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Self diffusion in sodium single crystals

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Self Diffusion In Sodium Single Crystals

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ABSTRACT

The diffusion coefficients of sodium tracers in single crystals of pure sodium were measured as a function of temperature over a range of 20 - 41°C. The relation $D = D_o \exp\left(\frac{-Q}{RT}\right)$ was found with Q 11,000 ± 170 cal/mole and D_o 0.313 ± 0.018 cm^2/sec. These values may be compared with $Q = 10,450$ cal/mole and $D_o = 0.242$ cm^2/sec. reported for polycrystalline sodium.

INTRODUCTION

There are two main reasons for studying diffusion in solids. First, the knowledge of diffusion is basic to an understanding of the structural changes that occur in solids at high or low temperatures. Secondly, the study of diffusion allows one to learn how atoms move in solids. Diffusion is intimately connected with the study of point defects in solids and their movements. Point defects are the simplest type of defects in a solid; yet, their concentrations and movements cannot be observed directly. Diffusion experiments have come to be the most frequently used means of studying point defects.

The simplest type of diffusion is self-diffusion. The term "self-diffusion" implies diffusion of one isotope into another isotope of the same chemical element. Three mechanisms are thought to give rise to diffusion in crystalline solids:

1. Ring Mechanism (atomic interchange between neighboring atoms).
2. Interstitial Mechanism (atoms that occupy interstitial positions diffuse by moving from one position to another).
3. Vacancy Mechanism (if one of the atoms in an adjacent site jumps into the vacancy, the atom is said to have diffused by vacancy mechanism).

The earlier experiments in self-diffusion in metals were performed by G. von Hevesy (1) and his collaborators using lead into which Thorium B, a radio-isotope of lead, was diffused. By analysing the distribution of the radio-isotope they were able to determine the rate of self-diffusion. Today, with the availability of radio-isotopes, it is possible to investigate many additional cases of self-diffusion.

The problem of the mechanism of diffusion in metallic copper was discussed by H.B. Huntington and Fredrick Seitz (2) from the standpoint of the modern theory of solids. The mechanisms of direct interchange of atoms, of interstitial diffusion, and of vacancy diffusion were considered in detail. Their results indicated that the interstitial mechanism was strongly preferred and yielded an activation energy in reasonable agreement with the theoretical value. On the other hand, the observed results for self-diffusion in polycrystalline sodium (3) indicated the possibility of the vacancy mechanism. Self-diffusion work has been done also on polycrystalline and single-crystal silver (4). The observed results indicated that the interstitial mechanism was strongly preferred and yielded an activation energy for polycrystalline silver in reasonable agreement with the theoretical value. However, for single-crystal silver the diffusion constant and activation energy differed from that for polycrystalline silver at low temperatures.

The purpose of this experimental investigation was to study self-diffusion in single-crystal sodium, using tracer techniques, in order to determine the diffusion constant and activation energy. No reports have been found in the literature on self-duffusion in single-crystal sodium.

THEORY

It is well known from the theory of specific heats that atoms in a crystal oscillate around equilibrium positions. Occasionally, these oscillations become so violent that atoms change sites. It is such jumps that give rise to diffusion in solids. The interpretation of diffusion as an example of the random-walk phenomena was shown many years ago. In view of the diffusion phenomena, an elegant method was put forward by Rayleigh (5) using a crystalline model.

For simplicity consider that C, the concentration gradient of the diffusing atoms, is along one of the principal axes of the crystal, taking this axis as parallel to the x-axis. Further, assume that each elementary act of diffusion consists of a jump forward or backward along the x-axis by an amount λ, a forward or backward jump has equal probability, fp, and the mean time between jumps is τ. Let C (x,t) be the number of diffusing atoms at time t on a plane of unit area passing through x. The model then gives for the increment of C (x,t) in the time interval δt, where $\delta t << \tau$,

$$C(x, t+\delta t) - C(x,t) = \delta t \left[C(x-\lambda, t) - 2C(x,t) + C(x+\lambda, t) \right] \quad (1)$$

The increase δC of the number of atoms on the plane located at x is given by the number of atoms jumping from $(x - \lambda)$ into x, plus the number of atoms jumping from $(x+\lambda)$ into x, minus the number of atoms jumping from the plane x (see Fig. 1). If it is specified that C changes very slowly over a distance λ, the difference equation (1) reduces to:

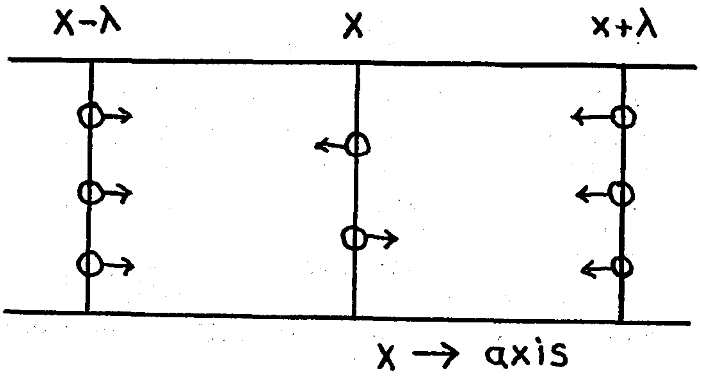

Fig. 1

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2} \qquad (2)$$

where $D = fp\lambda^2$ is the diffusion coefficient. In the expression $D = fp\lambda^2$, since f is determined solely by the geometry of the lattice and λ is nearly independent of the temperature, the temperature dependence of the diffusion coefficient must enter via the jump probability. The equation (2) is called Fick's second law of diffusion with the quantity D a scalar in cubic metals and a tensor in non-cubic metals. The solution to the differential equation (2) is given by:

$$C = \frac{C_0}{2\sqrt{\pi D t}}\,\exp\left(-\frac{x^2}{4Dt}\right), \qquad (3)$$

where C_0 = the initial concentration

C = the final concentration

D = the diffusion coefficient

x = the diffusing distance

t = the time in seconds

A simple model that can be used to determine the temperature dependence of p is to consider a particle moving in a fixed potential energy curve of the type illustrated in Fig. 2. Let the potential minimum A correspond to the position of the atom in which the particle finds itself and A' correspond to the neighboring vacant position. The barrier B of height ϵ_i is a result of the fact that as the particle moves from one position to another it must be squeezed between the atoms constituting the host lattice. Assuming the potential to be parabolic, the atom will vibrate as a harmonic oscillator. The frequency of vibration ν_i may be considered as the number of attempts per second made by the atom to cross the barrier. Any attempt can succeed only if the energy of the atom is $\geqslant \epsilon_i$.

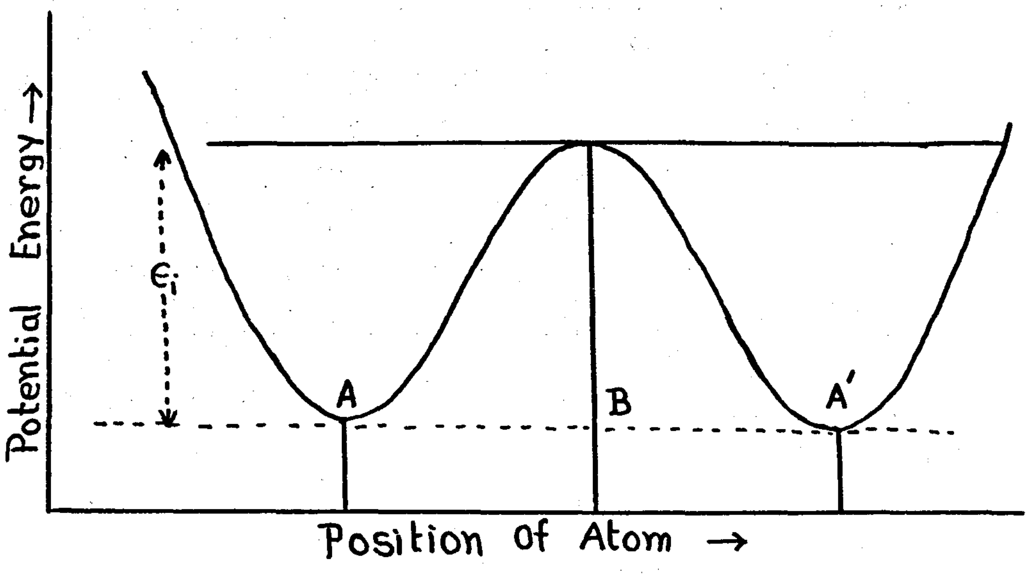

Fig. 2

The fraction of time spent by the atom in energy states $\gg \epsilon_i$ is given by $\exp\left(\frac{-\epsilon_i}{RT}\right)$, where R is a gas constant and T the absolute temperature. Hence, the probability that the atom would jump from A to A' per second is given by,

$$P_i = \nu_i \exp\left(-\frac{\epsilon_i}{RT}\right) \tag{4}$$

When the jumping problem is considered in terms of the entire lattice (6) one obtains a formula of the same form as equation (4), but ϵ_i is replaced by the free energy, $\Delta G_i = \Delta H_i - T\Delta S_i$ and equation (4) becomes, summing over all P_i,

$$P = \nu \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right), \tag{5}$$

Where ΔS is the entropy difference for an atom in the states A and B (Figure 2).

Substituting equation (5) into $D = fp\lambda^2$, one obtains

$$D = f\lambda^2 \nu \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right), \tag{6}$$

Equation (6) is the fundamental equation for the diffusion coefficient D and can be written in the form,

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \tag{7}$$

with $D_0 = f \lambda^2 \nu \exp(\Delta S/R)$ and $\Delta H = Q$,

where f and λ are determined by the geometry of the lattice and ν is the average frequency of the vibrating atom. The thermodynamical quantities ΔS and ΔH are called the entropy of activation and the associated enthalpy.

It has been shown by Zener (7) that equation (3) is applicable for small concentrations of the diffusion atom. The method of radioactive tracers is ideally suited for measuring diffusion rates at very small concentrations. A very accurate and systematic study in this respect has, in recent years, been carried out by Slifkin, et al (8). They measured, besides self-diffusion of silver, the diffusion of Cd, In, Sn and Pb into silver. Since radio-active tracer techniques were employed, the traction of diffusing atoms was kept very low (10^{-4}-10^{-5}).

In this study, a low concentration of radio-active sodium was diffused into single-crystal sodium and the diffusion constant and activation energy were determined by making use of equations (3) and (7).

EXPERIMENTAL

Introduction

For this experiment sodium single crystals, of 99.99 percent purity, were grown by the Czochralski method and supplied by the Virginia Institute for Scientific Research. The crystals were grown in cylindrical shapes ranging from 3/4 inch to 1 inch in diameter. In all of these diffusion experiments it was found that preparation of the crystals such as embedding, cutting, and polishing was of great technical importance and required careful attention. For example, a high degree of precision polishing was required before an attempt was made to deposit the tracer atoms. After preparation of the crystals the tracer atoms were deposited electrolytically and the specimens were subjected to a diffusing anneal at a constant temperature for a known length of time. Following the diffusion anneal, the specimens were sectioned on a microtome into slices of 50 microns thickness for radioactive assay.

Procedures

Etching was performed to see whether the specimen was a single crystal. One surface of the sodium specimen was cleansed with methanol and isopropyl alcohol and then placed in a etching bath consisting of xylene with about one part in fifty of isopropyl alcohol. After about 20-30 minutes at room temperature, the single crystal nature of the specimen became clearly visible by reflection from a directional white light source.

The etched crystals were suspended by thin wires in the center of moulds and molten paraffin at 40°C was poured in each mould. The embedded crystals were removed from the moulds after five hours. While embedding precautions were taken to exclude any air bubbles adhering to the crystal surface. Embedding was necessary to keep the crystal from being strained during the cutting process. Further, it was found essential to prevent distortion during microtome sectioning.

If an accurate value of the slope of ln C vs the square of depth using equation (3) was to be determined it was necessary to cut an initial surface on the crystal. Since sodium metal is soft, special care must be taken in cutting a single crystal (9). A single crystal when cut very carefully with a sharp razor will exhibit a polycrystalline structure which is 1-2mm deep. In order to keep the strain in the crystals to a minimum a chemical cutting saw was used (see Fig. 3). All parts of the string saw were exposed to a 50% water-methanol cutting agent. A spool of mercerized thread was immersed in the cutting fluid. The thread ran through the two guide posts, across the specimen which rested on the microtome groove, and to a rewinding spool. After the entire thread was rewound it was exchanged with the one in the cutting fluid and the entire process was repeated. The thread would last for about three passes through the sodium before it became weakened and expanded by the sodium hydroxide formed during cutting. 350 yards of thread passing across a 1/2 inch diameter specimen would normally take about 45 minutes to complete the cutting process. It is undesirable to stop the moving thread in the middle of the cutting process, since the cut surface will deviate markedly from its initial direction when cutting is resumed. The cut surface, although slightly irregular, is a single crystal.

After cutting further preparation of the crystal was done in a vacuum system for the following two reasons:

1. To prevent oxidation of the polished surface of the crystal specimen during the period of electropolishing and electrodeposition.

Fig. 3 Microtome and String Saw.

A and B	Driving and Winding Motors.
C and D	Guiding Posts.
E	Mercerised Spool.
F	Microtome.
G	Embedded Sodium Crystal.
H	Mercerised Thread.

2. To prevent absorption of CO_2 by ethylenediamine, used in the preparation of the crystal, from atmospheric air.
The system consisted of a bell jar 24 inches long and 16 inches in diameter (see Fig. 4). Mounted upright at the center of the base plate of the bell jar was a copper cylindrical tube 6 inches in length and 1½ inches in diameter. The top three inches of this copper tube was cut into a semicylinder. Two vertical grooves were cut in the lower part of the cylindrical copper tube, diametrically apart. Through the center of the tube ran a fine threaded screw which was connected at the top to a reversible 120 rpm motor. A movable arm, I, ran along the threaded screw and moved horizontally and vertically through the grooves in the copper tube. This arrangement facilitated the horizontal and vertical motions of the arm. Resting on the base plate of the bell jar was a glass dish "D" and a stainless steel cup "E" which was kept insulated from the base plate. The glass dish "D" and the stainless steel cup "E" held mineral oil and ethylenediamine. Two separate polyethylene tubes, each 1/8 inch in diameter and 6 feet in length, were passed through the base plate (see Fig. 4). One tube connected bottle "A" containing mineral oil with the mineral oil bath "D". The second tube connected bottle "B" containing ethylenediamine with the stainless steel cup "E". The bell jar enclosing the whole arrangement was made vacuum tight and was evacuated sufficiently by a mechanical pump linked with an oil diffusion pump. A Pirani Vacuum Gauge was used to record the vacuum produced in the bell jar.

An electrolytic method of polishing was ideally suited for the final preparations of the sodium single crystal. The suitable electrolyte used in the case of sodium was 99.99 per cent pure anhydrous ethylenediamine (10), an ideal ionising solvent of a highly basic type, which

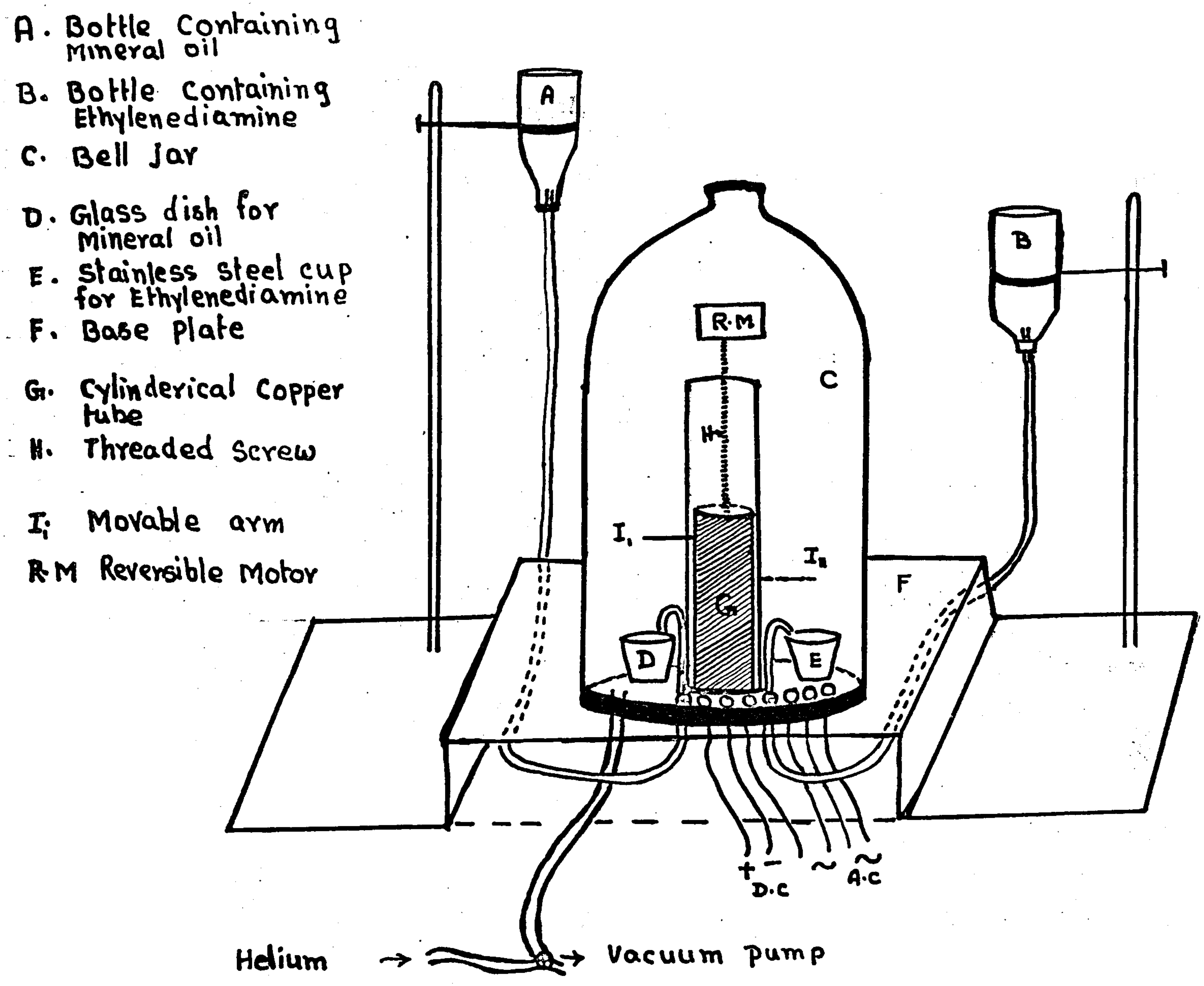
A. Bottle Containing Mineral oil
B. Bottle Containing Ethylenediamine
C. Bell Jar
D. Glass dish for Mineral oil
E. Stainless steel cup for Ethylenediamine
F. Base Plate
G. Cylinderical Copper tube
H. Threaded Screw
I. Movable arm
R.M Reversible Motor
A
B
R.M
C
H
I₁
I₂
F
G
D
E
+ − D.C
~ ~ A.C
Helium →
→ Vacuum pump

FiG. 4

was found to dissolve the alkali salts. Commercial ethylenediamine contained about 0.5% of moisture. A dehydrating method was used in order to eliminate the moisture content. Commercial ethylenediamine was digested for about three hours with sodium shavings and refluxed for three hours and finally vacuum distilled in distilling bottles. The pressure in the distilling system was about 700 microns. Ninety per cent of the material was distilled over a boiling range of less than ± 0.5° C. The first and the last fractions were discarded while the middle fraction was collected and estimated to be of 99.99 per cent purity. Precautions were taken to exclude atmospheric CO_2 and water.

The electropolishing of sodium single crystals required determination of the most suitable operating conditions for a given concentration and electrode arrangement. The results for some concentrations and electrode arrangement have been tabulated in Table I. The most important factor upon which successful polishing depended was of the control and initial adjustment of the current density for a given concentration. Too low a current density introduced etching on the surface of the specimen: whereas for too high a current density, excessive gassing was found to occur at the anode causing an uneven polishing. The current density was considered to be properly adjusted when no change was observed in the current when the applied voltage was altered. The relation between the current and the voltage may be altered either by the concentration of the electrolyte or by changes in the position of the electrodes. Voltage vs Current for given concentration and electrode arrangement are shown in figure 5. It was found desirable to operate around the plateau regions.

Table I. Concentration of salts in ethylenediamine and the current in milliamperes at the polishing region.

Salts	concentration gms./cc	electrodes apart	volts in D.C.	current in milliamperes per sq. inch
Potassium Iodide + Sodium Iodide	0.04	1/2 inch	17	180
Potassium Iodide	0.018	1/2 inch	17	120
Sodium Bromide	0.018	1/2 inch	17	60

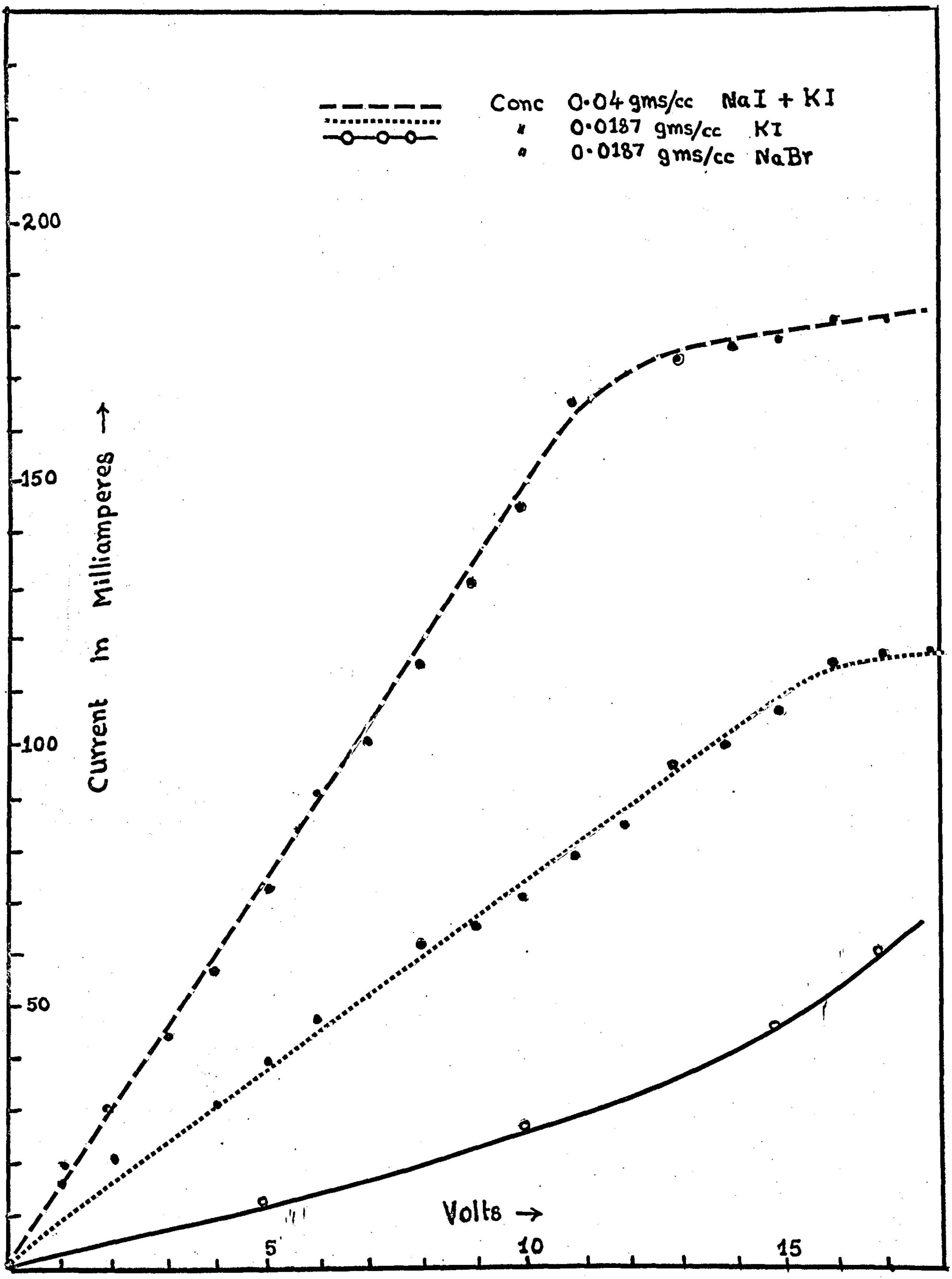

Fig. 5. Volts Vs Current

Various ethylenediamine solutions were prepared by dissolving weighed amounts of pulverized salts in known weights of the purified solvents. In view of the conductivity of various salts in ethylenediamine solutions only one mixture, 20% by weight sodium iodide and 80% by weight potassium iodide, when dissolved in the known weight of the solvent gave satisfactory results. The salts, sodium iodide and potassium iodide, were pulverized overnight and the amount required for a concentration of .04 grams per c.c. of ethylenediamine were added to the stainless steel cup "E". (Refer to Table I for concentrations of salts and the electrode arrangement).

The sodium single crystal was attached to the movable arm and was partially submerged in the mineral oil bath "D". The bell jar was evacuated to 20 microns with the mechanical and oil diffusion pumps. The pressure dropped to 20 microns in about 3 hours. At the end of 3 hours the vacuum was cut off and a purified helium jet was slowly introduced into the bell jar. The crystal was then transferred to the other side of the bell jar and was kept suspended in the electrolyte vessel "E" (the stainless steel cup), ready for electropolishing. (see Fig. 4).

Ethylenediamine, which had already been collected in the distilling bottle "B", was then slowly introduced into the vessel "E" for each run of the experiment. Electropolishing was carried out under helium pressure, since ethylenediamine was found to evaporate at low pressures, i.e. 20 microns. During polishing, the sodium specimen was kept at a positive potential and the electrolytic vessel "E" at a negative potential. 17-18 volts d.c. were applied across the electrodes, 1/2 inch apart, and the current density was observed to be 180 ma/sq. inch. Commercial helium was found to contain traces of hydrogen and oxygen and was purified by passing through potassium shavings and bubbling through an alloy of sodium and potassium. The quality of the polished surface produced by this method was superb.

After electropolishing, the movable arm was employed to transfer the sodium single crystal to mineral oil bath "D". The total time taken during the transfer was about four minutes. During this interval the polished surface of the crystal remained bright and untarnished.

Ten λ ($\lambda = 10^{-3}$ ml) of $Na^{22}Cl$*, supplied in a weak hydrochloric acid, was transferred with the help of a micropipette and a pipette control onto a thin glass plate. The pipette control consisted of a glass syringe connected to the pipette by means of Tygon tubing. To obtain the entire contents it was found necessary to thoroughly rinse the pipette. The 10 λ $Na^{22}Cl$ tracer sample, together with the washings on the glass plate, were dried under an infrared lamp for about 30 minutes. Evaporation of the $Na^{22}Cl$ solution was found to be the most convenient method to form a solid residue containing the material to be deposited. The dried tracer sample on the glass plate was introduced into the electrolytic vessel "E". The whole system was enclosed by the bell jar and was evacuated to 20 microns. After reaching 20 microns the vacuum pump was turned off and a helium jet was slowly introduced. The crystal was then transferred from the oil bath "D" to the electrolytic cup "E". Fifty cc of ethylenediamine were introduced into the electrolytic vessel containing the tracer isotope. During the process of

*$Na^{22}Cl$ was supplied by the Nuclear Science and Engineering Corporation, Pittsburgh 36, Pa.

electrodeposition the polished crystal surface was kept at a negative potential with respect to the electrolytic vessel. The electrodes were then adjusted 1/2" apart. The initial current density was 80 microamps/sq. inch and steadily decreased with time. After about 2-3 hours the current density dropped to zero, indicating complete deposition of the Na^{22} tracer.

The plated sodium crystal was then transferred into a Pyrex test tube. During the transfer precautions were taken to protect the plated surface. The test tube was evacuated, and maintained, at 0.1 mm of Hg pressure and immersed in an insulated water bath for the annealing process. The temperature of the bath was controlled by a thermoregulator* used with a mercury plunger type power relay capable of maintaining temperatures to within ± .05°C. The water in the bath was kept homogenous by two stirrers around the sample. The readings on four thermometers surrounding the sample were taken periodically during the diffusion anneal which on the average was 10^6 seconds. Over this period of time the probable error of the temperature readings was ± .05°C for all bath temperatures used.

After the diffusion anneal the sample was removed from the Pyrex tube for sectioning on a hand microtome. Uniform slices of 50 microns were taken out of each sample. Two successive slices were dissolved in test tubes which contained ethyl alcohol. The blade of the microtome was thoroughly washed with absolute alcohol after each slice. The washings were transferred to their respective tubes for radio-active measurements. Sectioning of the crystal was continued until the radioactivity of the slice approached the background count of the scalar.

* American Instrument Co., Silver Spring, Maryland.

The instruments used for the radioactive assay were a Model 135 scalar and a Model 810B well type scintillation detector made by Baird-Atomic, Inc. Since the tracer isotope Na^{22} emits gamma radiation, the use of the well type scintillation detector was found to be more appropriate to detect the gamma radiation. The optimum operating voltage, 1500v, for the counter was determined using a Na^{22} source obtained from Baird-Atomic, Inc. The test tubes, containing the dissolved 100 microns of materials, were introduced into the detector and the radiation was recorded for ten one minute intervals. The average number of counts per minute was obtained from these. Precautions were taken to avoid contamination of the crystal detector. No corrections were made for the decay of the tracer isotope Na^{22} since its half life was 3 years.

Results

Three crystal samples were prepared by the previously described techniques for diffusion anneal at various temperatures. The diffusing temperature, the diffusion anneal time, and the counting rates for the various sections are given in Table II, III, and IV. The section numbers correspond to slices 100 microns thick and the counting rate is that of the entire section. Where no counting rate is shown the loss of a section or some of the solution would have resulted in inaccurate measurements. The counting rate has been corrected for the background counting rate as determined at the beginning of the radioactive measurements of each crystal.

The diffusion coefficients D are obtained by plotting lnC vs x^2 as given in equation (3). The data, through the counting rates, give the concentration of the radio-isotope in the 100 microns sections rather

Table II. Counting rates for the sections of the sodium crystal annealed at the temperature of 20.00 ± 0.05°C for 7.54×10^6 seconds.

Background: 1076 CPM

Section Number	Av. counts per minute	Corrected counts per minute
1	2008	932
2	1891	815
3	1846	770
4	1831	755
6	1766	690
7	1711	635
8	1565	489
10	1601	525
11	1546	470
12	1526	450
13	1536	460
14	1496	420
15	1467	391
17	1425	349
18	1399	323
19	1391	315
20	1386	310
21	1346	270
22	1356	280
24	1301	225

Table III. Counting rates for the sections of the sodium crystal annealed at the temperature of 31.00 ± 0.05°C for 1.8718×10^6 seconds.

Background: 1076 CPM

Section Number	Av. counts per minute	Corrected counts per minute
1	23,000	21,924
2	18,500	17,424
3	16,500	15,424
4	23,500	22,424
5	15,500	13,424
6	13,486	12,410
10	10,500	9,434
11	10,326	9,250
14	10,234	9,158
15	7,510	6,434
16	7,500	6,424
17	6,583	5,507
18	5,215	4,139
19	4,900	3,824
20	4,200	3,124
21	3,872	2,796
22	4,500	3,424
23	3,596	2,520
25	3,500	2,424
26	1,778	702
28	2,859	1,703
29	2,600	1,524
30	2,156	1,080

Table IV. Counting rates for the sections of the sodium crystal annealed at the temperature of 41.00 ± 0.05°C for 9.64×10^5 seconds.

Background: 1083 CPM

Section Number	Av. counts per minute	Corrected counts per minute
1	96,977	95,894
2	72,582	71,499
3	48,188	47,105
4	44,910	43,833
5	23,860	22,777
6	19,592	18,509
7	16,713	15,630
8	12,938	11,855
9	11,209	10,126
10	9,536	8,453
11	7,135	6,052
12	8,163	7,080
13	6,496	5,413
14	7,862	6,779
15	7,184	6,101
16	4,265	3,182
17	5,103	4,020
18	3,864	2,781
20	3,599	2,516
21	2,816	1,733
22	2,345	1,262
23	2,764	1,681
26	2,539	1,456

at a depth x. The lnC has been plotted as a function of the square of the average depth of each section and are shown in Fig. 6, 7, and 8 corresponding to the data in tables II, III, and IV, respectively. The data has been plotted for sections 10 and above so that the width of the section will be small compared to the depth. The curves shown in Figures 6, 7, and 8 were obtained by the method of least square fit and the corresponding diffusion coefficients are given in table V. The best least square fit was determined by RPC 4000[*] computer, Scientific Computation Laboratory, Medical College of Virginia. The data were not corrected for the fact that all distances of the sectioned slices were measured at room temperature rather than at the diffusion temperature.

The logarithm of the diffusion coefficients obtained from figures 6, 7, and 8 are plotted against the reciprocal of the absolute temperature in figure 9. The slope of this curve gives the activation energy and from the ordinate intercept at $1/T = 0$ the diffusion constant is obtained. The diffusion constant and the activation energy for sodium single crystal was found to be 0.313 ± 0.018 cm^2/sec and 11,000 ± 170 cal/mole, respectively. Therefore for sodium single crystal equation (7) becomes,

$$D_{Na} = 0.313 \quad \exp\left(\frac{-11,000}{RT}\right)$$

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[*] General Precision Corp., Tarrytown, N.Y.

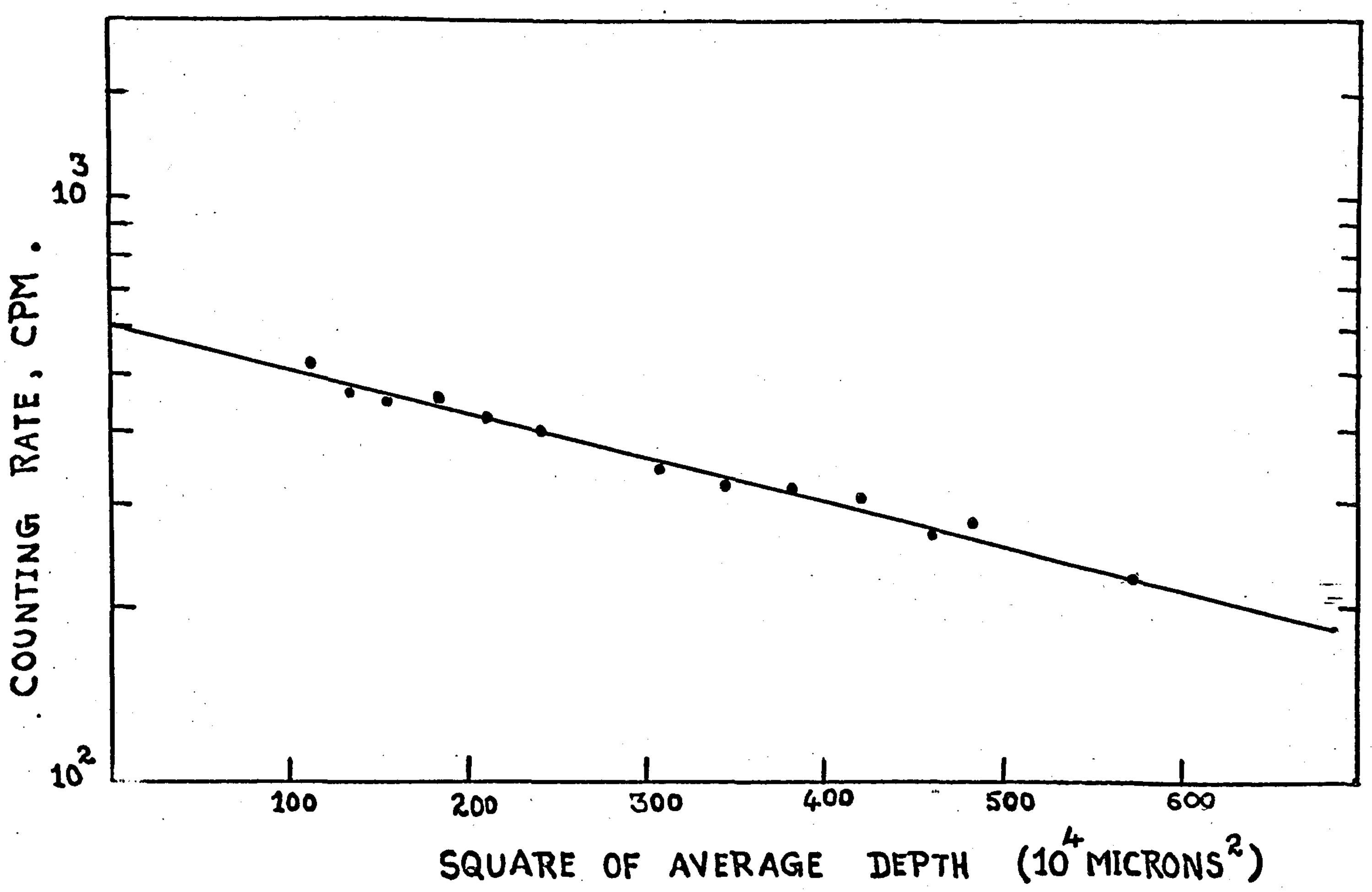

Fig. 6 Variation of C With Square of Average Depth.

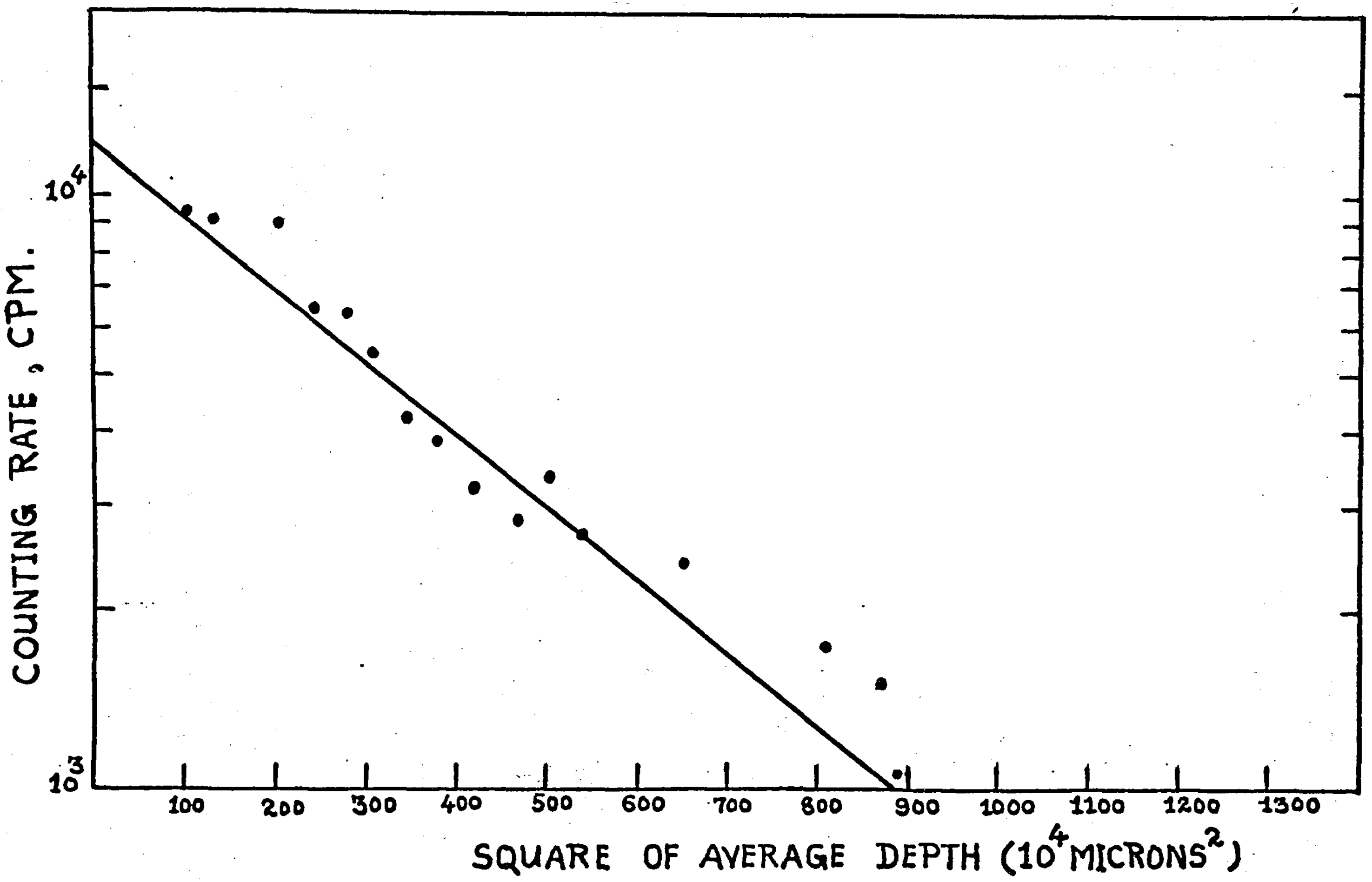

FiG. 7 Variation Of C With Square Of Average Depth.

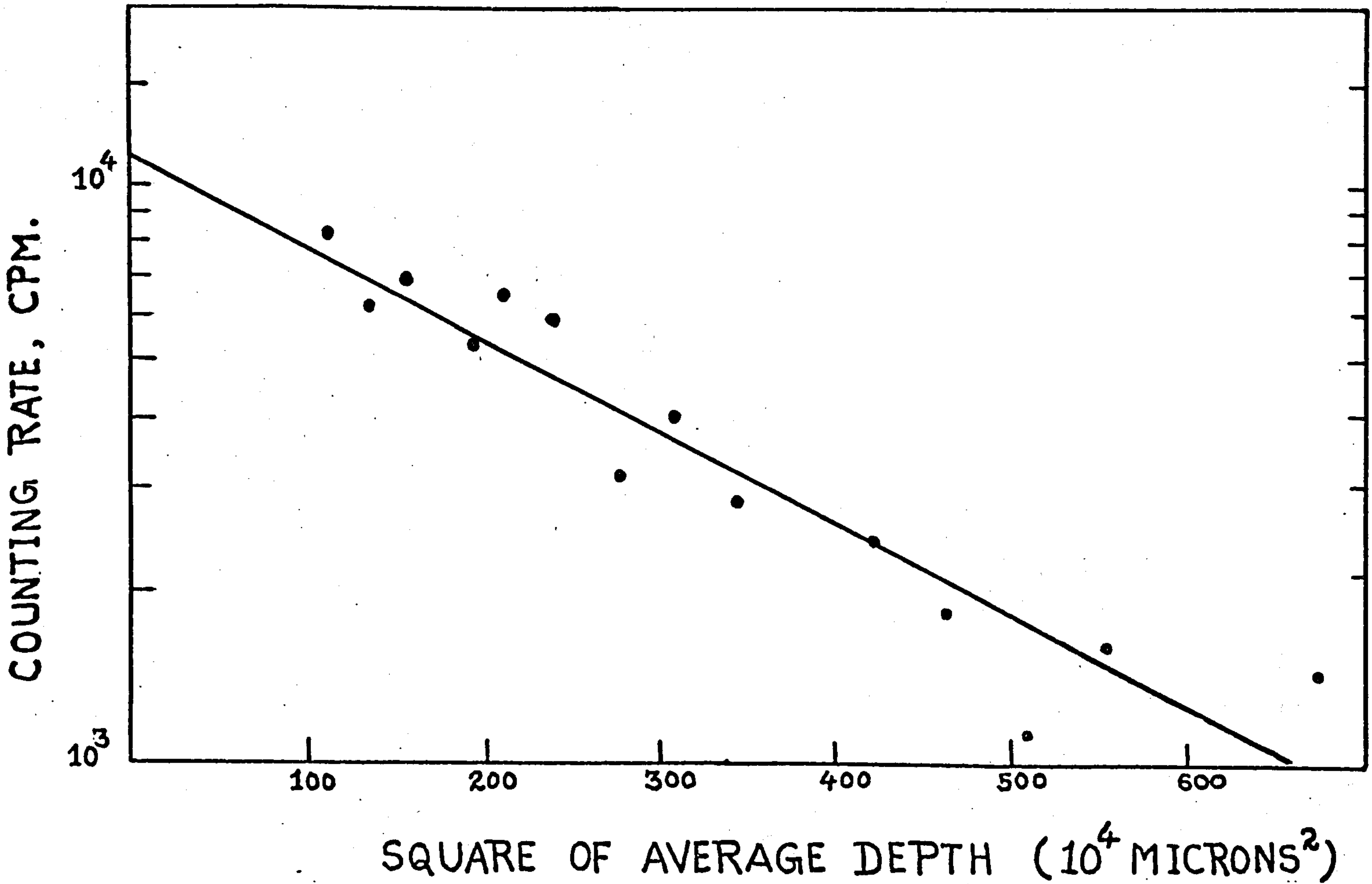

FIG. 8 Variation of C with Square of Average Depth.

Temperature on Absolute scale °K	Diffusion Coefficient D cm^2/sec.	Activation Energy Q cal/mole.	Δ Q cal/mole	Diffusion Constant D_o cm^2/sec.	Δ Do cm^2/sec.	$\frac{\Delta H}{Tm}$
293.0	2.01×10^{-9}					
304.0	4.07×10^{-9}	11,000.0	±170.0	0.313	± 0.018	30.0
314.0	7.17×10^{-9}					

Table V. Summary of Diffusion Data.

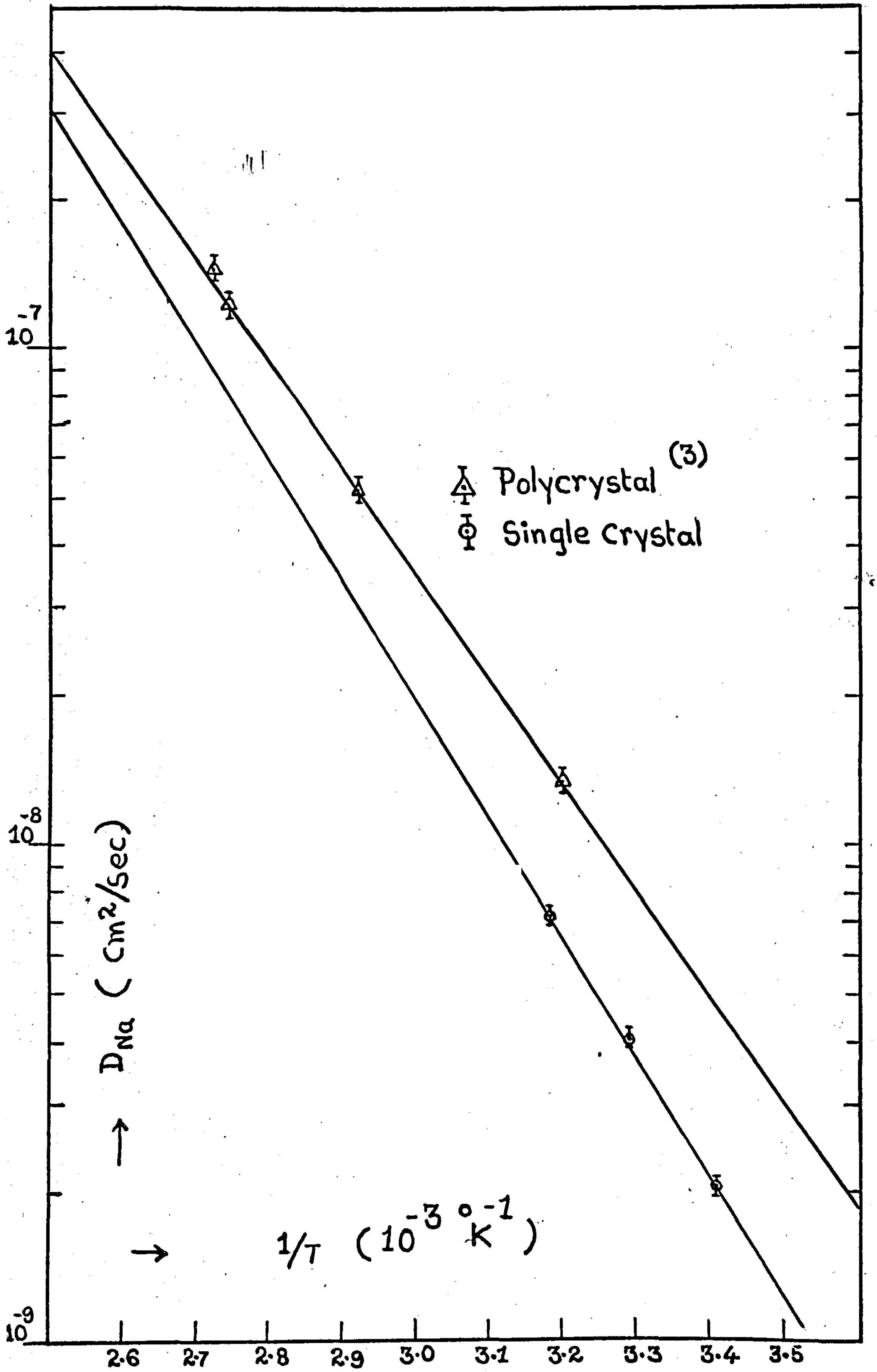

FIG. 9 Variation of D_{Na} With the reciprocal of Absolute Temperature.

DISCUSSION

The results obtained for sodium single crystals in this study can be compared with the results given by N.H. Nachtrieb and E. Catalano (3) for polycrystalline sodium. Their results have been reproduced in Figure 9 for comparison and give 10450 cal/mole for the activation energy and 0.242 cm^2/sec for the diffusion constant. It is observed that the values of D for single crystals lie consistantly below the values obtained for polycrystals. Similarly, the activation energy and the diffusion constant for the single crystals are greater than those for the polycrystals.

While detailed comparisons of the differences for single crystals and polycrystals cannot be given, these results are consistent with results found for single-crystal and polycrystalline silver (4). For silver the lower activation energy found for polycrystals was attributed to the influence of grain boundaries. However, at higher temperatures (above about 700°C) where the influence of the grain boundaries was small, the slope of the curve, and hence the activation energy, approached that for single crystals. The diffusion constants are determined by extrapolating the ln D vs 1/T curves to where $1/T = 0$, thus, a change in the slope of the curve would mean a change in the calculated value of the diffusion constant with the result that the extrapolated value obtained from the polycrystalline curve would be less than the extrapolated value from the single crystal curve. In Fig. 9 the curves for the polycrystalline sodium and the single-crystal sodium give the appearance of converging at higher temperatures (higher than the melting point of sodium, 98°C). Since the reported diffusion constant for the polycrystalline case was obtained by linear extrapolation of this curve it would be less than that for the single crystal case. That this is the case would be difficult to show for sodium since diffusion anneal would have to be made at temperatures above the melting point. Further comparison of the activation energies cannot be made since the kind, number, and effect of defects in the single-crystal sodium are not known.

There exists a relation between the associated enthalpy and the melting points of solids. According to Van Liempt (11) and C. Zener (7) the relation $\Delta H/T_m = 32$ cal/deg applied to cubic metals. Using the melting point of sodium $\Delta H_{cal} = 11,840$ cal/mole compared to the experimentally measured value of 11,000 cal/mole.

No unique conclusion can be drawn concerning the mechanism of diffusion in metals from diffusion rates and the activation energy alone. Such a decision must depend upon direct measurement of the mean jump frequency, which cannot be done with precision. The thermodynamical relations, associated enthalpy and entropy of activation, coupled with other evidences would permit tentative and suggestive conclusions to be drawn concerning the mechanism of self-diffusion.

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