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IDENTIFICATION OF UNCOMMON NON-CRYSTALLINE SOLIDS  
AS "REAL" GLASSES

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IDENTIFICATION OF UNCOMMON NON-CRYSTALLINE SOLIDS


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ABSTRACT

Non-crystalline solids can be prepared by many methods. For instance, besides the conventional cooling of a melt, condensation of the vapor or chemical deposition from solution at room temperature can also yield non-crystalline solids. In the former case, the resulting product is commonly referred to as a "glass".

To ascertain whether non-crystalline solids formed by some of the uncommon techniques are similar to the "glass" obtained by cooling the melt, an examination was made of the available pertinent physical properties of amorphous silica, alumina, magnesium fluoride, and a gold-silicon alloy. From a consideration of refractive index, density, infra-red absorption and/or crystallization kinetics, it is concluded that these materials can be classified as "real" glasses. In some systems, it is shown that grossly different techniques yield essentially the same non-crystalline solid.



## Introduction

Glass is generally made by the fusion together of several oxides followed by controlled solidification. As a result of this widespread practice for the preparation of glass, the American Society for the Testing of Materials has adopted the following definition:<sup>1</sup> "Glass is an inorganic product of fusion which has cooled to a rigid condition without crystallizing." A common glass is thus a rigid non-crystalline solid. A non-crystalline solid, however, can also be prepared by many other methods; for instance, vapor deposition. It has been suggested that some such non-crystalline solids cannot be considered as "real" glasses.<sup>2,3</sup> This suggestion is of course valid as long as the above ASTM definition is adhered to. A more logical consideration as to whether a vapor-formed non-crystalline solid is a "real" glass is to compare its structure and physical properties with those of the corresponding fusion-formed product.

One known example in which a direct comparison of the physical properties of two forms of non-crystalline solids has been made is ethyl alcohol.<sup>4</sup> Jones reported that the glass transition temperature,  $T_g$ , and the specific heats at

temperatures both below and above  $T_g$  are identical for two samples of non-crystalline ethyl alcohol prepared respectively by vapor deposition and melt quenching. For inorganic systems, silica is one of the few examples in which non-crystalline phases have been prepared by various techniques. For many other non-crystalline solids, however, crystallization invariably occurs when the melt is quenched. A direct comparison of the properties of these materials with those of the "real" glass is therefore not possible. In this paper, indirect methods of characterization are described.

Some examples of non-crystalline solids and their methods of preparation to be discussed are shown in Table I. All of these substances are non-crystalline by either X-ray or electron diffraction analysis. An amorphous gold-silicon alloy can be prepared in the form of a thin film by the rapid quenching ("splat cooling") of a droplet at liquid nitrogen temperature. <sup>5</sup> Duwez has reported that such an alloy crystallized after a 24 hour period at room temperature. Kingery et al. <sup>6</sup> have prepared amorphous alumina by an electron bombardment technique. Condensation of the resultant vapors on a room temperature substrate produced a thin film which was stable to 900°C when crystallization occurred. A similar

result was reported with magnesium fluoride which crystallized after 30 minutes at 300°C. These solids typify the systems which we will attempt to characterize in this paper.

### Non-Crystalline Silica

Before proceeding to the unusual non-crystalline systems of Table I, the common oxide, silica, will be considered. In Table II, the index of refraction and density of various samples of non-crystalline silica as prepared by eight different methods are listed. In most cases, the index of refraction and density values are identical to three significant figures. (The densities are within 0.1% of one another). The refractive index of samples 1, 2, and 8 are actually identical to the third decimal place. In addition, Simon<sup>19</sup> has reported that the X-ray diffraction patterns and infra-red absorption curves of non-crystalline silica formed by the conventional cooling of a melt and by neutron irradiation are similar. If the non-crystalline form of silica prepared by the conventional cooling of a melt is now designated "glass", then it seems logical to apply this term to the other forms of non-crystalline silica as well.

It is interesting to note the many possibilities by which

$\text{SiO}_4^{-4}$  tetrahedra can be packed together, Table III. It is known that the Si-O bond lengths and Si-O-Si angles are similar in the various forms of silica.<sup>20</sup> The unoccupied volumes listed are based on a 100% spherical packing density of oxygen ions,  $\rho_{100}$ , as defined by

$$\rho_{100} \equiv \frac{M_{\text{SiO}_2} (0.74)}{V_o} \quad (1)$$

where  $M_{\text{SiO}_2}$  = molecular weight of  $\text{SiO}_2$

$V_o$  = molar volume of oxygen ions in  $\text{SiO}_2$

0.74 = the densest packing of spheres

The calculated value of  $\rho_{100}$  from equation (1) is 3.22 gms/cm<sup>3</sup>. The densified glasses were prepared by either allowing solidification to occur under large hydrostatic pressure (equilibrium glass) or by non-hydrostatic compression of a rigid glass at low temperatures (non-equilibrium glass). The void volume varies from approximately 9% for coesite to about 31% for silica glass formed by fusion. Since even with a single Si-O-Si angle many packing arrangements are available by the simple variation of the mutual orientation of  $\text{SiO}_4^{-4}$  tetrahedra, one would expect the modifications of non-crystalline silica listed in Table II to assume different values of densities. However, they are the same. The similarity between

the refractive indices and densities of these samples may be partially due to the small variation of volume with temperature,  $dV/dT$ , of vitreous  $\text{SiO}_2$ . Structural evidence for a short-range similarity is demonstrated by the infra-red absorption spectra, Figure 1.

The position and intensity of the 9.2 and 12.5 micron Si-O absorptions are similar. In scan (B), the absorption at 7.1 microns is due to the incomplete hydrolysis of tetraethyl silicate. A water band is visible at 6.2 microns.

#### Uncommon Non-Crystalline Solids and the Glassy State

In order for a material to be identified as a glass, it must, of course, be both non-crystalline and rigid. Although all of the uncommon solids discussed in this paper satisfy these criteria, a more convincing description can be made by comparing their general characteristics with those of the amorphous product formed by the cooling of a melt. It would be ideal if films of such uncommon materials had been seen to flow or to form a droplet on heating. However, the flow properties of such films are usually restricted by the adherence to a substrate, even if the film is of low viscosity. In most cases only limited data are available for the uncommon non-

crystalline systems, making the choice of parameters which adequately characterize glass a difficult task. In general,

- (1) The index of refraction and density of a glass are less than that of the corresponding crystalline modification.
- (2) Flow properties are important.

Alumina has not been prepared in the glassy state by supercooling a melt. However, amorphous alumina can be formed by anodization, condensation of the vapor phase, or deposition from organic solutions, Table IV. The index of refraction and density values of these materials are similar, and yet markedly different from the crystalline values listed. These data are compatible with the observed results, that the index of refraction and density of a glass are generally lower than that of the crystalline modification. In all cases the alumina was deposited in the form of a thin film. Flow properties were not reported.

For many undercooled systems, the growth rate can be described in terms of the reciprocal viscosity<sup>23</sup> as

$$\mu = \frac{\Delta H_f (T_f - T)}{3 T_f \pi \lambda^2 \eta N} \quad (2)$$

where  $\mu$  = rate of growth (cm/sec)  
 $T$  = undercooled temperature ( $^{\circ}$ K)  
 $\eta$  = viscosity (poises)



$\lambda$  = mean jump distance (cm)  
 $N$  = Avogadro's number  
 $\Delta H_f$  = latent heat of fusion

Equation (2) can be written as:

$$\mu = \frac{K \Delta T}{\eta} \quad (3)$$

where  $K = \text{a constant} = \frac{\Delta H_f}{3 T_f \pi \lambda^2 N}$

If this relationship is valid for a system, then an approximate estimation of the viscosity at the crystallization temperature can be made if the rate of growth (crystallization) is known. Kingery<sup>6</sup> has reported that amorphous  $\text{Al}_2\text{O}_3$  crystallizes after 30 minutes at  $900^\circ\text{C}$ . Similarly, amorphous  $\text{MgF}_2$ <sup>5</sup> "devitrifies" after 30 minutes at  $300^\circ\text{C}$ . Duwez has observed that an amorphous 75 a/o Au - 25 a/o Si alloy crystallized after 24 hours at room temperature. An approximate rate of crystallization can be calculated for these materials if we assume that in all cases the particles grew from some arbitrary value, for example  $10 \text{ \AA}$  to  $110 \text{ \AA}$ , before crystallinity was detected. The "jump distance",  $\lambda$ , is taken as approximately  $2 \text{ \AA}$  units. For  $\text{Al}_2\text{O}_3$ , the heat of fusion is  $\sim 26 \text{ kcal/mole}$ <sup>24</sup>. The gold-silicon system forms a eutectic at 31 a/o silicon and a temperature of  $370^\circ\text{C}$ . The heat of fusion is approximately

5 kcal/mole for the 75 a/o gold composition if the mixture can be considered ideal.

The calculated viscosities for these materials below their melting points, based on the foregoing data, are shown in Table V at their respective crystallization temperatures. The range of viscosities indicated by the calculation would classify the materials as highly viscous supercooled liquids since the viscosity values are slightly below  $10^{13}$  -  $10^{14}$  poises. Since viscosity is approximately an exponential function of temperature, it is reasonable to conclude that at some slightly lower temperature than the above observed crystallization temperatures, the viscosities of these materials are characteristic of solid glasses,  $10^{13}$  -  $10^{14}$  poises. The calculated viscosities are not unreasonable since films with viscosities greater than  $\sim 10^8$  poises will support their own weight. Another method of ascertaining the correctness of the viscosity values in Table V is from the evaluation of the activation energy for viscous flow.

The activation energy for viscous flow,  $H_{\eta}^*$ , can be considered as a second flow parameter. An approximation of this quantity can be obtained from the empirical Arrhenius equation:

$$\eta = A \exp (H_{\eta}^* / RT) \quad (4)$$

where  $\eta$  = viscosity (poises)

A = constant

R = gas constant

A two-point plot of logarithm  $\eta$  vs.  $1/T$  will yield a straight line, the slope of which provides an average value of  $H_{\eta}^*$ , Figure 2. Normally,  $H_{\eta}^* = f(T)$  - the dashed curves would be more representative of the expected experimental data if available. Hence, at the melting point, the slope and corresponding  $H_{\eta}^*$  would be smaller than at lower temperatures.

For most metals and halides,  $H_{\eta}^* < 10$  kcal/mole.<sup>25</sup> The  $H_{\eta}^*$  values obtained from Figure 2 may therefore appear to be too large. However, the  $H_{\eta}^*$  for a glass-forming system is generally larger than the same quantity for a non-glass-forming material of a similar class.

A relationship discovered by Eyring,<sup>26</sup> which holds for most liquids, can be applied to these data to examine their validity:

$$\Delta H_{\text{vap.}} / \Delta G_{\eta} = 2.45 \quad (5)$$

where  $\Delta H_{\text{vap}}$  = latent heat of vaporization

and  $\Delta G_{\eta}$  = free energy change for viscous flow.

The heat of vaporization for gold and silicon are 82.0 and 72.6 kcal/mole, respectively. A weighted average can be used

in the calculation without introducing serious error.

For  $MgF_2$ ,  $\Delta H_{vap}$  has been reported as 88 kcal/mole.<sup>27</sup>

In the case of  $Al_2O_3$ , which dissociates, a rough estimate of  $\Delta H_{vap}$  can be made by using the vapor pressure data of Navias<sup>28</sup> and assuming that the vapor pressure at the "boiling" point is one atmosphere. This gives  $\Delta H_{vap}$  for alumina as  $\sim 216$  kcal/mole.

The free energy change for viscous flow,  $\Delta G_\eta$ , can be calculated from:

$$\Delta G_\eta = \Delta H_\eta - T \Delta S_\eta \quad (6)$$

where  $\Delta H_\eta$  = the calculated  $\bar{H}_\eta^*$

The entropy change for viscous flow,  $\Delta S_\eta$ , can be extracted from equation (7):

$$\eta = \frac{Nh}{V} e^{-\Delta S/R} e^{\Delta H/RT} \quad (7)$$

where  $\eta$  = calculated viscosity from the growth rate at T(°K)

V = molar volume at T(°K)

$\Delta H$  = activation energy,  $\bar{H}_\eta^*$

R = gas constant

The molar volumes are based on the densities of these

materials at their crystallization temperatures when available. The ratio  $\Delta H_{\text{vap}}/\Delta G_n$  thus calculated yields the values 2.56, 2.23, and 2.15 for  $\text{Al}_2\text{O}_3$ ,  $\text{MgF}_2$ , and the gold-silicon alloy, respectively. A calculation made for  $\text{B}_2\text{O}_3$  based on experimental data<sup>29</sup> gives  $\Delta H_{\text{vap}}/\Delta G_n = 2.57$ . These values are not too far different from the expected value of 2.45. The values of  $H_n^*$  calculated from Figure 2 are therefore reasonable. It would seem, then, that these films were indeed glassy at low temperatures. On heating, devitrification apparently took place at a viscosity between  $10^8 - 10^{13}$  poises. Flow was not observed simply because of the adherence of these thin films to the substrate.

### Conclusions

It has been demonstrated that glasses may be formed by many methods other than the cooling of a melt, as exemplified by the case of silica. By extending this analogy to amorphous alumina, it can be stated that this system may be glass-forming even though the glassy state has not been attained by the conventional supercooling of the melt.

For systems other than  $\text{SiO}_2$ , if crystallization rates are available, an approximate estimation of the viscosity at the

crystallization temperature and the corresponding  $H_n^*$  can be made, the values of which appear to be compatible with those directly obtained for common or "real" glass-forming systems. The systems described were  $Al_2O_3$ ,  $MgF_2$ , and a 75 a/o Au - 25 a/o Si alloy.

For  $SiO_2$ , grossly different techniques can lead to essentially the same non-crystalline solid. Whether this is generally true for other systems having normal coefficients of thermal expansion must await further study.

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TABLE I

Examples of Uncommon Non-crystalline Systems

<u>System</u>	<u>Method of Preparation</u>	<u>Reference</u>
Au-Si Te-Ge	Rapid "Splat" Cooling	Duwez <sup>5</sup>
MgO MgF <sub>2</sub>	Condensation of Vapor	Kingery <sup>6</sup>
Al <sub>2</sub> O <sub>3</sub>	Anodization	Weiskirchner <sup>7</sup>
ZnO	Reactive Sputtering	Mickelsen <sup>8</sup>
TiO <sub>2</sub>	Hydrolysis of Organics in Solution	Krylova <sup>9</sup>
Bi	Condensation of Vapor	Hilsch <sup>10</sup>

TABLE II

Comparison of the Index of Refraction and Density of  
Non-Crystalline SiO<sub>2</sub>, as Formed by Different Methods

No.	Method	Index of Refraction	Density (gms/cc)	Reference
1	Conventional Melting	1.458	2.203	Morey <sup>11</sup>
2	Vapor Phase Hydrolysis	1.458	2.202	Corning <sup>12</sup>
3	Reactive Sputtering	1.455	2.2	Sinclair & Peters <sup>13</sup>
4	Deposition from Organic Solution	1.40- 1.45	--	Schroeder <sup>14</sup>
5	Thermal Decomposition	1.430	--	Klerer <sup>15</sup>
6	Glow Discharge Decomposition	1.456	--	Secrist & Mackenzie <sup>16</sup>
7	Shock Wave Transformation	1.46	2.22	DeCarli & Jamieson <sup>17</sup>
8	Neutron Bombardment*	1.458	2.205	Primak <sup>18</sup>

\* Dosage:  $1.8$  to  $3 \times 10^{20}$  neutrons/cm<sup>2</sup>  
followed by annealing at 1100°C.



TABLE III

Unoccupied Volume in Various Forms of SiO<sub>2</sub>

	Density (gms/cm <sup>3</sup> )	% Unoccupied Volume Based on 100% Spherical Packing Density
Silica Glass	2.20	31.6
Densified Silica Glass (Equil.)	2.29	29.7
Densified Silica Glass (Non-equil.)	2.62	18.5
Cristobalite	2.32	28.0
Quartz	2.66	17.5
Coesite	2.93	9.0

TABLE IV

Comparison of the Index of Refraction and Density  
of Non-Crystalline Alumina with that of  
Crystalline Alumina

<u>Solid</u>	<u>Method of Preparation</u>	<u>Index of Refraction</u>	<u>Density (gms/cc)</u>	<u>Reference</u>
Non-Crystalline	Anodization	1.59	3.1	Young <sup>21</sup>
Non-Crystalline	Condensation of Vapor	1.61	2.9 (2% porosity)	Kingery <sup>6</sup>
Non-Crystalline	Deposition from Organic Solution	1.61- 1.65	---	Schroeder <sup>14</sup>
Crystalline	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> as grown	E=1.760 O=1.768	3.97	Larson & Berman <sup>22</sup>

TABLE V

Viscosities of Several Systems as Calculated  
From Their Rates of Crystallization

	$\mu$ (cm/sec)	T(°K)	$\eta$ CALC(poises)
Au-Si	$1 \times 10^{-11}$	300	$4.3 \times 10^{12}$
Al <sub>2</sub> O <sub>3</sub>	$5.5 \times 10^{-10}$	1173	$4 \times 10^{11}$
MgF <sub>2</sub>	$5.5 \times 10^{-10}$	573	$1.6 \times 10^{11}$

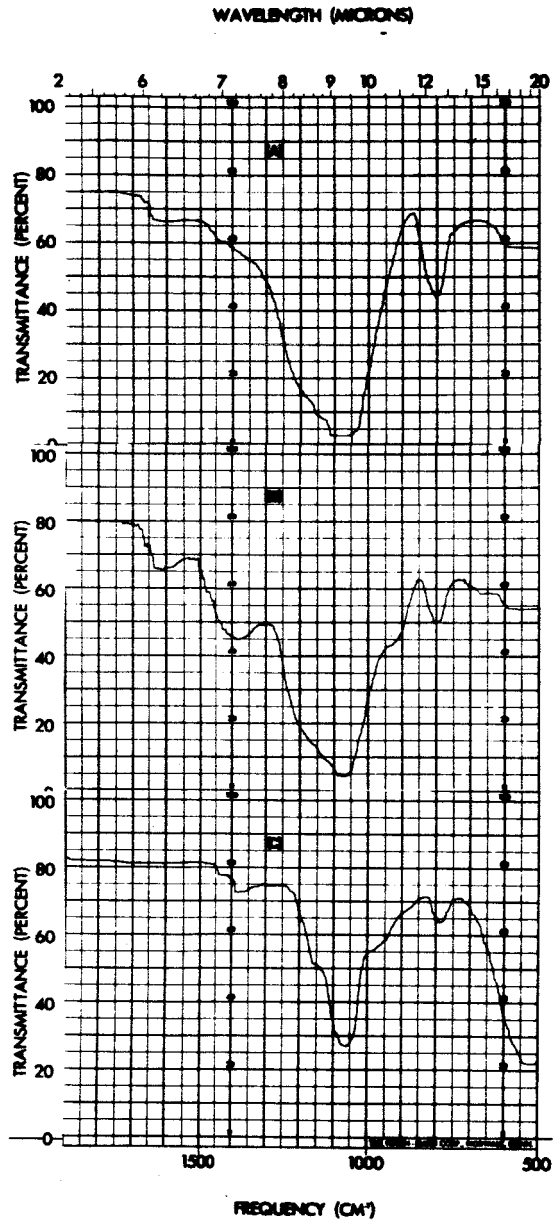


Figure 1

Infra-red transmission of non-crystalline  $\text{SiO}_2$  as prepared by different methods:  
 A---fused  $\text{SiO}_2$ ; B--- $\text{SiO}_2$  from hydrolysis of  $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ ; C--- $\text{SiO}_2$  from glow discharge decomposition of  $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ .

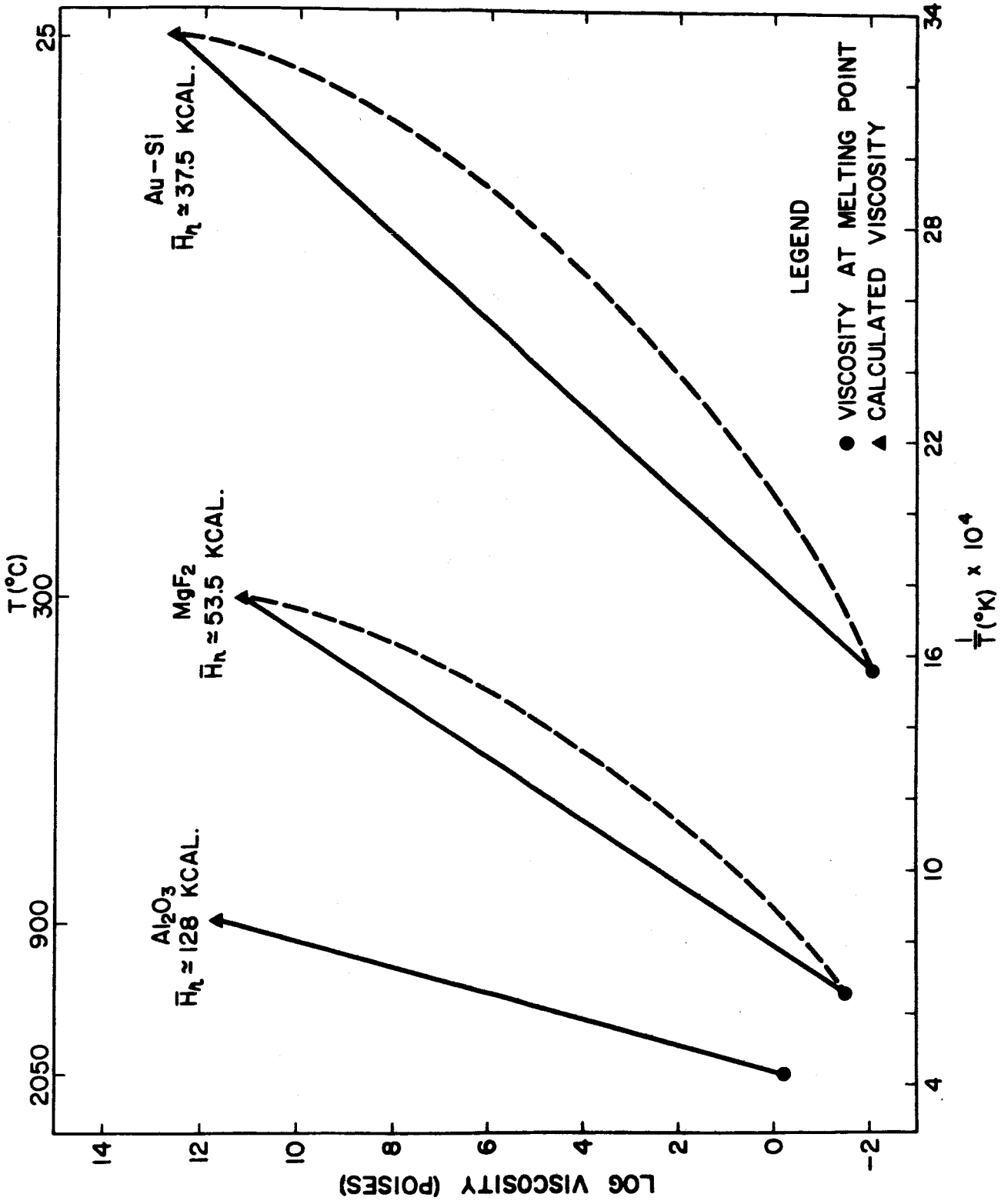


Figure 2

Expected relation of log viscosity and  $1/T$  for various systems

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