increase in the author's frequency factor, D_0 . Since this is well within the inherent error in D_0 (19), it is felt that the disagreement is slight. The plot of these coefficients shows that the author's values differ to a greater degree at higher temperatures. This indicates that the author's D_0 value is

Fig. 13. Relation of the diffusion coefficients to the zinc concentration in the alpha brass system. Values of $\log D$ at 0 and 31 per cent zinc from data of Hino, et al. (17), at 27 per cent zinc from data of Inman, et al. (18), and at 17 per cent zinc from data of author.



lower than the true D_0 value.

8.4 General Comparison of Tracer and Chemical Diffusion Measurements in Alpha brass.

With the availability of radioisotope data for several alloy compositions, it is interesting to make a general comparison with the results obtained by the sectioning-and-chemical-analysis technique. The variation of the activation energy with the composition as determined by the tracer technique does not agree with the variations obtained by Rhines and Mehl(1), da Silva and Mehl(3), or Horne and Mehl(5). The maximum difference in the activation energies between the two methods is 8.2, 12, and 12 kilocalories per mole for the above studies respectively. The only chemical measurement which has a point of fit with isotope data is that of da Silva which fits at approximately 10 atomic per cent zinc.

Tracer data and chemical data for values of D_0 are again in disagreement. The tracer measurements indicate an increase in D_0 with increasing solute concentration, while those of da Silva and Mehl(3) indicate a decrease, and those of Horne and Mehl(5) indicate a maximum. In the latter case, a minimum disagreement of $0.5 \text{ cm}^2/\text{sec}$, exists. In the former, there is a point of fit at approximately $0.4 \text{ cm}^2/\text{sec}$, but large general disagreement exists over the remainder of the curve.

In general it may be said that there is no agreement between diffusion data obtained by the chemical technique and that obtained by the tracer technique.

8.5 Comparison with Theory of Hoffman, Turnbull, and Hart.

It is difficult to determine the agreement of the present measured data with the theory of Hoffman, et al. (10). Only a semi-quantitative evaluation of these equations can be made since enough basic data, such as vacancy concentration, solute-vacancy exchange frequency, solvent-vacancy exchange frequency, etc. are not well known, and can only be approximated.

Assuming that diffusion in this system is governed primarily by the solute-vacancy exchange mechanism, then equation (3.24) applies, and:

$$D = 1/6 \lambda^2 v_2 X_v^1.$$

The value of the exchange frequency can be approximated by dividing the value of the speed of sound in the alloy by the distance of closest approach. The distance of closest approach can also be used as the value of λ . The speed of sound in brass is approximately 3,500 meters/sec (20), the value of the distance of closest approach in a face-centered-cubic crystal is simply $a_0/\sqrt{2}$, where a_0 is the lattice

parameter. For an alloy of 17 atomic per cent zinc, a_0 is approximately 3.6×10^{-8} cm. Evaluating the above, $\lambda^2 \approx 6.5 \times 10^{-16}$, $v_2 \approx 1.4 \times 10^{13}$, the value of D for this alloy at 1002°K is 2.1×10^{-10} cm²/sec. Evaluating equation (3.2-4), X_v^1 , the fraction of vacancies in the first coordination shell of the solute is approximately 1.39×10^{-7} or approximately 7 vacancies per million lattice sites. If this value of X_v^1 is substituted into the following equation developed by Cottrell (8):

$$\frac{n}{N} = \exp. -(U/RT) \quad (8.5-1)$$

in which n/N is the equilibrium vacancy concentration at temperature T , and U is the energy required to form a mole of vacancies, then U is determined to be approximately 31,200 calories per mole. Unfortunately there are no data available for comparison with this value. However, such data are available for pure copper. Huntington and Seitz (21) have made theoretical calculations on the vacancy mechanism of diffusion in pure copper using a quantum mechanical approach based on the distribution of the electronic cloud surrounding a vacancy. From these calculations, they have derived an energy of 32,000 calories per mole for the formation of a mole of vacancies. Using a value of $D = 3.75 \times 10^{-11}$ for the

diffusion coefficient of zinc into pure copper at 1000 °K determined by Hino, et al.(17), a value of 2.47×10^{-8} is determined for X_v' , and a corresponding value of 35,100 calories per mole is obtained. This agreement is surprising when one considers the relative coarseness of the approximations. In further work, Huntington(22) has determined the range of energy for the formation of a mole of vacancies in pure copper to be from 20,000 to 40,000 calories per mole depending on temperature. In all cases the values of this energy determined by the theory of Hoffman, et al.(10) and equation (8.5-1) are within this range.

9. CONCLUSIONS

The conclusions reached as a result of this investigation are as follows:

1. The equation relating the diffusion coefficient to temperature for a brass alloy containing 17 atomic per cent zinc is:

$$D_{Zn} = 0.44 \exp -(42,800/RT).$$

2. Correction of diffusion coefficients to a uniform composition can be made over a composition of ± 2 per cent through the use of the following equation:

$$D(N) = D(X) \exp b(N - X/RT),$$

where N is the nominal composition, X is the measured composition, and b is a calculated correction factor.

3. The equation relating the composition correction factor to the absolute temperature in the alpha brass system is:

$$b_{Zn} = 228.9 \exp (9560/RT).$$

4. The diffusion measurements obtained by the technique of sectioning and chemical analysis are not precise or consistent. There is little agreement with results obtained by different workers using this technique, and even less with results obtained from tracer measurements.

5. There is very good agreement between results obtained by different workers using the tracer technique on the alpha brass system.

6. There is an exponential relationship between diffusion coefficients in the alpha brass system and the solute concentration. This is in agreement with the linear dependence of the activation energy with solute concentration. The exact relationship of the frequency factor is not known, but shows a regular increase with solute concentration.

7. Calculations of the energy requirements for the formation of vacancies based on the theory of Hoffman, Turnbull, and Hart (10) and experimental data, are in good agreement with the theoretical calculations of Huntington and Seitz (21) and Huntington (22).

REFERENCES

1. F. N. Rhines and R. F. Mehl Trans. Amer. Inst. Min. Met. Eng. 128, 135 (1938).
2. C. E. Birchenall and R. F. Mehl Trans. Amer. Inst. Min. Met. Eng. 171, 143 (1947).
3. L. C. da Silva and R. F. Mehl Trans. Amer. Inst. Min. Met. Eng. 191, 155 (1951).
4. E. O. Kirkendall Trans. Amer. Inst. Min. Met. Engr. 203, 88 (1955).
5. G. T. Horne and R. F. Mehl Trans. Amer. Inst. Min. Met. Engr. 203, 104 (1955).
6. A. D. Le Claire Phil. Mag. 62, 673 (1951).
7. C. T. Tomizuka Methods of Experimental Physics 2, 370 (Academic Press, New York, 1960).
8. A. H. Cottrell Theoretical Structural Metallurgy pp 180, 119 (St. Martins Press, New York, 1960).
9. W. Jost Diffusion in Solids, Liquids, and Gases p 17 (Academic Press, New York, 1952).
10. R. E. Hoffman, D. Turnbull, and E. W. Hart Acta Met. 3, 417 (1955).
11. E. W. Hart, R. E. Hoffman, and D. Turnbull Acta Met. 5, 74 (1957).
12. A. B. Lidiard and A. D. Le Claire Phil Mag. 1, 521 (1956).
13. C. T. Tomizuka and D. Zimmerman Improvements On a Simple Temperature Controller ASTIA Document No. 205084 (University of Chicago, 1958).
14. A. H. Low Technical Methods of Ore Analysis, p 90 (John Wiley and Sons, New York, 1927).
15. D. Lazarus and C. T. Tomizuka Phys. Rev. 103, 1156 (1956).

16. J. C. Fisher J. Appl. Phys. 22, 74 (1951).
17. J. Hino, C. T. Tomizuka, and C. Wertz Acta Met. 5, 45 (1957).
18. M. C. Inman, D. Johnston, W. L. Mercer, and R. Shuttlesworth Radioisotope Conference 2, 93 (Buttersworth, London, 1954).
19. D. Lazarus Second United Nations International Conference on the Peaceful Uses of Atomic Energy, p. 1 (New York, 1956).
20. Handbook of Chemistry and Physics 36th Edition, p. 2311 (Chemical Rubber Pub. Co., Cleveland, 1954).
21. H. B. Huntington and F. Seitz Phys. Rev. 61, 324 (1942).
22. H. B. Huntington Phys. Rev. 61, 325 (1942).