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Marcus P. Borom

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ABSTRACT

Diffusion couples of elemental iron and degassed sodium disilicate glass rod were prepared under neutral to reducing conditions at several temperatures and at varying times. The diffusion profiles were analyzed by using electron microprobe techniques. Diffusion-coefficient calculations and activation-energy determinations indicated that a change in mechanism was occurring between 1000 and 1050°C. An indication is given by the magnetic-susceptibility measurements that atomic iron is the diffusing species at 900°C and that ferrous iron is the diffusing species at 1050°C. These observations are supported by the transmission-spectroscopy measurements and by theoretical thermodynamic considerations. A discussion of the possible mathematics of the diffusional processes is given.

I. INTRODUCTION

Enameling, the application of a glassy coating to a metal substrate, is a ceramic art which had its origins in very ancient times. In more recent times new demands for coatings for metals which would be both decorative and protective, protective particularly against corrosive materials often at elevated temperatures, has moved this ancient art into the realm of technology. A more recent cousin of enameling, born of the age of electronics, is the technology of the glass-to-metal seal. The basic approach to the solution of problems in both of these fields remains today to be primarily a pragmatic one, and only a small effort has been made toward converting these technologies into sciences.

One of the basic questions asked concerning glass - metal systems relates to the production and nature of the adherence produced between the glass and the metal. A number of theories of adherence have been advanced, but a complete understanding of the glass - metal interface still remains to be resolved. A significant contribution to the understanding of the chemical nature of the glass-to-metal bond has been made by Pask and Fulrath[1] from wetting and adherence studies conducted at the University of California over the past ten years. The basic concept arising from this work is that a balance of bond energies at the glass-metal interface is necessary for the production of good chemical adherence. This balance of bond energies may be achieved by the solution of the oxide of the base metal by the glass. According to theory, the amount of oxide dissolved should be sufficient to saturate the glass at the interface. In so doing, a balance is achieved between the demand for oxygen anions by the network forming silicon cations and the demand for oxygen anions by the metal cations at the immediate interface. The result is a smooth chemical transition from the elemental metal through an intermediate "equilibrium phase" to the unreacted glass. A requirement for the saturation of the glass at the interface is that the rate of solution of the oxide by the glass be faster than the rate of diffusion of the "oxide" into the glass.

A considerable amount of material is to be found in the literature regarding diffusion in glass, and Williams[2] has published a review on the subject. The majority of the diffusion studies deal with the more common cation components of glasses, such as the alkali and alkaline earth metals. In contrast to the wide usage of iron in glass-metal systems as the substrate metal or as the predominant metal in an alloy substrate, very little data are available on the diffusivity of iron in glass. Yang[3] has reported values for the self-diffusion of iron in an iron silicate melt in the temperature range from 1250 to 1300°C, with no specific mention of the valence of the diffusing species. Yang reported a value of 7.9×10^{-5} cm^2/sec for the diffusion coefficient of iron at 1250°C with an activation energy of 40 kcal. Tashiro[4] has reported the "diffusion velocity" of FeO in a typical enamel at 885°C to be 6.6×10^{-8} cm^2/sec.

The purpose of the present investigation is to supply fundamental information regarding the kinetics of the reactions that occur at glass - metal interfaces at elevated temperatures. A simple model system—elemental iron as the substrate metal and sodium disilicate glass as the diffusion medium—is chosen for study.

II. EXPERIMENTAL WORK

A. Preparation of Diffusion Couple

Metal specimens 5/8 in. in diameter were cut from 1/8-in.-thick Armco magnetic ingot iron (typical analysis: 0.015%C, 0.285% Mn, 0.005% P, 0.025% S, and 0.003% Si). The iron specimens were polished with dry papers and given a final polish with a suspension of Linde A-5175. Just prior to its use in a diffusion study, the metal specimen was heated in vacuum (less than 10^{-3} torr) at the test temperature in an alumina crucible until there was no further evidence of outgassing. The surface of the metal had a bright metallic luster after this treatment.

Degassed sodium disilicate glass rod approximately 5/8 in. in diameter was prepared by Corning Glass Works at their research laboratories in Corning, New York. The glass was vacuum-smelted in a platinum container at 1480°C and held at 0.015 torr pressure for 2 h before drawing the cane under an argon atmosphere. The glass contained 0.005% Cu as the only reported impurity. Three-quarter-inch lengths were cut from the rod to serve as diffusion specimens. A lateral cut was made in the glass specimen to accommodate the measuring thermocouple (Pt/Pt-10% Rh). The ends of the glass specimen were polished through a set of dry polishing papers prior to a diffusion experiment.

A vertical diffusion furnace was utilized which was capable of operation under conditions of vacuum or controlled atmosphere. The diffusion cell (shown in Fig. 1) could be raised or lowered in the furnace by means of an external magnet without affecting the furnace atmosphere. The vertical gradient in the diffusion cell under operating conditions was less than ±1°C. A schematic diagram of the diffusion furnace is shown in Fig. 2.

The diffusion cell was outgassed in the cold zone of the furnace at approximately 100°C for up to 12 h before being lowered into the hot zone. The sample temperature was monitored by the Pt/Pt-10%

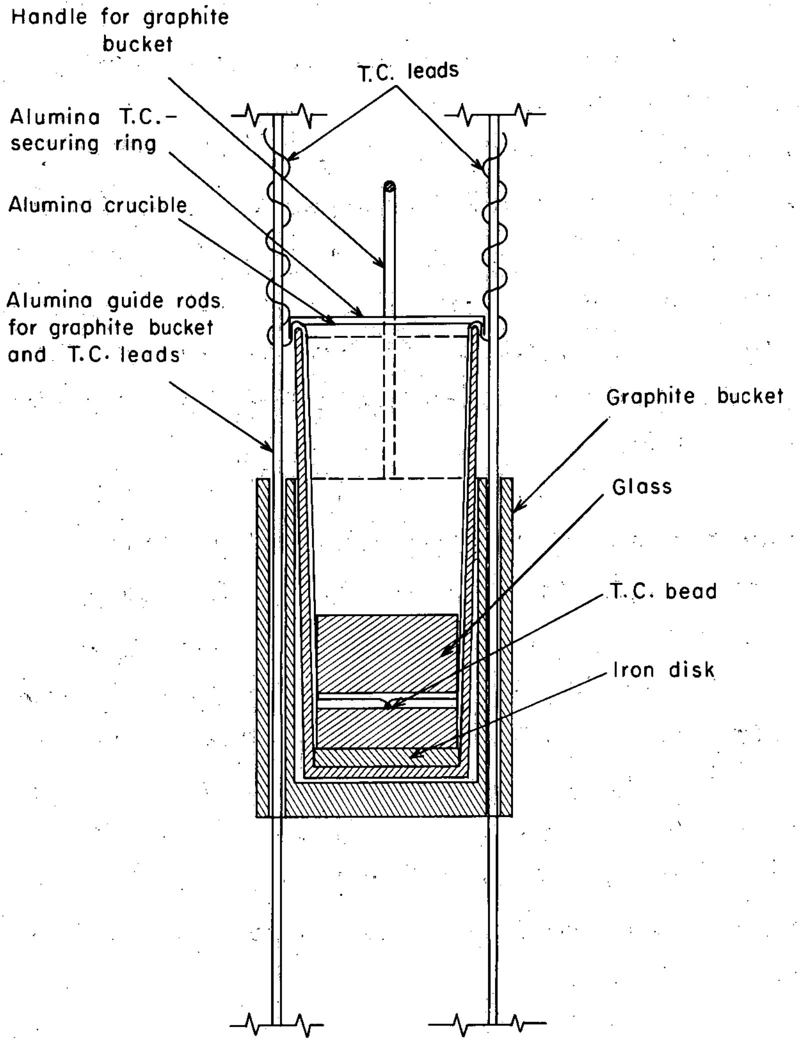

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Fig. 1. Schematic of diffusion cell.

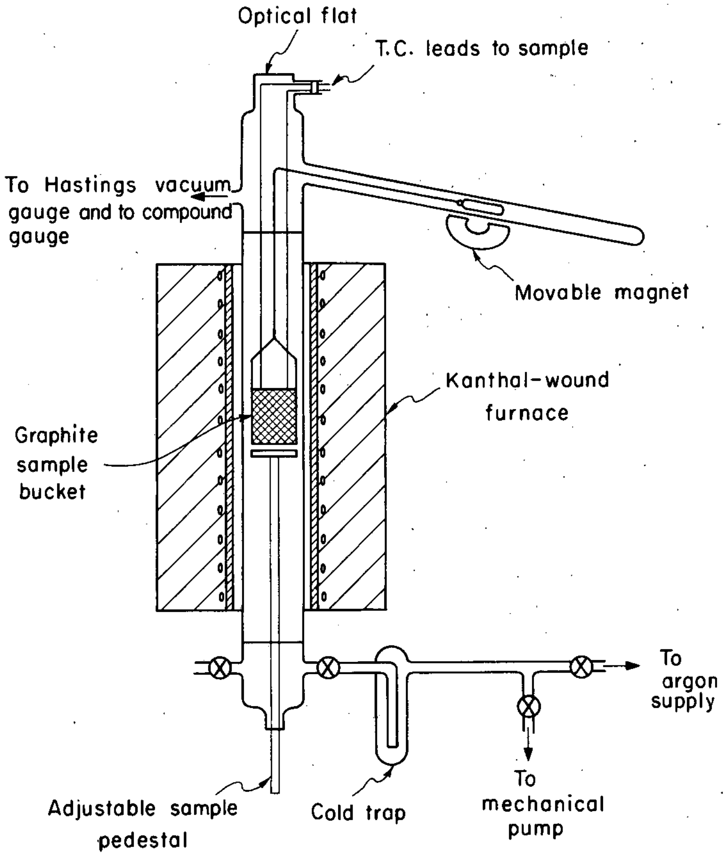

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Fig. 2. Schematic of diffusion furnace.

Rh thermocouple mounted in the glass portion of the diffusion couple, and the temperature was automatically recorded on a Leeds and Northrup Adjustable Span Adjustable Range (ASAR) Speedomax recorder. This technique permitted further outgassing of the diffusion cell at about 400°C. From this point the cell was completely lowered into the hot zone and the pressure was held at approximately 0.015 torr until the softening point of the glass (598°C) was exceeded and the glass - metal interface sealed. After the glass had wetted the metal, the furnace pressure was raised to approximately 125 torr with 99.99% argon which was passed through a liquid-nitrogen cold trap before entering the furnance. The pressure of the system was raised in order to minimize convection in the glass due either to further possible outgassing of the crucible and of the substrate metal at the higher temperature or to the production of a gas at the glass - metal interface due to a reaction.

Temperature variations of the sample during the diffusion run were indicated on the Leeds and Northrup ASAR Speedomax strip chart with a full-scale sensitivity of 2 mV adjusted to the range of the diffusion temperature. The temperature range covered during the experiments was from 900 to 1050°C in increments of 50°. This range was bounded by crystallization of the glass between 800 and 900°C and by furnace limitations above 1100°C.

Upon conclusion of the diffusion run the sample was withdrawn and allowed to cool rapidly to just above the annealing point (452°C) of the glass. Approximately 15 min were allowed for the sample to pass through the annealing point, after which the sample was withdrawn to the cold portion of the furnace and allowed to cool to room temperature.

B. Electron Microprobe Analysis

The lack of adherence between the glass and the iron permitted the easy removal of the glass column from the metal substrate. The glass column was mounted in a plastic casting resin, and a cross section of the diffusion zone perpendicular to the glass-metal interface was removed from the center of the column with the aid of a diamond saw. This cross section was remounted in the casting resin so as to expose the length of the diffusion path for analysis. The cross section was polished down through a 1-μ diamond polish with a Syntron polisher. After coating the surface of the sample with carbon it was submitted for electron microprobe analysis.

The electron microprobe is essentially an x-ray tube that uses the sample in question as the target material. A finely focused electron beam bombards the sample and fluorescent x-rays are produced. The characteristic fluorescent radiation from the particular element being analyzed is resolved by a proper positioning of a diffracting crystal, and the intensity of the radiation is measured with a suitable counter. The position of the sample in relation to the electron beam can be stepwise or continuously changed by means of a gear-and-motor-drive mechanism. A plot of intensity of radiation vs diffusion distance can be made with a strip-chart recorder, thereby yielding a record of the diffusion profile. The present samples were scanned at a rate of 96μ per min. The intensity of the radiation from the sample is calibrated against a known standard (in this case, olivine containing 8.7% Fe by weight). After appropriate corrections for absorption, atomic number, counter sensitivity, dead time, etc., the intensity is reported as weight percent. In order to obtain a meaningful diffusion profile the weight-percent values must be converted to atomic-percent values. This is done in order to conform more closely to the mathematics of the diffusion equations, which are derived on the basis of chemical potential gradients. Sample calculations are to be found in the Appendix. A.

C. Analysis by Transmission Spectroscopy

Cross sections were prepared as for electron microprobe analysis with two exceptions. The final polish was on a lap wheel with 4- to 12-μ B_4C, and both the front and the back side of the cross section of the glass were polished to improve transmission qualities. An aluminum-foil mask was prepared that exposed only the portion of the glass containing the diffused iron to the light source. The transmission spectra of the various samples in the visible and the ultraviolet regions were obtained with a Cary No. 14 recording spectrophotometer manufactured by the Applied Physics Corporation. The recorder plots sample optical density vs wavelength on a strip chart. Sample thickness varied from piece to piece, which required that different density standards be used in the reference beam. Since diffusion produces an inhomogeneity in the sample along its length and since the total iron diffused in each sample is different, no attempt was made at expressing the data in absolute units. The samples are compared on the basis of the relative shapes of the optical density vs wavelength curves.

D. Analysis by Magnetic Susceptibility Using a Faraday Balance

The Faraday balance (shown in Fig. 3) consists of a large electromagnet whose field strength may be varied, a sample chamber which permits a few milligrams of sample to be suspended in an inhomogeneous portion of the magnetic field, a telescope for viewing the position of the sample in the field, and a micrometer adjustment for measuring the deflection of the sample from the zero-field position. The sample chamber consists of a vertical tube surrounded by a dewar and illuminated from beneath for viewing. This permits convenient measurements at a variety of temperatures from room temperature to liquid-nitrogen temperature. The sample holder itself consists of a fused silica test tube approximately 6 by 1 mm which is suspended in the sample chamber from a fine fused silica fiber. A material of accurately known mass susceptibility is used to calibrate the suspending fiber. This calibration results in a set of apparatus constants that is used in calculating the susceptibility of an unknown sample. Sample calculations are given in Appendix C.

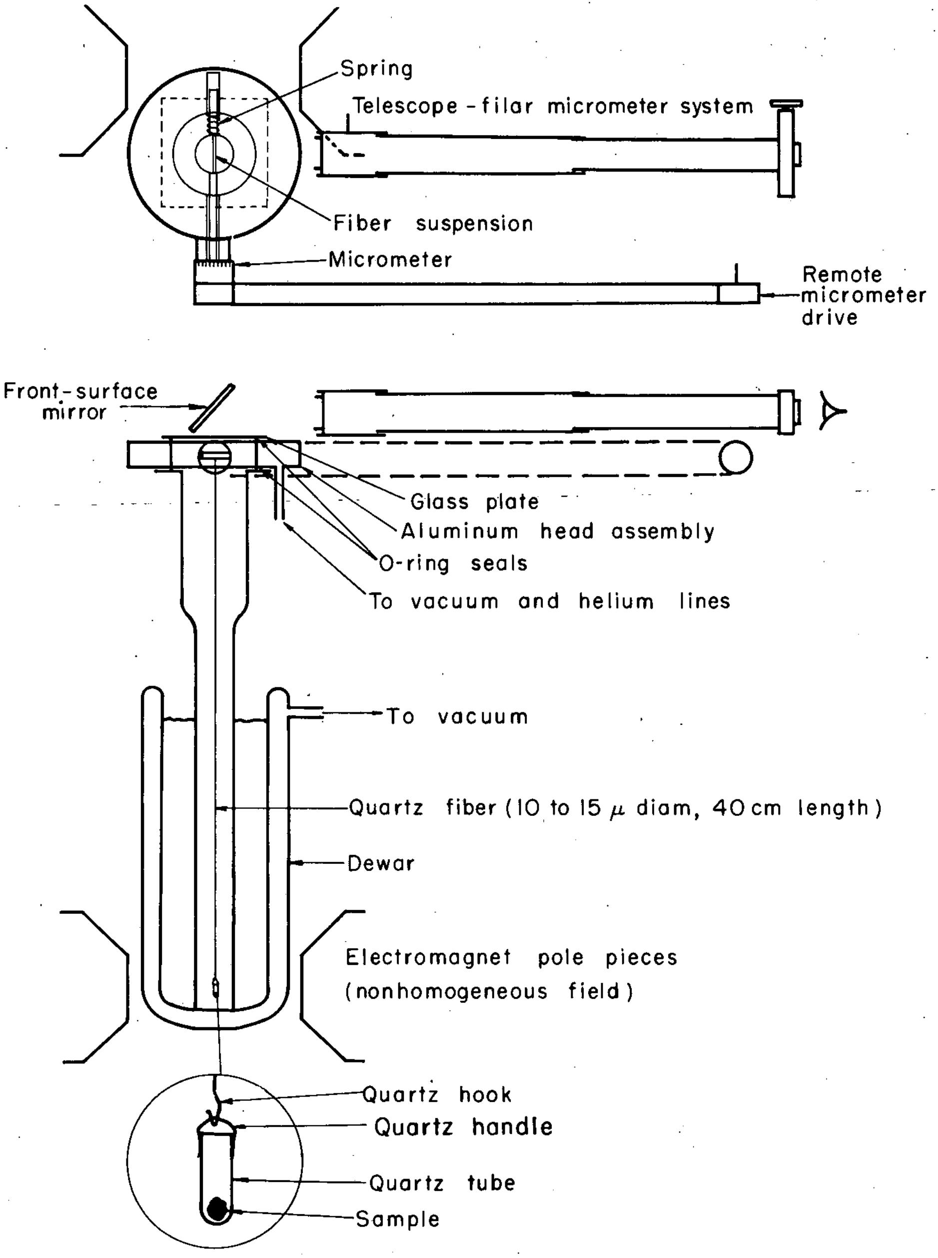

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Fig. 3. Magnetic-susceptibility apparatus.

A cross-sectional sample of the diffusion path was taken from the glass portion of the diffusion couple and crushed into small pieces in a glazed porcelain mortar previously cleaned with concentrated HCl. An attempt was made to obtain a random sampling of the total diffusion path. A few milligrams of sample was placed in the sample container and was accurately weighed. The deflection of the sample plus container in the magnetic field was measured at several field strengths at both room temperature and liquid-nitrogen temperature.

III. RESULTS AND DISCUSSION

A. Diffusivity Determinations

Before any approach to a solution of the diffusion equation can be made it is necessary to define and establish the boundary conditions and the initial conditions for the diffusional process under consideration. The system is represented by diffusion into a semiinfinite medium with $x > 0$.[5] The simplest approach to the boundary conditions is to assume that a constant concentration is maintained at the interface and that the diffusion coefficient is constant. This leads to the well-known error function or Gaussian solution for which tables are readily available.[6] This constant surface concentration may be considered as the equilibrium concentration for the process and should, therefore, increase with temperature. Table I shows that this is not the case, and indicates that a time as well as a temperature dependence must be considered in the solution.

A reasonable approach to the time - temperature dependence of the interfacial concentration is to assume that the rate of entry of the iron into the diffusion medium is directly proportional to the difference between the actual concentration, C_s, in the surface at any time and the concentration, C_0, which would be in equilibrium with the source of iron after an infinite time. A detailed discussion of the mathematics of this solution along with appropriate tables and master charts is given by Dorn and Gier.[7] This approach should be equally valid either for the surface evaporation of iron into the medium or for the proposed reaction at the interface, $Fe^0 + 2\,Na^+ = Fe^{++} + 2\,Na_{(g)}$, assuming that the diffusion of sodium is not a rate-controlling step. This latter assumption is not unreasonable since Williams[2] reports values of the diffusion coefficient of sodium in sodium disilicate glass between 10^{-5} and 10^{-6} cm^2/sec in the range of temperatures under consideration, which is relatively rapid.

To solve for the diffusion coefficient by using the solution discussed by Dorn and Gier it is necessary to know the actual value of the equilibrium surface concentration, which requires data from time

Table I. Time - temperature - surface concentration of iron in sodium disilicate glass.

Sample No.	Time (sec × 10^{-4})	Temp. (°C)	Interfacial iron concentration in glass (at.%)
A	17.9	905±1	0.159
B	3.78	946±3	0.142
C	3.63	1001±1	0.188
D-1	2.88	1056±1	0.333
D-2	16.6	1051±4	0.368

studies at each temperature. Such time studies are utilized in determining the equilibrium surface concentration by plotting surface concentration vs 1/time, and extrapolating to infinite time. The present data are not sufficient to make the above calculations since there is neither prior knowledge of the equilibrium surface concentration nor adequate information to calculate it. An assumption that the rate of entry of iron into the diffusion medium is relatively rapid can be made, however, which permits a rough calculation of the diffusion coefficients and consequently of the activation energy of the process. If the rate of entry of the iron into the diffusion medium is relatively rapid the solution of the diffusion equation based on surface reaction reduces to the Gaussian solution mentioned earlier, and diffusion coefficients are easily calculated.

As shown in the calculations in Appendix A, a small difference results in converting weight percent to atomic percent, depending on what assumptions are made regarding the reaction at the interface. These differences occur in the denominator of the conversion factor, however, and play no part in the Gaussian type solution since ratios rather than actual concentrations are used in the calculations. Table II shows the diffusion coefficients calculated for each of the samples by using standard error function tables such as given by Darken and Gurry.[8] A typical diffusion profile is shown in Fig. 4.

Diffusivity shows an exponential dependence upon temperature, which can be expressed by

$$D = D_0 \exp(-Q/RT),$$

where

D = the diffusion coefficient,

D_0 = pre-exponential constant valid for a specific temperature range,

Q = the activation energy for the process,

R = the gas constant,

T = the absolute temperature.

Table II. Diffusivity data for iron in sodium disilicate glass.

Sample No.	Time (sec × 10^{-4})	Temp. (°C)	C/C_s	$D \times 10^8$ (cm^2/sec)	Log D	$10^4/T$ (°K^{-1})
A	17.9	905±1	0.7773	4.52	-7.345	8.50
			0.5000	4.59	-7.338	
			0.2031	5.11	-7.292	
B	3.78	946±3	0.7773	8.36	-7.078	8.22
			0.5000	8.33	-7.080	
			0.2031	8.31	-7.080	
C	3.63	1000±1	0.7773	9.92	-7.004	7.85
			0.5000	10.9	-6.962	
			0.2031	11.2	-6.951	
D-1	2.88	1056±1	0.7773	7.02	-7.154	7.54
			0.5000	7.08	-7.150	
			0.2031	6.46	-7.190	
D-2	16.6	1051±4	0.7773	5.33	-7.274	7.55
			0.5000	5.13	-7.290	
			0.2031	4.34	-7.353	

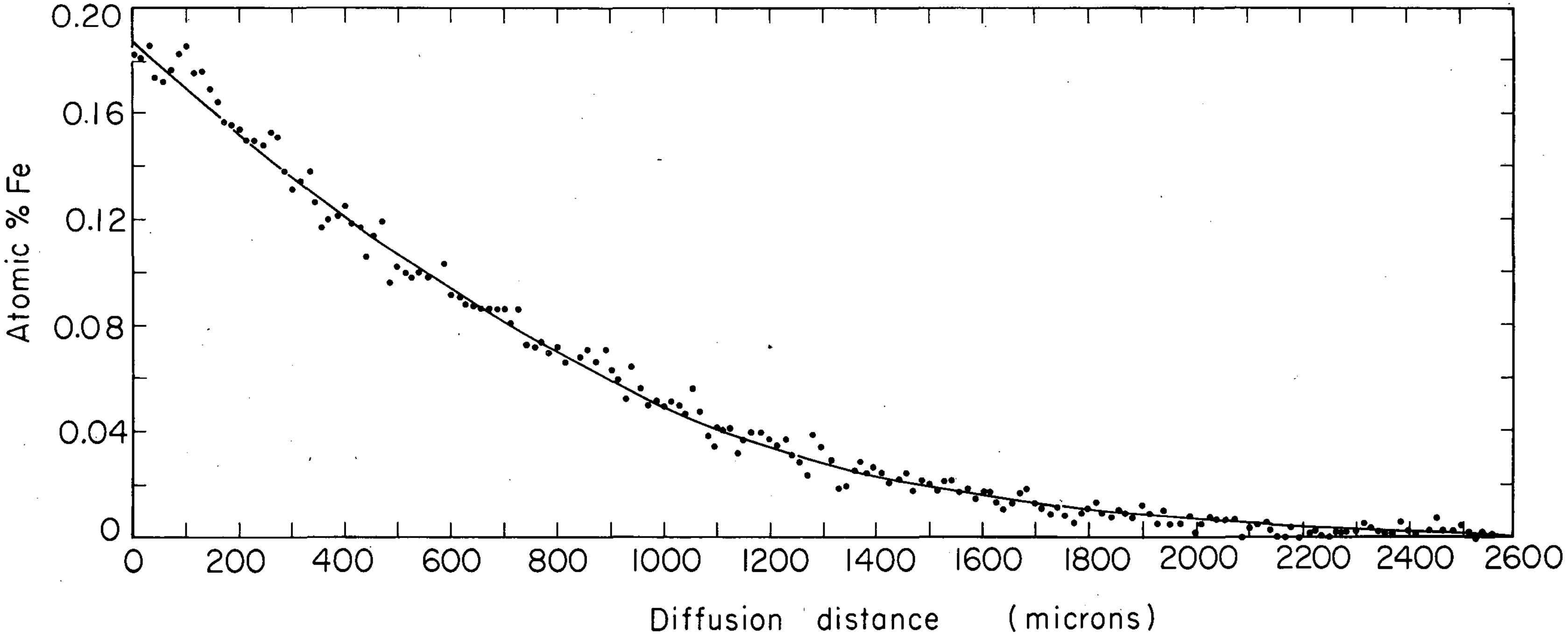

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Fig. 4. Typical diffusion profile for iron in sodium disilicate glass. Sample C: 1000°C, 3.63×10^4 sec.

An Arrhenius plot of ln D vs 1/T should give a straight line with a slope of -Q/R from which the activation energy, Q, can be calculated.

An Arrhenius plot of the data given in Fig. 5 shows the three lowest temperature points falling approximately on a straight line whose slope gives an activation energy of 24.3 kcal. The two 1050°C points, however, deviate markedly from this line, indicating a possible change in mechanism for the process. This is further supported by visual observation of the samples. Between 900 and 1000°C the diffusion zone appears as a neutral gray filter varying in intensity along its length. Above 1000°C there is a distinct change in the physical appearance of the zone. At 1050°C the zone at 8 h shows a cyan blue color in the region of the interface and a neutral gray filter appearance beyond; at 50 h the entire profile possesses a distinct cyan blue color. This indicates a time-dependent transition or reaction occurring above 1000°C. The following transmission spectroscopic data present a more objective analysis of these diffusion zones.

B. Transmission Spectroscopy

The transmission spectrographs of the various diffusion profiles are given in Fig. 6. The various curves have been placed on the coordinates with arbitrary shifts of the ordinate to avoid confusion among the individual curves. As was mentioned earlier, no attempt has been made to place absolute values on the optical density figures; the important consideration is the relative transmission and absorption bands indicated by the graphs.

The blank sodium disilicate glass containing no diffused iron shows a rather uniform transmission throughout the visible region, with a slightly higher transmission in the blue region due to the copper impurity. Sample A (905°C) exhibits a transmission band from about 6600 to 7000 Å, with a general absorption increasing toward the blue and uv region. Samples B (946 °C) and C (1001°C) show patterns similar to that of sample A. Sample D-2 (1051°C) shows transmission predominantly in the blue region, with the maximum transmission at

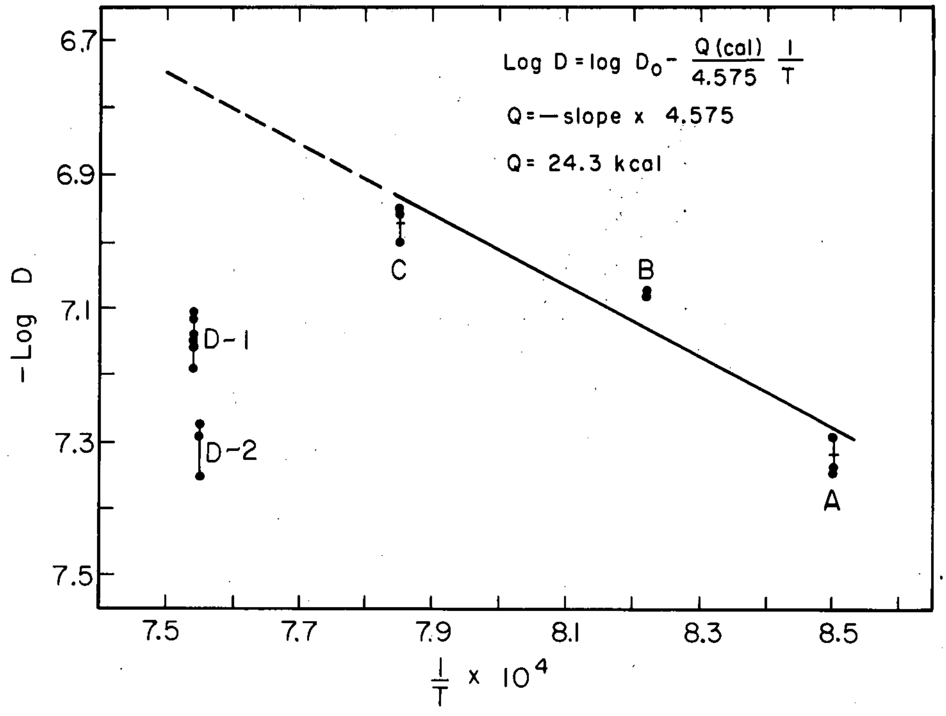

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Fig. 5. Activation-energy plot for diffusion of iron in sodium disilicate glass.

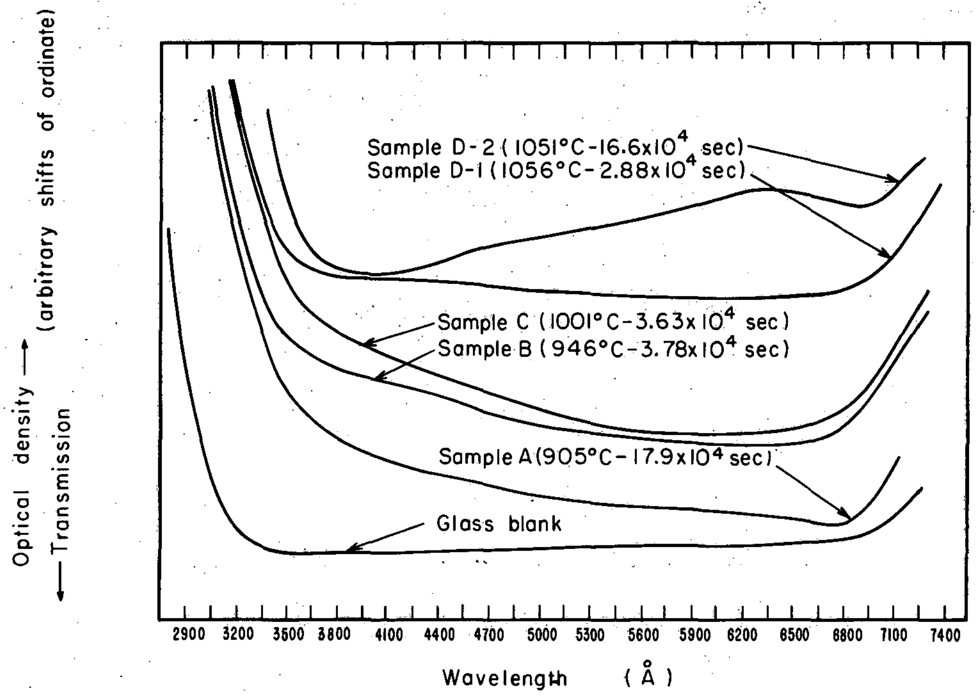

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Fig. 6. Transmission spectrographs of the diffusion zone from iron-sodium disilicate glass diffusion couples.

approximately 4000 Å. Sample D-1 which contains both the "low temperature" and the "high temperature" forms of the diffusing iron exhibits a curve which might well result from an addition of the curves for samples A and D-2.

It has been shown by Moore and Prasad[9] and by others that ferrous iron in sixfold coordination in network-modifying positions in a glass gives rise to a transmission curve very similar to that shown by sample D-2. The curves for the remaining samples show no particular correspondence to any transmission curves for iron in glass reported in the literature. Bishay,[10] however, has attributed an overall loss in transmission in the visible region for high-alkali silicate glasses containing iron to the formation of ferrous iron in fourfold coordination with oxygen in the glass network. There is an indication that no ferric iron exists in the glasses under study since ferric alone in a sixfold coordination gives rise to a yellow coloration or, when in combination with sixfold coordinated ferrous iron, to a green coloration.

C. Thermodynamic Considerations

The oxidation of elemental iron by sodium disilicate glass has been shown empirically by Ravitz and Hagan[11] to occur by the reduction of sodium ions in the glass to sodium vapor. Inspection of the $FeO-SiO_2-Na_2O$ phase diagram indicates that this reaction may possibly be represented by

$$2Fe_{(s)} + 2Na_2Si_2O_{5\,(glass)} = Fe_2SiO_{4(s)} + 3SiO_{2\,(glass)} + 4Na_{(g)}.$$

From the thermodynamic tables[12] compiled by the U. S. Bureau of Mines, the standard free energy for the above reaction was found to be 242 160 cal at room temperature. High-temperature enthalpy and entropy data were utilized in calculating the standard free energies for the reaction at elevated temperatures. Sample calculations of this sort are given in Appendix D. By using the expression $\Delta F_T^0 = - RT \ln a_{Na}^n = - RT \ln P_{Na}^4$ the equilibrium partial pressure of sodium for the reaction was calculated at several temperatures, and is plotted vs temperature in Fig. 7. It is understood that the above reaction is used only as an approximate model for the system. This is particularly apparent when one considers that there is no information regarding the extent to which sodium may be replaced by iron in the glass without the formation of an additional phase, and that there is no information regarding the activity of either iron or sodium in these intermediate glass compositions.

Figure 7 shows a rapid increase in the equilibrium partial pressure of sodium vapor above 1000°C leading to more easily attained conditions for reaction above this temperature. It is conceivable at this point to imagine that the kinetics of the oxidation-reduction reaction prevent it from occurring to any appreciable degree below 1000°C, and allow it to occur only under proper conditions of time at 1050°C. If this is the case, it must follow that the iron present in the glass at or below 1000°C must be prodominantly either elemental iron or iron with a valence of plus one.

D. Magnetic Susceptibility

Magnetic-susceptibility measurements were made only on samples A and D-2, which represent the low temperature and the high temperature diffusing species of iron, respectively. The gram susceptibility and the molar susceptibility values for these samples are given in Table III along with the effective electron spin moment calculated from the average value of the molar susceptibility by the standard relation

$$\mu_{eff} = 2.84 \, (\chi_{molar} \cdot T)^{1/2} .$$

Repeated measurements on the same sample show a reproducibility of ±2% in the values. The value of the gram susceptibility of sodium disilicate glass that was used in the calculations as shown in Appendix C was that reported by Bamford.[13] The error of greatest possible magnitude in the calculations of the magnetic susceptibility arises from the estimation of the mass of iron in the glass sample.

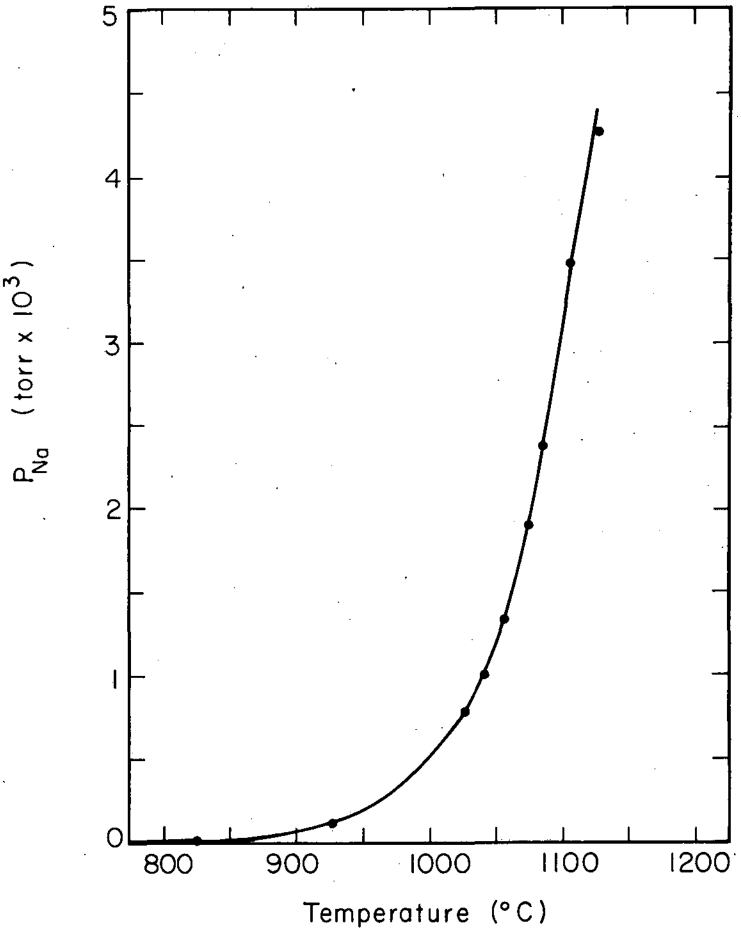

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Fig. 7. Equilibrium partial pressure of sodium gas vs temperature for the reaction

$$2Fe_{(s)} + 2\ Na_2Si_2O_{5(glass)} = Fe_2SiO_{4(s)} + 3\ SiO_{2(glass)} + 4\ Na_{(g)}.$$

Table III. Magnetic-susceptibility data.

Sample	Magnet current (A)	Gram susceptibility[a] χ_g (cgs units) $\times 10^6$		Molar susceptibility[a] χ_m (cgs units) $\times 10^6$		μ_{eff}	μ_{eff}
		25°C	-196°C	25°C	-196°C	25°C	-196° C
A	1.00	460.0	649.0	25 750	36 350	7.90	4.74
	1.25	472.0	654.0	26 400	36 600		
	1.50	476.0	639.0	26 620	35 800		
	1.75	462.0	637.0	25 820	35 700		
	2.00	457.0	647.0	25 580	36 200		
D-2	1.00	240.2	538.0	13 450	30 200	5.76	4.46
	1.25	242.8	540.0	13 600	30 220		
	1.50	248.6	552.0	13 920	30 900		
	1.75	248.7	544.0	13 940	30 450		
	2.00	251.4	557.0	14 080	31 300		

[a] Of iron in sodium disilicate glass.

A random sampling of the diffusion path was assumed and the average weight percentage of iron in the diffusion zone was used in the calculations. The reciprocal of the mass of iron is a common multiplier in the calculations, and it can be seen that an error in sampling could result in an equivalent but inverse error in the value of the magnetic susceptibility. The author feels that an upper limit of ±10% can be set on the magnitude of this error.

It is to be noted from Table III that the paramagnetic properties of iron are in evidence both in the positive values of the susceptibility and in its temperature dependence; however, ferromagnetic properties as would be shown by a field-dependent susceptibility are absent. This latter evidence does not, however, eliminate the possibility of atomically dispersed elemental iron in the glass since there is speculation that even dispersed colloidal particles of iron tend to lose their ferromagnetic properties. This is due to the fact that the particles have become too small to appreciably interact with one another.

The theoretical value for the effective electron spin moment of ferrous iron with all orbitals quenched is 4.90 Bohr magnetons. This is calculated from the relation $\mu_{eff} = [n(n+2)]^{1/2}$, where n is the number of unpaired electrons. Figgis and Lewis[14] point out that the experimental values range between 5.1 and 5.7 because of incomplete quenching of the orbitals. The experimentally determined values for sample D-2 compare favorably with these observations. In addition, Table IV gives the room temperature gram magnetic-susceptibility values for various states of iron in glass as reported by Moore and Kumar;[15] it can be seen that the values for sample D-2 are in agreement with those of ferrous iron in glass.

The outer-shell ground-state electronic configuration of elemental iron can be expressed as $3d^6 4s^2$, which leaves four unpaired electrons in the d orbitals. This is the same number as for ferrous iron and, therefore, the resulting theoretical effective electron spin moment in Bohr magnetons is the same, 4.90. If, however, one considers that the particles are small and are free of any effects from the

Table IV. Gram susceptibility of various forms of iron in glass according to Moore and Kumar.[a]

Species		χ_g (cgs units) × 10^6
Ferrous iron		220
Coloring ferric iron		> 300
	probably	> 350
Ferroso-ferric iron	probably	> 350
Colorless ferric iron		< 210
	probably	< 200

[a] Reference 15.

surrounding field, the theoretical value becomes 6.69. This value is obtained from the expression

$$\mu_{eff} = g\,[J(J+1)]^{1/2},$$

where

$$g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2\,J(J+1)}.$$

The values of J, L, and S are the same for both ferrous and elemental iron; therefore, one obtains the same value, $\mu_{eff} = 6.69$, as for elemental iron if the restriction of field-free conditions are placed upon ferrous iron.

Table III shows that the empirical room temperature μ_{eff} for sample A is within 10% of the theoretical value for elemental iron (or ferrous iron) in a field-free condition. The empirical μ_{eff} at -196°C for sample A has a value close to that of elemental iron (or ferrous iron) with all the orbitals quenched. This temperature dependence of μ_{eff} can be explained by a greater interaction between the iron atoms and the surrounding field at the lower temperatures, which results in a more effective quenching of the orbitals.

If elemental iron exists atomically dispersed in glass, one might expect that it would exhibit less interaction with the surrounding field than ferrous iron. This is due to two factors: (a) elemental iron would bear no charge, and (b) the larger atomic radius of the elemental atom would increase its nearest-neighbor distance as compared with that for ferrous iron. For this reason, the author associates the higher room-temperature value for μ_{eff} with iron in the elemental state.

The magnetic-susceptibility measurements for sample A eliminate the possibility of ferrous iron in a tetrahedral site as the low-temperature diffusing species of iron. Bishay[10] has proposed that fourfold coordinated iron bonds covalently in the d-shells resulting in an effective spin moment of zero, which is far from the value observed here.

IV. SUMMARY AND CONCLUSIONS

Diffusivity and activation-energy calculations have shown that a change in the mechanism of diffusion of iron from an elemental iron substrate into sodium disilicate glass occurs between 1000 and 1050°C. This change in mechanism could result from either a change in the position in the glass structure occupied by the diffusing species or by a change in the valence of the diffusing species.

Both spectroscopic and magnetic-susceptibility measurements have established that sixfold coordinated ferrous iron becomes the predominant, if not the only, diffusing species at 1050°C if sufficient time is allowed for the transition from the low-temperature to the high-temperature form. The remaining question is the nature of the low-temperature species. Thermodynamic—along with kinetic—considerations indicate that the low-temperature species could easily be a lower valence of iron, very possibly iron in the elemental state.

Magnetic-susceptibility measurements on the low-temperature sample support the observation that the iron exists either in a different coordination or in a different valence state from that in the high-temperature sample. Bishay's observations regarding iron in a fourfold coordination eliminate a change in coordination as a possible explanation for the anomaly in the temperature dependence of the diffusivity. Furthermore, the magnetic-susceptibility measurements tend to support the case for elemental iron at the lower temperatures.

The present experimental data permit the following general statements to be made:

(a) A change in the mechanism of the diffusion process occurs between 1000 and 1050°C.

(b) The change in the diffusion mechanism is very likely the result of a change in the valence of the diffusing iron from zero to plus two.

In order to reach more definite conclusions the following steps are suggested for future consideration:

(a) Time studies at various temperatures covering the ranges for both the high-temperature and the low-temperature species to establish the equilibrium concentration in order to improve the diffusion and activation-energy calculations.

(b) Allow samples from the various temperatures to homogenize under the conditions of the diffusion experiments, and use these samples for magnetic-susceptibility measurements.

(c) By using an homogenized low-temperature sample, attempt to establish the valence of the diffusing iron by wet analysis.

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APPENDICES

A. Calculations from Electron-Probe Data

1. Conversion of Chart Reading to Weight Percent

Let

A = chart reading for FeK_{α} radiation from diffusion profile at sensitivity a,

A_b = background chart reading from profile,

B = chart reading for FeK_{α} radiation from olivine standard at sensitivity b,

B_b = background chart reading from olivine standard,

C = weight percent Fe in olivine standard,

D = sensitivity correction,

X = weight percent Fe in sample.

Then

$$X = \frac{A - A_b}{B - B_b} \cdot D \cdot C \ .$$

The following usual corrections are, for this system and probe conditions, negligible:

(a) Counter dead time,

(b) Atomic number,

(c) Absorption.

2. Conversion of Weight Percent to Atomic Percent

Weight content of each of the constituents in 100 g:

$Na_2O \cdot 2\,SiO_2$ Glass

Na = 25.3

O = 43.9

Si = 30.8

100.0

a. Conversion based on solution of atomic iron (i.e., no counter diffusion of sodium).

Let

X = grams Fe in 100 grams material = weight percent Fe,

M_{gl} = molecular weight of $Na_2O \cdot 2\,SiO_2$ glass,

M_{Fe} = molecular weight of Fe,

Y = mole percent Fe.

Then

$$Y = \frac{X/M_{Fe}}{[(100 - X)/M_{gl}] + [X/M_{Fe}]} \cdot 100$$

$$= \frac{100X}{30.8 + 0.69X} .$$

b. Conversion based on counter diffusion of sodium (two sodium atoms for each iron atom)

Let

X = grams Fe replacing Na from 100 grams $Na_2O \cdot 2\,SiO_2$ glass $\approx$ weight percent Fe,

$Z = \left(\frac{25.3}{23} - \frac{2X}{56}\right)(23)$ = grams Na in glass after interchange with X grams Fe,

Y = atomic percent Fe.

Then

$$Y = \frac{(X/56) \text{ moles Fe} \cdot 100}{\frac{30.8}{28} \text{ moles Si} + \frac{44}{16} \text{ moles O} + \frac{X}{56} \text{ moles Fe} + Z \text{ moles Na}}$$

$$= \frac{100X}{276.5 - X} .$$

B. Diffusion Equations:[16] Diffusion into Semiinfinite Media with Constant Diffusion Coefficient

1. Condition of Constant Surface Concentration

a. Initial conditions: $t = 0$,

$C = 0$ at $x > 0$.

b. Boundary conditions: $t > 0$,

$C = C_0$ at $x = 0$.

c. Diffusion equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} .$$

d. Solution given by:

$$C = C_0 \operatorname{erfc} \frac{x}{2(Dt)^{1/2}} .$$

where the error function complement,

$$\operatorname{erfc} Z = 1 - \operatorname{erf} Z = 1 - \frac{2}{\pi^{1/2}} \int_0^Z e^{-\eta^2} d\eta .$$

The error function has the properties that $\operatorname{erf}(-Z) = -\operatorname{erf}Z$, $\operatorname{erf}(0) = 0$, $\operatorname{erf}(\infty) = 1$.
Extensive tables of the error function are available.[6]

2. Condition of Surface Evaporation

a. Boundary conditions: at $x = 0$,

$$-D\frac{\partial c}{\partial c} = \alpha(C_0 - C_s) ,$$

where

D = diffusion coefficient,
α = constant of proportionality,
C_0 = equilibrium surface concentration,
C_s = actual surface concentration.

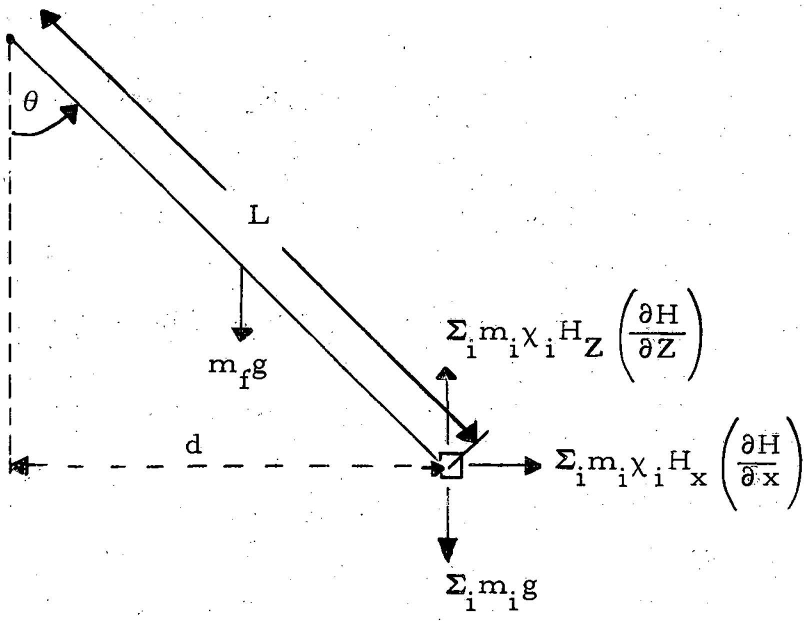
b. Solution of the diffusion equation

$$\frac{C}{C_0} = \operatorname{erfc} \frac{x}{2(Dt)^{1/2}} - \exp(hx + h^2Dt) \operatorname{erfc}\left[\frac{x}{2(Dt)^{1/2}} + h(Dt)^{1/2}\right] .$$

For master charts and tables of the solution see Dorn and Gier.[7]

C. Magnetic Susceptibility: Equations

1. Gram Susceptibility of a Given Sample



where

χ = gram susceptibility,
m = mass,
g = gravitational constant,
d = deflection,
H = magnetic field,
L = length of fiber,
θ = angle of deflection,

subscripts t = sample tube,
s = sample,
f = fiber.

The gram susceptibility is calculated from the balance of forces as follows:

$$[m_t + m_s + m_f/2]\,gd = [m_t\chi_t + m_s\chi_s]\,H\,\frac{\partial H}{\partial X}\,L\cos\theta, \tag{C-1}$$

where

$\cos\theta \approx 1.$

Upon simplification,

$$m_t\chi_t + m_s\chi_s = \frac{g}{H\frac{\partial H}{\partial x}L}\,[m_t + m_s + (m_f/2)]\,d, \tag{C-2}$$

and finally,

$$\chi_s = K[m_t + m_s + (m_f/2)]\frac{d}{m_s} - \frac{m_t\chi_t}{m_s}, \tag{C-3}$$

where K = apparatus constant (varies with field strength).

2. Gram Susceptibility of Iron in Glass

Subscripts gl = glass,
Fe = iron.

By substituting $m_s\chi_s = m_{gl}\chi_{gl} + m_{Fe}\chi_{Fe}$ in (C-2) one obtains

$$m_t\chi_t + m_{gl}\chi_{gl} + m_{Fe}\chi_{Fe} = K[m_t + m_s + (m_f/2)]\,d,$$

and therefore

$$\chi_{Fe} = \frac{1}{m_{Fe}}\left[Kd(m_t + m_s + m_f/2) - (m_t\chi_t + m_{gl}\chi_{gl})\right],$$

where m_{Fe} = (wt. % Fe) (m_s) .

D. Thermodynamic Calculations

1. Represent the proposed reaction

$$Fe^{0} + 2\ Na^{+}_{(in\ glass)} = Fe^{++}_{(in\ glass)} + 2\ Na^{0}_{(gas)} \qquad (1)$$

by the reaction

$$2\ Fe_{(s)} + Na_2Si_2O_{5\,(glass)} = Fe_2S_iO_{4\,(s)} + 3\ S_iO_{2\,(glass)} + 4\ Na_{(gas)}, \qquad (2)$$

where for reaction (2),

ΔS_{298} = 114.0 eu,

ΔH_{298} = 276 150 cal,

ΔF^{0}_{298} = 242 160 cal.

The ΔS_{298}, ΔH_{298}, and ΔF^{0}_{298} values for reaction (2) are obtained from the values[12] listed in Table D-I.

Table D-I. Thermodynamic functions for reaction (2).

	S_{298}(eu)	ΔH^{0}_{f298}(cal)
$Fe_{(s)}$	6.49	0
$Na_2Si_2O_{5\,(glass)}$	44.1	-581 450
$Fe_2S_iO_{4\,(s)}$	34.7	-346 000
$SiO_{2\,(glass)}$	11.2	-214 850
$Na_{(gas)}$	36.72	25 950

2. To determine the ΔF^0_T for reaction (2) at a higher temperature, T, one uses the formula:

$$\Delta F^0_T = \Delta H_{298} + \Delta(H_T - H_{298}) - T[\Delta S_{298} + \Delta(S_T - S_{298})] , \qquad (3)$$

where the values $(H_T - H_{298})$ and $(S_T - S_{298})$ have been tabulated[9] for the products and the reactants.

3. The equilibrium partial pressure of sodium, P_{Na}, for reaction (2) may then be calculated for any temperature T by means of the equation

$$\Delta F^0_T = - RT \ln P^4_{Na} . \qquad (4)$$

Values of P_{Na} are given in Table D-II.

Table D-II. ΔF^0_T and P_{Na} for reaction (2).

T(°K)	t(°C)	ΔF^0_T(cal)	P_{Na}(atm)	P_{Na}(torr)
1000	727	168 800	6.03×10^{-10}	4.58×10^{-7}
1100	827	159 800	1.15×10^{-8}	8.75×10^{-6}
1200	927	151 100	1.38×10^{-7}	1.05×10^{-4}
1300	1027	142 700	1.05×10^{-6}	7.98×10^{-4}
1400	1127	134 400	5.63×10^{-6}	4.27×10^{-3}
1500	1227	129 100	1.95×10^{-5}	1.48×10^{-2}

Values of P_{Na} for additional temperatures in the range 1000 to 1500°K can be calculated with the aid of Fig. D-1.

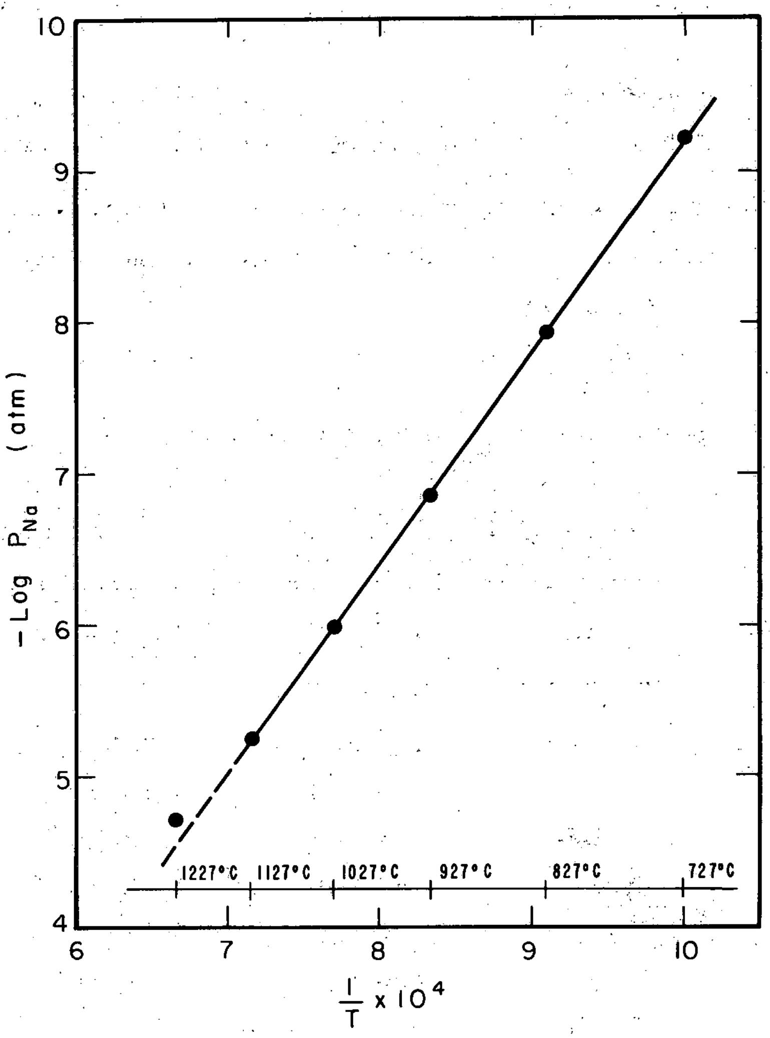


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Fig. D-1. Plot of -log P_{Na} vs 1/T for reaction (2).

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