

DIFFUSION IN MINERALS

by

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ERRATUM

1. Abstract I, 3rd line from bottom, change ( $D \sim 2.6 \times 10^{-10}$ ) to ( $D \sim 2.6 \times 10^{-11}$ )
2. p. 23, lower right corner of Plate. Change "Oil Diffusion Pump" to "Diffusion Pump".
3. p. 28, line 20. Change "some solid inorganic com-" to "some solid organic com-".
4. p. 33, line 13. Change "slumps" to "sumps".
5. p. 71, line 20. Change "15 to 50 cal./mole" to "15kto 50 K cal./mole".

Mead LeRoy Jensen

DEPARTMENTAL COPY:

## ABSTRACT

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Mead LeRoy Jensen

Submitted for the degree of Doctor of Philosophy  
in the Department of Geology on May 11, 1951.

The thesis is an attempt to initiate laboratory investigation on the long-neglected subject of solid diffusion in minerals using radioactive nuclides. A fundamental review of the subject is given. Experimental techniques and methods have been developed, the effect of a disordering transformation on diffusion rates has been determined in the case of the mineral chalcocite, and approximate diffusion rates through a few minerals have been measured.

The diffusion coefficients of copper in chalcocite have been determined at temperatures above ( $D = 1 \times 10^{-9}$  cm.<sup>2</sup>/sec. at 127° C) and below ( $D = 1.3 \times 10^{-11}$  cm.<sup>2</sup>/sec at 60° C) the critical temperature of complete disorder of copper in this mineral. The activation energy of copper in high chalcocite has been determined to have a value of approximately 4,000 cal./mole. Values have been obtained on the approximate diffusion rates of copper in tetrahedrite ( $\sim 10^{-8}$  cm.<sup>2</sup>/sec. at 182° C), in quartz ( $\sim 10^{-10}$  cm.<sup>2</sup>/sec. at 600° C), and in cuprite containing blebs of chalcopyrite ( $\sim 2 \times 10^{-8}$ )cm.<sup>2</sup>/sec. at 92° C). The investigation of the diffusion of sodium in perthite ( $D \sim 2.6 \times 10^{-10}$  cm.<sup>2</sup>/sec. at 550° C) has been accomplished and some geologic conclusions have been deduced from this experiment.

## ABSTRACT

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There has been much disagreement upon the geologic and mineralogic importance of solid state diffusion. Many contradictory hypotheses have been expressed by geologic authorities based upon their interpretation of field evidence. There have been, however, very few fundamental laboratory investigations made upon this problem.

This thesis is an attempt to begin the laboratory investigation using radioactive nuclides of solid diffusion rates in minerals by developing experimental techniques, by determining the effect of disorder transformations on diffusion rates, and by measuring diffusion rates through some minerals. The diffusion coefficients of copper in chalcocite have been determined at temperatures above and below the critical temperature of complete disorder of copper in this mineral. The activation energy of copper in high chalcocite has also been determined. Approximate diffusion rates of copper in tetrahedrite, in quartz, and in cuprite containing unmixed chalcopyrite blebs have also been measured. The investigation of the diffusion of sodium in perthite at a temperature of 550 degrees centigrade has been accomplished and some important geologic conclusions have been deduced from this experiment.

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## II INTRODUCTION

Diffusion of ions and atoms in, through, and around minerals and rocks has been a subject of much controversy and speculation during the past half century. The geologic importance of diffusion has received varying degrees of acclaim and censure; for example, it has been accredited with the formation of all,<sup>1</sup> fifteen percent,<sup>2</sup> some,<sup>3</sup> and none<sup>4</sup> of the granitic masses.

The geologic literature contains many discourses on the "proof" of diffusion over great distances from field interpretations. In fact, an interesting symposium has been held, due to the controversy created by the subject, where noted authorities further aired their opinions on this enigmatic problem.<sup>5</sup> The extreme lack of laboratory investigations on diffusion rates in minerals, nevertheless, is appalling.

An attempt was made in 1915<sup>6</sup> to begin quantitative experimental work on solid diffusion in minerals. Even with this early start, the laboratory work has been neglected while the metallurgical literature of the past fifteen years abounds with experimental information on solid diffusion in the degenerate crystallographic case of metals.<sup>7</sup> It is interesting to note that the International Critical Tables give the diffusion coefficient of only one silicate, Natrolite, a zeolite which is listed as having a diffusion coefficient of

$1.5 \times 10^{-10} \text{ cm.}^2/\text{sec.}$  at 20 degrees centigrade.<sup>8</sup>

A unique laboratory experiment was performed in 1921,<sup>9</sup> which seemed to indicate that the rate of diffusion of magnesium and calcium ions into plagioclase glasses was about  $3.5 \times 10^{-6} \text{ cm.}^2/\text{sec.}$  at the high temperature of 1500 degrees centigrade.

Recently, more and more experimental diffusion results in minerals have been appearing in the geologic literature.<sup>10</sup> The laboratory work, however, is still in its infancy, if not still in the prenatal stage. There is no doubt, however, that the seed of laboratory investigation has been planted.

### III SCOPE AND PURPOSE OF WORK

It is the attempt of this thesis to begin the quantitative investigation of diffusion rates in minerals by the development of experimental techniques, to study the effect of structural and disordering transformations on diffusion rates, and to perform some experiments with the developed techniques on some interesting minerals.

The thesis is limited to true solid state diffusion and no attempt has been made to study the further effect upon diffusion rates by introducing other factors such as pressure, obvious fractures in the specimens, and by using water saturated samples. Whenever possible, single crystals have always been used and crystals containing obvious flaws and fractures have been rejected. Important factors, however, such as lineage structure and impurities could hardly be avoided. There is no doubt that these factors and many more will noticeably effect diffusion coefficients and it is the author's desire to investigate these other parameters in the future.

## IV GENERAL

### A. Mathematical Treatment

Diffusion may be defined as the process by which, under the influence of a concentration gradient and/or a chemical potential gradient, atoms or ions move from one position to another. When the phase is a gas, a liquid, or a solid, the diffusion process is more closely defined by the modifying adjectives gaseous, liquid, or solid, respectively.

The rate of migration of atoms through a phase may be treated rationally by equations based on Fick's First and Second Laws.<sup>11</sup> According to Fick's First Law the amount of material ( $dm$ ) per unit time ( $dt$ ) which diffuses in a direction ( $+x$ ) is proportional to the cross-sectional area ( $A$ ) through which it passes and to a driving force or concentration gradient ( $\frac{\partial c}{\partial x}$ ). That is:

$$\frac{dm}{dt} \propto A \left( -\frac{\partial c}{\partial x} \right) \quad (1)$$

A proportionality constant  $D$ , is introduced giving:

$$\frac{dm}{dt} = -D \cdot A \left( \frac{\partial c}{\partial x} \right) = -D \cdot A \cdot g^*$$

where,  $\frac{dm}{dt}$  is the rate of transfer of solute.

$D$  is the diffusivity or diffusion constant.

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\* A more rigorous derivation of this equation is given in Appendix A.

and  $g = \frac{\partial c}{\partial x}$  is the concentration gradient.

The following units are most commonly used:

$$m = \begin{cases} \text{mols} \\ \text{grms.} \\ \text{atoms} \end{cases}$$

$$t = \text{seconds}$$

$$A = \text{cm.}^2$$

$$x = \text{cm.}$$

$$g = \begin{cases} \text{moles/cm.}^3 \\ \text{grms./cm.}^3 \\ \text{atoms/cm.}^3 \end{cases}$$

In order that the units should agree in the equation,  $D$  must be expressed in units of  $\text{cm.}^2/\text{sec.}$  The diffusion coefficient, therefore, is the amount of solute per unit time which diffuses through a unit cross-section under a unit concentration gradient.  $D$  values obtained from the study of diffusion in metals vary from about  $10^{-5} \text{ cm.}^2/\text{sec.}$  to values less than  $10^{-15} \text{ cm.}^2/\text{sec.}$  at given temperatures ranging from a few hundred degrees to over 1500 degrees centigrade. A diffusion coefficient of  $10^{-6} \text{ cm.}^2/\text{sec.}$  for a specific solute in a solvent means that one gram of the solute diffuses through an area of one square centimeter of the solvent in one million seconds.

Fick's Second Law shows the time rate of change with concentration and the distance rate of change with concentration. It is usually written as follows:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{where } D \neq f(c) \quad (3)$$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \quad \text{where } D = f(c)^* \quad (4)$$

It has been found that the diffusion coefficient may actually vary from one position to another in a given substance depending upon the concentration of solute at the position. In other words, the diffusion "constant" of a solute in a solvent is a function of the solute concentration. Unfortunately, the diffusion equations which have been used in the past and which are still being used (with one exception known as the Matano Analysis<sup>12</sup>) were derived with the assumption that  $D \neq f(c)$ . This is not as serious as it first appears, since in many experiments the change in concentration is extremely small and the corresponding change in the diffusion coefficient is usually overshadowed by experimental errors. It is possible, furthermore, to determine from a series of experiments when the results obtained are in error due to diffusion being a function of concentration.

Diffusion equations are very similar to heat flow equations with the constants in each being the diffusion coefficient and the coefficient of thermal conductivity respectively. For this reason diffusion equations have stemmed

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\*The derivation of this equation is given in appendix B.

from heat flow equations, and texts<sup>13</sup> on this subject are prime sources for diffusion equations with variable boundary conditions.

The equation used for the experiments done for this thesis will be the only diffusion equation dealt with in any detail. Several texts and many papers<sup>7a,14</sup> are good sources for the mathematical treatment of other diffusion equations with given boundary conditions.

The mathematical treatment used in this thesis was first applied to diffusion studies by W. A. Johnson<sup>15</sup> in his study of the self diffusion of silver. I know of no published derivation of this equation, therefore, the derivation is given in Appendix C. The equation is:

$$c_x = \frac{c_o \cdot a}{\sqrt{\pi D t}} \cdot e^{-\frac{x^2}{4Dt}} \quad (5)$$

where,  $c_x$  = the concentration at a distance  $x$  from the interface

$c_o$  = the initial concentration

$a$  = thickness of solute layer

$x$  = the distance from the solute film

$t$  = time of diffusion

$D$  = diffusion coefficient

It should be noted from the derivation that the equation is based upon Fick's Second Law, equation (3), with

the geometrical boundary conditions specifying that the solute be placed in crystallographic contact with a planar surface of the solvent as shown in figure 1. The thickness of the solute should theoretically approach zero but practically it may be as much as from five to ten percent of the measurable diffusion distance, a distance of usually a few tenths of one millimeter. With proper techniques, however, it is fairly simple to keep the thickness easily within one percent of the measurable diffusion distance.

After a given diffusion time, successive sections are cut from the specimen at known distances  $x$  from the

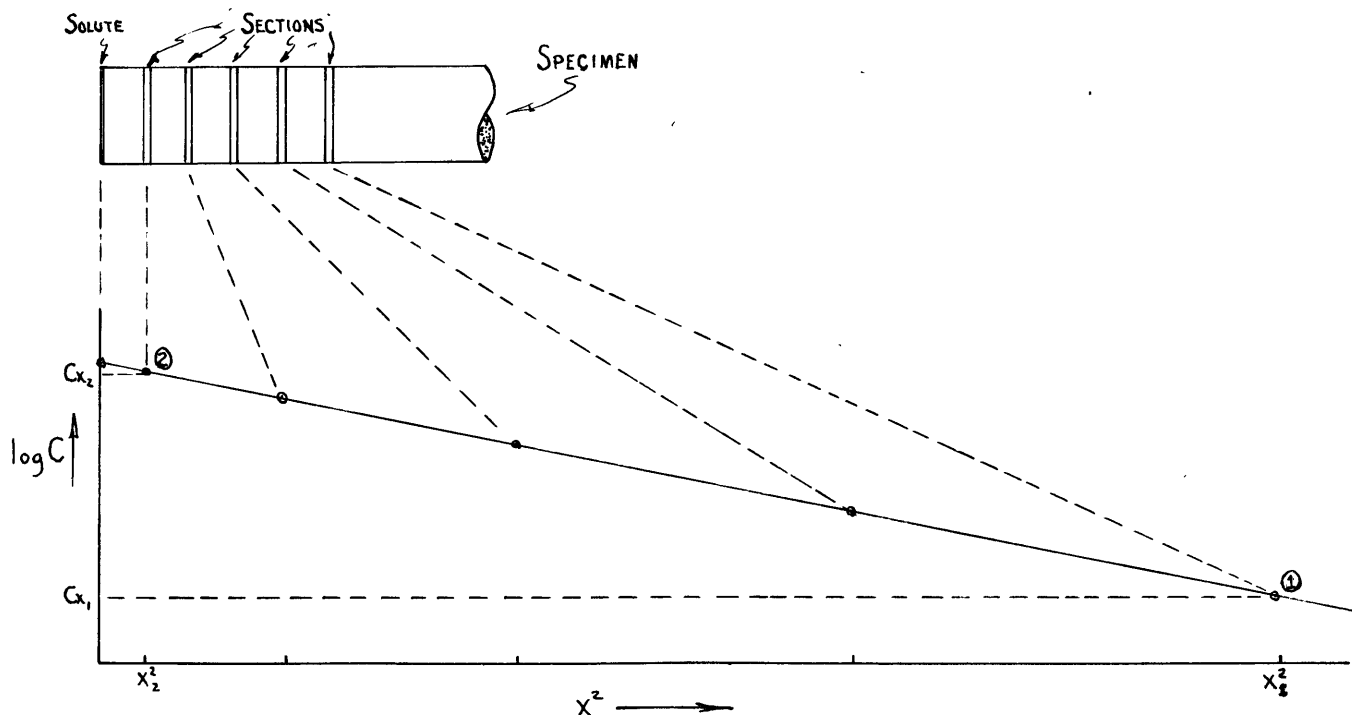


Figure 1. Plot of concentration versus distance.

solute film and the concentration of the solute is determined in each section. This data is plotted on semi-logarithmic paper with the concentration plotted logarithmically versus the distance squared. The purpose in doing this will become obvious after the following considerations. The equations for the concentration of two sections located at a distance  $x_2$  and  $x_1$  from the solute layer are:

$$\text{For section 2, } \ln c_{x_2} = \ln \frac{c_0 \cdot a}{\sqrt{\pi D t}} - \frac{x_2^2}{4Dt} \quad (6)$$

$$\text{For section 3, } \ln c_{x_1} = \ln \frac{c_0 \cdot a}{\sqrt{\pi D t}} - \frac{x_1^2}{4Dt} \quad (7)$$

$$\text{The difference is: } \ln(c_{x_2} - c_{x_1}) = \frac{1}{4Dt} (-x_2^2 + x_1^2)$$

$$\text{Therefore, } -\frac{1}{4dt} = \frac{\log (c_{x_2} - c_{x_1}) \cdot 2.303}{x_2^2 - x_1^2} \quad (8)$$

$$\text{or, } -\frac{0.1086}{D \cdot t} = \frac{\log (c_{x_2} - c_{x_1})}{x_2^2 - x_1^2}$$

Notice that the right side of equation (8) is the slope of the line as shown on the previous page. If the experimentally determined points give a straight line, the slope may be determined graphically and the diffusion coefficient will be given by the equation:

$$D = -\frac{0.1086}{\text{slope} \times t} \quad (9)$$

If the time of diffusion ( $t$ ) is measured in seconds and the distances ( $x$ ) are measured in centimeters, the diffusion coefficient has the dimensions of  $\text{cm.}^2/\text{sec.}$

If the slope is not a straight line, experimental errors being neglected, the diffusion coefficient is not a constant and it varies with concentration. (It should be remembered that equation (5) was derived from equation (3) where  $D \neq f(c)$ .)

#### B. Experimental Methods and Techniques.

In order to perform diffusion experiments it is necessary that the solute or diffusing ions be placed in a position where they may readily begin diffusing through, or exchanging position, with the solvent. This requires that the solute and solvent atoms be within "atomic reach" of each other; i.e., not separated by a gap of the order of more than a few angstroms. This can be accomplished by many different methods but each method has its limitations which become fairly obvious when any given solute and solvent pair are considered. The following is an outline of several successful methods which have been used in the study of diffusion; it also includes modification of existing techniques, development of new methods, and suggestions of other techniques.

Welding is one of the more common methods used when both the solute and solvent material are metals. It has been used in the study of solid diffusion rates of cadmium, indium, tin, antimony, and copper into silver;<sup>16</sup> iron into gold, copper into platinum, nickel into platinum,

nickel into gold,<sup>17</sup> and many others.<sup>15</sup> This method merely requires that the two metals be joined together over the entire area of a planar surface by a good weld.

Another common method used when the substance under investigation are conductors is electroplating. This has an advantage over the welding technique in that a very thin film of solute atoms may be electroplated on a planar surface of the solvent material. It has been used in the study of diffusion of nickel into copper,<sup>18</sup> copper into copper alloys,<sup>19</sup> and the study of self diffusion of silver using radioactive silver.<sup>15</sup>

An electroplating technique was developed in this thesis during the investigation of the diffusion rates of copper into minerals of the semi-conductor type. Since radioactive copper was used, the experiments had to be made in such a way that radiation hazards were minimized. It was also desirable that the process should be observable. This was arranged by using the technique shown on Plate 1. Since  $\text{Cu}^{64}$  is almost entirely a beta emitter of 0.571 and 0.657 Mev energies, the particles were easily stopped by approximately one millimeter of pyrex glass. The water jacket increased the shielding much more than necessary and it also provided an easy means of measuring the temperature of the electroplating solution without placing a thermometer in the active solution. The copper made a much better coating when the electroplating solution had a temperature of about 35 degrees centigrade.

The radioactive copper was obtained in the form of copper foil. In order to obtain a dilute solution of copper sulphate, the foil was dissolved in 2N  $H_2SO_4$ . Since copper is only moderately soluble in hot  $H_2SO_4$ , a few cc's of hydrogen peroxide were added to the solution. This rapidly oxidized the copper which then reacted with the acid very easily and at a temperature as low as 40 degrees centigrade. Preparation of the solution was carried out under the chemical hoods in the Cyclotron Building, Massachusetts Institute of Technology.

The electroplating solution had the following composition:

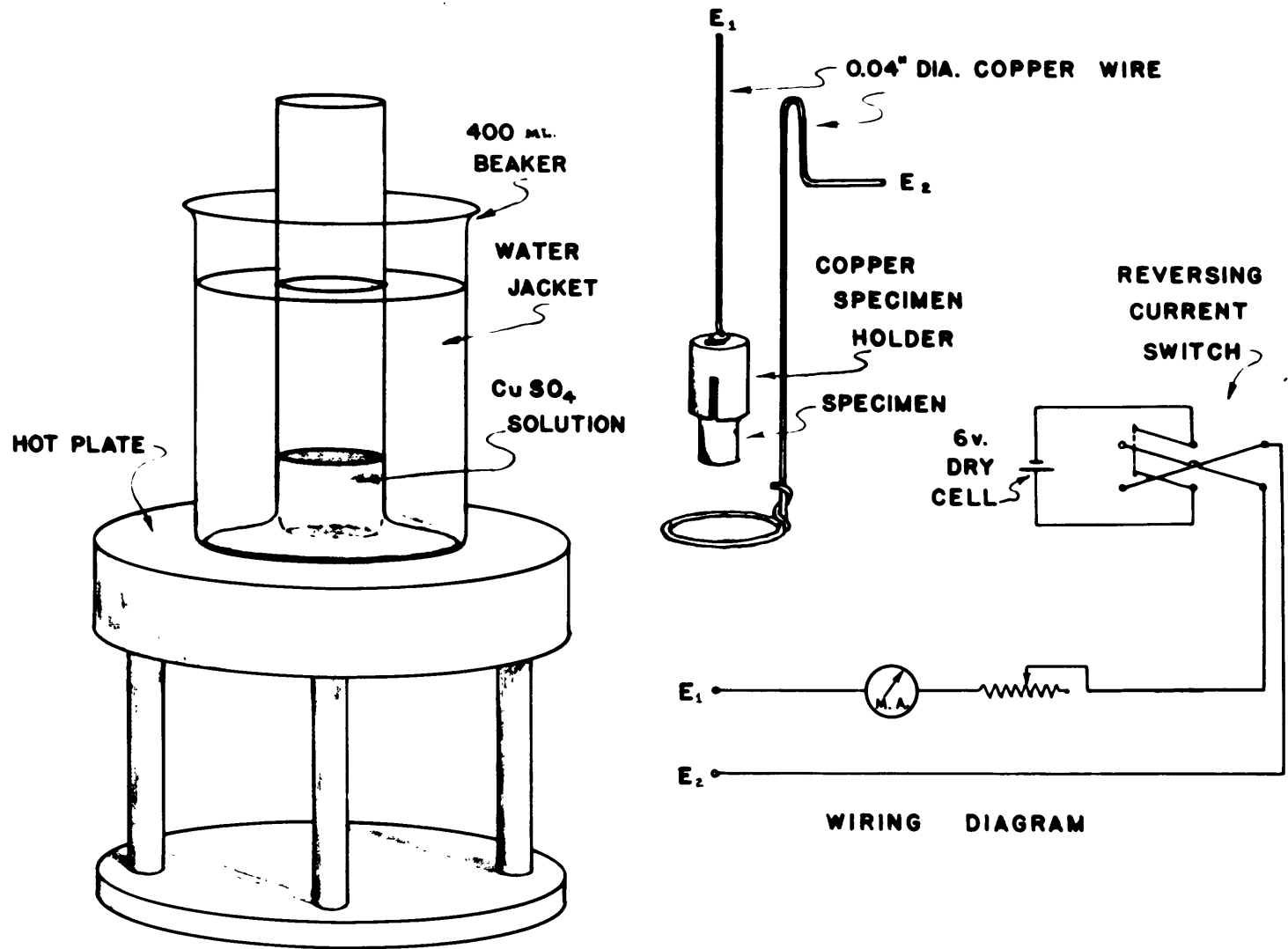
0.5 grms. Cu foil

25 cc's 2N  $H_2SO_4$

10 cc's  $H_2O_2$

This solution was heated at a few degrees below its boiling temperature for several minutes after all of the copper had been dissolved in order to remove any excess  $H_2O_2$ . The solution was then poured into the electroplating cell where the copper wire anode was already in place. The water jacket was heated to 25 degrees centigrade and the specimen was lowered into the cell. The planar end surface of the specimen had previously been thoroughly cleaned, washed in cleansing alcohol and distilled water, and held so that no finger prints were left on the cleansed surface. The cylindrical surface was covered with scotch tape which prevented deposition on that surface.

PLATE I



EXPERIMENTAL SETUP FOR ELECTROPLATING TECHNIQUE

The electroplating required from twenty to thirty minutes with a current density of 200 milliamperes/in.<sup>2</sup> before a thin adherent coating was obtained. The current direction was reversed for a few seconds each minute during the first 10 minutes of electroplating.

A method of rolling or drawing can be used in the case of malleable metals. This technique can be used in the study of diffusion of magnesium and silicon from an aluminum alloy into pure aluminum.<sup>20</sup> This was done by rolling the aluminum onto both sides of the alloy, but only after the surfaces had been thoroughly cleansed. This method was used in order to prevent initial diffusion which would occur during casting of the alloy against the aluminum. It is possible, however, that the cold work induced by the rolling could cause more rapid diffusion and, thereby, increase the true coefficient of diffusion.

It is very obvious that none of the above methods is applicable to the study of diffusion in ionic crystals or minerals; however, there are several methods whereby a metal or an ionic substance may be caused to adhere to another ionic material. One of the most obvious methods, and one which may become as useful with ionic minerals as welding and electroplating have proven with metals, is by using a glaze. The ceramists have made noted contributions on determining the physical and chemical properties of glazes of different compositions; however, their object was to develop a glaze which would react favorably with the body to which it was being

applied in order to form a good adherent coating which would not spall nor craze.<sup>21</sup> This inter-reaction of the glaze and body must be avoided if the technique is to be used for the study of diffusion. In other words, a glaze which is used for diffusion studies must not only adhere to an applied surface but there must be as little initial diffusion or reaction between the body and the glaze as possible.

This is not too difficult to obtain. If diffusion studies are being investigated at temperatures of one-hundred or more degrees below the melting temperature of the crystal, a suitable substance can usually be chosen for the glaze which has a melting temperature slightly above the temperature region being studied. After the raw glaze has been allowed to dry on the crystal, it is placed in a furnace, which has already been heated to a temperature about 20 degrees above the fusing temperature of the glaze. If the specimen is removed from the furnace within one minute after the glaze fuses, there will normally be little reaction between the crystal and the glaze. This can and should be ascertained by removing thin sections from the specimen shortly after firing the glaze and, thereby, measure the extent of initial diffusion due to the glazing process. If the initial diffusion during the glazing is negligible, other specimens prepared in the same manner can be used for diffusion determinations at temperatures below the fusion temperature of the glaze.

If true solid diffusion studies (where both the

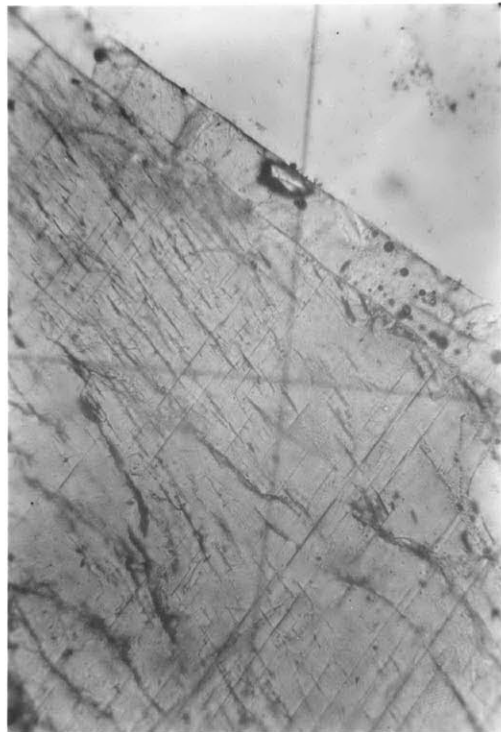
crystal and the glaze are in the solid state) are to be made in the region just below the melting temperature of the crystal, it becomes more difficult to select a suitable glaze which will fuse just below the fusing temperature of the crystal and will not react appreciably with the crystal which is, itself, almost ready to melt. This requirement can usually be met if the glaze and the body are essentially of the same composition, the only difference being that a small amount of flux is added to the glaze. The glaze material should be finely ground so that it will tend to fuse at a temperature as far below that of the crystal as possible. It is then thoroughly mixed with enough water to form a thin slip. A thin film of the slip is then applied to the chosen planar surface of the crystal under investigation, but only after the crystal face has been thoroughly cleaned and, if possible, treated in a dilute acid solution in order to remove any scum or oil from the surface. The thickness of the coating should be as thin as possible and this can be controlled by the amount of water dilution of the slip, since the surface tension between the slip and the crystal allows only so much slip solution to be applied before running over the side of the crystal. After the slip on the prepared specimen has been allowed to dry at a temperature of 110 degrees centigrade, it is rapidly placed in a furnace which is controlled at the desired temperature; it is removed within one or two minutes after the glaze fuses. It should

not be removed as soon as the glaze melts since it requires a short time for the air bubbles to migrate to the surface of the glaze and escape.

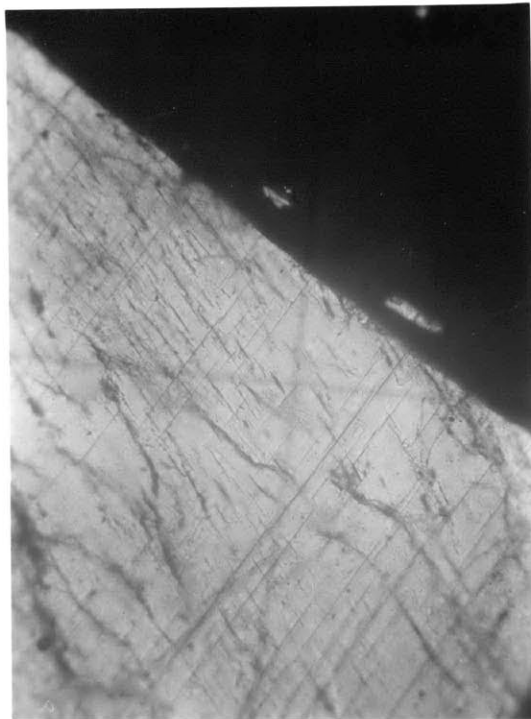
The above method was successfully used on several one-cubic-centimeter and smaller specimens of cleavlandite and microperthite. In the case of cleavlandite, the glaze slip was made from ground cleavlandite from the same specimen. The glaze had the following composition:

2.0 grms of cleavlandite  
0.3 grms. of  $\text{Na}_2\text{CO}_3$

This was thoroughly ground in a mortar and pestle and then mixed with 3 cc's of water and applied to the crystal. The glazing was done on different specimens at temperatures of approximately 1080, 1090, 1100, 1110, and 1120 degrees centigrade. A suitable glaze was formed only at the latter two temperatures. The specimens fired at the lower three temperatures remained in the furnace for five minutes and in each case there resulted only a surface fusion of the glaze. The specimens fired at the latter two temperatures remained in the furnace for eight minutes. Plate II is a photomicrograph of a thin section cut normal to the glazed surface of one specimen which was fired at 1110 degrees centigrade for eight minutes. There is no apparent reaction between the glaze and the crystal and it is of interest to note that this specimen was fired in a carbon arc furnace at a temperature about ten degrees above the crystals melting temperature. It is not known if the crystal itself reached the fusing tem-



Plane  
polarized  
light



Crossed  
nicols

Thin-section of Microperthite  
with adherent glaze coating. (X50)

Plate II

perature since it remained in the furnace for only eight minutes. It is well known, however, that fused potash and soda feldspar are extremely viscous due to their high silica content, and possibly, this may preserve their crystalline structure if they are heated to a temperature a few degrees above their fusing temperature for a short time and then allowed to cool. This hypothesis is worthy of investigation. It is obvious that the crystal in the photograph never fused while the glaze is definitely in the glassy state.

The author planned to have the sodium in the crushed cleavandite activated by slow neutrons, forming the  $\text{Na}^{24}$  isotope, which would then be used as the glaze material and applied to a crystal of cleavandite. The diffusion coefficient could then be determined at a temperature only a few degrees below the fusing temperature of the crystal. This plan did not materialize due to the lack of a suitable furnace and the insufficient activity provided by thermal neutrons at the Massachusetts Institute of Technology cyclotron.

Rosenqvist<sup>10b</sup> has used a glaze process in his study of the rates of solid diffusion of radium and lead (RaD) through feldspar crystals. He merely mixed his active nuclide with crushed window glass, fritted and recrushed it several times, and applied a drop of the viscous material to each feldspar crystal. Since he applied only a point source of solute atoms, his mathematical treatment differs from that

used when a thin film of solute atoms is applied to the solvent crystal.

A preliminary investigation of diffusion rates of sodium into quartz and feldspars was accomplished in this thesis by use of the following glaze technique: Three cubic centimeters of radioactive sodium ( $\text{Na}^{22}$ ) were obtained in the form of a solution of  $\text{NaNO}_3$ . The specific activity of the solution was more than enough to allow over ten parts of either  $\text{Na}_2\text{CO}_3$  or  $\text{NaCl}$  to be added to one part of the solution. When this had been done, a drop or two of the prepared solution was then spread over the flat clean end of a cylindrical specimen, of 0.271 inch diameter, which had been drilled from a suitable crystal. The water was allowed to evaporate leaving a fine white coating of crystals which, in the case of both solutions, was fused to form a glaze at a temperature of 800 degrees centigrade. The diffusion runs were done at temperatures from 550 to 700 degrees centigrade. Upon visual inspection, the glaze containing the  $\text{NaCl}$  appeared to form the better coating; however, for some unknown reason, more successful experimental results were obtained from the specimens prepared from the  $\text{Na}_2\text{CO}_3$  glaze. The activity of the thin glaze coatings on the 0.271 inch diameter specimens varied from ten to twenty microrutherford when measured at a distance of one-half inch from a thin mica window Geiger-Mueller tube. Each specimen was enclosed in 0.5 inch diameter hard glass tubing capsules during the diffusion runs to pre-

vent escape of radioactive sodium into the atmosphere by vaporization.

It was further observed, during the above experiments, that the soluble NaCl glaze could be removed after glazing by immersing and agitating the active end of the specimen in a beaker of hot water. This was repeated several times until no further glaze could be detected on the surface; it was then found that an activity of about one-tenth the glaze activity could be measured. This was due to an initial diffusion or ion exchange mechanism which took place during the glazing process. Upon sectioning the specimen it was further found that the penetration of active ions was negligible compared to the penetration obtained after approximately 24 hours of diffusion at temperatures of 500 degrees centigrade and higher.

Ion exchange techniques, whereby an active isotope exchanges position with a stable isotope of the same element located on the surface of the solvent crystal, should prove to be a suitable technique for diffusion studies. It has been found that active lead and sulphur nuclides will rapidly exchange with the same ions respectively of a tarnished surface of galena, while there is very little exchange with an untarnished surface.<sup>22</sup> The same investigator found that radioactive calcium and phosphorus films could be formed on the surface of the mineral apatite by an ion-exchange mechanism.

It is well known that delicate optical mirrors can be made by evaporating aluminum or silver on to glass. With

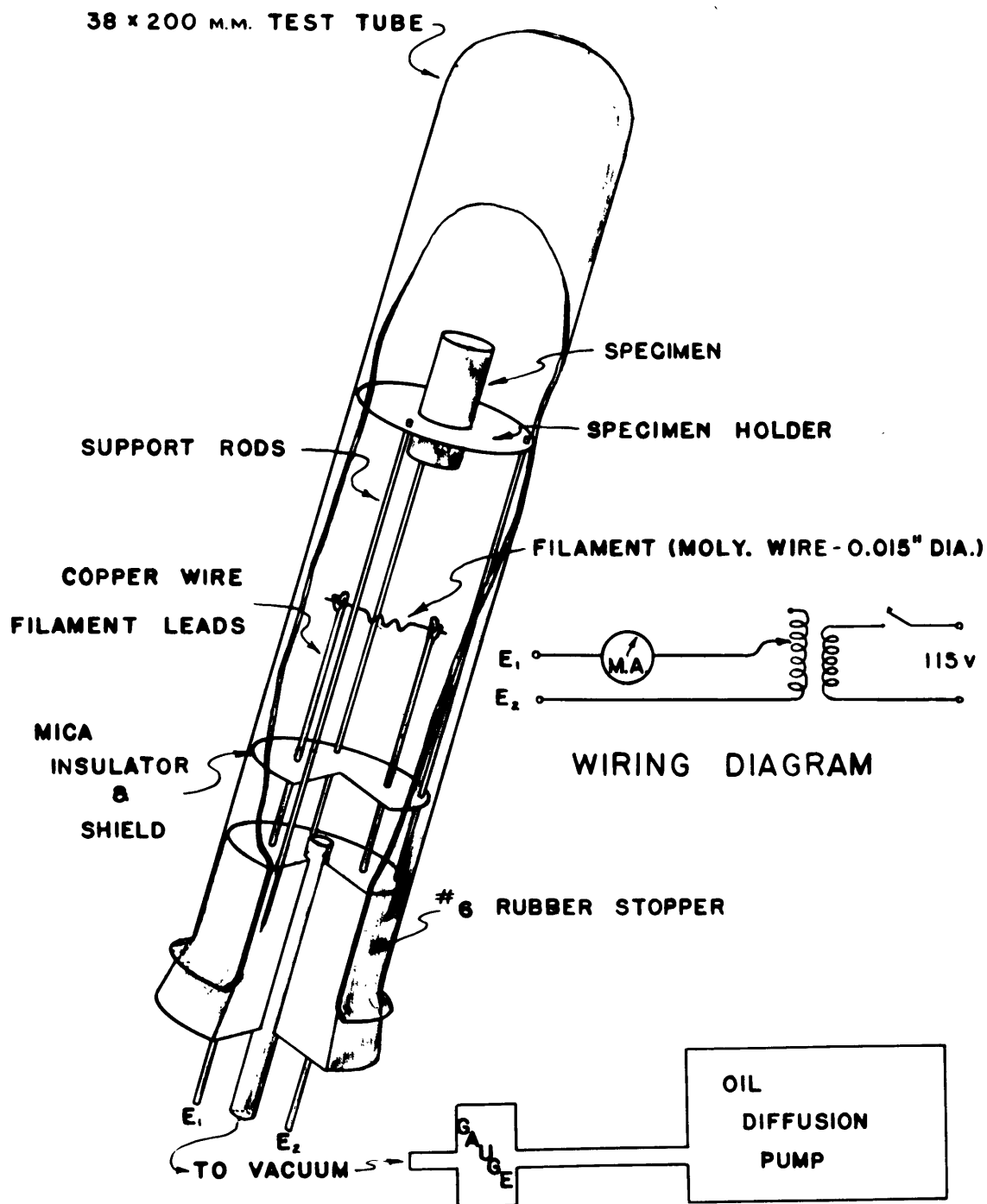
this knowledge, a method was developed whereby thin coatings of copper could be applied to metals, semi-conductors, and ionic minerals. A perspective drawing of this technique is shown on Plate III. It consists essentially of an evacuated chamber containing a tungsten filament and a support for the specimen to be coated. Thin strips of copper foil, containing radioactive copper ( $\text{Cu}^{64}$ ), are hung over the filament. The tube is evacuated and the filament is heated by increasing the current through the filament by means of a variac until the copper strips melt and the bright globules of molten copper adhere to the filament by surface tension.\* At this stage the copper evaporates rapidly. The process depends upon obtaining a suitable vacuum which will increase the free mean path of the copper atoms to a distance greater than the distance from the filament to the specimen. This requires a vacuum pressure of the order of a few microns of mercury or less.

An improvement of the evaporating method described above is a technique known as sputtering. It differs from the former method in that a high potential, varying from 1,000 to 20,000 volts, is applied between the filament and the plate or surface to be coated.

It seems possible that diffusion studies could be

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\* A molybdenum wire was used as the filament when evaporating copper since the surface tension between molybdenum and molten copper is greater than that between tungsten and molten copper.



EXPERIMENTAL SETUP FOR EVAPORATING TECHNIQUE

carried out on minerals which occur naturally with a variable ion concentration; e. g., zoned crystals or minerals which show the phenomenon of unmixing or exsolution. If the concentration of an ion in a zoned crystal was determined at several points in a plane normal to the zoned bands and the change in concentration was again determined after a diffusion time at a given temperature, the change in concentration would give a concentration variation curve which would lead to a diffusion coefficient. Indeed, it has already been found by several investigators<sup>23</sup> that structural homogeneity occurs in some perthitic intergrowths when heated in the region of 700 to over 800 degrees centigrade.

The second important aspect of the experimental techniques used in the study of solid diffusion rates is the method of determining the concentration gradient of the solute in the solvent.

There are numerous methods used in determining the concentration of solute atoms at a known distance from the solute-solvent interface. The method of measurement used depends upon several factors, such as the physical properties of the solvent, e. g., metallic or brittle, radioactive or stable nuclides, and other factors which make it possible to quantitatively determine the amount of solute present per unit volume of solvent. The following is an outline of several methods of concentration measurement.

One of the most obvious methods is visual investigation with the aid of a microscope. If the solvent is non-

opaque, the index of refraction of the solvent will vary in proportion to the concentration of solute atoms present.<sup>24,9</sup>

If the solvent is opaque, it may be investigated metallographically.<sup>25</sup>

A test based on the variation of microhardness with concentration of solute present has been used in the study of diffusion of copper, magnesium, manganese, and silicon into aluminum,<sup>26</sup> and surprisingly enough, it is fairly accurate. For example, in the study of diffusion of copper into aluminum, the microhardness varied from about 25 to 90 kgs./mm.<sup>2</sup> over a distance of about 400 microns.

One of the most common methods used is to determine the concentration of solute in given sections by chemical analyses or metallurgical assaying of each section. If the solvent is a metal, thin slices may be cut using a metal lathe, or preferably, a jeweler's lathe. The cuttings are collected from each slice or section and chemically analyzed. This method was used by Rhines and Mehl<sup>19</sup> during their study of diffusion of copper into copper alloys.

The sections may be analyzed for the amount of solute using the spectrograph. This has been done by Seith and Peretti<sup>16</sup> on the investigation of diffusion rates of cadmium, indium, tin, antimony, and copper into silver.

Quantitative measurements of the concentration of solute in a section cut from the solvent have been made by means of X-ray investigation.<sup>17</sup> This method is based on the

premise that the lattice parameter of a substance X varies with almost a straight line relation when plotted versus the atomic fraction of substance Y present. Data can be obtained<sup>27</sup> which seem to show that in the case of two materials with the same structure, their lattice parameter varies essentially as a straight line when plotted versus the atomic percent of the two materials present in the mutually soluble structure.

The investigation of the self diffusion of any element can only be studied by the use of nuclides or isotopes of that element. This, in itself, is not truly self-diffusion since the nuclides of a given element differ in properties such as mass and the number of particles in their nucleus. The approximation, however, is very close, except for the nuclides of the first few light elements of the atomic table; for example, deuterium ( $H^2$ ) weighs twice as much as the  $H^1$  nuclide.

A mass spectrometer may be used to determine the respective concentrations of nuclides in a sample. The use of this instrument, needless to say, is not limited to studies in self-diffusion; in fact, it has been used in the investigation of diffusion of stable isotopes of nickel into copper.<sup>18</sup>

The availability of radioactive nuclides has been one of the greatest stimulants to the study of diffusion. The first application of radioactive nuclides in the study

of diffusion was accomplished over 30 years ago.<sup>28</sup> This was an investigation on the rate of diffusion of radiogenic lead into common lead at a temperature of 340 degrees centigrade; the lead was fused. This was followed by the determination of the diffusion rate of lead in the solid state.<sup>29</sup> Of course, only naturally occurring radiogenic nuclides were used at that time but since the discovery of artificial tracers, about seventeen years ago, many investigations on the subject of diffusion, self diffusion in particular, have been made.<sup>30</sup>

There are essentially two methods of measuring the concentration of radioactive solute atoms which have diffused into a solvent. The first is known as the sectioning method, whereby sections are cut from the specimen and the activity of each section is determined by measuring the radiation given off by each sample. The second method is referred to as the surface decrease method. The activity of a thin film of radioactive solute atoms, in contact with the solvent, is measured before and after a diffusion period. The decrease in activity, neglecting decay factors, is proportional to the concentration of active atoms which have diffused into the solvent. A calibration curve of the logarithm of activity of solute material versus the  $\text{mg./cm.}^2$  of solvent needed in order to decrease the activity a given amount is required before this method can be used.<sup>31</sup> Diffusion results based on the surface decrease method have not proven to be as accurate as the sectioning method. A recent

investigation<sup>32</sup> of the self diffusion of iron, however, has shown that this need not be true if sufficient precautions are taken.

The sectioning method was used entirely in the investigations made for this thesis. The sectioning process requires special care and techniques not only because of the "hot" atoms present but also because of the requirement of accurately determining the distance of each section from the solute-solvent interface. Since the sections vary from less than 0.001 inch to a few one-thousands of an inch in thickness, extreme care must be exercised in measuring the width of each section removed. When using a metal lathe or micrometer calipers, one must estimate to the nearest 0.0001 inch which limits results to two significant figures, which is poor. When a jeweler's lathe is employed, the accuracy becomes much better.

Sectioning by means of a lathe is limited to materials which can be cut without chipping, breaking, or fracturing. This limits the method to most metals and alloys, a few semi-conductors, and some solid ~~in~~organic compounds; e.g., lucite. It is, however, a property lacking in practically all silicates and many other ionic minerals, especially if they have pronounced cleavage directions.

Chalcocite can be sectioned fairly well by means of a metal lathe if certain precautions are heeded. The technique developed for this thesis was as follows: Cylindrical specimens, of 0.371 inch diameter and about 0.75 inch

long, were cut from select specimens of massive chalcocite. A brass collar was prepared which would clasp the specimen firmly when tightened in the lathe chuck. This binding about the chalcocite prevented it from chipping when the lathe tool was removing material near the edge of the chalcocite. Each section of material removed was caught on waxed paper and gently brushed into special counting receptacles. It was found that the fine particles did not cling to this paper while a trace of the material always seemed to adhere to other papers. The width of the section removed was recorded from the lathe micrometer and the weight of the section was determined after the counting had been accomplished. A generalized flow sheet of the technique used is shown on plate IV.

In the case of the minerals such as quartz, perthite, and feldspar, which could not be sectioned using a lathe, another technique was developed. Square disks, one inch in width, were cut from size 1 emory paper. These were pressed into special capsules which were also used as containers of active material during the counting stage. The mineral to be sectioned was then mounted in a drill press and a small amount of material, approximately one milligram, was ground from the revolving specimen when it was brought into contact with the emory paper. A brass collar fitted about the brittle specimen prevented the lathe chuck from crushing the specimen. The remainder of the specimen was then weighed

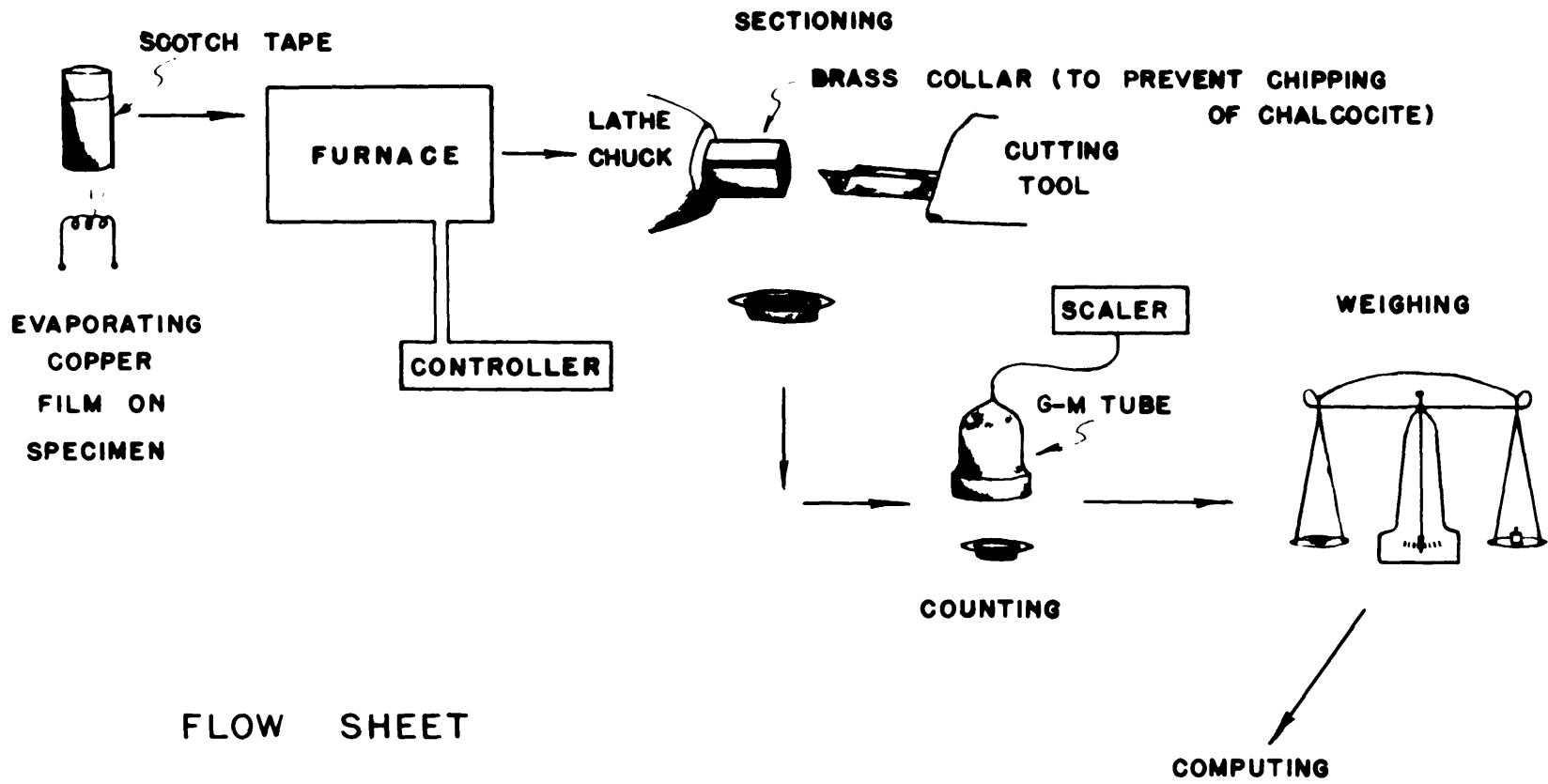


PLATE IV

FLOW SHEET  
FOR  
CHALCOCITE INVESTIGATION

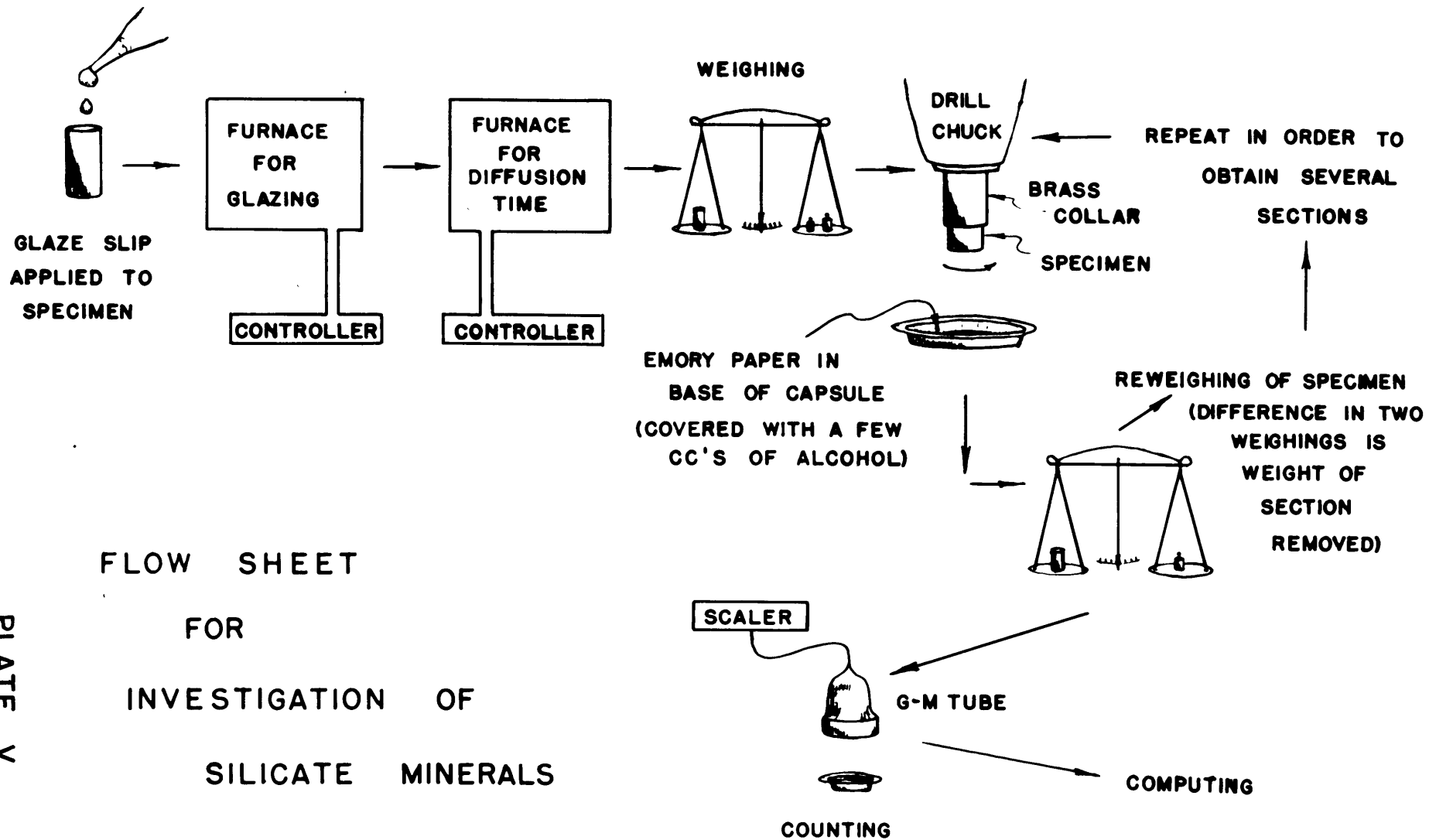
and the thickness of the section determined by measuring the decrease in length using microcalipers. Since the width of each section removed was of the order of a few thousands of a millimeter and the micrometer was calibrated to read to 0.01 millimeter, it was found to be much more accurate to plot concentration versus the weight of a section instead of versus thickness. The total thickness of material removed was, however, recorded. A generalized flow sheet of this technique is given on plate V.

During the grinding process, many of the silicates may give off extremely fine powder, which undoubtedly contains some active atoms that may be easily inhaled. To eliminate this hazard, the base of the capsule is covered with approximately 0.4 cc's of alcohol. This prevents dust from rising during the grinding and the alcohol evaporates soon after the sectioning has been completed.

### C. The Effect of Temperature

The importance of temperature in mineralogy as a source of energy has already been pointed out by Professor Buerger.<sup>33</sup> Its effect on diffusion rates is of extreme interest, not only because of the rapid increase of diffusion of ions with increase in temperature, but also because of the effect on diffusion rates of first and second order transformations which are also functions of temperature.

The prevailing concept of the behavior of an atom



FLOW SHEET  
FOR  
INVESTIGATION OF  
SILICATE MINERALS

PLATE V

is that it tends to oscillate about its equilibrium position with a frequency which is determined by its mass and the bond strength between neighboring atoms. When the atom receives energy, as in the form of heat, its frequency does not change significantly but the magnitude of its oscillations increases. If the magnitude becomes great enough to break some of the bonds holding the atom in place, the atom may jump to a new position. The energy which it must overcome in order to accomplish this is known as the activation energy.

It is common to represent this activation energy graphically by a curve of varying amplitude showing energy slumps, or atom equilibrium locations, and energy peaks of height proportional to the activation energy. A typical diagram is shown in figure 2 where it is evident that the probability of atom A exchanging position with atom B is more likely than atom B exchanging position with atom C since the energy barriers differ. If the energy barrier is represented by a value of  $\epsilon$  cal/atom, the probability that either atom B or C will reach the activation energy is proportional to  $e^{-\frac{\epsilon}{kT}}$  where  $e$  is the natural logarithm,  $k$  is the Boltzmann constant, and  $T$  is the absolute centigrade temperature.

If  $e^{-\frac{\epsilon}{kT}}$  is the probability that  $\epsilon$  will be reached during one oscillation, then the probability per unit time

is  $K = f \cdot e^{-\frac{\epsilon}{kT}}$  where  $f$  is the vibrational frequency. Dushman and Langmuir<sup>34</sup> have proposed that the diffusion coefficient is approximately equal to the product of the probability per unit time that an atom will jump and the jump distance squared ( $\delta^2$ ), or:

$$D = K \cdot \delta^2 \quad (10)$$

therefore,  $D = \delta^2 \cdot f \cdot e^{-\frac{\epsilon}{kT}} \quad (11)$

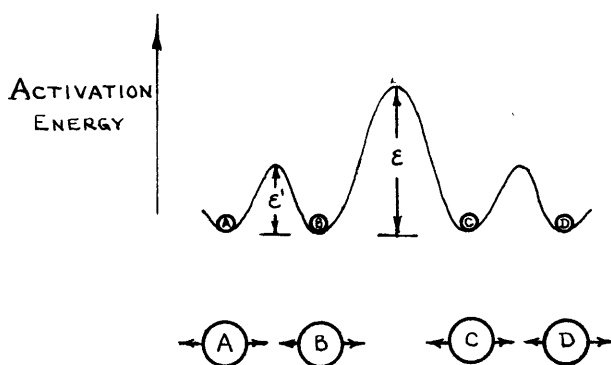


Figure 2. Graphical Representation of Activation Energies.

Since the oscillation frequency and the jump distance are fairly independent of temperature, a constant ( $D_0$ ) is introduced, and:

$$D = D_0 \cdot e^{-\frac{\epsilon}{kT}} \quad (12)$$

If both  $\epsilon$  and  $kT$  are multiplied by Avogadro's number,  $N_0 \cdot k$  will be replaced by the gas constant ( $R$ ), and  $N_0 \cdot \epsilon$  is defined as the activation energy ( $Q$ ) measured in

cal./mole, thus:

$$D = D_0 \cdot e^{-\frac{Q}{RT}} \quad (13)$$

The equation has proven to be fairly accurate when checked with experimental diffusion results which are limited to the temperature ranges of a crystal structure which is undergoing very slow disordering rates, but it has been found that the value of  $D_0$  varies considerably. This should not be too surprising since it was assumed that  $D_0$  did not vary with temperature and it is common knowledge that  $\delta$ , the jump distance, usually increases with temperature. It is further assumed that the activation energy is not a function of temperature and this also is not true.

The value of equation (13), however, lies in its usefulness for determination of the activation energy of a particular species of solute atom in a given solvent system over a given temperature range. First, it is required to determine experimentally the diffusion coefficient at, at least, two different temperatures and preferably at several intermediate temperatures for improved precision. Therefore, if  $D_2$  and  $D_1$  are the two diffusion coefficients determined at temperatures  $T_2$  and  $T_1$  respectively, it follows that:

$$D_2 = D_0 \cdot e^{-\frac{Q}{RT_2}} \quad \text{and} \quad D_1 = D_0 \cdot e^{-\frac{Q}{RT_1}} \quad (14)$$

therefore,  $\ln D_2 = \ln D_0 - \frac{Q}{RT_2}$

and

$$\ln D_1 = \ln D_0 - \frac{Q}{RT_1}$$

$$\text{Subtracting} \quad \ln(D_2 - D_1) = \frac{Q}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (15)$$

$$\text{therefore, } \frac{Q}{R} = \frac{\ln(D_2 - D_1)}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (16)$$

This is the slope of the line shown in figure 3. Therefore if the slope of the line is determined graphically, where the logarithm of diffusion coefficients is plotted

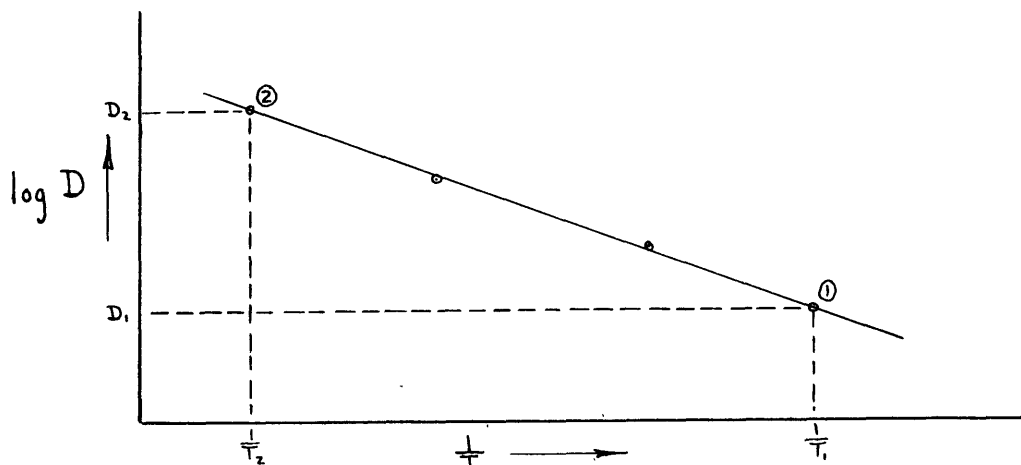


Figure 3. Graph of Diffusion results at given Temperatures versus the reciprocal of the absolute centigrade temperature (Kelvin), the activation energy is:

$$Q = 2.303 \times R \times \text{slope} \quad (17)$$

$$\text{or, } Q = 4.583 \times \text{slope} \quad (18)$$

In equation (18), R has the value of 1.99 cal./K./mole, 2.303 is the conversion factor used to convert from natural to base 10 logarithms; hence, Q will have the units of cal./mole.

The effect of second order transformations on diffusion coefficients may now be considered. If the diffusion rates of a solute, such as sodium, were measured in a solvent such as  $\alpha$  quartz and the logarithms of the diffusion coefficients were plotted versus the reciprocal of the given temperatures on semi-logarithm paper, the result should be approximately a straight line as previously explained. If, however, the line were extended with the same slope to temperatures over 573 degrees centigrade, it would be in error. Sodium ions would tend to diffuse through  $\beta$  quartz at a higher rate due to the more open structure, and this increase in diffusion would take place over a few degrees below 573 degrees, in which the  $\alpha$  quartz structure inverts to the  $\beta$  quartz structure. Diffusion experiments would need to be made at temperatures over 573 degrees centigrade. The resulting curve would probably be similar to that shown in figure 4. The slope of the two fairly straight lines need not be the same and, therefore, the energies of activation for sodium in quartz would be different depending upon whether the quartz solvent was in the  $\alpha$  or  $\beta$  state.

Plate VI shows the relationship of diffusion coefficients for first and second order transformations when they are plotted versus the reciprocal of temperature. The left side of the plate is taken from Professor Buergér's work.<sup>35</sup> The log D versus  $1/T$  curve for a disordering transformation

is based upon results obtained in this thesis on the investigation of diffusion rates in high and low temperature structural modifications of chalcocite. The  $\log D$  versus  $1/T$

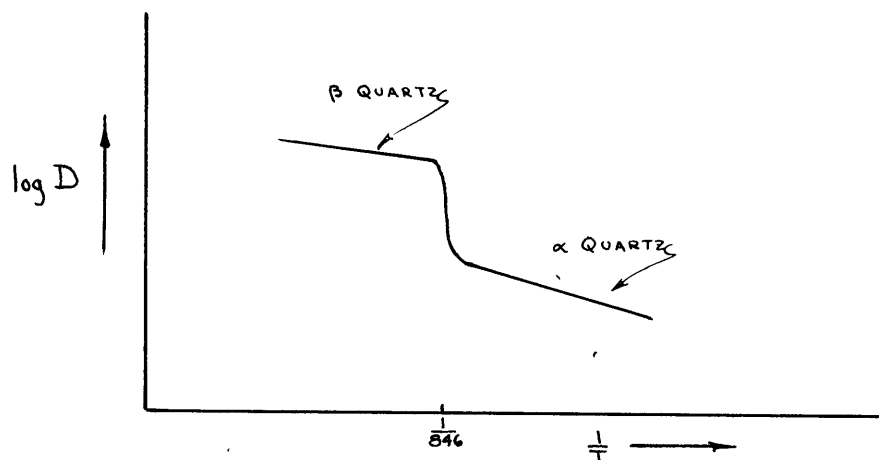
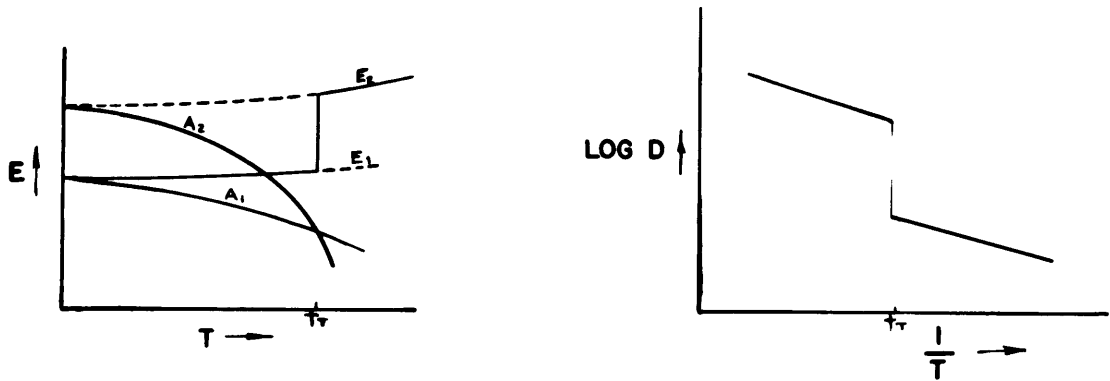


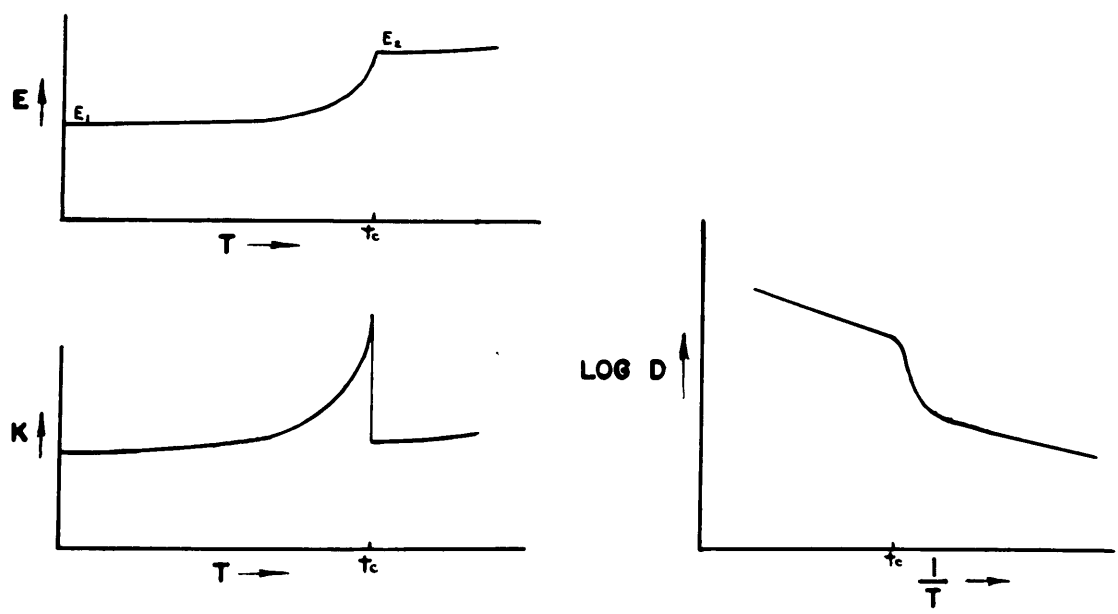
Figure 4. Variation of Diffusion in  $\alpha$  and  $\beta$  Quartz

diffusion curves shown on this plate should serve as a warning against attempts to determine the energy of activation of a particular system when based on only two diffusion runs at widely different temperatures, especially so when the structural transformations of the mineral are not known. This is particularly true of the feldspar minerals.

It is interesting to note the special case of the transformation of  $\alpha$  iron to  $\gamma$  iron. The self diffusion coefficients of iron suddenly decrease when  $\alpha$  iron transforms to  $\gamma$  iron, where  $\gamma$  iron is a higher temperature form than  $\alpha$  iron.<sup>32</sup>



FIRST ORDER TRANSFORMATION



SECOND ORDER TRANSFORMATION

#### D. Mechanism of Diffusion

The relative importance of grain surface, boundary, and volume diffusion rates is of considerable interest. Grain boundary and surface diffusion would normally be expected to be rather significant when compared to diffusion through a solid. This has been found to be true in the study of diffusion of thorium along tungsten filament wires.<sup>36</sup> In this case, surface diffusion was found to be more rapid than grain boundary diffusion and much more rapid than volume diffusion.

Several investigators<sup>37</sup> have found that grain boundary diffusion through metals is quite negligible, especially at high temperatures. Wagner\* also believes this to be true of semi-conductors and several ionic minerals; i.e., at high temperatures,<sup>‡</sup> grain volume diffusion seems to be of primary importance, while at low temperatures, grain surface and boundary diffusion rates are much more significant.

This effect can be determined by diffusing a solute through pressed tablets which are composed of grains, or crystals, of given size; in this way, the degree of grain surface and boundaries can be varied from one specimen to another by varying the grain size of different speci-

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\* Dr. Carl Wagner, oral communication.

‡ The terms low and high temperature become much more specific when applied to a given mineral; e.g., a temperature over 105 degrees centigrade would be high for chalcocite since the diffusion rate shows a significant increase at this temperature and higher.

mens. Identical diffusion experiments can then be performed on the tablets and the effect of grain boundaries and surface area can then be ascertained.

The relative importance of grain surface, grain boundary, and volume diffusion is extremely important when applied to various geologic phenomena such as replacement, pseudomorphs, basic fronts, reaction rims and zones, and ichor flow. Investigations<sup>38</sup> have already been made on the rates of diffusion of solutions into granular material with the interesting result that the rate is not dependent upon the permeability or porosity of the rock. There seems to be little disagreement upon the fairly rapid migration of solutions through fractures, joints, and openings in rocks. The importance of diffusion in geologic phenomena, nevertheless, ultimately depends on the rate of grain volume diffusion, or true solid diffusion, in order to have a crystal of one composition changed to a crystal of another composition by addition of ions.

Solid diffusion is usually broken down into three basic mechanisms, especially in the case of metals. These are interstitial diffusion, diffusion by direct interchange, and the so-called vacancy diffusion mechanism. These three mechanisms are shown on plate VII.

Interstitial diffusion takes place by movement of ions through space surrounded by normal atomic sites. This is probably a more common process in the case of a small atom

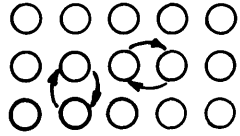
such as carbon or aluminum diffusion through a crystal structure made up of larger atoms such as carbon or copper respectively.

A series of calculations have been made by several investigators<sup>39</sup> on the energy requirements needed for the different diffusion mechanisms in the case of self diffusion of f.c.c. copper. It was found that the activation energy needed to cause a copper atom to jump from its equilibrium site to an interstitial position is approximately 220,000 cal./mole, but the energy needed for a copper atom to move from one interstitial position to another is only about 11,500 cal./mole.

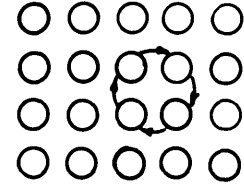
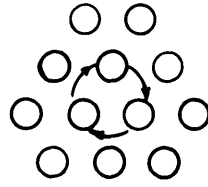
Diffusion by direct interchange may occur by the simultaneous exchange of position of two atoms, which is known as pair interchange, or it may occur by a cyclic interchange of three, four, or more atoms. This has recently been called ring diffusion but a more descriptive term, "cyclic", was proposed almost twenty years ago.<sup>40</sup> The energy of activation needed in the copper system for pair interchange is approximately 110,000 cal./mole. For cyclic interchange, it is lowered to a value of about 91,000 cal./mole. In order to have a direct interchange of two atoms the crystal structure would need to be strongly distorted during the interchange. Because of this "space problem", the mechanism is not accepted with much favor. It is important to note,

## DIRECT INTERCHANGE

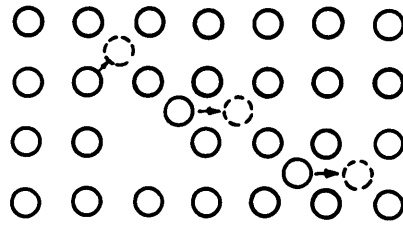
PAIR



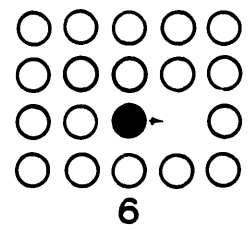
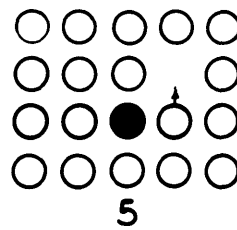
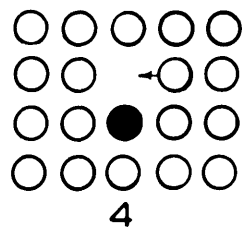
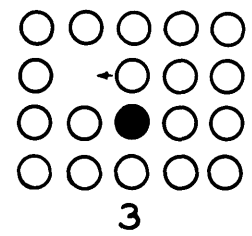
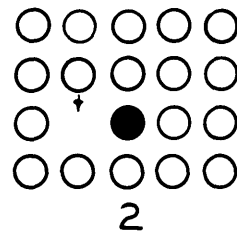
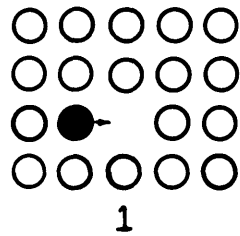
CYCLIC (RING)



## INTERSTITIAL DIFFUSION



## VACANCY DIFFUSION



## MECHANISM OF DIFFUSION

PLATE VII

however, that the cyclic type of interchange need not require much distortion of the crystal structure.

The third mechanism, vacancy diffusion, takes place by an atom moving to a vacant site and thereby creating a vacancy in the site previously occupied. In the case of copper, once again, the activation energy required for a copper atom to move to a vacant site is about 23,500 cal./mole. The energy needed to create a vacancy within the copper structure has already been given as having a value of 220,000 cal./mole; however, the energy needed to cause an atom to move on the surface of the crystal and form a vacancy there is much less; it is of the order of 41,500 cal./mole. It is known, furthermore, through thermodynamic reasoning that a given substance has a finite number of vacant atomic sites at any temperature above absolute because of the increase in entropy that results from the disorder that they introduce. For example, the number of vacant sites in a sodium chloride crystal is about one percent of the total sites at a temperature near 800 degrees centigrade.<sup>41</sup>

The activation energy determined experimentally from self diffusion studies of copper is about 47,000 cal./mole. This seems to indicate that vacancy diffusion is a favored mechanism. It is very probable, however, that all other mechanisms occur but to a lesser extent.

The probable mechanism of solid diffusion in minerals, in silicates in particular, differs from the above

mentioned methods in a very basic manner. The silicates are composed of specific structures or networks based not only upon various arrangements of the silica tetrahedron but also upon the number of shared oxygen atoms of each tetrahedron. The result is a structural framework, formed from the tetrahedrons, with positive ions located in the larger openings of the framework. When the structure receives energy in the form of temperature, it tends to become more open and the atoms are then more capable of migrating or diffusing from one open space or cage to another. Basically, this is an interstitial type of diffusion but it might be more descriptive to refer to the mechanism as interstitial diffusion through a network or interstitial network diffusion.

#### E. Driving Force for Diffusion

An examination of Fick's Laws suggests that the concentration gradient between two bodies is the driving force which causes net diffusion from one body to the other. Other investigations show that this is not the sole solution of the driving force problem. Darken<sup>42</sup> investigated the diffusion of carbon in two specimens of austenite iron which were joined together along a planar contact. One specimen contained 3.80% Si and 0.48% C; the second specimen contained 0.05% Si and 0.44% C as shown in the diagram below. If the concentration gradient is the driving force, one would expect

the carbon concentration to approach the concentration as shown by the dotted line during diffusion; however, the concentration after a diffusion time  $t_1$  was found to have the values as shown by the diagram. The explanation for

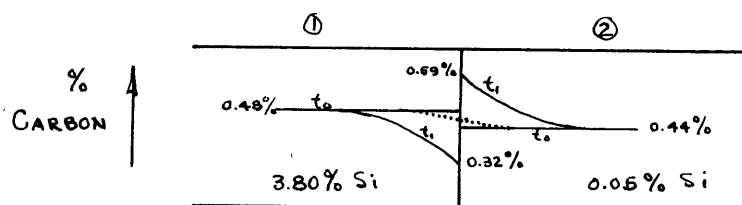


Figure 5. Diffusion of Carbon in Iron

this is that carbon has a higher than normal thermodynamic activity when in the presence of silicon; therefore, activity may also be a driving force for diffusion.

A third factor, however, seems to be the omnipotent driving force for diffusion. This is the chemical potential which is based upon the premise that a force ( $f$ ) acts upon an impurity or solute atom in a solvent system causing the solute to move in a direction  $+x$ , or:

$$f = - \text{potential gradient} = - \frac{\partial u}{\partial x} \cdot \frac{1}{N_0}$$

where  $-\frac{\partial u}{\partial x}$  is the molar chemical potential gradient of the solute atom along the  $\pm x$  direction and  $N_0$  is Avogadro's number.

A common crude comparison is often given as an

illustration of chemical potential, which states that diffusion depends upon differences in chemical potential in the same way that electrical conductivity depends upon differences in electrical potential. The importance of chemical potential as a driving force for solid diffusion in minerals and rocks has already been elaborated upon by Bugge.<sup>43</sup>

The subject of self diffusion becomes more interesting when considered with relation to chemical potential since chemical potential gradient is a force acting upon an impurity or solute atom in a system and in the case of self diffusion both the solute and the solvent atoms are identical; therefore, there is no chemical potential gradient since all atoms are identical. Of course, no one has yet measured true self diffusion since there is no means of distinguishing the solute from the solvent. The closest approximations are obtained using stable or radioactive nuclides as tracers, but this of course is not truly self diffusion since a given nuclide of any element differs from the other nuclides of that element in properties such as mass, number of neutrons, and stability.

#### F. The Effect of Impurities

The diffusion measurements made by the chemists and metallurgists in the past have been carried out almost entirely upon pure elements or compounds prepared in the laboratory. Now a mineral, according to its definition, is

"a naturally occurring product" and, as a result, it is loaded with impurities. The significance of this is extremely important when one realizes the effect of impurities upon diffusion results. The effect is almost always an increase in the diffusion rate over the rate where no impurities are present.

Wagner<sup>44</sup> has shown the effect of adding given amounts of strontium chloride,  $\text{SrCl}_2$ , as impurity, to potassium chloride,  $\text{KCl}$ . Measurements were made of the ionic conductivity of potassium chloride at given temperatures with varying amounts of strontium chloride in solid solution. The amount of strontium chloride present was always less than one percent. The result was that the ionic conductivity of potassium chloride, which is directly proportional to ionic diffusion, increased considerably with slight additions of impurity. For example, at a temperature of 650 degrees centigrade, the ionic conductivity of potassium chloride, containing 0.8 percent strontium chloride, was found to be over 270 times the conductivity of pure potassium chloride.

Minerals may contain several percent of impure material which may easily vary from place to place in one crystal. Therefore, it should not be surprising at all if diffusion measurements vary considerably from one specimen to another of a given mineral. Rosenquist\* has found that the

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\* Written communication, Nov. 11, 1950.

diffusion rates in feldspars "seem to be very variable from specimen to specimen". I have also found this to be true of chalcocite, optically clear quartz, and, of course, perthites which are not only impure but vary in the amount of potash and soda feldspar present.

The probable effect of impurities on diffusion rates is represented in the standard diffusion-temperature diagram below.

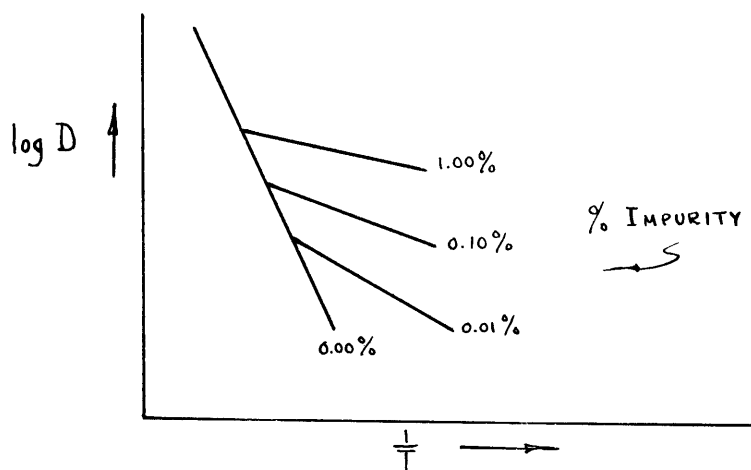


Figure 6. Effect of Impurities on Diffusion Rates

The slope of the straight lines shown in this figure determines the energy of activation of the solute atoms in the system under investigation. It is significant to note that the activation energy is lowered (the slope is decreased) when impurities are added and, also, that the effect of impurities is decreased or overshadowed at higher temperatures.

## V EXPERIMENTAL RESULTS

### A. Diffusion of Copper in Chalcocite

The experimental investigation of the diffusion of copper ( $\text{Cu}^{64}$ ) in chalcocite was done on two massive chalcocite specimens. The first was a massive chalcocite specimen from Butte, Montana. Although this specimen was used mostly on developing and perfecting the experimental technique, three diffusion coefficients were obtained during this investigation. The second specimen was a massive chalcocite from Kennecott, Alaska. (Both specimens were obtained from the Harvard Mineralogy Collection.) Four diffusion coefficients were experimentally determined on the second specimen.

The results of the investigation on chalcocite are shown on the standard graph, Plate VIII, of the logarithm of diffusion coefficients plotted versus the reciprocal of the absolute centigrade temperature. The temperature in degrees centigrade is shown at the top of the graph.

The activation energy of copper in high chalcocite has been computed for both specimens. The values are given in Table I.

The results from the seven individual experiments performed on chalcocite, which resulted in reasonably accurate diffusion coefficients, are shown on Plates IX to XV. The experimental data obtained in order to plot these graphs is

tabulated on Table II.

TABLE I  
Activation Energy of Copper in High Chalcocite

Specimen	Slope of line	Activation Energy
1. Butte, Montana	725	3,320 cal./mole
2. Kennecott, Alaska	1020	4,680 cal./mole

An example of the method of computing the diffusion coefficient is given in some detail for specimen number nine (Plate IX) on Table III. The slope of the lines and the resulting diffusion coefficients for all seven chalcocite experiments are tabulated on Table IV.

#### B. Diffusion of Sodium into Perthite

The results of the diffusion of sodium ( $\text{Na}^{22}$ ) into microcline-perthite are shown on Plates XVI and XVII. Plate XVI shows the curve obtained when the concentration is plotted versus the distance of penetration of the solute. (The plot also shows the weight of each section removed.) Plate XVII is the curve needed in order to determine the diffusion coefficient by measuring the slope of the line. The first slope is not a straight line. The second two slopes, however, have been used to compute the diffusion coefficient. The results are tabulated on the graph. The experimental data obtained in order to plot the graphs is tabulated on Table V.

TABLE II

## CHALCOCITE

Butte, Montana  
Harvard Collection

Section	Thickness		Distance (Cm.)			Counting			Counts per Second	Wt. Mg.	Counts per Second per Mg.
	Inches	Centimeters	Center to Center	Interface to Center	(I-C) <sup>2</sup>	Time: Counts Began	Counts	Time (Sec.)			
Specimen # 12 Time: 20.5 hrs.			Plate XI Temperature: 48.5° C								
1	0.0004	1.02 x 10 <sup>-3</sup>	-----	-----	-----	1602	256	438	0.585	1.8	0.324
2	0.0010	2.54 x 10 <sup>-3</sup>	1.78 x 10 <sup>-3</sup>	1.78 x 10 <sup>-3</sup>	3.16 x 10 <sup>-6</sup>	1611	256	569	0.450	5.2	0.086
Specimen # 9 Time: 20.8 hrs.			Plate IX Temperature: 85° C								
1	0.0010	2.54 x 10 <sup>-3</sup>	-----	-----	-----	1455	512	756.3	0.677	3.2	0.211
2	0.0010	2.54 x 10 <sup>-3</sup>	2.54 x 10 <sup>-3</sup>	2.54 x 10 <sup>-3</sup>	6.43 x 10 <sup>-6</sup>	1508	512	924.4	0.553	2.8	0.198
3	0.0010	2.54 x 10 <sup>-3</sup>	2.54 x 10 <sup>-3</sup>	5.08 x 10 <sup>-3</sup>	25.8 x 10 <sup>-6</sup>	1524	512	702.3	0.730	4.6	0.159
4	0.0020	5.08 x 10 <sup>-3</sup>	3.81 x 10 <sup>-3</sup>	8.89 x 10 <sup>-3</sup>	78.9 x 10 <sup>-6</sup>	1537	512	493.5	1.038	11.7	0.089
Specimen # 11 Time: 6.33 hrs.			Plate X Temperature: 187° C								
1	0.0008	2.03 x 10 <sup>-3</sup>	-----	-----	-----	1902	128	319.8	0.401	3.2	0.125
2	0.0012	3.05 x 10 <sup>-3</sup>	2.54 x 10 <sup>-3</sup>	2.54 x 10 <sup>-3</sup>	6.46 x 10 <sup>-6</sup>	1908	128	169.0	0.758	7.1	0.107
3	0.0012	3.05 x 10 <sup>-3</sup>	3.05 x 10 <sup>-3</sup>	5.59 x 10 <sup>-3</sup>	31.3 x 10 <sup>-6</sup>	1914	128	289.2	0.443	5.2	0.085
4	0.0028	7.11 x 10 <sup>-3</sup>	5.08 x 10 <sup>-3</sup>	10.67 x 10 <sup>-3</sup>	114 x 10 <sup>-6</sup>	1919	128	260	0.492	16.3	0.030

TABLE II  
(cont'd)

CHALCOCITE

Kennecott, Alaska

Section	Thickness		Distance (Cm.)			Counting			Counts per Second	Wt. Mg.	Counts per Second per Mg.
	Inches	Centimeters	Center to Center	Interface to Center	(I-C) <sup>2</sup>	Time Counts Began	Counts	Time (Sec.)			
Specimen # 25 Time: 22 hrs.						Plate XIII Temperature: 186.6° C					
1	0.0005	1.27 x 10 <sup>-3</sup>	----	----	----	1806	1024	841.0	1.22	7.86	0.154
2	0.0008	2.03 x 10 <sup>-3</sup>	1.65 x 10 <sup>-3</sup>	1.65 x 10 <sup>-3</sup>	2.72 x 10 <sup>-6</sup>	1821	512	430.0	1.19	8.21	0.145
3	0.0013	3.33 x 10 <sup>-3</sup>	2.66 x 10 <sup>-3</sup>	4.32 x 10 <sup>-3</sup>	18.65 x 10 <sup>-6</sup>	1830	512	291.0	1.76	12.76	0.138
4	0.0019	4.83 x 10 <sup>-3</sup>	4.06 x 10 <sup>-3</sup>	8.38 x 10 <sup>-3</sup>	70.3 x 10 <sup>-6</sup>	1835	512	264.0	1.94	12.94	0.149
5	0.0020	5.08 x 10 <sup>-3</sup>	4.92 x 10 <sup>-3</sup>	13.30 x 10 <sup>-3</sup>	179.5 x 10 <sup>-6</sup>	1843	512	235.5	2.17	15.23	0.142
6	0.0030	7.62 x 10 <sup>-3</sup>	6.31 x 10 <sup>-3</sup>	19.60 x 10 <sup>-3</sup>	384 x 10 <sup>-6</sup>	1852	1024	373.3	2.74	19.90	0.138
7	0.0030	7.62 x 10 <sup>-3</sup>	7.62 x 10 <sup>-3</sup>	27.22 x 10 <sup>-3</sup>	743 x 10 <sup>-6</sup>	1859	1024	364.6	2.81	21.24	0.132
Specimen # 26 Time: 25 hrs.						Plate XIV Temperature: 22° C					
L.	0.0005	1.27 x 10 <sup>-3</sup>	----	----	----	1455	256	585.0	0.437	2.09	0.209
2.	0.0010	2.54 x 10 <sup>-3</sup>	1.91 x 10 <sup>-3</sup>	1.91 x 10 <sup>-3</sup>	3.64 x 10 <sup>-6</sup>	1510	1024	773.	1.327	7.79	0.171
3.	0.0038	9.65 x 10 <sup>-3</sup>	6.10 x 10 <sup>-3</sup>	8.00 x 10 <sup>-3</sup>	64 x 10 <sup>-6</sup>	1525	1024	2617.	0.392	15.28	0.025

TABLE II  
(cont'd)

CHALCOCITE

Kennecott, Alaska

Section	Inches	Centimeters	Center to Center	Interface to Center	(I-C) <sup>2</sup>	Time Counts Began	Counts	Time (Sec.)	Counts per Second	Weight Mg.	Counts per Second per Mg.
Specimen # 28 Time: 24.5 hrs.						Plate XV Temperature: 75° C					
1	0.0005	1.27 x 10 <sup>-3</sup>	-----	-----	-----	1653	256	617.3	0.415	1.19	0.349
2	0.0012	3.05 x 10 <sup>-3</sup>	2.16 x 10 <sup>-3</sup>	2.16 x 10 <sup>-3</sup>	4.65 x 10 <sup>-6</sup>	1712	1024	322.0	3.18	8.82	0.361
3	0.0015	3.81 x 10 <sup>-3</sup>	3.43 x 10 <sup>-3</sup>	5.59 x 10 <sup>-3</sup>	31.3 x 10 <sup>-6</sup>	1716	1024	322.0	3.18	10.43	0.305
4	0.0028	7.12 x 10 <sup>-3</sup>	5.46 x 10 <sup>-3</sup>	11.05 x 10 <sup>-3</sup>	122.2 x 10 <sup>-6</sup>	1722	1024	181.2	5.65	19.39	0.291
Specimen # 23 Time: 10.5 hrs.						Plate XII Temperature : 116° C					
1	0.0004	1.015 x 10 <sup>-3</sup>	-----	-----	-----		512	331.3	1.547	2.88	0.537
2	0.0020	5.08 x 10 <sup>-3</sup>	3.04 x 10 <sup>-3</sup>	3.04 x 10 <sup>-3</sup>	9.2 x 10 <sup>-6</sup>		1024	392.0	2.61	5.12	0.510
3	0.0030	7.62 x 10 <sup>-3</sup>	6.35 x 10 <sup>-3</sup>	9.4 x 10 <sup>-3</sup>	88.2 x 10 <sup>-6</sup>		1024	153.5	6.67	13.33	0.501
4	0.0015	3.81 x 10 <sup>-3</sup>	5.72 x 10 <sup>-3</sup>	15.1 x 10 <sup>-3</sup>	228 x 10 <sup>-6</sup>		1024	208.0	4.92	10.60	0.464
5	0.0023	5.84 x 10 <sup>-3</sup>	4.82 x 10 <sup>-3</sup>	19.9 x 10 <sup>-3</sup>	397 x 10 <sup>-6</sup>		1024	293.7	3.49	8.82	0.395

TABLE V

## PERTHITE

Section	Weight of Section (mg)	Weight			Counting		Counts per Second	Counts per Second per mg.
		Center to Center	Interface to Center	(I-C) <sup>2</sup>	Counts	Time (Sec.)		
1	1.78	--	--	--	4096	33.1	123.6	69.5
2	0.74	1.25	1.25	1.56	4096	104.8	39.1	52.8
3	0.78	0.76	2.01	4.03	4096	146.3	27.9	35.9
4	0.84	0.81	2.82	7.94	4096	190.1	21.5	25.6
5	0.95	0.89	3.72	13.8	4096	246.3	16.6	17.5
6	0.91	0.93	4.64	21.6	4096	361.5	11.3	12.4
7	1.42	1.16	5.81	33.8	4096	349.7	11.7	8.26
8	1.13	1.28	7.09	50.2	4096	404.1	10.1	8.95
9	1.46	1.31	8.40	70.6	4096	447.7	9.1	6.26
10	1.28	1.37	9.77	95.8	4096	949.9	4.3	3.36
11	1.28	1.28	11.05	122.0	4096	710.0	5.8	4.50
12	1.15	1.22	12.26	150.0	2048	674.7	3.0	2.64

TABLE III

Method of Computing Diffusion Coefficient

Chalcocite Specimen # 9

The slope of the line is:

$$\begin{aligned}
 \text{slope} &= \frac{\log (c_{x_2} - c_{x_1})}{(x_2^2 - x_1^2)} \\
 &= \frac{\log \frac{0.211}{0.211} - \log \frac{0.093}{0.211}}{0 - 75 \times 10^{-6}} \\
 &= \frac{\log (4.41 \times 10^{-1})}{75 \times 10^{-6}} \\
 &= \frac{0.644 - 1}{75 \times 10^{-6}} = -1.825 \times 10^3
 \end{aligned}$$

$$\begin{aligned}
 \text{Since } D &= \frac{-0.1086}{\text{slope} \times \text{time}}, \text{ where time} = 20.8 \text{ hrs.} \\
 &= \frac{-0.1086}{-1.825 \times 10^3 \times 20.8 \times 3600} \\
 &= \frac{0.1086}{3.55 \times 10^8} \\
 &= \underline{3.1 \times 10^{-10} \text{ cm.}^2/\text{sec}}
 \end{aligned}$$

TABLE IV

Compilation of Diffusion Data for Chalcocite

Specimen Number	Temperature (°C)	Diffusion Time (hrs.)	Diffusion Coefficient (cm. <sup>2</sup> /sec)
9	85	20.8	3.1 x 10 <sup>-10</sup>
11	187	6.33	8.75 x 10 <sup>-10</sup>
12	48.5	20.5	8.1 x 10 <sup>-12</sup>
23	116	10.5	8.43 x 10 <sup>-9</sup>
25	186	22.0	2.1 x 10 <sup>-8</sup>
26	22	25	8.5 x 10 <sup>-11</sup>
28	75	24.5	1.94 x 10 <sup>-9</sup>

C. Diffusion of Copper into Various Minerals

The results of the diffusion of copper ( $\text{Cu}^{64}$ ) into quartz, into tetrahedrite, and into cuprite containing unmixed chalcopyrite blebs are given in Table VI. These results are only semi-quantitative.

TABLE VI  
Semi-Quantitative Results  
of  
Diffusion of Copper into Various Minerals

Mineral	Temperature	D. ( $\text{cm.}^2/\text{sec.}$ )
1. Quartz crystal ( (Diffusion Cv.)	600° C	$1.1 \times 10^{-10}$
2. Tetrahedrite crystal	182° C	$1. \times 10^{-8}$
3. Cuprite containing chalcopyrite blebs	92° C	$2. \times 10^{-8}$

← CENTIGRADE

# PLATE VIII DIFFUSION COEFFICIENTS

VS.

## RECIPROCAL OF TEMPERATURE FOR CHALCOCITE

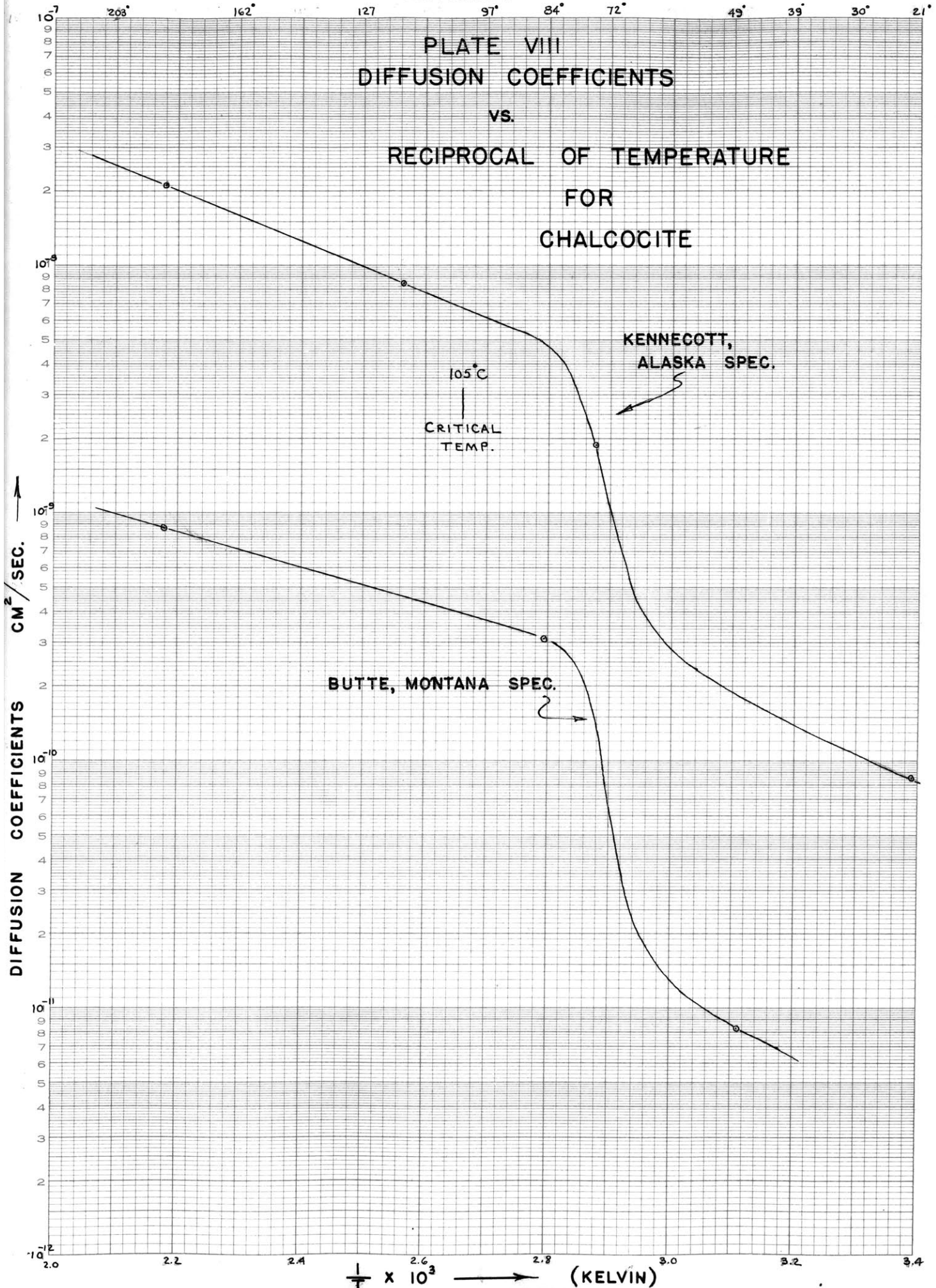


PLATE IX

CONCENTRATION vs. DISTANCE SQUARED  
FOR  
DIFFUSION OF COPPER  
INTO  
CHALCOCITE

SPEC. #9

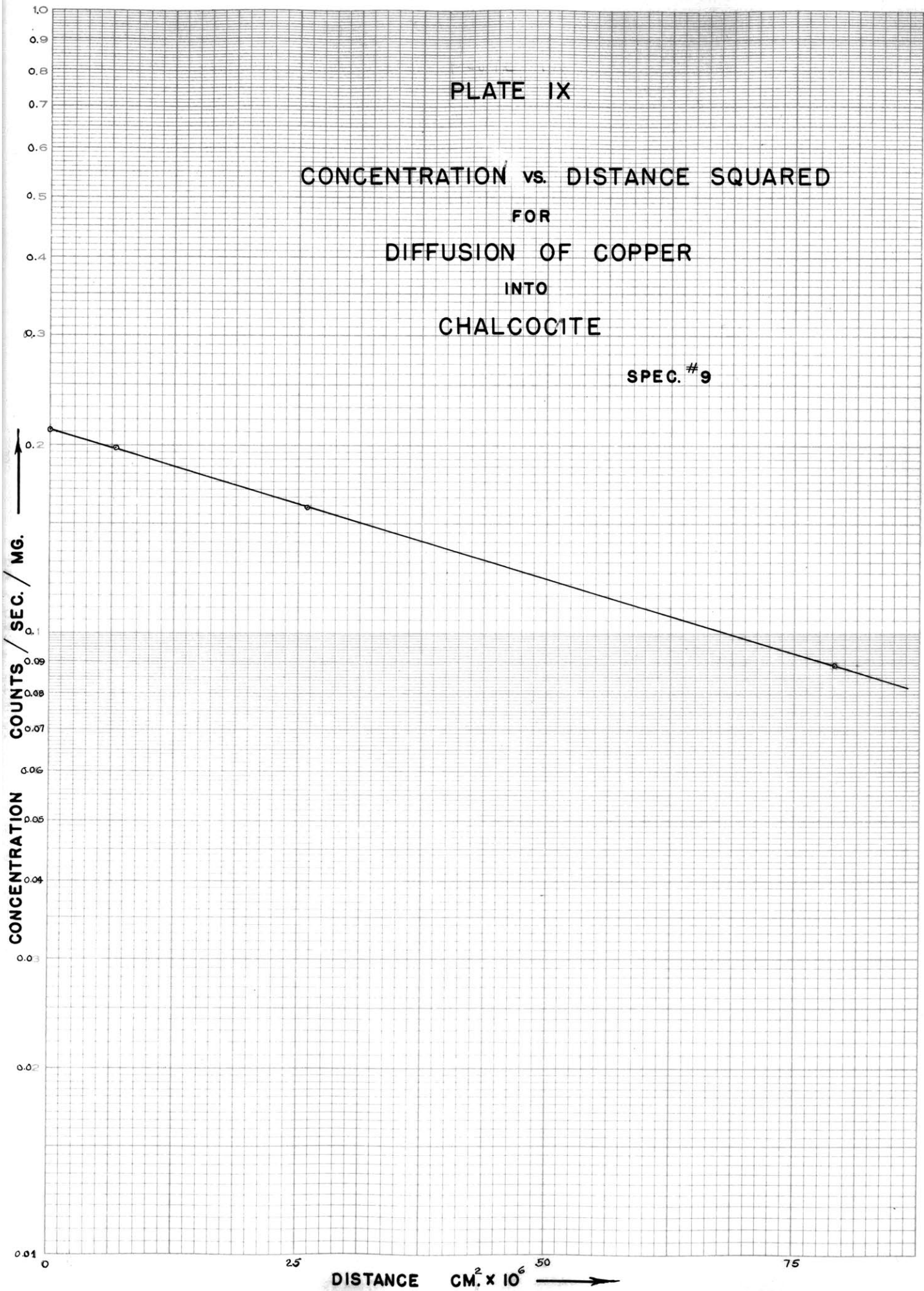
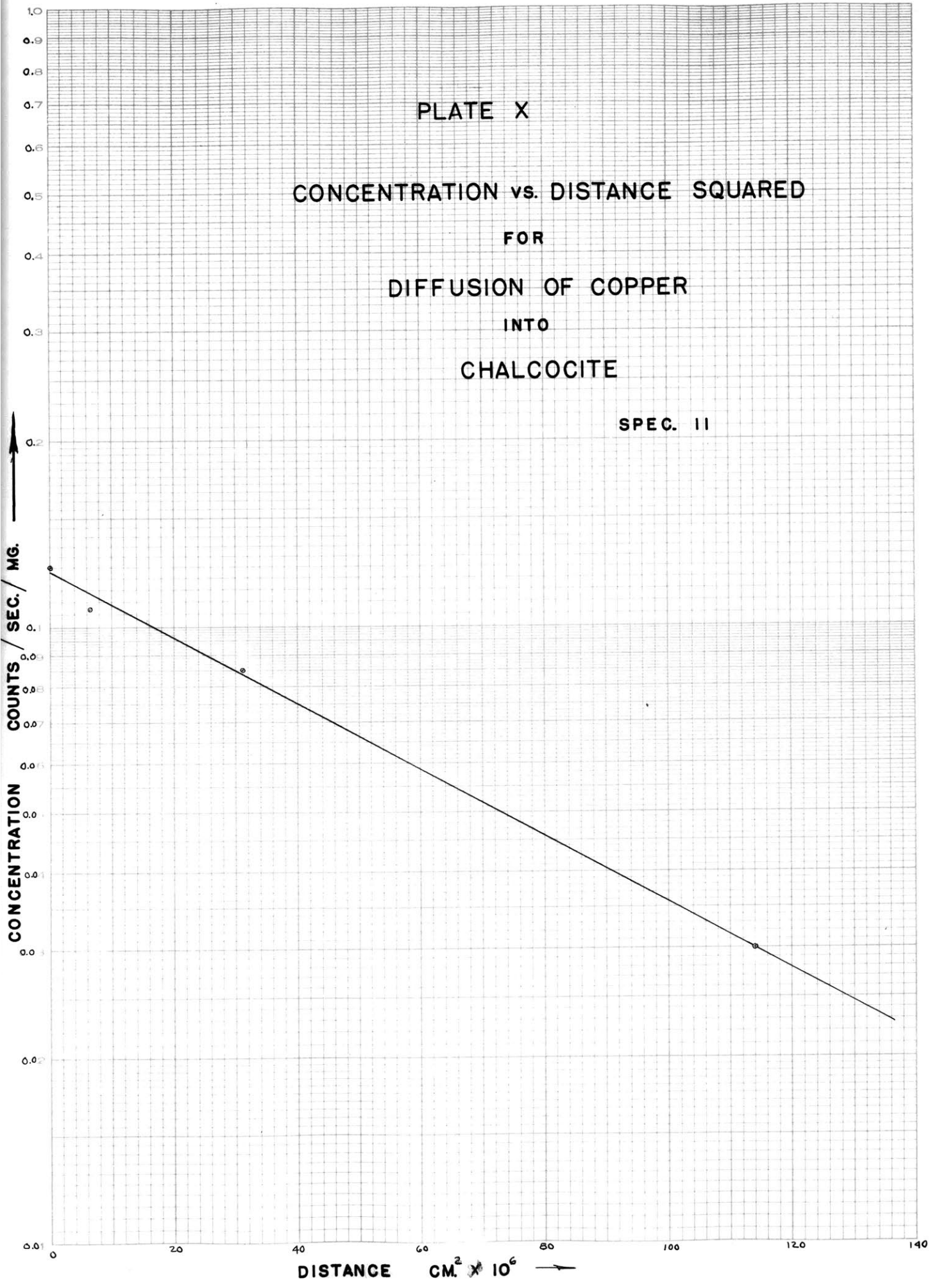


PLATE X

CONCENTRATION vs. DISTANCE SQUARED  
FOR  
DIFFUSION OF COPPER  
INTO  
CHALCOCITE

SPEC. II



# PLATE XI

## CONCENTRATION vs. DISTANCE SQUARED

FOR

### DIFFUSION OF COPPER

INTO

### CHALCOCITE

SPEC. 12

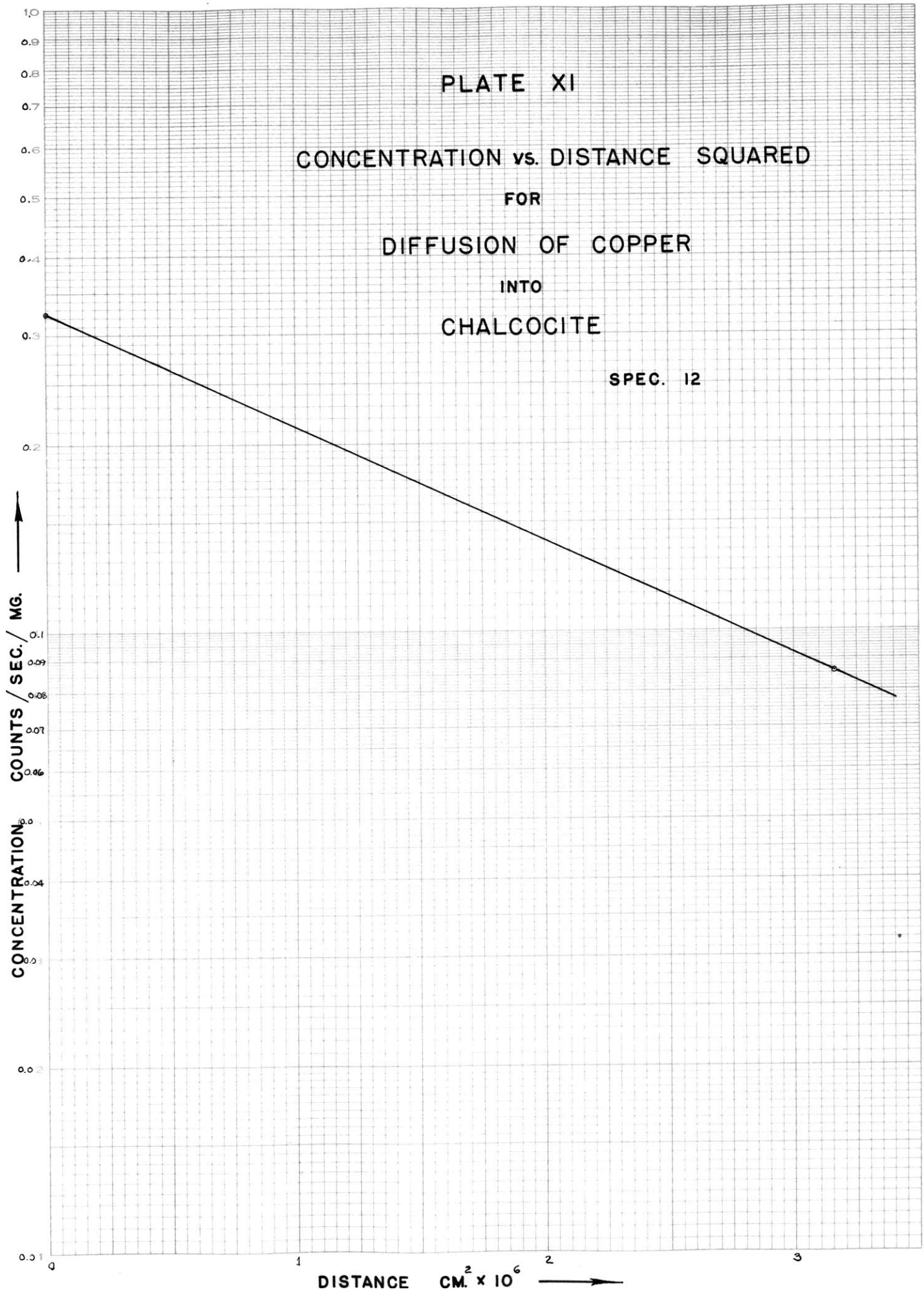


PLATE XII

CONCENTRATION vs. DISTANCE SQUARED  
FOR  
DIFFUSION OF COPPER  
INTO  
CHALCOCITE

SPEC. 23



COUNTS / SEC. / MG.

CONCENTRATION

0.1

100

200

300

400

DISTANCE  $CM^2 \times 10^6$

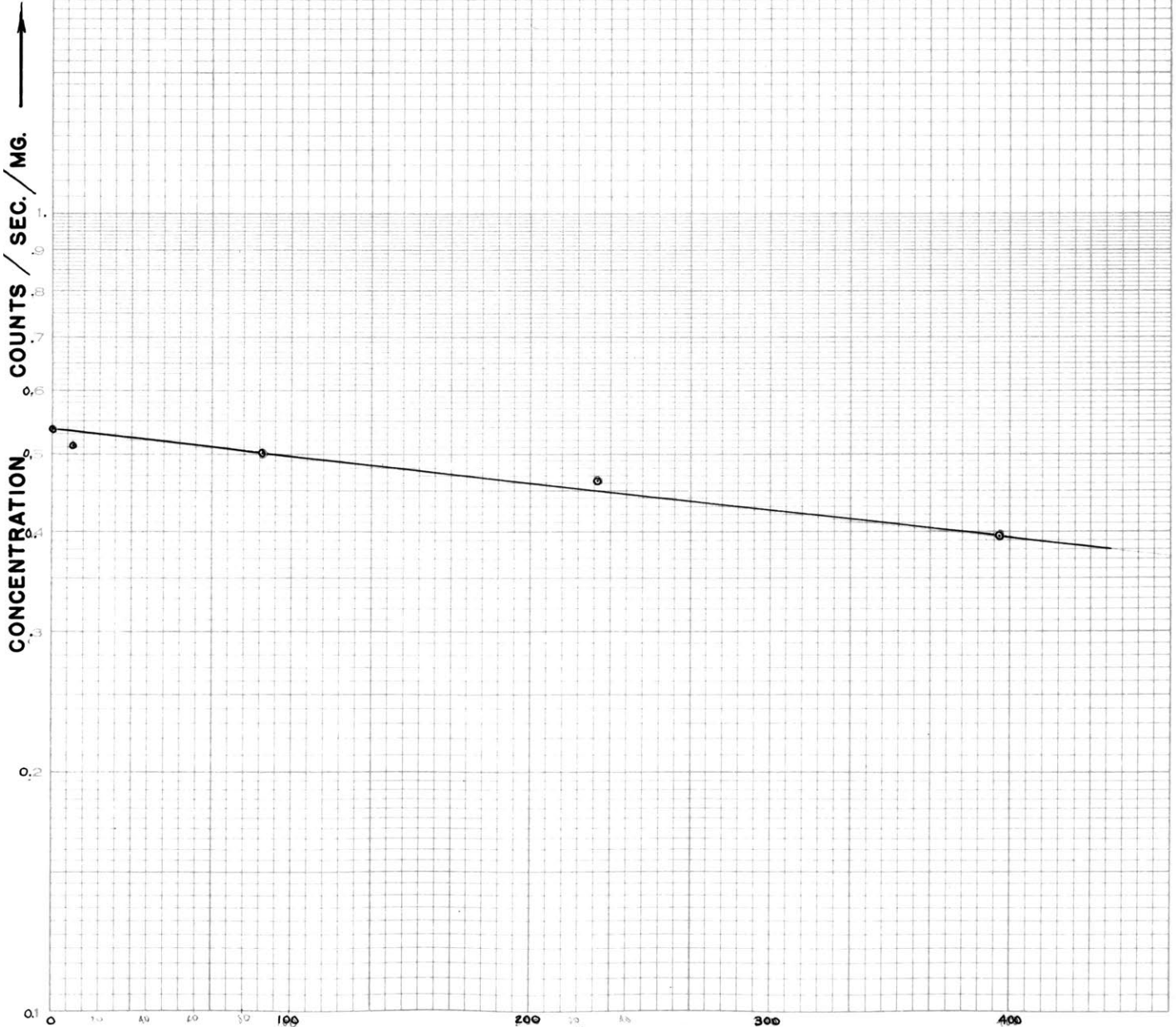


PLATE XIII

CONCENTRATION vs. DISTANCE SQUARED  
FOR  
DIFFUSION OF COPPER  
INTO  
CHALCOCITE

SPEC. 25

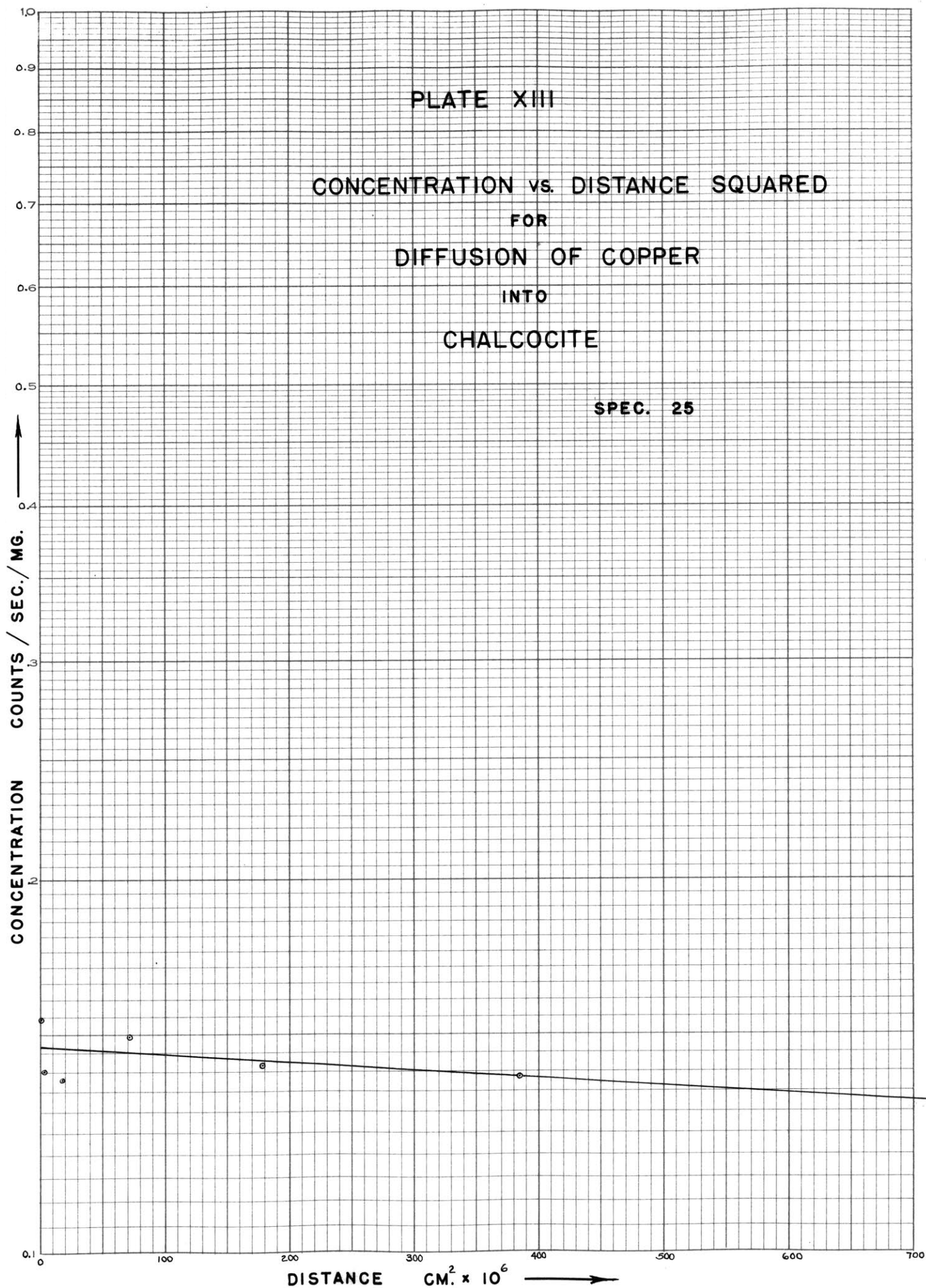


PLATE XIV  
CONCENTRATION vs DISTANCE SQUARED  
FOR  
DIFFUSION OF COPPER  
INTO  
CHALCOCITE

SPEC. 26

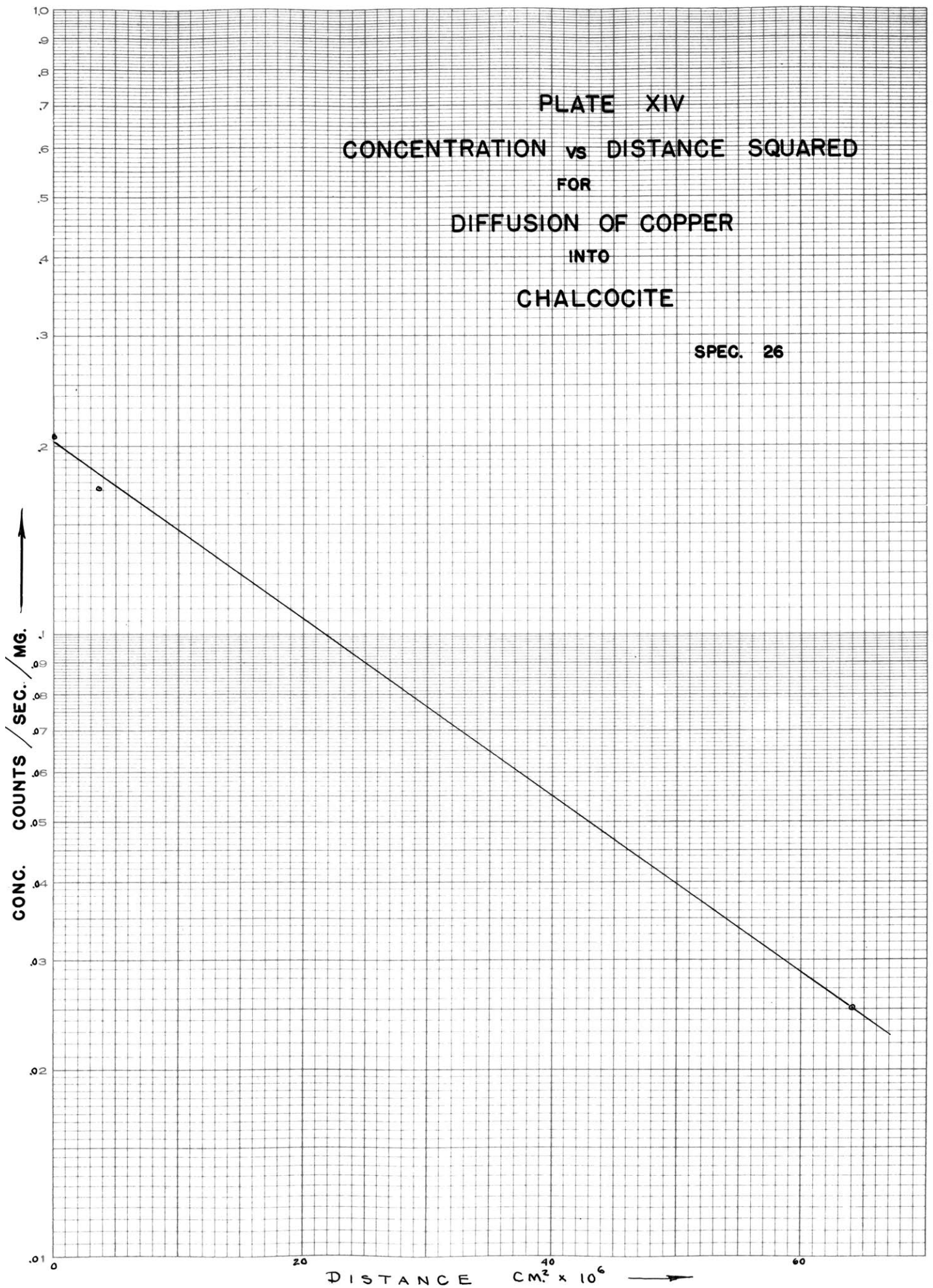
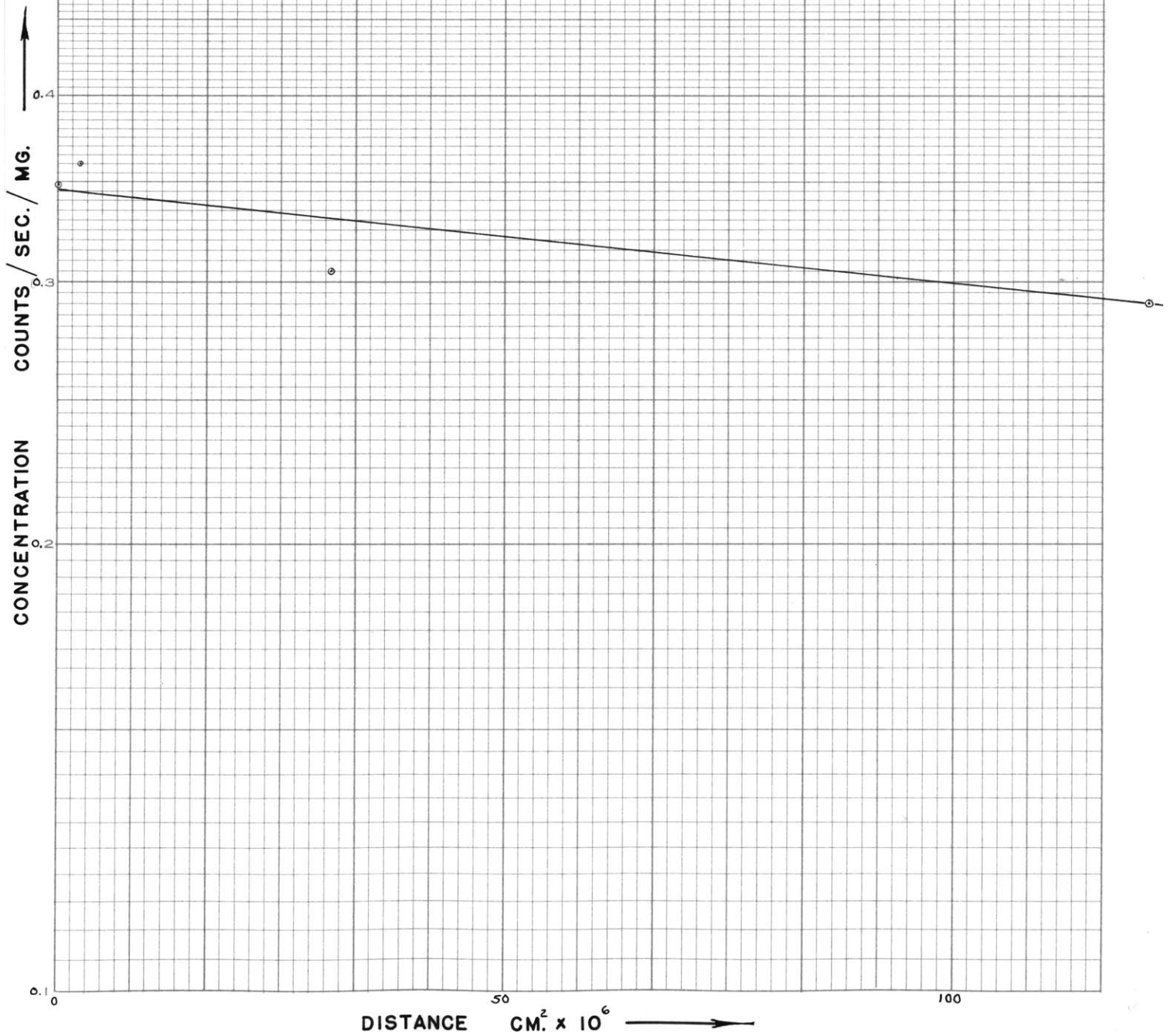


PLATE XV

CONCENTRATION vs. DISTANCE SQUARED

FOR  
DIFFUSION OF COPPER  
INTO  
CHALCOCITE

SPEC. 28



CONCENTRATION vs DISTANCE  
 FOR  
 DIFFUSION OF SODIUM  
 INTO  
 PERTHITE

PLATE XVI

CONCENTRATION  
 COUNTS / SEC. / MG.

WEIGHT MG. →  
 DISTANCE MM. →

0.1

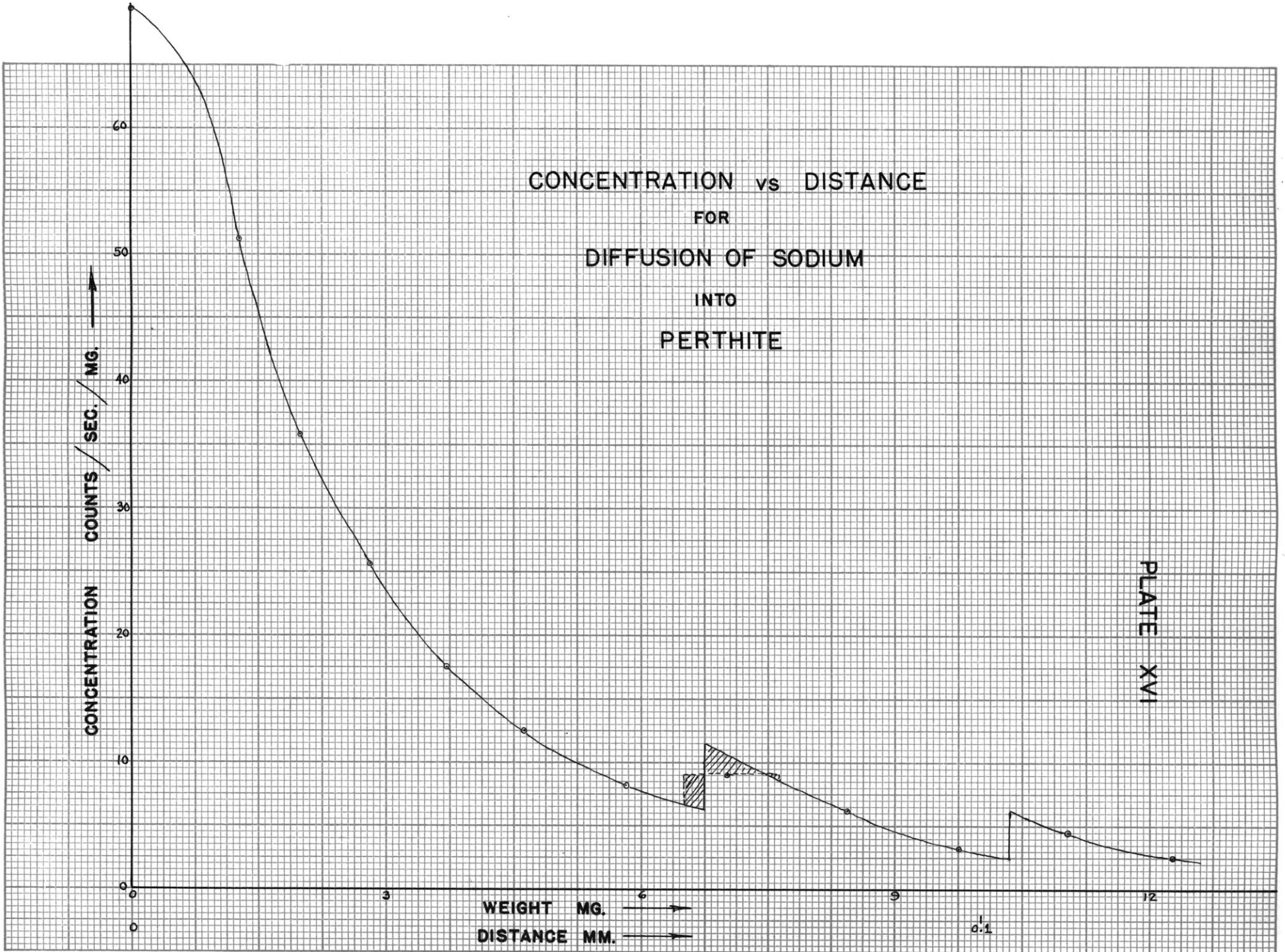
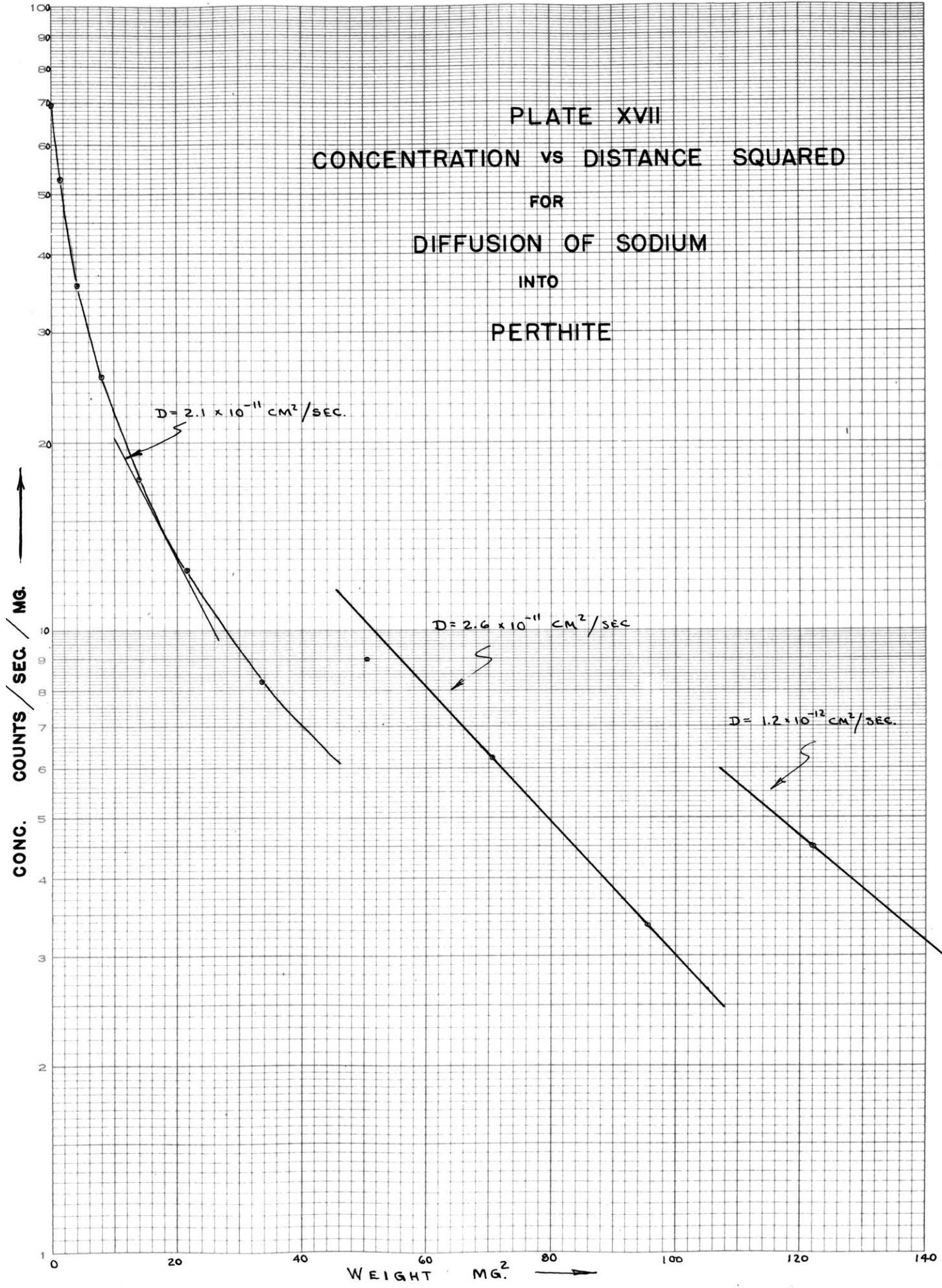


PLATE XVII  
CONCENTRATION vs DISTANCE SQUARED  
FOR  
DIFFUSION OF SODIUM  
INTO  
PERTHITE



## VI DISCUSSION OF EXPERIMENTAL RESULTS

### A. Diffusion of Copper into Chalcocite

The study of diffusion rates into chalcocite was of interest for several reasons.\* It was possible to obtain radioactive copper at the Massachusetts Institute of Technology cyclotron, the chalcocite could be cut fairly easily using a metal lathe, the active copper could be placed in crystallographic contact with the chalcocite by either electroplating or evaporating techniques, and finally, but most important of all, this mineral provided an excellent example to determine the effect of disordering upon diffusion coefficients. It has been shown by Buerger<sup>45</sup> that relatively pure chalcocite begins to disorder noticeably at a temperature of about 75 degrees centigrade and reaches complete disorder at a temperature of 105 degrees centigrade. As previously mentioned, one purpose of this thesis was to determine the order of magnitude of change in diffusion rates due to a disordering transformation. Chalcocite was thought to be

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\* Several adverse factors encountered during this investigation should also be noted. The copper nuclide used was  $\text{Cu}^{64}$ , the longest lived active nuclide of copper, which has a half-life of only 12.8<sub>g</sub> hours. This prevented diffusion runs from lasting much longer than 24 hours even when the experiment was begun with copper having an initial activity of about 0.1 millicurie. Massive chalcocite, furthermore, had to be used due to the lack of crystals of sufficient size. It was also very difficult, if not impossible, to select chalcocite specimens which were relatively pure; i.e., containing none or very little bornite, digenite, or other commonly associated minerals.

a suitable mineral for this investigation.

It was expected that the diffusion rate of copper through chalcocite would increase by a factor of several thousands or tens of thousands at a temperature slightly over 105 degrees centigrade when compared to a temperature of about 50 degrees centigrade. It was, therefore, quite surprising to obtain diffusion results of only  $10^{-9}$  cm.<sup>2</sup>/sec. at a temperature near 200 degrees centigrade as compared to  $10^{-11}$  cm.<sup>2</sup>/sec. at a temperature about 150 degrees lower. This is an increase of only 100 cm.<sup>2</sup>/sec. The increase in diffusion coefficients during the disordering (from about 70° C to 90° C) is even less; it is of the order of 15 to 20 cm.<sup>2</sup>/sec. This value is essentially the same in the investigation on the chalcocite from both Butte, Montana, and Kennecott, Alaska.

Since the solute atoms were in the form of copper metal against the solvent, or chalcocite (Butte Montana specimen), it was thought that the rate of self diffusion of copper in the solute film might limit the "availability" of the solute atoms at the solute-solvent interface and, thereby, lower the true diffusion rate through chalcocite. In order to avoid this possible effect, further experiments were carried out by placing the copper solute film near a small amount of heated sulphur. This rapidly changed the film to a sulphide of copper. The assumption was made that the solute copper

atoms would diffuse through the sulphide of copper film more rapidly and, thereby, increase the availability of the solute copper at the interface. These later experiments were performed on the massive chalcocite from Kennecott, Alaska.

The results obtained from the latter investigation on chalcocite from Kennecott, Alaska, gave diffusion coefficients which were larger than those of the previous investigation, but only by a small factor of approximately 20  $\text{cm.}^2/\text{sec.}$ . The diffusion coefficient, at a temperature near 200 degrees centigrade, determined in the latter experiments has a value of about  $2.5 \times 10^{-8} \text{ cm.}^2/\text{sec.}$  as compared to a value of  $1 \times 10^{-9} \text{ cm.}^2/\text{sec.}$  obtained in the former experiments. In the opinion of the author this small difference in diffusion coefficients is probably due to impurities in the two specimens and not due to the state of the solute film.

The magnitude of the energies of activation of copper in high chalcocite (obtained in this thesis) is of considerable interest. This is especially true when one realizes that the activation energies obtained from diffusion studies in metals are usually of the order of 15 to 50Kcal./mole. The author has no knowledge of any investigation on metals where an activation energy has been reported as low as that determined here for high chalcocite, a non-metal. He believes, however, that the values obtained, approximately 4000 cal./mole, are very reasonable. The copper atoms in high chalcocite

are in complete disorder which is proof enough that they have overcome the energy barriers between each other and have done so at the relatively low temperature of about 100 degrees centigrade. Upon further increase in temperature diffusion rates can not be aided by further disordering since disorder of the copper atoms is already complete. The apparent result is that the diffusion coefficients of high chalcocite do not increase too rapidly with increase in temperature (the slope of the curve of  $\log D$  versus  $1/T$  is low) and the result is a low activation energy.

No attempt has been made to compute the energy of activation of low chalcocite from the results obtained. This should be obvious since a line of practically any slope could be drawn through the one point determined for low chalcocite in both specimens.

The author believes that the curves shown on Plate VIII are not a contradiction of the critical temperature of complete disorder for chalcocite (105 degrees centigrade) determined by Buerger.<sup>45</sup> The planar end surface of the specimens was cut and prepared using a metal lath. This preparation undoubtedly added a certain amount of cold work energy to the material which would allow the critical temperature of complete disorder to be reached at a somewhat lower temperature.

### B. Diffusion of Sodium into Perthite

The results obtained from the diffusion of sodium into the perthite specimen at a temperature of 550 degrees centigrade are extremely interesting and significant. The concentration versus distance curve obtained, Plate XVI, was not predicted but after some thought a possible interpretation became apparent.

First let us consider two end members, A and B, of a binary system which are placed in contact with each other, and a third component, solute C, is applied to a planar surface parallel to the interface planes of A and B as shown in figure 7. If a diffusion run is made at a temperature where A and B are not in solid solution the resulting concentration-distance curve will show a sudden rise at the A-B interface if the diffusion rate of solute C in member B has a lower value than the diffusion coefficient of solute C in member A. If the coefficients were reversed (solute C diffuses through B more rapidly than through A) there would then be a sudden drop or fall of concentration at the interface of A and B.

Apparently, the result obtained from diffusion of sodium into the perthite specimen is analogous to the above consideration. The perthite specimen used consisted of thin laminae of albite and microcline which, roughly speaking, can be considered to be end members of the  $\text{NaAlSi}_3\text{O}_8$ - $\text{KAlSi}_3\text{O}_8$

binary feldspar system. Furthermore, the diffusion temperature of 550 degrees centigrade is very probably in a region

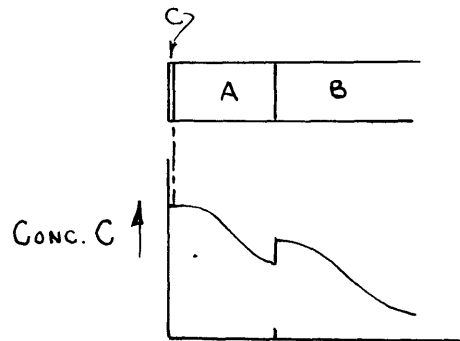


Figure 7. Diffusion of Solute C through Binary Members A & B of non-solid solution.<sup>23a</sup> The analogy, however, now becomes less clear. The perthite consists of innumerable alternating lamellae of the two end member components whereas the example given above of the A and B end members consisted of only one specimen of each member. The numerous interfaces between the microcline and the albite were, furthermore, not parallel to the thin solute film but intersected the plane at an angle of approximately 30 degrees. During the sectioning, different ratios of microcline to albite were removed due to the non-uniform width of the lamellae and the general variation of the ratio of albite to microcline from place to place in a perthite. Referring to Plate XVI, it appears that the ratio may have varied abruptly at a distance from the solute film of about 0.066 millimeter and again at about 0.103 millimeter. It

seems possible that the sodium tended to diffuse through one of the two members at a more rapid rate. When a section was cut containing a sudden increase of the component through which diffusion is more rapid, the concentration of radioactive sodium, therefore, increased.

Considering the results in the light of Darken's<sup>42</sup> investigation on diffusion of carbon in two welded specimens of austenite iron (described on page 46), it seems possible that the sudden changes in the sodium concentration curve could be due to unequal amounts of a component in the microcline and albite lamellae, possibly even impurity, which would vary the chemical activity of sodium. In fact, it is even possible that the difference in the ratio of initial sodium and potassium in the two components could be the cause of the effect. The result would be that the sodium ions would tend to diffuse more rapidly in that material or mineral having the higher thermodynamic activity for sodium.

The application of this experiment to zoned crystals is rather interesting. Bowen<sup>46</sup> has expressed doubts about the existence of zoned crystals in granitized bodies. He wonders why a small crystal should remain zoned when the granitizers speak of diffusion over several miles. The granitizers have not answered his question except by ridicule or "argumentum ad hominae". It seems possible, however, that a zoned crystal could actually be formed by solid diffusion under special con-

ditions. For instance a quartz crystal may possess zones formed during the growth of the crystal which contain slight differences in the amount of impurities present. Any one, or all, of these impurities might change the thermodynamic activity of an ion which diffuses into the quartz crystal and the result would be different concentrations of the solute ion in zones corresponding to the growth zones of the original quartz crystal. The major criticism of this theory is that the impure ions would probably also tend to diffuse within the crystal and the sharp growth zones would, therefore, tend to become diffuse with the result that sharp zoning, due to diffusion of other ions into the crystal, would become less and less probable.

Geologic contacts may be another example of the effect of thermodynamic activity on diffusion rates. Several investigations have been made in the Department of Geology, Massachusetts Institute of Technology, through spectrographic methods, on the variation of elements across geologic contacts.<sup>47</sup> It has been observed, (quite often) that the concentrations of an element on each side of a contact become even more divergent as the contact is approached. This is shown diagrammatically in figure 8. It is believed a concentration variation curve such as this may be due almost entirely to the thermodynamic activity of the element in the two rock types on each side of the contact. In figure 8, the diffusing element

has a higher thermodynamic activity value in rock A than it has in rock B. As a result of this variation in activity, more of the element moves across the contact to the right than to the left and the concentration curves vary as shown in figure 8.

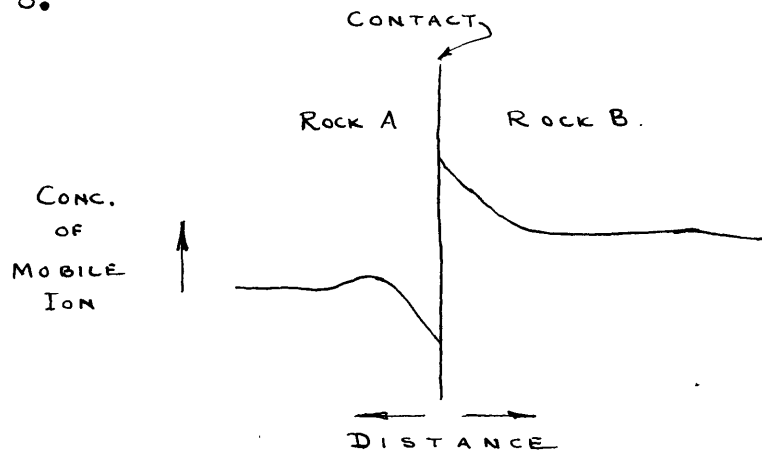


Figure 8. Variation of an Ion across a Contact

## VII CONCLUSIONS

There is little doubt that the study of diffusion in minerals is a somewhat more difficult task than the study of diffusion in metals. It would be rather enjoyable to be able to crystallize synthetically a silicate mineral, place it in a lathe or milling machine and cut it to desired dimensions, weld or electroplate another substance to the mineral, and be able to allow rather rapid thermal fluctuations of the material with little fear of it disintegrating to smithereens. We must, however, be appreciative of the metallurgists and physicists for their fundamental research on solid diffusion and the development of the mathematical approach to the problem.

I have been rather surprised not only by the slow rates of diffusion found for minerals during this investigation, but also by the numerous low diffusion coefficients reported in the literature for other solids. The concept of rather large channelways through the structure of a crystal, usually a silicate, which allows an atom practically to fall through these openings appears to be a misconception. Rather it seems that these passageways are more aptly described as a series of cages containing the diffusing ion, with fairly large interconnecting openings. The size of these openings is not of primary importance. Rather the electrostatic field existing

about each cage is of more importance. Even though a polymorphous mineral may show larger and larger channel-ways with increase in temperature, the total expansion in the size of the cages forming the passageways is of the order of only one or two angstroms, usually much less. This rather insignificant expansion does not noticeably decrease the electrostatic field or potential barriers existing about each cage for the diffusing ions. The result is that the bond strength is not decreased appreciably by expansion of the structure and diffusing ions still have some difficulty in jumping rather rapidly from one cage to another. This difficulty of overcoming electrostatic repulsions and attractions is even encountered in under-cooled liquids, such as glasses, which contain very large openings. The diffusion coefficient of sodium migrating through sodium glass is as low as  $10^{-8}$  cm.<sup>2</sup>/sec. at a temperature of about 850 degrees centigrade.

In conclusion, I shall become somewhat quantitative but far from dogmatic. In the light of the above discussion, I have some doubts if solid diffusion coefficients of the alkali metals in silicate minerals are much greater than  $10^{-5}$  cm.<sup>2</sup>/sec. I wish to emphasize that this value might be easily increased by factors such as pressure, impurities, and application of a potential across the mineral in order to pull the solute atom through the crystal. There is no doubt, furthermore, that diffusion rates through fractures and openings in rocks are extremely more rapid, especially when solu-

tions are present, but I am referring only to pure solid diffusion.

In making the above suggestion, I realize I am doing so on the basis of very meager experimental data but it is one of the stronger multiple hypotheses which I shall attempt to study in the future.

The importance of diffusion in the phenomenon of geologic replacement should be briefly mentioned. It is possible that the diffusion of sodium ions into perthite (as performed in this thesis) may result in a replacement or albitization of the microcline due to the sodium ions being added to the microcline. This would be very true if the potassium ions would diffuse from their positions in the solvent back across the interface into the solute so that the solute sodium ions diffusing in the opposite direction could occupy the vacant potassium sites. It is a sort of Pfeil (Kirkendall) effect<sup>7b</sup> with, however, no movement of the interface as long as the replacement is volume for volume.

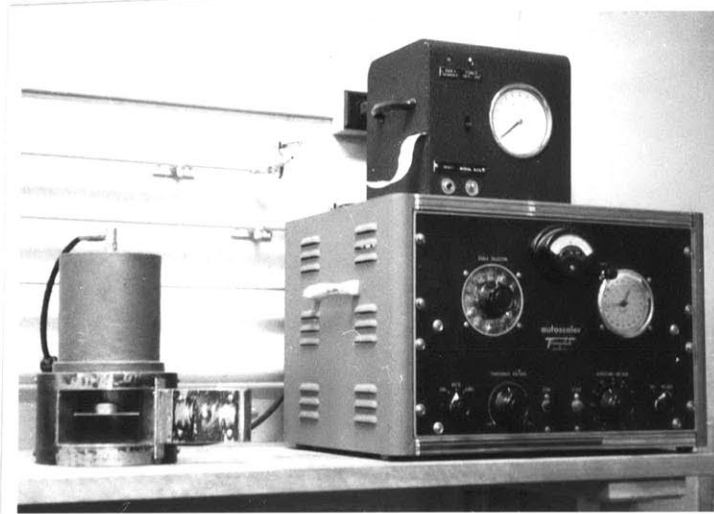
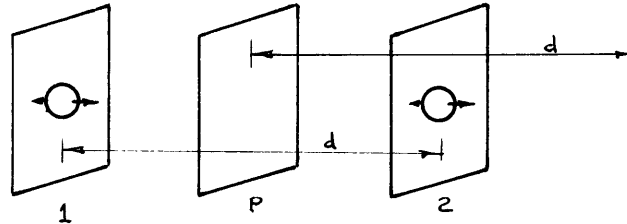


Plate XVIII

Scaler instrument, time recorder,  
and lead-shielded Geiger-Mueller  
tube counting set-up, showing counter  
with door open and active sample on  
shelf.

## VIII APPENDIX

A. Derivation of Fick's First Law

Conditions:

	Plane 1	Plane 2
Concentration	$c_1$	$c_2$
Number of atoms	$N_1$	$N_2$
Cross-sectional area	$A$	$A$
Atomic fraction of solute atoms present	$\beta_1$	$\beta_2$
Number of solute atoms present	$N_1 \cdot \beta_1$	$N_2 \cdot \beta_2$
Therefore,	$c_1 = \frac{N_1 \cdot \beta_1}{d \cdot A}$	and $c_2 = \frac{N_2 \cdot \beta_2}{d \cdot A}$

also, let  $\nu$  jump frequency in the x direction

$\nu_1$  jump frequency in the x direction in plane 1

$\nu_2$  jump frequency in the x direction in plane 2

$\frac{\nu_1}{2}$  is the probability of a solute atom moving to the right from plane 1, and  $\frac{\nu_2}{2}$  is the probability of a solute atom

---

\* The derivations of Fick's First and Second Laws given here in Appendix A & Appendix B are essentially the same as those presented by Professor M. Cohen in Adv. Physical Metallurgy. (3.34T)

moving to the left from plane 2.

$$\text{Therefore, } \frac{dm}{dt} = \frac{N_1 \cdot \beta_1 \cdot \lambda_1}{2} - \frac{N_2 \cdot \beta_2 \cdot \lambda_2}{2} \text{ where } \frac{dm}{dt} \text{ is the}$$

number of solute atoms per unit time which pass through plane P.

$$\text{and, } \frac{dm}{dt} = \frac{N_1 \cdot c_1 \cdot d \cdot A}{2 \cdot N_1} - \frac{N_2 \cdot c_2 \cdot d \cdot A}{2 \cdot N_2} = \frac{A \cdot d}{2} [c_1 \lambda_1 - c_2 \lambda_2]$$

If the assumption is made that  $\lambda \neq f(c)$

$$\text{then, } \lambda_1 = \lambda_2 = \lambda$$

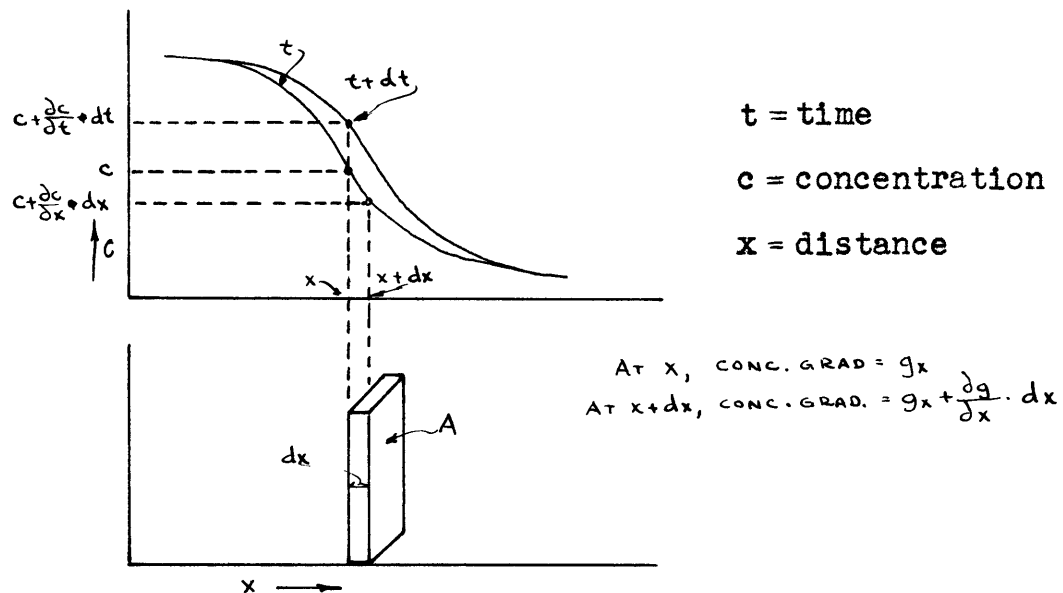
$$\text{and } \frac{dm}{dt} = \frac{A \cdot d \cdot \lambda}{2} [c_1 - c_2] \text{ but } c_2 = c_1 + \frac{\partial c}{\partial x} \cdot d$$

$$\text{therefore, } \frac{dm}{dt} = \frac{A \cdot d \cdot \lambda}{2} [c_1 - (c_1 - \frac{\partial c}{\partial x} \cdot d)] = -\frac{A \cdot d^2 \cdot \lambda}{2} \cdot \frac{\partial c}{\partial x}$$

$$\text{Now let } D = \frac{d^2 \lambda}{2}$$

$$\text{then, } \frac{dm}{dt} = -D \cdot A \cdot \frac{\partial c}{\partial x}$$

## B. Derivation of Fick's Second Law



In the elementary volume  $dV$ , which equals  $A dx$ , and at a time  $t$ , the weight of solute is  $c \cdot A dx$ . At a later time  $t+dt$ , the weight of solute is  $(c + \frac{\partial c}{\partial t} dt) \cdot A dx$ . In  $dt$  seconds, the change in weight of solute in  $dV$  is the difference in the above two expressions, or:

$$(c + \frac{\partial c}{\partial t} \cdot dt) \cdot A dx - c \cdot A dx = \frac{\partial c}{\partial t} A dx \cdot dt \quad (1)$$

In  $dt$  seconds, the weight of solute entering from the left is, according to Fick's First Law,  $-D \cdot A \cdot g_x \cdot dt$ .

In  $dt$  seconds, the weight of solute entering from the right is,  $-D \cdot A \cdot (g_x + \frac{\partial g_x}{\partial x} \cdot dx) \cdot dt$ .

Therefore, in  $dt$  seconds, the change in weight of solute in the elementary volume  $dV$  is the difference in the above

two expressions, or:

$$-D \cdot A \left( g_x + \frac{\partial g}{\partial x} \cdot dx \right) dt - (-D \cdot A \cdot g_x \cdot dt) = -D \cdot A \cdot \frac{\partial g}{\partial x} \cdot dx \cdot dt \quad (2)$$

On equating (1) and (2).

$$\frac{\partial c}{\partial t} \text{ Adx} \cdot dt = -D \cdot A \cdot \frac{\partial g}{\partial x} \cdot dx \cdot dt$$

$$\frac{\partial c}{\partial t} = -D \cdot \frac{\partial g}{\partial x} \quad \text{but } g = \frac{\partial c}{\partial x}$$

Therefore, 
$$\frac{\partial c}{\partial t} = -D \frac{\partial^2 c}{\partial x^2}$$

or, 
$$\frac{\partial c}{\partial t} = D \frac{\partial}{\partial x} \left( \frac{\partial c}{\partial x} \right) \quad \text{and} \quad \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right)$$

for  $D \neq f(c)$

for  $D = f(c)$

C. Solution of Fick's Second Law for the Semi-infinite Solid

The differential equation is:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{where, } \begin{array}{l} c = \text{concentration} \\ D = \text{diffusion constant} \\ x = \text{distance of penetration} \\ t = \text{time of diffusion} \end{array}$$

The boundary conditions are:

$$c = f(x, t) \quad \text{for } t > 0$$

$$c = f(x) \quad \text{for } t = 0$$

Assume the solution  $c = X(x) \cdot T(t)$

$$\text{therefore, } \frac{\partial c}{\partial t} = X \frac{\partial T}{\partial t} \quad \text{and} \quad \frac{\partial^2 c}{\partial x^2} = T \frac{\partial^2 X}{\partial x^2}$$

so, substituting in the differential equation,

$$X \frac{\partial T}{\partial t} = DT \frac{d^2 X}{dx^2}, \quad \begin{array}{l} \text{let } X'' = \frac{d^2 X}{dx^2} \\ \text{and } T' = \frac{\partial T}{\partial t} \end{array}$$

therefore,  $XT' = DX''T$ , which is set  $= -\beta^2$

$$\text{and } \frac{T'}{T} = \frac{X''}{X} = -\beta^2$$

Now,  $X(x) = A \cos \beta x + B \sin \beta x$ , (sol. of  $X'' + X \beta^2 = 0$ ) (1)

and  $T(t) = G_0 e^{-\beta^2 Dt}$  (sol. of  $\frac{T'}{T} = -\beta^2 D$ ) (2)

where  $A$ ,  $B$ ,  $G_0$ , and  $\beta$  are real constants

$$\text{and } c = G_0 e^{-\beta^2 Dt} (A \cos \beta x + B \sin \beta x)$$

A sum of such solutions is also a solution, and by application of Fourier Series in order to evaluate constants:

$$c = (a_n \cos \beta_n x + b_n \sin \beta_n x) \cdot e^{-\beta^2 Dt}$$

$$\text{where, } a_n = \frac{1}{\pi} \int_{-\pi}^{+\pi} f(x') \cdot \cos \beta x' \cdot dx'$$

$$\text{and } b_n = \frac{1}{\pi} \int_{-\pi}^{+\pi} f(x') \cdot \sin \beta x' \cdot dx'$$

Putting in integral form and applying boundary conditions:

$$c = \frac{1}{\pi} \int_0^{\infty} e^{-\beta^2 Dt} d\beta \int_{-\infty}^{+\infty} f(x') \cdot \cos \beta (x-x') dx'$$

Note: Since  $f(x')$  is an even function,

$$[f(-x) = f(x)]$$

therefore,  $b_n = 0$

$$c = \frac{1}{\pi} \int_{-\infty}^{+\infty} f(x') \left[ \int_0^{\infty} e^{-\beta^2 Dt} \cos \beta (x-x') \cdot d\beta \right] dx'$$

$$\int_0^{\infty} e^{-a^2 x^2} \cos bx \cdot dx = \frac{\sqrt{\pi} \cdot e^{-\frac{b^2}{4a^2}}}{2a} \quad (\text{from handbook})$$

if  $a > 0 \therefore a^2 = Dt$  and  $b = (x-x')$

$$\text{therefore, } c = \frac{1}{\pi} \int_{-\infty}^{+\infty} f(x') \left[ \frac{\sqrt{\pi} \cdot e^{-\frac{(x-x')^2}{4Dt}}}{2Dt} \right] dx'$$

$$= \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^{+\infty} f(x') \cdot e^{-\frac{(x-x')^2}{4Dt}} dx'$$

Remembering that  $c = f(x)$  at  $t = 0$ , and that  $c = f(x, t)$  at  $t > 0$ , assume at  $t = 0$  that there is a thin film concentration ( $c = c_0$ ) of solute atoms between planes  $x = -a$  and  $x = +a$ , then:

$$c = \frac{1}{2\sqrt{\pi Dt}} \int_{-a}^{+a} c_0 e^{-\frac{(x-x')^2}{4Dt}} dx'$$

$$\text{Now, as } a \rightarrow 0, \quad c = \frac{c_0 \cdot a}{2\sqrt{\pi Dt}} \cdot e^{-\frac{x^2}{4Dt}}$$

But the concentration curve is symmetrical about the origin, so when there is diffusion in one direction only (+x), the resulting equation is:

$$c = \frac{c_0 a}{\sqrt{\pi Dt}} \cdot e^{-\frac{x^2}{4Dt}}$$

D. Biographical Note

The author's parents are Joseph Mead and Gertrude Grayson Jensen. He was born in Salt Lake City, Utah, on June 11, 1925, and received all of his primary and secondary education in that state.

He entered the University of Utah in 1942 and graduated with the degree of Bachelor of Science in Geological Engineering in June, 1948. His undergraduate training was interrupted from 1944 until 1946 at which time he served with the Amphibian Corp of the United States Navy as an electronic technician.

In September, 1948, he entered the Graduate School of Geology, Massachusetts Institute of Technology, and in June, 1951, received the degree of Doctor of Philosophy in Geology. He received appointments as teaching fellow during his first two academic years at the Institute and was the recipient of the William S. Knudsen Fellowship during the third year, 1950-51.

His professional experience has been limited to summer employment. During the summer of 1948, he was employed by the Pacific Western Oil Corporation as a Field Assistant. In 1949 and 1950, he served as Geologist and Party Chief for the Standard Oil Company of California in the investigation of stratigraphy and structural geology in the states of Utah, Idaho, and Nevada.

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