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PHYSICAL CHEMISTRY OF GLASS-METAL INTERFACES[*][†]

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SUMMARY

The phase equilibria of glass-metal heterogeneous systems are discussed; thermodynamic equilibrium is established in the presence of oxygen when the molten silicate becomes saturated with the low valence oxide of the metal. When the glass contains transition metal oxides whose metals have a lower oxidation potential than the base metal and form alloys with the base metal, reactions occur that result in adjustments of the compositions of the alloy and glass at the interface in a drive to achieve and maintain equilibrium. Presence of multivalent cations in the glass also assists in this drive by providing a transport mechanism for atmospheric oxidation of the base metal. If glass and metal are not at equilibrium and oxygen is not readily available, reactions of a redox type occur. Maintenance of equilibrium compositions at the interface while the whole system moves toward thermodynamic equilibrium is dependent upon the kinetics of the various reactions.

It is theorized that when thermodynamic equilibrium is present in heterogeneous systems, chemical bonding can occur between the phases providing there are no complications of a physical nature. This condition then corresponds to an equal attraction between the atoms at the

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interface leading to a balance of bond energies and a continuity of the electronic structure. This hypothesis is applied to glass-metal systems. Furthermore, with the development of a chemical bond the surface energy of the metal is lowered by an amount approximately equivalent to the surface energy of the molten glass; this condition corresponds to a zero contact angle in a sessile drop experiment.

I. INTRODUCTION

The nature of glass-metal interfaces is all-important in all types of macrocomposites using these dissimilar materials. Good bonding is necessary for such composites as glass-to-metal seals, porcelain enamels, and protective coatings; no bonding, on the other hand, is desired in the shaping of glass articles in metal molds. Although adherence can be achieved physically by such means as roughening of the metal surface, the best and strongest seals are associated with the existence of chemical bonding across the interface zone. Recent studies[1] indicate that an understanding of the conditions under which chemical bonding occurs at interfaces is associated with an understanding of the thermodynamics of glass-metal heterogeneous systems. If two phases forming an interface are not at equilibrium, then a driving force exists for the occurrence of the appropriate reactions to attain equilibrium. With the occurrence of such reactions at the interface, chemical potential gradients result in the bulk of the phases and their homogenization proceeds by diffusion processes. These processes continue until the entire system is at thermodynamic equilibrium; in the meantime, the kinetics and thermodynamics of all the individual processes determine the success of attaining and maintaining equilibrium compositions at the interface.

These studies have also resulted in the development of a theory that under equilibrium conditions at the interface a balance of bond energies exists allowing the formation of a continuous electronic structure, i.e., a chemical bond, across the interface. Under these conditions the interfacial energy between the two phases is at a minimum. Wetting, or sessile drop, experiments that provide information on the interfacial energy changes are thus important.

This paper will explore in detail the principal subject areas mentioned. The discussion will be based primarily on interpretations and generalizations of experiments performed in the authors' laboratories. Only the chemical factors will be of concern; the physical factors that play a role in matching dissimilar phases and that must be considered in the making of successful composites will not be discussed.

II. THERMODYNAMICS OF GLASS-METAL SYSTEMS

In the development of the general principles related to chemical bonding at interfaces of glass-metal heterogeneous systems, the sodium disilicate ($Na_2Si_2O_5$) and iron (Fe) system will be used as an example. Since enameling processes are performed in air, some oxidation of iron occurs; therefore, iron oxide will also be included in the discussion of this system.

A. Glass with No Multivalent Cations

1. In Contact with Metal Oxide

If a molten glass placed in contact with a metal oxide is not saturated with the oxide, then a driving force for solution of the oxide by the glass exists. If the diffusion rates of the components of the substrate oxide in the glass are slower than the rate of solution of the substrate oxide, the glass at the interface immediately becomes saturated and a concentration gradient into the bulk glass forms from the interface. Solution of the oxide is, therefore, dependent upon these diffusion rates and it will continue until the entire glass phase is saturated with the oxide, assuming that an excess of oxide is present. At this point the saturated glass will be in equilibrium with the oxide.

As an example, Fig. 1 shows the published equilibrium phase diagram for Na_2O-SiO_2-FeO.* It also shows an isothermal section at 1000° C. A join between FeO and $Na_2Si_2O_5$ indicates that about 40% FeO can be dissolved in the liquid phase at this temperature.[2]

The driving force for solution of the oxide is basically due to a reduction of the internal energy of the glass. The internal energy is related to the degree of screening of the cations, the dominant cation being Si^{+4} because of its high charge. The screening of a cation is determined by the number of coordinating anions and the nature of the secondary neighbors. In the case of Si^{+4}, there are four coordinating oxygen anions; each of these oxygen anions, in turn, is coordinated with either another Si^{+4} or the necessary number of Na^+ or Fe^{2+} cations to provide an electrovalent balance for the oxygen which will be determined by the glass structure. It has been shown that the Si-O bond length is not constant in a number of silicates but that it is dependent on the second cation neighbor, being shorter and stronger when the other cations coordinating the oxygen are of lower valence.[3] The schematic Si-O-Si configuration, therefore, is at a higher energy state than Si-O-Na or Si-O-Fe; or, in effect, a structure with bridging oxygens is at a higher energy state than one with nonbridging oxygens. The nonbridging oxygens can be increased by increasing the O/Si ratio of the glass which can be accomplished by solution of an oxide, in this case FeO. Solution continues at a given temperature until the glass is saturated with the oxide at which point equilibrium exists, and a balance of bond energies and an electronic structure also exist across the interface.

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*The formula FeO is used throughout the text for convenience; in actuality the compound is nonstoichiometric with the formula Fe_xO where x is 0.875 - 0.946 at 1000° C.

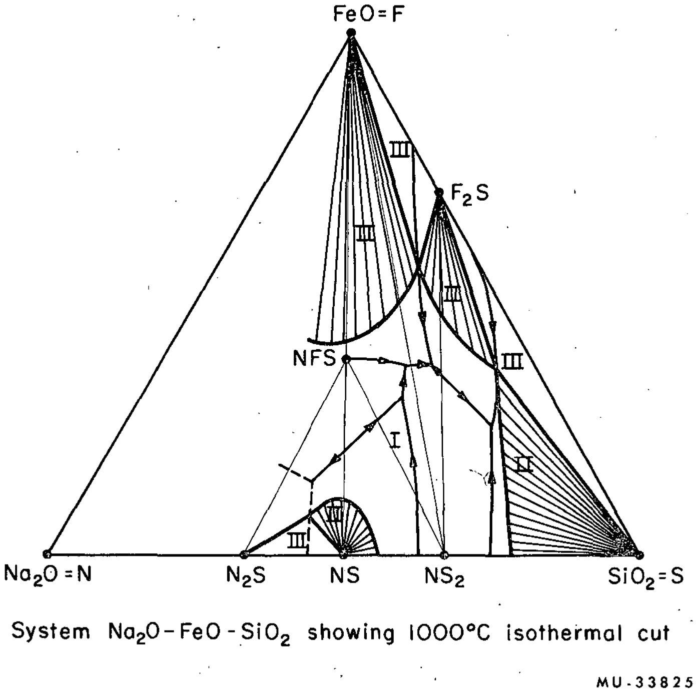

Fig. 1. Na_2O-SiO_2-FeO phase diagram showing 1000°C isothermal cut.

2. In Contact with Oxidized Metal

If a molten glass is placed in contact with a metal surface that has been oxidized, the glass will dissolve the oxide as described in the previous section. A similar type of solution-diffusion zone is the result. The diffusion into the glass is the controlling step. Prior to complete solution of the oxide, a cross section through the composite would reveal the following transition in phases: metal-metal oxide-glass saturated with metal oxide grading in composition away from the substrate interface to the composition of the original metal oxide-free glass. Although equilibrium compositions exist at the interfaces, the entire system remains in a state of nonequilibrium as long as any of the phases possess a concentration gradient.

Such a situation continues until the oxide is completely dissolved, if the amount present is not sufficient to saturate the bulk glass. With continuation of the diffusion processes, the glass at the interface becomes unsaturated. This loss of equilibrium results in a driving force for reactions that would tend to restore equilibrium compositions at the interface.

These situations can be best illustrated by the use of the diagram in Fig. 2 which shows schematically the change in the activity of iron across the cross section at various time intervals. The curve at t_o represents the activities just at the time of contact when a discontinuity exists at the glass-oxide interface. The curve t_1, a short time later, shows that the activities of iron in the oxide and in the glass phase at the glass-oxide interface are equivalent which is the requirement for saturation of the glass and equilibrium. As solution of the oxide continues, the length of the diffusion path increases but the activity of

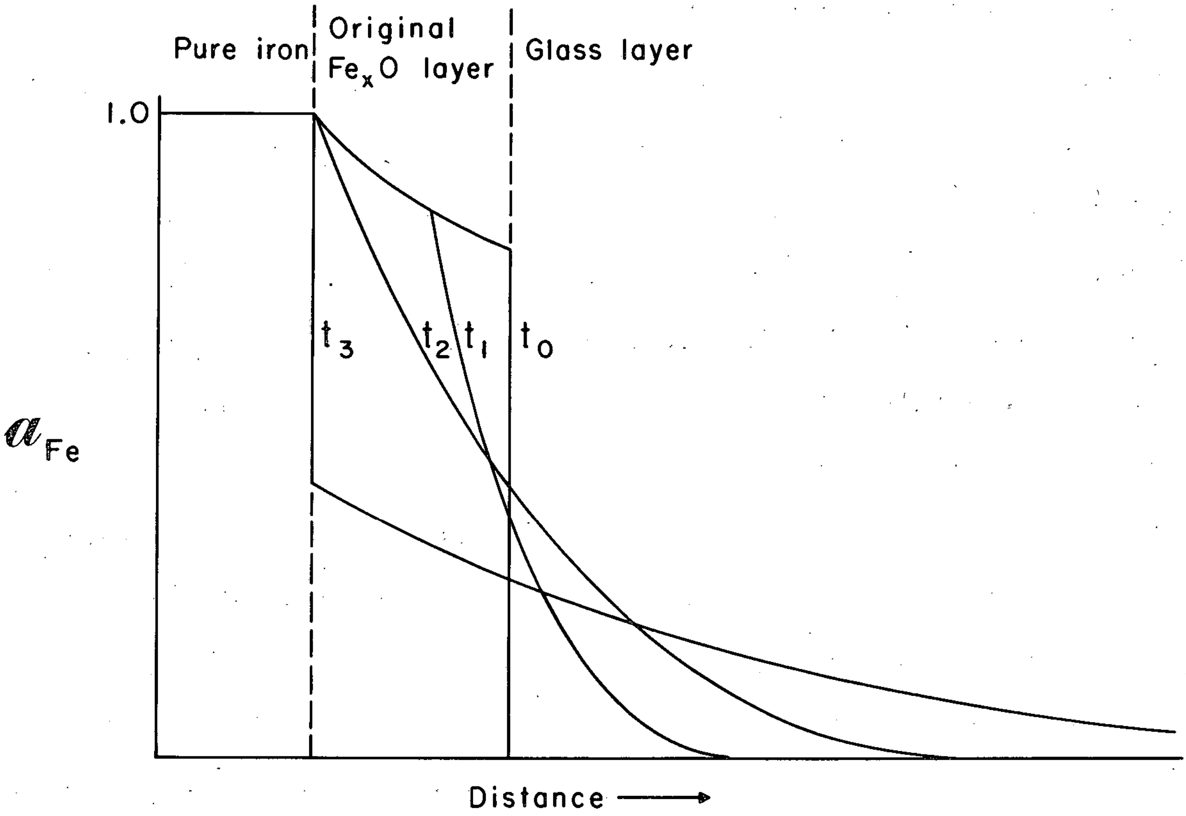

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Fig. 2. Hypothetical iron activity vs penetration distance diagram for oxidized iron-glass contact zone showing ferrous iron activity in the oxide and the glass relative to metallic iron as the standard state.

the iron in the two phases remains equal at the interface. This situation continues until the last trace of discrete oxide is dissolved, represented by t_2 in the figure; at this point the activities of iron in the metal and glass are equal, and these two phases are then in equilibrium. (An isothermal component tetrahedron of Na-Fe-Si-O would be necessary to show the complete relationships of the different phases.) The curve t_3 represents the situation when the iron oxide concentration in the glass at the interface has dropped because of diffusion rates that are faster than the oxidation reactions for the iron, as described in the next section.

3. In Contact with Unoxidized Metal

If a metal oxide-unsaturated glass is placed in contact with an unoxidized metal surface, a similar situation exists as that occurring at time t_3 in the previous section. A driving force for a reaction then exists in an effort to attain equilibrium. In the iron-glass system two types of reactions are possible. In the presence of oxygen, iron may be oxidized and enter the glass structure as iron oxide. With unavailability of oxygen a redox reaction may occur with some component in the glass which, in the model system under discussion, is sodium.

$$Fe^o = Fe^{2+} + 2e^- \qquad (1)$$

$$1/2\ O_2 + 2e^- = O^= \qquad (2)$$

$$Fe^o + 2Na^+(\text{glass}) = 2Na^o(g) + Fe^{2+}(\text{glass})\ . \qquad (3)$$

Equations (1) and (2) are the half cell reactions associated with the atmospheric oxidation of the iron substrate. Since oxygen has to enter the system at the surface of the glass and iron is only available at the interface, some transport process through the glass either for electrons or atoms is necessary. According to our present understanding, no electron conduction mechanism is present in sodium disilicate glass and the diffusion of oxygen or iron through the glass is extremely slow. Atmospheric oxidation is thus not expected to be prominent.

Equation (3) has been experimentally observed by Hagan and Ravitz[4] in mixtures of powdered iron and powdered sodium disilicate glass in the temperature range 900 to 1000°C under vacuum conditions. The reaction proceeds only through the maintenance of a low partial pressure of sodium gas. In contrast to the reaction of Eqs. (1) plus (2), Eq. (3) proceeds with no change in the O/Si ratio since only sodium and iron are involved as long as no reaction phases are precipitated. Reference to Fig. 1 indicates that SiO_2 will first precipitate as a result of this reaction; the final phases which would be in thermodynamic equilibrium with Fe are not certain because of lack of information on phase equilibria with elemental iron. Borom,[5] however, has shown that Eq. (3) does not take place at the interface. Studies of diffusion couples of bulk iron and sodium disilicate glass annealed in the above temperature range in a flowing argon atmosphere indicated that the iron evidently enters the glass as atoms with some coalescence into colloidal particles also occurring. Richardson[6] observed a similar phenomenon on heating CaO-SiO_2-Al_2O_3 melts in contact with copper where a dispersion of microscopic particles of metallic copper formed as a rosy fog. Reaction (3) thus occurs primarily within the glass rather than at the interface. The transfer of elemental iron into the glass is a slow step which results in an interfacial iron concentration that increases with time. As the concentration of elemental iron increases, reaction (3) begins to proceed to the right. The ferrous ions that are produced diffuse into the bulk glass faster than the elemental iron with the result that the maximum interfacial iron concentration obtained in the experiments was less than 1.5 wt %.[5] This does not represent an equilibrium condition at the interface; consequently no adherence was observed with the base metal. It should be noted that Eq. (3) would not be operative if the metal-glass interface is saturated with FeO.

B. Glass with Multivalent Cations

It has been found by practice that porcelain enamel adherence is improved by the addition of a small percentage of certain multivalent cations, such as Co, Mn, Ni, and Cu. These cations normally are present in the low valence form and are of the network modifier type. The glasses that will be used for illustrative purposes in this analysis are $Na_2Si_2O_5$ with about 4% of CoO and a complex low-melting enamel glass of composition shown in Table I.

1. In Contact with Metal Oxide

The nature of the solution process of a metal oxide is similar to that described in Section II-A-1 for a glass without multivalent cations. Table II shows that the solubility of FeO in enamel glasses with and without multivalent cations is essentially the same when the glasses are placed in contact with FeO (concentration in table expressed in terms of elemental iron). An iron concentration gradient is set up in the glass as a result of the solution of the oxide which subsequently establishes a counter diffusion profile for the cobalt and other cations in the glass. Establishment of equilibrium at the interface may also involve some diffusion of the multivalent cations into FeO until the activities for the respective elements would be equal in the two phases.

Table I. Frit glass compositions

	Glass A wt %	Glass B wt %
SiO_2	38.2	36.8
B_2O_3	19.0	18.2
Al_2O_3	3.7	3.5
Na_2O	18.2	17.4
K_2O	2.0	1.9
CaO	10.3	9.9
BaO	4.7	4.5
F_2	2.9	2.8
P_2O_5	1.0	1.0
CoO	-	0.7
NiO	-	1.3
MnO	-	1.7
CuO	-	0.3

Table II. Tabulation of experimental conditions.

Expt. No. type glass		Approx thick. of preoxidized layer on iron (microns)	Temp (°C)	Time (hr-min)	Crucible material	Atmos.	Net wt gain (mg)	Conc. Fe at interface (wt %)
I -	A	150	870	24 - 0	Pt	air	36	19.1
	B	110	"	"	"	"	41	*
II -	A	3	900	27 - 30	"	"	60	13.8
	B	3	"	28 - 0	"	"	85	19.8
V -	A	110	980	8 - 0	Al_2O_3	"	2	*
	B	110	"	"	"	"	80	*
FeO -	A	∞	900	0 - 30	Al_2O_3	argon	-	25.8
	B	∞	"	"	"	"	-	24.5

*not determined.

Note: glass B = glass A + adherence oxides.

2. In Contact with Oxidized Metal

If oxidized metal is used, the conditions for the first stages of solution while the oxide is still present are similar to those described in Section II-A-2. Equilibrium compositions are maintained at the oxide-glass interface as long as any oxide remains, and also the saturated glass at the interface is in equilibrium with the metal at the instant the last trace of oxide is dissolved. At this point, however, an imbalance in equilibrium occurs as the iron continues to diffuse into the bulk glass, and a driving force for oxidation with atmospheric oxygen and re-establishment of equilibrium develops.

Reactions (1), (2), and (3) are again potentially operative. The previously described difficulties in regard to reaction (3) still exist in this case, but those in regard to reactions (1) and (2) are not the same. The glass containing cations capable of attaining several oxidation states possesses a mechanism for transport of electrons as indicated by the data for weight gains for several glasses listed in Table II (experiment V; experiments I and II indicate that the Pt crucible provides a conduction path[7]).

An additional reaction with the formation of an alloy, however, becomes possible as the Co ions reach the interface as represented by Eq. (6) which is a summation of the step reactions indicated by Eqs. (4) and (5).

$$xFe + xCo^{+2} \rightleftharpoons xFe^{+2} + xCo \qquad (4)$$

$$(1 - x)Fe + xCo \rightarrow Fe_{(1 - x)}Co_x \qquad (5)$$

$$Fe + xCo^{+2} \rightleftharpoons xFe^{+2} + Fe_{(1 - x)}Co_x \qquad (6)$$

Written in terms of a general alloy equilibrium with the metal ions in the glass, Eq. (6) becomes:

$$Fe_{(1-p)}Co_p + xCo^{+2} \rightleftharpoons xFe^{+2} + Fe_{(1-p-x)}Co_{(p+x)}. \qquad (7)$$

Two distinct situations exist regarding alloy formation as a result of the dynamics of the system. The flux of the iron is away from the substrate metal and the flux of the cobalt is toward the substrate. The system is complicated by the fact that it is composed of, in essence, an infinite supply of Fe and a limited supply of Co^{+2}. At the original interface and in the region immediately adjacent to it the change with time is initially one of increasing cobalt concentration and decreasing iron; however, a plane far removed from the interface constantly experiences an increase in iron concentration due to the advancing Fe concentration gradient and a corresponding decrease in cobalt concentration. Equation (8) to the right describes the necessary adjustment of the compositions at the substrate interface which have lost equilibrium due to the decreasing Fe^{+2} and the increasing Co^{+2} concentration resulting in the formation of a new alloy and a change in the Fe^{+2} and Co^{+2} content of the glass to re-establish equilibrium.

$$Fe_{(1-x)}Co_x + mFe^{+2} + nCo^{+2} \underset{\text{dendrite}}{\overset{\text{substrate}}{\rightleftharpoons}} Fe_{(1-x-p)}Co_{(x+p)}$$

$$+ (m+p)Fe^{+2} + (n-p)Co^{+2} . \qquad (8)$$

The reverse direction expresses the changes occurring at a dendrite far removed from the interface. The effect of these changes will be discussed in more detail in Section II-B-5.

In a glass-metal system involving "adherence oxides" and resultant alloy formation, the half cell reaction of Eq. (1) must be expressed in the more general terms of Eq. (9) in which the summation of the subscripts for the alloys is not intended to be equal to one:

$$Fe_xCo_y = Fe_{(x-p)}Co_{(y-q)} + pFe^{+2} + qCo^{+2} + (p+q)2e^- . \qquad (9)$$

The half cell reactions (9) plus (2) then represent atmospheric oxidation. Preferential or selective oxidation is indicated by use of the subscripts p and q.

It is evident that, in order to maintain equilibrium, the drop of activity or chemical potential of the iron in the glass at the interface due to diffusion into the bulk unsaturated glass must be counteracted. The first reactions to occur are atmospheric oxidation of the iron [Eqs. (1) and (2)] and the formation of an alloy as cobalt diffuses to the interface [Eq. (6)]. Equilibrium is maintained subsequently by the necessary adjustments in the compositions of the phases at the interface through alloy composition modifications [Eq. (8)] and atmospheric oxidation [Eqs. (9) and (2)]. The extent to which each of these reactions will occur will be determined by their relative kinetics. Theoretically, these reactions will continue until the chemical potential gradients in the overall system have been eliminated. The system will then consist of homogeneous glass and alloy phases in which the activity of iron and of cobalt in each of the phases is equal; further atmospheric oxidation would only lead to the conversion of the alloy to a discrete oxide phase.

3. In Contact with Unoxidized Metal

If glass with multivalent cations is placed in contact with unoxidized metal, reactions (8) and (9) with (2) still apply as described in the previous section. However, in this case, since the activity of iron in the glass at the start is essentially zero and the activity of the cobalt in the glass is relatively high, the driving force for reaction (8) is at first much greater than in the previous case resulting in the formation of an alloy considerably higher in cobalt. The rate for reaction (9) is then retarded because of the much lower oxidation potential of high cobalt alloy. Therefore, although the relative rates and phase compositions are different, the same types of reactions carry on until no further chemical potential gradients exist in the system. However, as before, the glass-metal interface itself can maintain equal activities of iron and of cobalt in both phases only when the kinetics of reactions (8) and (9) are sufficiently rapid.

4. Experimental Evidence

The experimental data of Borom and Pask[7] can be used to illustrate the foregoing discussions. For this purpose an analysis will be made of the weight gain-vs-time curves shown in Fig. 3 which pertain to the data given in Table II. The curves were obtained by heating specimens in air that were formed by sandwiching disks of oxidized iron between relatively thick disks of glasses, whose compositions are given in Table I, and sealing the composite at the test temperature in argon.

Comparison of the total weight gains of experiments I-A and II-A with V-A demonstrates the importance of the choice of crucible material. The enhanced transport mechanisms resulting from the presence of "adherence cations" is evident from the much higher weight gain of experiment V-B relative to V-A; however, this difference is not as pronounced with the use of platinum crucibles as shown by experiments I and II. The platinum crucible serves as an external path for the transfer of electrons and thereby enhances the coupling of the interface and surface reactions involved in atmospheric oxidation of the base metal through

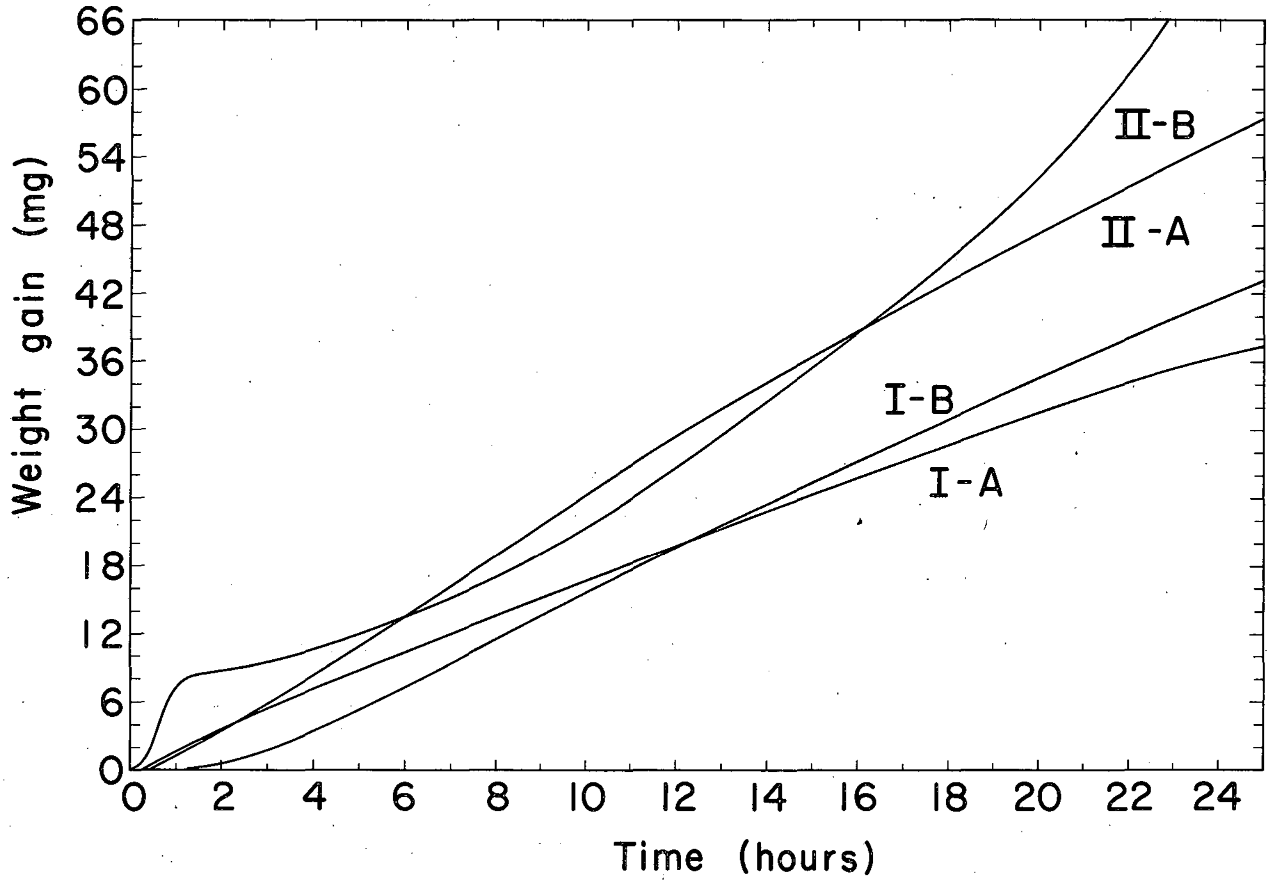

Fig. 3. Net weight gain vs time curves for oxidized iron-glass composites. Experimental conditions are given in Table II.

the glass. Because of this amplification of atmospheric effects, experiments conducted in platinum crucibles have been chosen for illustrative purposes.

Curves I-A and II-A are essentially parabolic in shape which is typical of diffusion controlled processes; the only reactions to consider with glass A then are the half cells corresponding to atmospheric oxidation, Eqs. (1) and (2). Curves I-B and II-B, however, deviate considerably from a parabolic shape and require a more careful analysis. Due to the light preoxidation in experiment II-B, the flux of iron away from the interface on complete solution of the oxide is rapid which results in an initially strong demand for additional oxidation of the base metal. The easy path for the transport of electrons provided by the crucible permits the loss in iron at the interface to be compensated in part by the action of Eqs. (9) plus (2) which is evidenced by the initially rapid rate of weight gain for curve II-B. As the "adherence cations" diffuse to the substrate metal interface from the bulk glass, alloy formation occurs by a reaction represented by Eq. (8). The alloy that is formed becomes increasingly more noble and serves as a "barrier layer" to the continuation of the initial rate of atmospheric oxidation. This effect can be observed in the change in slope of curve II-B in the initial stages. As the rate of supply of "adherence cations" to the interface becomes insufficient to maintain the required equilibrium compositions, atmospheric oxidation once again becomes the predominant reaction. The rate of weight gain increases as the alloy "barrier layer" is by-passed by preferential attack along high energy sites such as grain boundaries, and as new surfaces are exposed that become richer in iron as the penetration proceeds. This "barrier layer" is left as a marker of the original interface and can be readily observed in Fig. 4. A similar analysis can be applied to curve I-B with the exception that the greater amount of preoxidation increases the total amount of iron which has been introduced into the glass at the time of complete solution of the oxide and, thereby, reduces the flux of the iron away from the interface. This effect eliminates the initially high demand for atmospheric oxidation exhibited by experiment II-B. Figure 4 also shows the cross section of the specimen from experiment II-A; absence of the "barrier layer" reflects its dependence upon the formation of an alloy which, in turn, is dependent on the presence of "adherence cations".

5. Formation of Dendrites in Glasses Containing "Adherence Oxides"

The presence of isolated dendrites in the diffusion zone, as observed in Figs. 4 and 5, is a phenomenon that was not covered in the previous discussion. The dendrites are composed of alloys whose iron content decreases with distance from the interface. Another feature of the dendrites is the cross-sectional composition as determined with an electron microprobe; the iron concentration was found to increase from the center of the dendrite to its surface, and the cobalt concentration to decrease. This feature is more pronounced in the dendrites furthest away from the substrate.

As the iron diffuses from the glass-substrate metal interface, a gradient is established into the bulk glass. Likewise, a counter gradient of cobalt toward the interface results as discussed previously. At some distance from the interface, then, the composition of the glass is such that the activities of the iron ions and cobalt ions are equivalent to those in a specific mixed oxide of these metals, i.e., the glass is saturated with this oxide. This mixed oxide, in turn, would be in

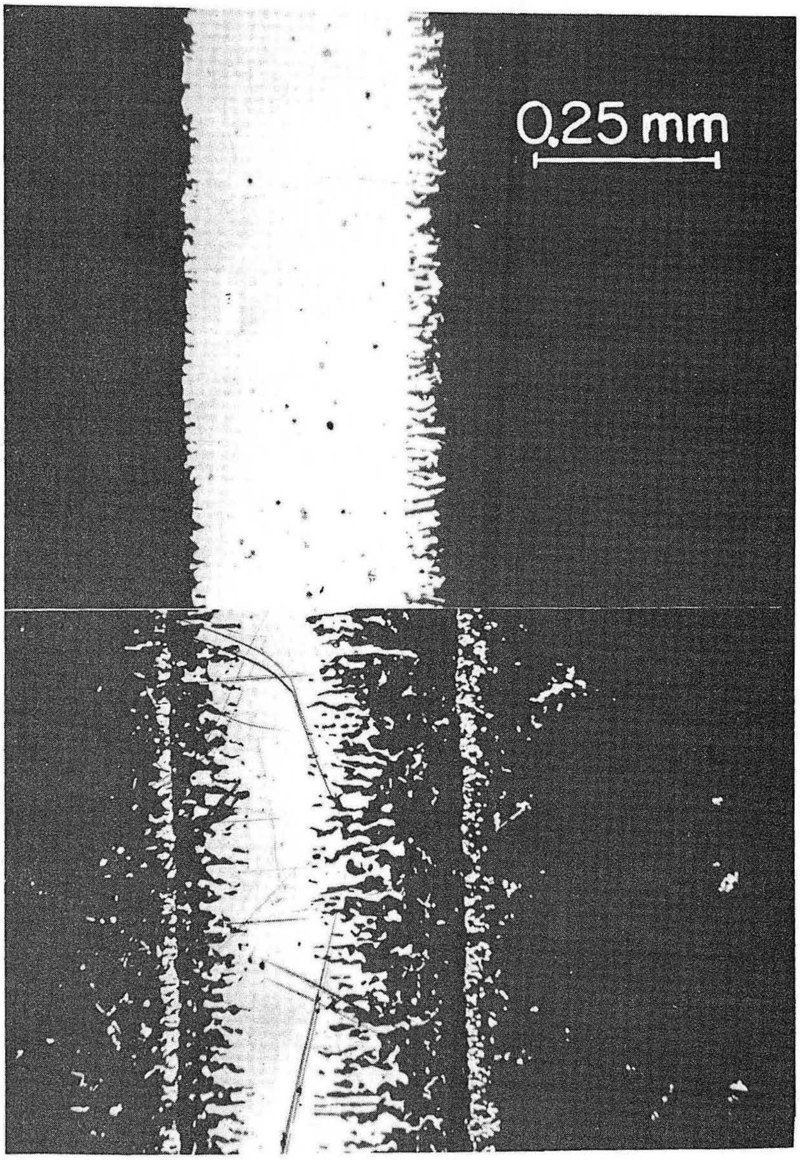

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Fig. 4. Photomicrographs of the glass-metal interfaces of experiments II-A (left) and II-B (right) taken with reflected light (X 100).

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Fig. 5. Photomicrograph of glass-metal interface from experiment II-B taken with dark field illumination showing extensive dendrite formation (X 100).

equilibrium with a specific alloy of iron and cobalt. In the presence of available electrons, and with a suitable nucleation site, it becomes thermodynamically more favorable for the appearance of the dendrite instead of the mixed oxide. The dendrite forms and grows according to Eq. (10).

$$mFe^{2+} + nCo^{2+} + (p + q)2e^{-} = Fe_pCo_q + (m - p)Fe^{2+} + (n - q)Co^{2+} \qquad (10)$$

The electrons become available through reaction (9) at the interface. The transmittance of electrons through the glass becomes possible by means of the mechanism provided by the multivalent cations in this zone, or possibly by means of the existing dendrites themselves. A type of galvanic cell action is thus established in which a flow of electrons occurs from the base metal to the dendrites, and a flow of cations also occurs in the same direction because the cations or plus charges that are necessary to replace the cations removed from the glass by the dendrite formation are also supplied through the same reaction (9). This action increases the corrosive attack on the base metal and also affects the glass compositions at the substrate interface.

With the continuation of oxidation and diffusion processes, the concentration of iron in the glass at a given point from the interface will increase relative to the cobalt. At this point, the corresponding alloy that would be in equilibrium with the glass would also be higher in iron. The necessary adjustment of the equilibrium compositions at the dendrite interface could be achieved by the reaction represented by Eq. (8) moving to the left with no growth of the dendrite. However, with the availability of an existing dendrite as a growth site and electrons by action of Eq. (9), an equilibrium alloy can grow by means of Eq. (10).

The predominance of the latter process is supported by the physical growth of the dendrite and the nature of the dendrite cross-section composition which would result from a continuation of the mechanism represented by Eqs. (9) and (10). Homogenization of a dendrite cannot be achieved as long as the glass composition adjacent to it is constantly changing, since the diffusion rates of cobalt and iron within the alloy are slower than those within the glass.

In these studies no dendrite growth from the substrate metal surface has been observed as indicated by careful examination of Figs. 4 and 5. The figures do show, however, that the roughening of the interface is considerably intensified when the glass contains multivalent cations; some of the resulting protuberances have a peninsular shape that could be interpreted as dendrites. The roughening is due to the oxidation of the surface with the attack being greater along high energy sites, like grain boundaries. This analysis was verified by Gaidos and Pask[8] who showed that no attack of the iron surface occurred when the glass was saturated with FeO, while glass saturated with Fe_2O_3 attacked and roughened the iron surface according to the reaction indicated by Eq. (11).

$$Fe^o + 2Fe^{3+} = 3Fe^{2+} \qquad (11)$$

The intensified roughening visible in Figs. 4 and 5 is due to increased oxidation rates resulting both from enhanced conduction mechanisms provided by the presence of multivalent cations, as described earlier, and from additional oxidation demands imposed on the substrate metal by the formation of dendrites in the bulk glass. However, there is a possibility of activity at the metal surface equivalent to many small galvanic cells due to alloy composition fluctuations brought about by faster reaction rates at grain boundaries; in this case, Eqs. (9) and (10) would also be operative. It will not be possible to prove this point until experimental techniques are developed for determining compositions on such a small scale.

III. GLASS-METAL INTERFACES

It is now of interest to examine the glass-metal interface in greater detail because its nature determines the behavior of composite systems. Part II discussed the conditions under which equilibrium was reached at the glass-metal interfaces and maintained as the overall system approached thermodynamic equilibrium by homogenization within the bulk phases.

A. Nature of Interfaces

As an introduction, it is of interest to consider the conditions across any arbitrary imaginary plane through a homogeneous condensed phase free of isolated defects. There are no discontinuities across such a plane: a) no physical discontinuity in the sense that no intermediate phase is present, b) the atomic structure is continuous in that there is no dissimilarity in the structure of the phases adjoining the plane, and c) the electronic structure is continuous whether it represents chemical bonding of a metallic, ionic, or covalent nature or some combination. The existence of the continuous electronic structure is associated with the existence of a balance of bond energies in the sense that the electrons in the interface are equally attracted to adjoining atoms. (The terminology of a balance of bond energies has no reference to bond lengths or the energy levels at which a balance may occur.)

Under these conditions, a thermodynamic equilibrium exists at such an imaginary plane and no driving force exists for chemical reactions to occur. Also, since there are no discontinuities and no real interface, it is obvious that the interfacial energy at such a plane (or the surface energy of a solid in contact with solid with a contiguous structure) is zero.

1. Metal Surface

The formation of a solid (as a metal) surface in a perfect vacuum represents a plane across which there is a discontinuity in both the atomic and electronic structures. Because of the discontinuities a higher energy level exists at the surface exposed to vacuum in comparison with a parallel plane through the bulk solid. This difference in energy level is referred to as the surface energy of the solid in contact with vacuum, or more correctly, the interfacial energy of the solid relative to vacuum. The reason for this energy level is the poorer screening of the atoms or ions at the surface; an atom at the surface has a lower coordination number than a corresponding atom in the bulk material. The degree of its screening determines the energy level.

The surface in all cases will attempt to reach the lowest possible energy level. Because of the rigid nature of a solid no major rearrangement of atoms can take place; a distortion and a polarization of atoms at and near the surface, however, can take place which results in better screening and a reduction of the surface energy. This polarization effect is more dominant for compounds and for certain atoms.

In the presence of a gas the surface atoms of a metal increase their screening and thereby reduce their energy level by adsorption of the gas. Whether this adsorption is physical or chemical is dependent on whether a chemical bond forms by a reaction which would be required for thermodynamic equilibrium of the system. A chemical bond leads to a lower energy state because of the continuity of the electronic structure and, thus, a lower surface energy of the metal in contact with the gas. Such a chemical reaction can lead to a solution of the product layer or its growth; in each case, adsorption of the gas will continue until thermodynamic equilibrium for the entire system is reached. The kinetics of the various reactions involved will determine the rates. If a definite product layer does form, reference to the surface energy of the metal in contact with the gas becomes meaningless because of a physical discontinuity due to the intermediate product pahse. In that case, reference only to the surface energy of the metal in contact with the product layer becomes meaningful.

2. Liquid Surfaces

The surface in contact with a vacuum, as before, represents a discontinuity in both the atomic and electronic structures. The preceding discussion in regard to surface energies is thus generally applicable. A liquid, however, because of the mobility of the atoms and of no long range order structure, can in addition experience a rearrangement of atoms at its surface in an attempt to reach the lowest possible energy level. This capability is of particular significance for liquids, like molten silicate glasses, that have complex compositions and structures.

The absolute or internal energy level of a bulk glass is determined by the degree of screening of the cations and the nature of the electronic structure, as discussed in Section II-A-1. A lower internal energy is normally attained with a higher O/Si ratio which is achieved by an increased amount of oxides that provide network modifying cations.

The structure at the surface of the glass, however, adjusts itself so that it is silica-rich with a minimum number of coordinated network modifying cations, i.e., a lower O/Si ratio. It can be shown structurally that such a surface can maintain an electrovalent balance without a decrease in the coordination number of four for the silicon; whereas, presence of modifying cations with coordination numbers normally greater than four would require a decrease in their coordination number at the surface. Of these two possibilities the former would have a lower energy level and would thus be preferred; it would, however, be at a higher energy level than a parallel plane through the bulk glass and hence the source of surface energy for the glass. Because of this drive for a silica-rich rearrangement at the surface, the surface structures do not vary greatly for different glasses and the surface energies of silicate glasses thus do not vary considerably; values quoted in the literature generally fall in the range of 275 to 350 ergs/cm^2.

3. Liquid-Solid Interfaces

If a solid and liquid placed in contact form an interface, no physical discontinuity in the form of a gap or an intermediate phase exists between them. There is a discontinuity in the atomic structure since the phases have dissimilar structures. The continuity of the electronic structure, however, is dependent upon the existence of chemical bonding or a balance of bond energies across the interface which occurs under conditions of thermodynamic equilibrium.

In the case of a metal, like iron and molten glass, since the surface energy of the metal is considerably greater than that of glass and will thus dominate the system, the formation of an interface indicates that the surface energy of the metal in contact with glass is less than when it is in contact with gas. If thermodynamic equilibrium does not exist, then the surface structure of the glass, although distorted by physical screening demands of the metal, remains intact and a van der Waals type of attractive forces develop. A discontinuity in the electronic structure across the interface then exists. If, on the other hand, thermodynamic equilibrium between the phases exists, the glass structure at the surface is modified because there are attractive forces between the atoms in the two phases equivalent to the bonding energies of the atoms in the surface of the glass, and a balance of bond energies or a chemical bond results. No discontinuity in the electronic structure across the interface exists under these conditions; the surface energy of the metal in contact with the glass is then reduced in comparison with the situation where chemical bonding does not exist. There is still, however, an interfacial energy, or a surface energy of the metal in contact with glass, because of the discontinuity in the atomic structure.

A more specific discussion of this phenomenon relative to the systems in question may be informative. A "clean" metal normally has a thermodynamically stable chemically adsorbed layer of oxygen. A molten glass placed on this surface will have its surface interact with the oxygen layer because of its effort to reach a lower energy level by increasing its oxygen-silicon ratio or the number of nonbridging oxygens. This process requires a preliminary step of breaking some of the bonds existing between the atoms in the original surface of the glass. If the bulk glass adjacent to the surface is not saturated with the oxide, i.e., not in thermodynamic equilibrium with the oxide, then an imbalance exists in the demand for the oxygen layer between the bulk glass and the metal.

The layer is absorbed by the liquid glass, and with no available free oxygen the glass surface again readjusts its structure to the lowest possible energy level; this surface is then in contact with metal atoms and an attractive force of a van der Waals type develops with a discontinuity in the electronic structure across the interface. On the other hand, if the bulk glass adjacent to the surface is saturated with the metal oxide, i.e., in thermodynamic equilibrium with the oxide, a balance exists in the demand for the oxygen layer between the bulk glass and the metal after the preliminary interaction of the surfaces. Consequently, a balance of bond energies and no discontinuity in the electronic structure exist.

B. Wetting Behavior

Wetting or sessile drop experiments become of interest because they provide quantitative information on interfacial energies which, in turn, provide information on the nature of bonding at the glass-metal interfaces.

If the surface energy of a metal is lowered when in contact with a liquid, the driving force resulting from the decrease in surface energy provides a spreading force around the periphery of a drop placed on the metal as shown in Fig. 6. The only restraining force is the surface tension of the liquid. A balance of the horizontal components of these forces determines the often quoted contact angle, the cross-sectional angle between the metal-glass plane and a plane drawn tangent to the liquid surface at the three-phase junction, represented by Eq. (12) where ${}_s\gamma_g$, ${}_s\gamma_\ell$, and ${}_\ell\gamma_g$ are the solid-gas, solid-liquid, and liquid-gas surface tensions, respectively.

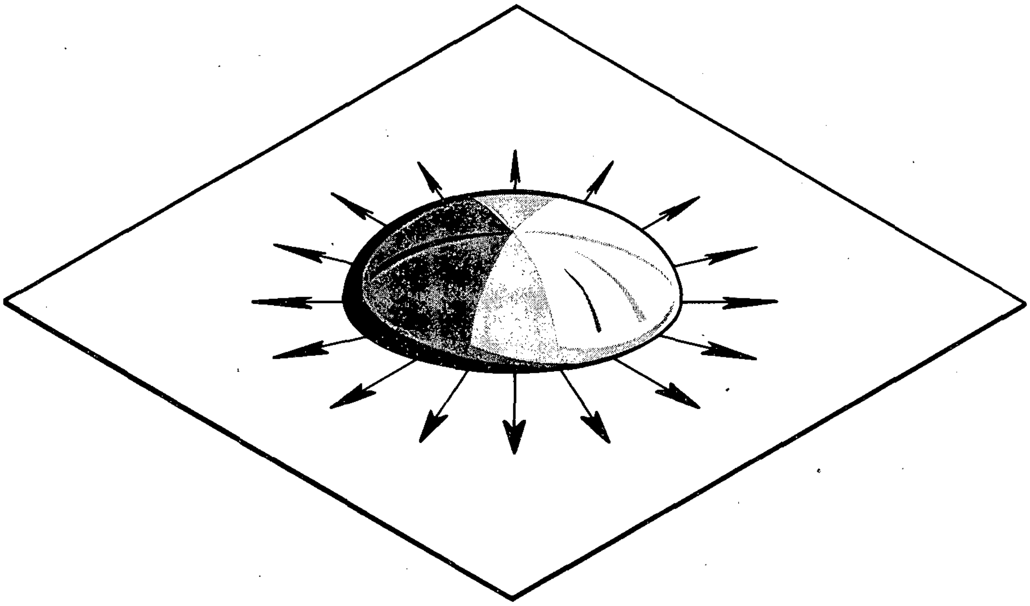

Fig. 6. The driving force due to a decrease in the surface energy of the solid by the liquid, ${}_sF_g - {}_sF_\ell$, manifests itself as a tensile force acting on the periphery of the drop in contact with the solid.

$$ {}_{s}\gamma_{g} - {}_{s}\gamma_{\ell} = {}_{\ell}\gamma_{g} \cos\theta \; . \qquad (12) $$

It can be seen that when the contact angle, θ, approaches zero, the amount of reduction in the surface tension of the metal (which is roughly equal to surface energy) by the liquid approaches the surface tension of the liquid. As discussed earlier this balance indicates that the bonding forces between the atoms at the interface are essentially equivalent to the bonding energies of the atoms in the glass which is the requirement for a continuous electronic structure or chemical bonding at the interface. This concept has been verified experimentally by measurements of adherence. A certain amount of leeway seems to exist in that good adherence begins to develop at contact angles smaller than about 30°, at which point the reduction of the surface energy of the metal by the glass is equivalent to about 85% of the surface energy of the molten glass. $Na_2Si_2O_5$ glass saturated with iron oxide on iron showed a contact angle of about zero degrees, and $Na_2Si_2O_5$ glass alone showed a contact angle of 55°; likewise, the former configuration showed good adherence by fracturing in the glass on deformation, and the latter showed poor adherence by easy separation of the glass drop from the metal.

If the spreading force manifested by the reduction of the surface energy of the metal exceeds the surface tension of the liquid, then the chemical bonds at the surface of the glass are exceeded and an extension of the surface occurs resulting in spreading. This phenomenon can be attributed either to faster kinetics that may occur under certain conditions or to reactions leading to the formation of lower energy bonds.

The formation of an obtuse angle in wetting experiments is an indication that the surface energy of the solid in contact with the liquid is greater than that of the solid in contact with the gas. Wetting of the solid by the liquid is thus unfavorable. The formation of an interface, however, in most cases indicates that the surface energy of the liquid in contact with the solid is lower than that of the liquid in contact with gas. This situation normally occurs when the surface energy of the liquid is considerably higher than that of the solid, i.e., molten metal on a refractory oxide.

IV. CONCLUSIONS

Fundamental interpretations of experimental observations of the behavior at glass-metal interfaces indicate that thermodynamic equilibrium exists in glass-metal systems in the presence of oxygen when the glass is saturated with the low valence oxide of the metal, element, or alloy. If thermodynamic equilibrium does not exist, then a driving force exists for reactions at the interface to achieve such an equilibrium whose success is dependent upon the kinetics of the reactions. The maintenance of equilibrium compositions at the interfaces while the rest of the system moves toward homogenization and thermodynamic equilibrium is dependent upon the kinetics of the associated reactions. Quantitative data to support these hypotheses, other than the experimental observations described, are quite meager. Thermodynamic data for equilibrium conditions in glass-metal heterogeneous systems are particularly lacking. Work in this area is presently in progress.

A second concept of particular importance which has been strengthened by this study is that a continuous electronic structure or chemical bonding can exist at the interfaces of phases only when they are in equilibrium. Glass-metal adherence is basically dependent upon this concept although there are many ramifications because of the complexities involved. Under equilibrium conditions, the interfacial energy of the metal is lowered by the molten glass by an amount approximately equivalent to the surface energy of the molten glass. Sessile drop experiments performed under controlled conditions thus are important; contact angles approaching zero degrees, indicating good wetting, represent the existence of conditions for chemical bonding and good adherence at the glass-metal interfaces.

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