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EXPERIMENTAL DETERMINATION and A MODEL FOR CALCULATION

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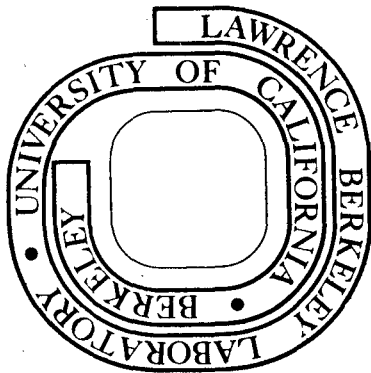
HIGH TEMPERATURE HEAT CONTENT AND HEAT
CAPACITY OF SILICATE GLASSES: EXPERIMENTAL
DETERMINATION AND A MODEL FOR CALCULATION

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High Temperature Heat Content and Heat Capacity
of Silicate Glasses: Experimental Determination
and a Model for Calculation

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Heat Content and Heat Capacity of Silicate Glasses

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Abstract

The high temperature heat contents, $H_T - H_{298}$, of two FeO-rich synthetic silicate glasses and five glasses and three supercooled liquids prepared from igneous rocks ranging from basalt to rhyolite have been measured by drop calorimetry. Data for the two synthetic glasses are combined with published heat content determinations on simple silicate glasses to yield the partial molar heat contents and heat capacities of SiO_2 , Al_2O_3 , FeO, MgO, CaO, Na_2O and K_2O in silicate glass, assuming/ no of necessity that there is compositional dependence over the range in question. The partial molar heat content of SiO_2 is essentially equal to that of pure SiO_2 glass. Experimental heat contents of the five natural compositions are reproduced by calculation from the partial molar heat contents. Experimental glass transition temperatures for the glasses studied range from 700 to 1080°K and bear no simple relation to liquidus temperature, calculated liquid thermal expansion or activation energy for viscous flow. The heat capacity of silicate glass generally approximates $3R \text{ cal} \cdot \text{g-atom}^{-1} \cdot \text{deg}^{-1}$ at the glass transformation temperature.

Introduction

The understanding of igneous processes would be greatly improved through knowledge of the thermodynamic properties of silicate liquids. For instance, it would then be possible to calculate the physical conditions of equilibration of a given mineral assemblage and silicate liquid (Carmichael, et al., 1974). Conversely, for designated values of intensive parameters the compositions of crystalline phases coexisting at equilibrium with a magma could be determined. Though far from complete, significant

advances have been made towards the thermodynamic characterization of crystalline phases occurring in igneous rocks. Silicate liquids have received less attention and there is only a small body of basic thermodynamic data.

A thermodynamic property which can be readily measured is the heat content, or the difference in enthalpy of a substance at a temperature T , and that substance in its reference state at 298.15°K ($H_T - H_{298.15}$).* From the temperature dependence of the heat content, values of the heat capacity at constant pressure, C_p , may be derived, since

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

If heat content data were available for a sufficient number of compositions the partial molar heat contents of the major oxide components of silicate liquids could be evaluated. The partial molar heat content, $\bar{H}_{T,i} - \bar{H}_{298,i}$, is the change in total heat content of the solution per mole of component i when an infinitesimal amount of i is added to the solution. The partial molar heat content or derived partial molar heat capacity, $\bar{C}_{p,i}$, could be used to evaluate the temperature dependence of the activity of component i , a_i , if the partial molar heat of solution of i in the melt were known at 298°K or some higher temperature, as

$$\begin{aligned} \left(\frac{\partial \ln a_i}{\partial T} \right)_p &= \frac{1}{RT^2} \left(H^\circ_{T,i} - \bar{H}_{T,i} \right) \\ &= \frac{1}{RT^2} \left[\left(H^\circ_{T,i} - H^\circ_{298,i} \right) - \left(\bar{H}_{T,i} - \bar{H}_{298,i} \right) + \left(H^\circ_{298,i} - \bar{H}_{298,i} \right) \right] \end{aligned}$$

where the superscript $^\circ$ refers to pure component i .

A consequence of knowledge of partial molar heat capacities of components of silicate liquids is the ability to calculate the specific heat of any magma

* In the following pages, 298°K will be used in place of 298.15°K , though the latter temperature is the actual reference temperature.

from a chemical analysis as a function of temperature. The accuracy of calculations involving the transfer of heat in magmatic systems would thus be improved.

It is often said that the glassy state provides the low temperature analog of the liquid. In some respects silicate glasses are structurally similar to liquids (Riebling, 1968) and, as heat content data from which heat capacities may be derived are far more abundant for glasses than for liquids, the following will be primarily concerned with the heat content and heat capacity of silicate glasses and the corresponding partial molar quantities. The present work includes new heat content data obtained on two synthetic FeO-rich glasses and five glasses and three of the corresponding supercooled liquids prepared from igneous rocks. Published data on glasses are evaluated and combined with the new data on the FeO-rich compositions to obtain the best-fit partial molar heat contents of the oxides SiO_2 , Al_2O_3 , FeO, MgO, CaO, Na_2O and K_2O in silicate glasses. Because of the limited number of compositions for which accurate heat content measurements have been made one must assume that the partial molar heat contents are independent of composition over the range in question. As calculated heat contents of the glasses of natural composition closely reproduce the measured values this assumption is acceptable.

Factors Contributing to the Heat Capacity of Silicate Glasses, Supercooled Liquids and Liquids

Before proceeding to a description of the data obtained in this study it is worthwhile to discuss the factors contributing to the heat capacity of silicate liquids and glasses and the differences between the liquid and glassy states.

Silicate liquids consist of free ions, polymer networks and discrete polymer species whose structure and relative concentration are dependent on temperature and composition (Bockris, et al., 1955; Masson, 1968; Hess, 1971; Anfilogov, 1973). The heat capacity of such liquids is determined by the accessibility of vibrational and rotational modes of individual ions and polymer groups. The number of modes available clearly depends not only on temperature but also on the shapes and size distribution of the polymers and the mobility of cations. Glasses, having properties quite similar to crystalline solids but lacking long range order, derive their heat capacity primarily from the thermally encouraged vibration of ions within a relatively rigid structure.

The heat capacity of a supercooled silicate liquid is higher than a glass of the same composition because of the greater rotational freedom of species in the liquid. In addition, in the glass transformation region an abrupt increase in C_p arises from the additional energy necessary to provide expansion of the glass structure through the formation of holes (Kauzmann, 1948). The effects of the glass transformation may be observed by cooling a glass-forming substance below its liquidus or melting temperature without the precipitation of crystals. This results in an equilibrium supercooled liquid (though metastable with respect to crystals) whose thermodynamic properties are continuous with those of the liquid. Upon further cooling, continuous but rather abrupt changes in slope of enthalpy and volume vs temperature functions are observed to take place simultaneously over a small range of temperature. This phenomenon is known as the glass transition and is correlated with a fundamental change in the structure of the supercooled liquid as it transforms to glass. Upon cooling through the glass transition the structure of the supercooled liquid is frozen in.

The degree of long-range disorder inherited from the supercooled liquid depends upon the cooling rate through the transition. For a given composition the degree of disorder retained and the packing (coordination) of cations determines the configurational contribution to the heat capacity of the glass. The glass transition temperature (T_g), defined here as that corresponding to the intersection of glass and supercooled liquid enthalpy curves, is dependent upon composition and cooling rate. Likewise, the magnitude of the observed change in heat capacity at T_g ($\Delta C_{p_{T_g}}$) is a function of composition and cooling rate.

The change in state from supercooled liquid to glass may be described in terms of the entropy of the substance. There are two components to the thermal entropy of a liquid or supercooled liquid: entropy arising from lattice vibrations and configurational entropy due to the lack of long range order and formation of holes. Contributions to heat capacity are analogous. Extrapolation of equilibrium supercooled liquid properties to low temperatures results in the paradox of a lower entropy for the liquid than the corresponding crystalline material at the same temperature (Kauzmann, 1948). It has thus become evident that at some temperature a second order transformation from equilibrium supercooled liquid to equilibrium glass takes place in order to maintain the higher entropy of the amorphous phase. Gibbs and DiMarzio (1958) identified this temperature with the "ideal" glass transformation temperature, T_0 , which corresponds to the operational glass transition temperature extrapolated to infinitely slow cooling rate. The configurational entropy of the "ideal" glass is zero. Neglecting differences in vibrational contributions to entropy between glass and crystal, the configurational entropy frozen into a real

glass during the glass transformation is equal to the residual entropy of the glass at 0°K (Adam and Gibbs, 1965). It is possible to determine this quantity calorimetrically for single component glasses (Gibson and Giaque, 1923). For glasses which are solutions of two or more oxides the additional residual entropy of mixing of components to form the solution must be included (Angell, 1968). The glass transition always occurs at $T_g > T_o$ because, upon cooling, a point is reached where the configurational entropy attains some critical minimum value below which kinetic barriers to ordering cannot be overcome under realizable experimental cooling rates (Chang, et al., 1966). The slower the cooling the lower will be the operational glass transition temperature and the smaller will be the configurational contribution to the entropy.

Angell (1968) gives a method whereby T_o may be calculated from measurements of viscosity. Unfortunately, insufficient data have been obtained from the supercooled liquid region to allow T_o to be calculated for very many silicate compositions. Angell (1968) noted that T_g/T_o is a measure of the "non-ideality" of a glass and the abruptness of the observed transition decreases as T_g/T_o increases. The "smearing out" of the transformation, hence T_g/T_o , increases with SiO_2 content in silicate glasses. Pure silica glass is far from ideal and shows no clear transition, but rather a gradual increase in heat capacity over about 300°K (Wietzel, 1921). For silicate glasses which contain appreciable tetrahedrally coordinated Al, T_g/T_o might be more successfully related to R , the ratio of oxygen to network forming cations (Si^{4+} and Al^{3+}) (Lacy, 1965), rather than to SiO_2 content alone.

Clearly, because of the time-dependent nature of the glass transformation,

in any calorimetric study the distinction must be made between measurements of $H_T - H_{298}$ obtained from the supercooled liquid state and those acquired from the glass. For both to refer to the same reference state it must be established experimentally that the final state attained in runs on supercooled liquid is the same as that for glass. This is not a matter of concern when heat capacity is measured directly but is critical to the interpretation of results obtained by the method of mixtures (drop calorimetry). Since the structural state of glassy materials depends

upon their cooling history, glasses prepared under different conditions (i.e. quenched vs. cooled slowly or annealed) may possess different degrees of order and, hence, heat contents. A common practice in drop calorimetry is to begin a series of experiments at low temperature (e.g. 400°K) and proceed to higher temperatures at regular intervals. Enthalpy measurements at temperatures below the glass transition region should be reproducible as long as they refer to essentially the same final state. Once the glass transition region is entered at a temperature near the experimentally determined glass transition temperature, T_g , structural rearrangement begins to take place and the final state of the glass will depend upon cooling rate through the transition. Above the glass transition the supercooled liquid state is attained in which the material develops the disordered structure of a liquid. Cooling from $T > T_g$ repeatedly produces the same glass structure (configuration) provided the cooling rate through the glass transition is identical for each experiment (Haggerty, et al., 1968). Again, enthalpy values will be reproducible. However, enthalpies measured starting from the supercooled liquid region may not relate to the same glass at 298°K as those determined at $T < T_g$. Consequently,

the heat content of the sample must be repeatedly checked at $T < T_g$ to ensure that the supercooled liquid heat content measurements refer to the same final state/ as those for the original glass. With two exceptions, one of which may be attributed to the structural changes following volatilization of H_2O and Cl and the other to devitrification, heat contents measured here were reproducible at low temperatures after passing through the glass transition region, indicating that essentially the same final state was attained within the precision of the measurements.

In the supercooled liquid region partial or complete devitrification of the sample is inhibited by very slow nucleation and growth of crystals. Fortunately, small amounts of devitrification are readily detected. Devitrification of the glass sample will result in measured enthalpy values which are too low (Schwiete and Wagner, 1932) by the difference in heat content between glass and crystals. This effect becomes pronounced at temperatures greater than T_g in basic melts, as in compositions 1, 2 and 7 (figures 1 and 3). Crystallization during cooling in the calorimeter will result in high values because the heat of fusion is given up. Heat contents determined from below T_g will then be lower than for the original glass, as in composition 6 (figure 3).

Experimental Determination of the Heat Content of Glasses and Supercooled Liquids.

Accurate heat content data are available on silicate glasses consisting of up to four major components (see appendix). Though the oxides SiO_2 , Al_2O_3 , MgO , CaO , Na_2O and K_2O are well represented, no glasses rich in FeO , one of the most abundant oxides present in igneous rocks, have been studied prior to this work. Consequently, two low melting compositions very rich in FeO were prepared by fusion of mixtures of silica glass, Al_2O_3 , Fe , Fe_2O_3 , CaCO_3 and Na_2CO_3 in Fe crucibles under an argon atmosphere and quenching in water. Wet chemical analyses of the resulting glasses are presented in table 1 (analyses 6 and 7).

table 1 about here

In order to add to the data on silicate glasses and supercooled liquids and test the hypothesis that partial molar heat capacities of oxide components derived from literature data and the two FeO -rich glasses could be applied to natural compositions five glasses prepared from igneous rocks/ were studied. The five compositions are: high-alumina basalt, andesite, rhyolite and two pantellerites. One of the pantellerites is a residual glass from a lava and was included in order to check effects of cooling rate since it probably cooled relatively slowly. The other four glasses were prepared from rock specimens by crushing to < 200 mesh in a tungsten-carbide ball mill, fusing under 1 atmosphere of nitrogen in a molybdenum crucible and quenching in water. This process was repeated 3 to 5 times to obtain a homogeneous glass.

The glasses prepared from rocks were analyzed for Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P and Mo with an ARL-SEMQ electron probe. Loss of Na was

minimized by using a large spot and a sample current of .01 μ a. Data were corrected by the method of Bence and Albee (1968), using their measured correction factors where possible and those calculated by Albee and Ray (1970) elsewhere. Ferrous iron was determined wet-chemically. Analyses of splits of glasses are given in table 1.

For measurement of heat content 7 to 9 grams of glass (50-100 mesh) were loaded into Pt-10% Rh capsules, evacuated and sealed by arc-welding under 1 atmosphere of argon. Heat contents ($H_T - H_{300^\circ K}$) were obtained at approximately 50 degree intervals for the FeO-rich compositions and 100 degree intervals for the others with a drop calorimeter similar in principle to that described by Hultgren, et al. (1958). The 2 cm diameter \times 2.5 cm Pt-10% Rh sample container is suspended in a vertical Pt-wound furnace by a .25 mm Pt-10% Rh wire. Temperature is measured with a Pt/Pt-10% Rh thermocouple placed about 2 mm above the sample container. The thermocouple is calibrated periodically against the melting point of gold (1063°C). Reported temperatures are believed to be accurate to $\pm 1^\circ K$ or better. After reaching thermal equilibrium two sets of gates between furnace and calorimeter are momentarily opened and the sample dropped into the calorimeter well, where it hangs from the wire. The calorimeter consists of a copper tube with horizontal fins enclosed in a double wall glass vessel which is immersed in a water bath maintained at a constant temperature ($\pm 0.001^\circ C$), slightly above the melting point of diphenyl ether (300.03°K). The space between the copper tube and glass is filled with diphenyl ether, a portion of which is frozen around the tube. A pool of mercury in the bottom of the glass vessel connects with a calibrated horizontal capillary. Addition of heat to the calorimeter by the introduction of a sample melts some of the diphenyl ether, forcing mercury along

the capillary. The amount of displaced mercury is directly proportional to the heat content ($H_T - H_{300}$) of the sample at the instant it entered the calorimeter. The calorimeter constant is taken to be $18.91 \text{ cal} \cdot \text{g}^{-1}$ of mercury displaced (Jessup, 1955).

The heat content of the Pt-10% Rh capsule and wire and the heat lost during the drop were accounted for by measuring the heat content of an empty capsule whose size, shape, and emissivity were similar to all other capsules. Small differences in mass between capsules were corrected for by assuming that the heat content of an empty capsule is directly proportional to its mass since all Pt-10% Rh components of the capsules are of the same thickness.

The precision of individual measurements is better than approximately $\pm 0.5\%$. Precision of measurements on the FeO-rich compositions is better than $\pm 0.2\%$, some improvements in the capillary system and furnace temperature control having been made before these materials were studied.

Accuracy was assessed by measuring the heat content of NBS standard sapphire 720. After subtraction of capsule heat content, data were fitted with an equation of the form (Maier and Kelley, 1932)

$$H_T - H_{\text{Ref.}T} = AT + BT^2 + CT^{-1} + D. \quad (1)$$

Smoothed values for $H_T - H_{300}$ and C_p are compared with those given by the NBS in table 2. The near agreement suggests accuracy of about $\pm 0.5\%$ in

table 2 about here

heat content and $\pm 1.0\%$ in heat capacity. Lindroth and Krawza (1971) reported similar deviation from the NBS values for standard sapphire 720. A few measurements on a natural, very pure quartz sample agreed with values from Kelley (1960) within similar limits. Measurements were made on the sapphire sample periodically to insure the accuracy of the other determinations.

Other sources of error in the glass experiments include the heat content of Ar gas within the capsule, vaporization, reduction or oxidation of Fe, loss of Fe to the capsule, dehydration and leakage of gas from the capsule. The heat content of the excess of Ar present in the empty capsule vs. filled amounts to about .01% of the measured enthalpy and was ignored. Vaporization of sample would absorb a quantity of heat equal to the heat of vaporization of the substance, liberating a similar quantity of heat upon condensation as the sample cools in the calorimeter. Anhydrous silicate melts exhibit such low vapor pressures at the temperatures considered here that this effect is of negligible significance. However, in the case of hydrous initial compositions, condensation phenomena cannot be ignored.

The magnitude of heat effects due to change in oxygen content of the melt and oxidation state of iron are difficult to assess, since it is impossible to monitor or control the fugacity of oxygen within the capsule. Little change is to be expected for the samples prepared by fusion under an inert atmosphere as long as the capsule remains sealed and iron is not lost to the Pt-10% Rh. The iron in these was initially largely reduced and, as the capsule was filled with argon, probably remained so. Assuming the difference in heat content between solid Fe_2O_3 and solid FeO plus O_2 gas (Kelley, 1960) is of the same magnitude/that between Fe_2O_3 in the liquid and FeO in the liquid plus O_2 gas, the effect of oxidation or reduction of Fe in sample 3 was estimated to be less than 1% at the highest initial temperatures. This effect would be so large for samples 6 and 7,

the FeO-rich glasses, that it certainly could be detected. The measurements show that no significant oxidation or reduction occurred in sample 7 and certainly not for composition 6 at temperatures below T_g .

Transfer of Fe from glass to capsule is probably ineffective at temperatures below T_g (700-750°K). At higher temperatures there must be some heat of reaction and difference in heat content between Fe dissolved in Pt-10% Rh and O_2 gas and FeO in melt. As it is likely that only a thin layer of melt participates in the iron loss the total heat effect is assumed to be within the precision of the measurements. Either Fe loss has no measureable effect on heat content or this process did not occur in the FeO-rich compositions for the measured heat contents at temperatures below T_g are thoroughly reproducible, with the exception of those made on composition 6 after exceeding T_g . The observed lower heat contents are probably in the right sense, considering the difference in the partial molar heat content of FeO in glass and the heat content of Fe metal plus O_2 gas, though this difference could also be attributed to partial devitrification.

The same procedure was followed in measuring the heat content of each of the five natural compositions. Starting at approximately 400°K heat contents were determined at roughly 100° intervals, each measurement being repeated at least once (table 3, figures 1 and 2). Reproducibility was

table 3, figures 1 and 2 about here

considered sufficient evidence for the attainment of essentially the same final state at the end of each experiment. A more precise method would be necessary to detect any gradual changes in configuration of these glasses during heating at temperatures below T_g .

Measurements were continued above T_g until the maximum operating

temperature was reached or devitrification was indicated by lack of reproducibility. In the three rhyolite compositions devitrification did not take place at high temperatures and it was possible to obtain super-cooled liquid and ^(presumably) liquid state enthalpy data. In order to check the validity of relating both liquid and glass data to the same final state several measurements were made on each glass at temperatures below T_g (see appendix for effects on composition 3). Glasses 4 and 5 were originally quenched very rapidly in water, while 3 is a natural, crystal-free residual glass from a lava. Effects on 4 and 5 were insignificant.

Heat contents of the synthetic FeO-rich samples were determined at approximately 50 degree intervals, each experiment being repeated at least once (table 3, figure 3). As higher temperatures were reached the heat

figure 3. about here

content at a low temperature (480°K for 6, 450°K for 7) was checked, revealing constancy of the final state of the glass. Measurements on sample 7 were terminated when devitrification set in. Since the estimated liquidus temperature of composition 6 is only about 975°K two pairs of drops were made from higher temperatures. These were quite reproducible, though a further experiment at 480°K resulted in a very low heat content. Some degree of crystallization apparently took place after the sample entered the calorimeter giving erroneously high values of heat content for drops from superliquidus temperatures due to liberation of heat of crystallization. Subsequent low values in the glass range are ascribed to the presence of crystals.

heat content

For each composition/data obtained from temperatures below T_g were fitted by least squares with an equation of the form of equation (1). A short extrapolation corrects the D term to the reference temperature of 298°K. Differentiation of this expression yields the heat capacity of the glass over the range 298 - T_g :

$$C_p = A + 2BT - CT^{-2}.$$

A small but significant temperature dependence of the heat capacity of all three rhyolitic supercooled liquids was noted. Supercooled liquid heat contents were fitted with an equation of the form

$$H_T - H_{300} = AT + BT^2 + D.$$

The final term was corrected to the 298°K reference temperature by adding the heat content of the glass between 298 and 300°K. Supercooled liquid data for composition 3 may not refer to the same final state as those obtained on the glass due to changes enumerated above. The heat capacity of the supercooled liquid becomes

$$C_p = A + 2BT.$$

Enough data were gathered on the basalt supercooled liquid before devitrification to define an approximate heat capacity up to about 130 degrees above T_g but were insufficient to detect its variation with temperature. The heat capacity probably increases further at higher temperatures. The coefficients for the above analytical expressions are given in table 4. The reasons for the slight positive curvature of the enthalpy

table 4 about here

vs. temperature curve for the composition 4 supercooled liquid (positive B term, table 4), while those for 3 and 5 display negative curvature (table 4), are not apparent.

In addition to the experimental points, figures 1, 2 and 3 also show the curves for mean specific heat derived from the analytical expressions given in table 4. It can be seen that the greatest inaccuracies occur at low temperatures, though the equations fit the actual enthalpy data very well. Figure 4 depicts the experimental points for composition 4 and enthalpy curves fitted to the data. The derived heat capacity is also shown, though the behavior of C_p in the vicinity of T_g is uncertain.

figure 4 about here

Partial Molar Enthalpies and Heat Capacities of Oxide Components of
Silicate Glasses

multi-component silicate

A simple model for calculation of glass heat contents can now be considered. It is based upon values for heat content of the FeO-rich glasses here reported and of 12 simple silicate glasses from the literature (see table in appendix) and gives apparent partial molar heat contents. The validity of the model for compositions similar to igneous rocks is substantiated by the data of this study on the five natural compositions. Previous efforts are first described and later compared with the present results.

Historically, the glass industry has required values for the specific heats of commercial glasses. Attempts to calculate specific heat from a chemical analysis have concentrated on accurately modeling the mean specific heat of the glass, rather than the extraction of meaningful partial molar heat capacities for the components chosen. It has long been known that the heat capacities of many crystalline substances may be approximated by the sum of those of their constituent oxides. Since Winklemann's first calculations (1893), a number of workers, notably Sharp and Ginther (1951), have attempted to demonstrate the additivity of heat capacities of oxide glasses. Because in systems of interest to ceramists no data existed on pure oxide glasses other than SiO_2 and B_2O_3 these workers derived "factors" for other oxides with the assumption that the partial molar heat capacities of SiO_2 and B_2O_3 dissolved in silicate glasses are identical with the molar heat capacities of pure SiO_2 and B_2O_3 glasses, respectively. Partial molar heat capacities of other components were assumed to be constant over the range of composition for which data existed. Mean specific heats, heat contents and heat capacities of glasses were calculated by summing the

product of oxide "factor" and weight fraction over all oxides. The most recent evaluations based on the above assumptions are those of Schwiete and Ziegler (1955) and Moore and Sharp (1958).

The approach adopted here has been to calculate the best fit apparent partial molar heat contents of major oxide components of silicate glasses at 50°K intervals (350-1000°K) by solving the over-determined matrix of equations of the form

$$(H_T - H_{298})_{\text{glass}} = \sum X_i (\bar{H}_{T,i} - \bar{H}_{298,i}). \quad (2)$$

Because accurate enthalpy data exist for only a few silicate glasses the assumption must still be made that the partial molar heat capacities of the components in question are constant at a given temperature over the range of composition for which measurements have been reported. That this is a valid approximation is evident from the accuracy with which measured heat contents may be reproduced by calculation. Were more data available a more rigorous model could be developed in which partial molar quantities reduce to molar quantities as the mole fraction of a component i , X_i , approaches 1. Of course, since glassy state data exist for only one component, SiO_2 , the standard state (glass) for the other components is purely hypothetical, though theoretically existent (Angell, 1968), and molar quantities remain as yet undefined.

Calculated partial molar heat contents were fitted for the coefficients of equation (1). Making no restricting assumptions about the behavior of SiO_2 resulted in a partial molar heat capacity of SiO_2 very similar to the molar C_p° of silica glass (figure 5). Since the curves for \bar{C}_p and C_p°

figure 5 about here

vs. T cross twice and are nearly coincident in the temperature range of

interest, the partial molar heat capacity of SiO_2 is assumed to be equal to the molar heat capacity of silica glass (Kelley, 1960). Re-calculation of the partial molar heat contents of Al_2O_3 , FeO , MgO , CaO , Na_2O and K_2O results in the coefficients given in table 5 and the partial molar heat capacities plotted in figures 5, 6 and 7. In the above calculations the partial molar heat contents of MnO and Fe_2O_3 , present in small amounts in some glasses were assumed to be equal to those of the solid oxides.

table 5, figures 6 and 7 about here

Referring to figures 6 and 7 it is not surprising that the partial molar heat capacities are generally greater than the molar heat capacities of the corresponding crystalline oxides. If physical significance may be attached to these trends then the higher heat capacity of the oxides dissolved in glass must be due to greater freedom of vibration of the monovalent and divalent cations within the relatively disordered, open structure of the glass. The near linearity of the $\bar{C}_{p_{\text{FeO}}}$ vs. T curve, its negative deviation from the hypothetical stoichiometric crystalline FeO curve at low temperatures and the positive curvature of the $\bar{C}_{p_{\text{Na}_2\text{O}}}$ curve elude explanation. Presumably, these anomalies are due to ignoring compositional dependence of the \bar{C}_{p_i} and the small set of data used the calculation. Considering the simplicity of the model, the values derived for the \bar{C}_{p_i} are quite reasonable, if not strictly quantitative.

Alumina behaves in a manner strikingly different from the other oxides. $\bar{C}_{p_{\text{Al}_2\text{O}_3}}$ is significantly less than the heat capacity of corundum over almost the entire temperature range in question. The most likely explanation for this phenomenon is that virtually all Al^{3+} is tetrahedrally coordinated in

most silicate glasses (Riebling, 1968), rather than octahedrally coordinated as in corundum. It thus participates in polymer formation as AlO_4^{5-} tetrahedra linked to SiO_4^{4-} tetrahedra. By analogy with crystalline silicates it is readily shown that the heat capacity of albite, in which Al^{3+} is in tetrahedral coordination, is considerably less than that of a mechanical mixture of α -quartz and jadeite, in which Al^{3+} is in octahedral coordination (Kelley, 1960). Though other factors certainly cannot be ignored, this difference is very nearly equal to the difference between \bar{c}_p and c_p° Al_2O_3 (corundum) over much of the temperature range. At high pressures aluminous silicate glasses, and probably liquids as well, would be expected to experience a progressive increase in heat capacity with increasing pressure as Al^{3+} transforms from tetrahedral to octahedral coordination (Waff, 1975).

The value of the excess partial molar heat capacity, where

$$\bar{c}_p^{XS} = \bar{c}_p - c_p^{\circ},$$

has important implications for the behavior of activity coefficients for components of silicate glasses. It has been shown that \bar{c}_p^{XS} SiO_2 is essentially equal to zero above 298°K. In cases where \bar{c}_p^{XS} differs from zero, solution models must be sufficiently complex to include an excess entropy of mixing.

A consequence of the lack of significant compositional dependence of the \bar{c}_p is that partial molar entropies, $\bar{s}_{T,i} - \bar{s}_{298,i}$, are also constant at a given temperature. This allows simple change of reference temperature for partial molar enthalpies and entropies reported at 298°K or above, as well as estimation of the corresponding molar quantities for silicate glasses. It is suggested that reference temperatures between 298 and about 500°K be

between the partial molar heat capacity of the oxide dissolved in a glass and molar heat capacity of the crystalline oxide is zero without introducing significant error in the calculated bulk heat capacity of the glass. Where data exist for more than one polymorph of a component, that with the greatest molar volume should be used (e.g. anatase rather than rutile for TiO_2). The solid oxide data are included in equation (3) or (4) in the same way as the coefficients for the partial molar quantities.

Glasses containing SO_3 or Cl require special treatment. An equal amount of Na is allocated to Cl and the data for NaCl are used. For SO_3 an equivalent amount of Na_2O is assigned to make Na_2SO_4 . Data for the high-temperature form of Na_2SO_4 are employed. The required A, B, C and D coefficients for NaCl, Na_2SO_4 and solid oxides are given by Kelley (1960).

The effect of H_2O content on the heat capacity of a silicate glass cannot at this point be estimated for more than one composition ($\text{NaAlSi}_3\text{O}_8$). The effect on the partial molar heat capacity of $\text{NaAlSi}_3\text{O}_8$ is insignificant in the system $\text{NaAlSi}_3\text{O}_8 - \text{H}_2\text{O}$ for mole fractions of H_2O less than 0.5 (Burnham and Davis, 1974). Here, the partial molar enthalpy of $\text{NaAlSi}_3\text{O}_8$ may be equated with the molar enthalpy of $\text{NaAlSi}_3\text{O}_8$ glass (at $P = 1$ bar) for $X_{\text{H}_2\text{O}}^{\text{melt}} \leq 0.5$. Thus, small amounts of H_2O are not likely to affect the partial molar enthalpies and heat capacities of oxide components significantly. Burnham and Davis' (1974) partial molar heat capacity of H_2O may probably be considered to apply to other silicate systems where H_2O is a minor component.

In order to convert calculated enthalpies and heat capacities to a per-gram basis it is necessary to know the mass of one mole of glass. In this study the mean molecular weight of a glass is taken as

$$\sum X_i M_i$$

the oxide component i .

where M_i is the gram formula weight of i . This quantity gives no indication of the mean mass of polymer groups in a melt but is merely a device for putting experimental data for a variety of compositions on a molar basis. Enthalpies calculated from the partial molar enthalpies and appropriate solid oxide data agree very well with the actual values. Similarly, derived heat capacity data are nearly concordant. As a measure of the ability of the calculations to reproduce experimental data, the quantity

$$100 \times \frac{\text{calculated enthalpy} - \text{measured enthalpy}}{\text{measured enthalpy}} \quad (5)$$

is plotted as a function of T in figure 8 for each glass studied here.

figure 8 about here

The good agreement between calculated and measured enthalpies and heat capacities confirms the hypothesis that the partial molar enthalpies and heat capacities are essentially constant with respect to composition at a given temperature over the range of compositions investigated. That there must be a slight compositional dependence is borne out particularly by the measurements on the FeO-rich glasses, since the differences between calculated and measured heat contents are an order of magnitude greater than the estimated experimental precision allows. The relatively poor fit of composition 4 must be due to undetected experimental error since heat contents of the other rhyolites are well reproduced by calculation.

In table 6 the ability of various sets of data to reproduce the measured enthalpies and derived heat capacities of 29 glasses (excluding compositions 6 and 7, see Appendix) is compared. Tabulated are the standard deviations of the quantity in equation (5) and an analogous value for heat capacity as calculated from the solid oxides (β -cristobalite for SiO_2), the data of

Schwiete and Ziegler (1955), Moore and Sharp (1958) and the present study, all corrected for minor components. It will be seen that the partial molar quantities obtained here yield slightly more accurate calculated values, particularly for heat capacity. Were the original data on many of the commercial glasses of higher quality the numbers given in table 6 would no doubt be considerable smaller.

table 6 about here

Heat Capacities of Silicate Liquids

Based on data in the literature (see Appendix) and the measurements reported here, some generalizations can be made concerning the heat capacity of silicate liquids.

Heat capacities of silicates in the supercooled liquid region tend to show only slight or no detectable dependence on temperature. This is commonly observed in systems where the glass C_p reaches a value of $3R$ $\text{cal} \cdot \text{deg}^{-1} \cdot \text{g-atom}^{-1}$ (Haggerty, et al., 1968). No silicate heat capacities have been reported for temperatures much above the liquidus or melting point. Since the degree of polymerization of silicate melts is a function of temperature a temperature-dependent heat capacity seems likely, at least until some limiting degree of depolymerization is reached.

On a gram-atom basis, measured heat capacities of silicate supercooled liquids are not strongly dependent upon bulk composition. Assuming constancy with temperature, the heat capacities of 15 silicate supercooled liquids of $2 \leq \underline{R} \leq 3$ average $6.9 \pm .3$ (1σ) $\text{cal} \cdot \text{deg}^{-1} \cdot \text{g-atom}^{-1}$. There appears to be no simple relation between C_p and the parameter \underline{R} .

Some indication of the behavior of partial molar heat capacities of

oxide components of silicate liquids may be gleaned from the literature on binary silicate-metal oxide systems. Charles (1967) showed from the temperature dependence of the activity of SiO_2 in liquids in the systems Li_2O -, Na_2O - and K_2O - SiO_2 that the partial molar heat of solution of SiO_2 relative to a standard state of SiO_2 liquid is essentially independent of temperature. Similar conclusions were reached by Schuhmann and Ensio (1951) concerning both FeO and SiO_2 for liquids in the system FeO - SiO_2 and by Nicholls and Carmichael (1972) for Al_2O_3 in liquids saturated with corundum in the ternary system Na_2O - Al_2O_3 - SiO_2 . It follows that \bar{C}_{p_i} in these systems must be nearly equal to $C_{p_i(\text{liquid})}^\circ$ over the temperature range studied. Thus, it is likely that essentially constant partial molar heat capacities may be derived for components of supercooled liquids and liquids in a like manner to glasses with the advent of more precise data on additional compositions.

Charles (1969) also noted that in order to explain activity data the partial molar enthalpy of solution of SiO_2 in binary alkali-silicate systems must be a strong function of composition, being endothermic at high and exothermic at low silica concentrations. It is the endothermic nature of this quantity at high silica concentrations that leads to the observed liquid immiscibility. Systematic study of the heats of solution of oxides in silicate melts, whether measured in the glass or liquid state, will require a great many measurements and a solution model which takes into account the compositional dependence of this quantity.

Estimation of T_g and $\Delta C_{p_{T_g}}$

In multicomponent silicate systems the compositional dependence of the glass transition temperature is complex. It is commonly observed that the

glass transition in inorganic substances corresponds to a viscosity of around 10^{13} poise. In a qualitative sense, more viscous compositions (e.g. rhyolites) possess higher T_g 's, as they attain sufficiently high viscosity at higher temperatures. However, the correlation is poor between T_g and activation energy for viscous flow as calculated by the methods of Shaw (1972) or Bottinga and Weill (1972).

Based on the assumptions that

$$\alpha_l \times T_m = k' \quad \text{and} \quad \alpha_l \times T_g = k''$$

where α_l is the coefficient of thermal expansion of the liquid, T_m is the melting or liquidus temperature and k' and k'' are constants, Sakka and MacKenzie (1971) suggested that $T_g/T_m \sim 2/3$ for inorganic glass forming systems. The experimental data of the present study contradict this empirical rule since T_g for rhyolite 5 is much higher than that for the basalt, 1. When coefficients of thermal expansion for the liquids investigated are calculated from the data of Bottinga and Weill (1970) the quantity $\alpha_l \times T_g$ is found to vary by a factor of 2. It is clearly impossible to predict T_g for silicate solutions with accuracy from either of these empirical rules. This applies to the data of Arndt and Häberle (1973) and Vergano et al. (1967) on feldspar glasses and supercooled liquids as well.

An estimate of the glass transformation temperature may be obtained from calculated or experimental values for heat capacity. The limiting value for the heat capacity at constant volume, C_V , of a solid is theoretically equal to $3R \text{ cal. deg.}^{-1} \text{ g-atom}^{-1}$, at which point all vibrational modes are excited. If the harmonic oscillator model is obeyed any further increase in heat capacity can only be brought about by disruption of the structure. As the difference between C_p and C_V for most silicate glasses

is very small* it should be possible to obtain an estimate of T_g from the temperature where C_p is equal to $3R$ cal. deg.⁻¹ g-atom⁻¹. Table 7 gives experimentally determined glass transition temperatures and temperatures (T_{3R}) where the measured $C_p = 3R$. For most compositions $T_g > T_{3R}$. Values of T_g much greater than T_{3R} probably result from the configurational component of the heat capacity of these non-ideal glasses. Since the glass transition takes place over a significant temperature interval, experimental T_g 's do not reflect the onset of the transformation but rather some higher temperature.

table 7 about here

The dependence of T_g on cooling rate in silicates amounts to less than 60°K for a change in cooling rate of three orders of magnitude (Sakka and Mackenzie, 1971). Of the glasses which did not devitrify only the natural glass (3) showed a significant change in heat content at $T < T_g$ after fusion, though in the opposite sense to that expected. Reasons for this have been discussed in a previous section. The determination of T_g from enthalpy measurements is sufficiently imprecise to allow a variation in T_g of many degrees to go undetected. The dependence of T_g on cooling rate is more readily elucidated by volumetric studies.

The difference in heat capacity between supercooled liquid and glass at T_g does not vary greatly among similar materials. Searching for a rule of constancy of this change in heat capacity, Wunderlich (1960) found that

$$C_{p, \text{liquid}} - C_{p, \text{glass}} = \Delta C_{p, T_g} = 2.7 \pm .5 \text{ cal. deg.}^{-1} \text{ mol}^{-1}$$

for glass-forming substances. Here mole refers to one mole of "beads."

A "bead" is defined as the smallest molecular unit whose movements may allow

* $C_p - C_v = \frac{TV\alpha^2}{\beta}$ where V is the molar volume, α the coefficient of thermal expansion and β the compressibility of the substance.

structural rearrangement of the liquid. It was suggested that ΔC_p is effectively independent of composition when this quantity is expressed per mole of "beads" and that oxygen be defined as the "bead" in oxide systems. Accordingly, ΔC_p per oxygen averages $1.1 \pm .4$ (1σ) cal. deg.⁻¹ mole⁻¹ for 8 silicate compositions. From what is known about the polymeric nature of silicate melts (Hess, 1971), the bead concept is clearly a gross oversimplification. Boyer (1973) summarizes relationships between T_g , ΔC_p and thermal expansion for organic high polymers. For these substances $\Delta C_p \times T_g$ is nearly constant. Clearly, this is not the case for the silicate compositions studied here. It is not surprising that ΔC_p should display some constancy in glass-forming silicate solutions, considering that C_p of the glass near T_g is generally about $3R$ cal. deg.⁻¹ g-atom⁻¹ and C_p of the liquid is approximately 6.9 cal. deg.⁻¹ g-atom for compositions of $2 \leq R \leq 3$. Therefore, ΔC_p is not likely to differ greatly from about $.9$ cal. deg.⁻¹ g-atom⁻¹ and will on the average be a bit less ($.7 \pm .3$ (1σ) cal. deg.⁻¹ g-atom⁻¹ for 8 compositions). Simple dependence of ΔC_p upon R is not evident.

Conclusion

three of

Five glasses and their supercooled liquids corresponding in composition to terrestrial igneous rocks and two synthetic FeO-rich glasses have been studied calorimetrically. Glass heat content data can be represented by the standard heat content equation of Maier and Kelley (1932). Supercooled liquid data on the three silica-rich compositions are extensive enough to display some temperature dependence of the heat capacity. A quadratic equation adequately represents the supercooled liquid heat content data. Glass transition temperatures obtained from heat content data increase from

basalt and pantellerite to rhyolite.

The partial molar heat contents and heat capacities of most of the major components of commercial and natural silicate glasses have been obtained from selected published heat content measurements and new data on the FeO-rich compositions. The precision of the data and number of different compositions limit the model to the assumption of compositional independence of the partial molar quantities over the range $0.4 \leq X_{\text{SiO}_2} \leq 0.8$. Despite such a simple model, heat contents and heat capacities of glasses can commonly be predicted to nearly ^{within} the precision of experimental measurements. Partial molar heat capacities of minor oxide components are taken as those of the solids. Partial molar heat capacities presented here will allow change in reference temperature for partial molar enthalpies or entropies measured between 298°K and T_g .

Correlation of glass^{and} liquid data is hampered by meager data on glass transition phenomena and supercooled liquid properties. The near constancy of the heat capacity of supercooled liquid silicates ($2 < R < 3$) on a gram-atom basis suggests little compositional or temperature dependence of partial molar heat capacities in the supercooled liquid region. Data are at present inadequate to allow the compositional dependence of the glass transition temperature or the magnitude of $\Delta C_{p_{T_g}}$ to be determined. Rules for calculating T_g from liquid thermal expansion, liquidus temperature or glass heat capacity fail to accurately predict experimental transition temperatures. Accurate enthalpy data on several more supercooled liquids would probably show that partial molar heat capacities can be obtained in a manner similar to that here advanced for glasses. In addition, the compositional dependence of the glass transition temperature is an important problem which might be

resolved by further systematic experiment of the sort successfully pursued by Arndt and Häberle (1973).

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Appendix: Sources of Heat Content Data and Comments on Composition 3 of This Study

Reviewed here are published heat content measurements of silicate glasses consisting largely of the oxides SiO_2 , Al_2O_3 , MgO , CaO , Na_2O and K_2O . Experimental data were fitted to an equation of the form of equation (1) except where measurements were confined to high temperatures. In the latter case the C term was not included. Glass transition temperatures were estimated by determining the intersection of the glass heat content vs. temperature curve with that portion of the curve where the slope became essentially constant.

Anderson (1946). Thirteen measurements are presented in graphical form for "plate glass" from about 780 to 1340°K. Data below an apparent glass transition at approximately 1070°K were fitted to a quadratic equation, excluding the points at 792 and 962°K. The five determinations above the glass transition suggest an anomalously high, constant heat capacity of the supercooled liquid.

Haggerty et al. (1968). Of the 17 measurements on the "Lillie 1" composition (~ 390 - 1220°K), 10 fall in the glass region ($T_g = 850^\circ\text{K}$). Values for the coefficients, A, B, and C of equation (2) were taken from this work. The D term was corrected to the 298°K reference temperature. A linear equation adequately represents the supercooled liquid data.

Hartmann and Brand (1953, 1954). Data were obtained from Schwiete and Ziegler's (1955) compilation. Reported enthalpies range from 373 to 1573°K but are too widely spaced with respect to temperature and imprecise to accurately define glass transitions. Coefficients of equation (2) were obtained for braunglas, grunglas, tafelglas and wirtschaftsglas to an arbitrary upper limit of 1000°K . Enthalpies at higher temperatures suggest near linear relationships to temperature, implying that these measurements refer to supercooled liquids.

Křivánek and Kříž (1959). Enthalpy measurements are reported for three glasses and supercooled liquids. Data for composition "bílá" cover the range 623 to 1476°K with a transition at about 1020°K . Compositions "hnědá" and "zelená" bear a resemblance to strongly peralkaline igneous rocks. Heat contents for these cover the range 574 - 1517°K ($T_g \sim 990$) and 574 - 1540°K ($T_g \sim 880$), respectively. Enthalpy data were fitted with parabolic equations in the glass region and linear in the supercooled liquid.

Naylor (1945). The enthalpies of $\text{Na}_2\text{Si}_2\text{O}_5$ glass and Na_2SiO_3 and $\text{Na}_2\text{Si}_2\text{O}_5$ liquid were measured. Coefficients for equation (1) were taken from Kelley (1960).

Parmlee and Badger (1934). A few measurements are given on three compositions, all above 1073°K . These data scatter considerably and are not included in the present study.

Schwiete and Ziegler (1955). Presented in this work are data on $\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$,

$K_2O \cdot 2.5SiO_2$, and $Na_2O \cdot CaO \cdot 6SiO_2$. The range 373 to 1273°K is covered for the first glass, which apparently undergoes a transition at about 860°K. Reported enthalpies on the other two compositions range from 373-1573°K, but are too widely spaced with temperature to permit evaluation of glass transition temperatures. Equations of the form of equation (1) were fitted to the reported heat contents.

Tydlitát, et al. (1972). When plotted against temperature, these enthalpy data scatter considerably, especially above 1200°K. Glasses 1, 2, 3 and 6 were found to be suited compositionally for the present work. Reported heat contents were fitted to quadratic equations for those data obtained from temperatures between 875 and 1190°K. The value given for glass 3 at 1164°K was excluded, being obviously too low. This was most likely due to devitrification. Reported heat contents for glass 6 are suspiciously high. No clear glass transitions are defined.

White (1919). Data are presented for several glasses. Coefficients of equation (1) were taken from Kelley (1960) for $CaSiO_3$, $MgSiO_3$, $CaMgSi_2O_6$ and $CaAl_2Si_2O_8$ glasses, valid to 1000°K. Reported heat contents for "andesine" ($Na_2O \cdot CaO \cdot 2Al_2O_3 \cdot 8SiO_2$), "albite" and "microcline" glass were fitted for the coefficients of equation (1). These measurements are valid to 1173, 1173 and 1373°K, respectively. The latter two glasses were prepared by fusion of natural minerals. The compositions of the feldspars used by White are given by Day and Allen (1905).

Glasses Used in Partial Molar Heat Content Calculation

<u>Composition</u>	<u>Investigator</u>
Composition 6	Bacon (this study)
Composition 7	"

Lillie 1	Haggerty, et al. (1968)
$\text{Na}_2\text{Si}_2\text{O}_5$	Naylor (1945)
$\text{K}_2\text{O}\cdot 2.5\text{SiO}_2$	Schwiete and Ziegler (1955)
$\text{Na}_2\text{O}\cdot 3.3\text{SiO}_2$	"
$\text{Na}_2\text{O}\cdot \text{CaO}\cdot 6\text{SiO}_2$	"
CaSiO_3	White (1919)
MgSiO_3	"
$\text{CaMgSi}_2\text{O}_6$	"
$\text{CaAl}_2\text{Si}_2\text{O}_8$	"
Andesine	"
Albite	"
Microcline	"

The relatively

/ slowly cooled glass (3) contained significantly less heat (2.4%) at $T - T_g \sim 100^\circ$ after fusion and quenching (figure 2). At lower temperatures measured enthalpies for composition 3 were indistinguishable ($T - T_g \geq 200^\circ$). On the basis of estimated water loss it was expected that the heat treated glass and vapor would contain about 1% more heat at higher temperatures. If the vapor escaped through a leak in the capsule a loss of at most 1% in heat content could be expected. Since the mass of the sample was not significantly less after the experiments than before, little H_2O or NaCl could have been lost. A decrease in heat content of the heat-treated material was also noted in the supercooled liquid region, suggesting a fundamental change in the structure of the supercooled liquid after prolonged heating at a temperature above its liquidus. Conceivably, the glass originally cooled under stress due to flow and was quenched in a strained state. Heating at temperatures above the glass transition would surely relieve such strain and, thus, possibly contribute to a slight decrease in heat capacity. Removal of OH^- and Cl^- from the melt would lead to an increase in the

number of bridging oxygens. Apparently, the degree of ordering of the liquid was increased, resulting in loss of configurational heat capacity.

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Figures

1. Individual measurements plotted as mean specific heat ($(H_T - H_{300}) / (T - 300)$) in $\text{cal} \cdot \text{g}^{-1} \cdot \text{deg}^{-1}$ for samples 1 and 2. Circles denote measurements made in order of increasing temperature. Squares represent measurements made after heating to 1360°K and quenching. Scale for 1 on right, 2 on left. Curves are obtained by dividing heat contents calculated from equation fit to enthalpy data (table 4) by $T - 300$.
2. Same quantities as in Fig. 1 but for compositions 3, 4 and 5. Scale for 4 is on right, 3 and 5 on left.
3. Same quantities as in Fig. 1 but for compositions 6 and 7. Triangles represent measurements made at low temperature after exceeding 700°K. Scale for 7 is on right, 6 on left.
4. Measured heat content of composition 4 in $\text{cal} \cdot \text{g}^{-1}$ and derived heat capacity in $\text{cal} \cdot \text{g}^{-1} \cdot \text{deg}^{-1}$. Symbols as in Fig. 1.
5. Heavy curves are calculated partial molar heat capacities for SiO_2 and Al_2O_3 , light curves molar heat capacities for silica glass and corundum ($\text{cal} \cdot \text{mol}^{-1} \cdot \text{deg}^{-1}$). The partial molar heat capacity of Al_2O_3 was calculated assuming that $\bar{c}_P^{\text{SiO}_2} = c_P^{\text{SiO}_2(\text{gl})}$.
6. Heavy curves are partial molar heat capacities of CaO, FeO and MgO calculated assuming $\bar{c}_P^{\text{SiO}_2} = c_P^{\text{SiO}_2(\text{gl})}$, light curves c_P° for corresponding solids ($\text{cal} \cdot \text{mol}^{-1} \cdot \text{deg}^{-1}$). The heat capacity of stoichiometric FeO was estimated as that of 1 mole of wustite + 0.053 moles of Fe metal. Scales for CaO and MgO on left, FeO on right.

(Figures Continued)

7. Heavy curves are partial molar heat capacities of Na_2O and K_2O calculated assuming $\bar{C}_p^{\text{SiO}_2} = C_p^{\text{SiO}_2(\text{gl})}$, light line $C_p^{\text{SiO}_2}$ for solid Na_2O ($\text{cal. mol}^{-1} \cdot \text{deg}^{-1}$).
8. Percent difference between measured and calculated enthalpies for the seven glasses investigated. The upper temperature limit of each curve is defined by the operational glass transition temperature, T_g . A positive difference means that the calculated enthalpy is the greater.

Tables

1. Chemical analyses of glasses. Analyses 1-5 by electron microprobe.
Analyses 6 and 7 and FeO in 1-5 by wet chemical techniques.

Composition 1 was prepared from high-alumina basalt (Smith and Carmichael, 1968, No. 187), 2 from andesite (Lowder and Carmichael, 1970, No. 114), 3 from residual glass from pantellerite (Carmichael, 1962, No. 3114G), 4 from pantellerite obsidian (Brown, 1970, No. 121), and 5 from rhyolite obsidian (Carmichael, 1967, No. Cam 66).

*Introduced during glass preparation.

†Includes .20 ZrO₂, .31 Cl, .17 H₂O⁺

††ZrO₂

†††BaO

2. Comparison of National Bureau of Standards data for sapphire 720 with smoothed data obtained in this study.
3. Individual heat content values in order of measurement. Temperature is reported in degrees K and heat content in cal·g⁻¹.

*Sample previously heated at 1360 ± 10°K, cooled in calorimeter or by removal from furnace.

†Erroneous value, probably due to crystallization.

4. Coefficients of equation (1) for glass and supercooled liquid data of table 3 corrected to the 298°K reference state ($H_T - H_{298}$) (cal·g⁻¹).
Temperature range based on glass transition, maximum temperature attained in furnace or last reproducible run. $\Delta C_{p,T_g}$ calculated by extrapolating experimental curves to T_g.
5. Coefficients of equation (1) for partial molar heat contents (cal·mol⁻¹).
Values for SiO₂ are those for silica glass (Kelley, 1960).

6. Standard deviation of percent difference between calculated and measured heat contents and heat capacities for 29 glasses using solid oxide data, the data of Schwiete and Ziegler (1955), Moore and Sharp (1958) and this work.
7. Operational glass transition temperatures compared with temperatures where $C_p = 3R \text{ cal}\cdot\text{g}\cdot\text{atom}^{-1} \text{ deg.}^{-1}$.

Table 1

	1	2	3	4	5	6	7
SiO ₂	51.9	57.7	69.6	70.5	73.5	44.71	39.37
TiO ₂	.90	.93	.62	.32	.30	---	---
Al ₂ O ₃	18.0	15.5	10.7	7.77	13.6	---	11.80
Fe ₂ O ₃	.79	1.02	2.14	1.13	.07	4.07	1.61
FeO	6.84	8.07	4.24	7.21	1.67	35.50	41.39
MnO	.13	.18	.27	.24	.02	.04	.03
MgO	7.53	3.50	.23	.03	.32	---	---
CaO	9.11	6.91	.37	.35	1.24	---	5.99
Na ₂ O	3.35	3.99	6.47	6.88	4.04	15.53	---
K ₂ O	.64	1.29	4.66	4.15	4.27	.03	---
P ₂ O ₅	.19	.26	.02	.01	.03	---	---
MoO ₃ [*]	.11	.24	---	.35	.02	---	---
Other	---	---	.61†	.22††	.11†††	---	---
Total	99.5	99.6	99.9	99.2	99.1	99.88	100.19

Table 2

T°K	$H_T - H_{300}$ This study cal. mol ⁻¹	$H_T - H_{300}$ NBS	% Devia- tion	C_p This study cal. deg. ⁻¹ mol ⁻¹	C_p NBS	% Devia- tion
400	2082.6	2114.7	-1.52	23.02	22.96	+ .26
500	4523.7	4540.9	-.38	25.56	25.36	+ .79
600	7160.7	7159.4	+ .02	27.07	26.90	+ .63
700	9922.3	9904.6	+ .18	28.10	27.94	+ .57
800	12773	12739	+ .27	28.87	28.71	+ .56
900	15692	15642	+ .32	29.50	29.32	+ .61
1000	18669	18599	+ .38	30.03	29.82	+ .70
1100	21696	21602	+ .43	30.49	30.26	+ .76
1200	24767	24650	+ .47	30.92	30.65	+ .88
1300	27879	27733	+ .53	31.32	31.01	+1.00
1400	31029	30850	+ .58	31.69	31.33	+1.15

Table 3

1		2		3		4		5		6		7	
T	H _T -H ₃₀₀	T	H _T -H ₃₀₀	T	H _T -H ₃₀₀	T	H _T -H ₃₀₀	T	H _T -H ₃₀₀	T	H _T -H ₃₀₀	T	H _T -H ₃₀₀
400.5	19.49	382.2	15.95	400.7	20.25	408.9	21.32	402.8	20.88	415.8	22.51	354.9	9.46
395.7	18.17	381.7	15.82	397.2	19.37	408.6	21.29	400.8	20.57	415.9	22.46	352.7	9.26
490.2	39.53	488.1	38.88	488.0	39.68	510.4	44.48	493.8	41.26	443.6	28.22	352.6	9.16
498.2	41.38	483.5	38.10	497.0	41.72	510.3	44.02	492.5	41.01	441.7	27.99	402.2	18.10
623.5	72.30	605.5	66.94	597.7	66.49	596.7	65.24	607.8	69.49	480.3	36.08	401.3	18.19
621.2	70.93	607.0	67.85	607.3	68.62	695.0	89.67	603.9	68.69	476.4	35.37	400.2	18.01
622.9	71.75	666.9	82.59	713.8	96.62	701.6	91.65	711.3	96.56	523.3	45.52	450.0	27.54
684.6	87.73	653.6	78.68	701.8	93.88	811.4	121.46	710.0	96.39	522.3	45.44	451.7	27.91
679.1	86.32	662.7	82.16	805.5	121.44	815.3	122.49	797.3	120.10	575.8	57.67	503.7	38.33
768.1	109.48	722.3	96.44	807.9	123.05	907.5	150.90	812.5	123.60	575.8	57.73	503.3	38.40
775.0	111.13	734.9	100.62	901.6	151.80	915.2	152.81	920.0	153.97	618.0	67.89	551.4	48.57
861.2	134.92	806.6	119.28	903.0	151.92	999.8	179.36	909.8	151.97	620.8	68.35	551.1	48.53
850.3	131.85	806.9	118.84	1008.2	183.21	996.7	178.62	1028.0	184.79	479.8	36.20	598.0	58.81
952.4	161.97	906.6	146.70	996.0	178.67	1097.0	209.13	1012.0	179.71	479.2	35.93	595.0	58.43
959.8	163.81	895.6	143.11	1162.4	231.64	1227.9	251.60	1106.3	208.40	673.6	81.52	450.2	27.63
1055.9	196.16	1023.8	183.81	1182.3	237.51	1234.8	255.02	1098.2	206.42	673.0	81.23	651.6	71.09
1047.5†	185.74	1012.1	179.19	1352.8	289.52	1358.6	295.00	1249.4	256.13	721.1†	94.22	651.5	71.11
691.8*	89.28	1125.4†	206.04	1360.0	288.87	1351.0	292.01	1268.8	262.16	720.1†	94.93	702.0	82.81
704.1*	92.86	1008.3†	172.34	1356.8	288.40	489.2*	39.48	1340.5	284.79	718.7†	94.16	702.4	82.85
		699.8*	91.54	701.3*	91.70	485.4*	38.53	1361.5	291.55	479.2†	35.20	447.4	26.89
		700.2*	90.90	702.1*	91.41	599.6*	65.80	497.2*	41.86	1074.4†	206.94	752.2	94.11
				586.2*	63.55	612.0*	68.38	490.3*	40.92	1074.7†	207.09	751.5	94.18
				594.1*	65.80			620.6*	72.94	478.8†	35.08	800.0	105.99
				701.9*	91.98			610.5*	70.51	1157.9†	238.33	799.0	105.82
				1015.6	181.80			610.1*	70.77	1154.7†	237.11	450.5	27.64
								603.9*	68.38	479.6†	33.35	851.8	119.94
								636.1*	77.17			853.0	119.94
								691.3*	90.64			902.0	136.03
								700.7*	93.45			903.2	136.61
												450.5	27.56
												960.4†	153.07
												958.2†	150.51
												451.6	27.77

00104306799

Table 4

		A	B × 10 ⁵	C × 10 ⁻³	D	Temperature Range °K	$\Delta C_{p_{T_g}}$ cal. deg. ⁻¹ g ⁻¹
1	glass	.2572	1.462	9.009	-108.2	298-833	
1	liquid	.2938	-	-	-117.7	833-1055	.0252
2	glass	.2205	3.535	5.921	-88.7	298-910	
3	glass	.1887	6.295	3.950	-75.1	298-830	
3	liquid	.3220	-.849	-	-131.8	830-1360	(.0206)
4	glass	.2302	2.907	6.638	-93.5	298-779	
4	liquid	.2568	2.774	-	-104.8	779-1360	.0439
5	glass	.2458	2.464	7.625	-101.0	298-1081	
5	liquid	.4527	-5.219	-	-227.8	1081-1360	.0474
6	glass	.1384	8.472	.569	-50.7	298-700	
7	glass	.1864	3.977	4.416	-73.9	298-750	

00004306800

Table 5

	A	$B \times 10^3$	$C \times 10^{-5}$	D
SiO_2	13.38	1.84	3.45	-5310
Al_2O_3	26.42	-.03	6.21	-9955
FeO	7.01	5.41	.28	-2665
MgO	9.64	2.04	1.57	-3581
CaO	10.36	2.98	2.38	-4151
Na_2O	6.44	13.00	-3.99	-1739
K_2O	36.18	.36	21.40	-17998

Table 6

T°K	Heat Content				Heat Capacity			
	Oxides	Schwiete & Ziegler	Moore & Sharp	This Study	Oxides	Schwiete & Ziegler	Moore & Sharp	This Study
400	5.01	4.37	4.42	4.56	12.82	3.65	3.59	3.28
500	6.31	3.29	3.49	3.16	6.31	4.41	4.87	3.31
600	5.31	3.22	3.65	2.75	4.25	3.99	4.86	2.93
700	4.15	3.10	3.71	2.48	5.59	3.33	4.05	2.41
800	3.47	2.86	3.53	2.20	7.89	3.32	3.23	2.28
900	3.58	2.61	3.18	1.93	10.20	4.14	3.31	2.77
1000	4.33	2.50	2.79	1.76	12.34	5.40	4.52	3.63

Table 7

Composition	Investigator	T _g	T _{3R}
$\text{Na}_2\text{Si}_2\text{O}_5$	Naylor (1945)	650	635
6	This study	~700	636
7	"	~750	725
4	"	779	986
3	"	830	795
1	"	833	994
Lillie 1	Haggerty, et al. (1968)	850	772
$\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$	Schwiete & Ziegler (1955)	860	689
Zelena	Křivánek & Kříž (1959)	880	805
2	This study	910?	896
Hneda	Křivánek & Kříž (1959)	990	675
Bila	"	1020	782
Albite	White (1919)	1036*	965
Andesine	"	1038*	932
Plate glass	Anderson (1946)	1070	718
5	This study	1081	1006
$\text{CaAl}_2\text{Si}_2\text{O}_8$	White (1919)	1086*	1066
Microcline	"	1178*	1050

*Taken from Arndt and Häberle (1973).

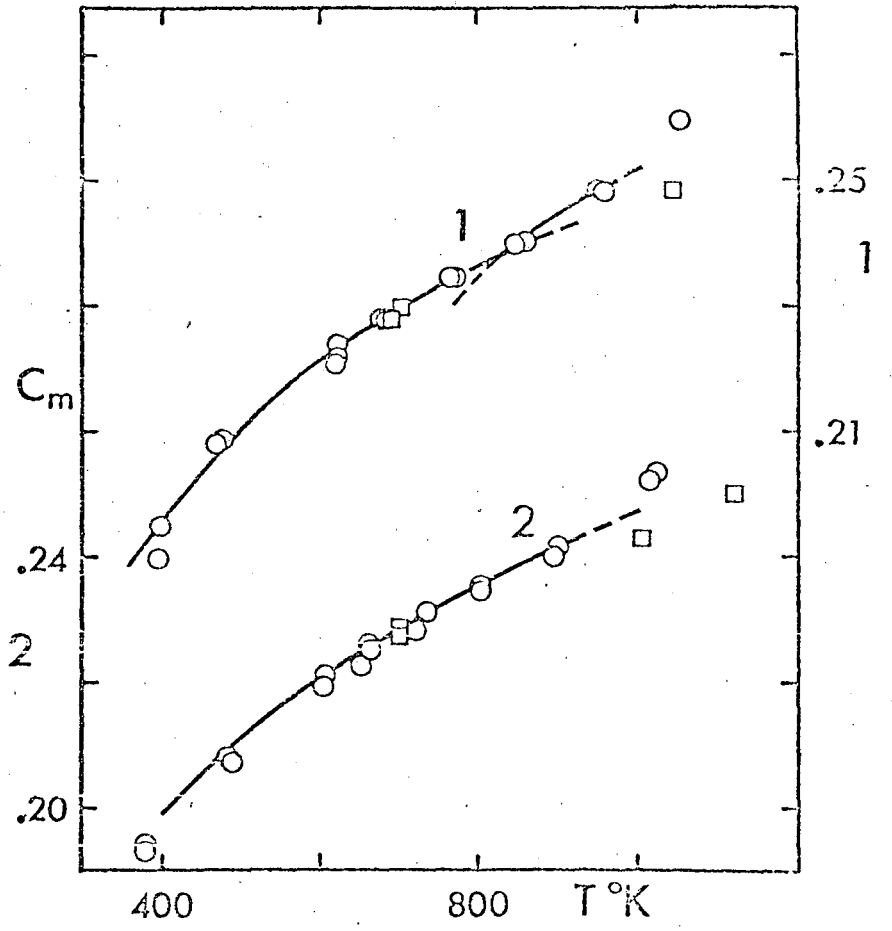


Fig. 1

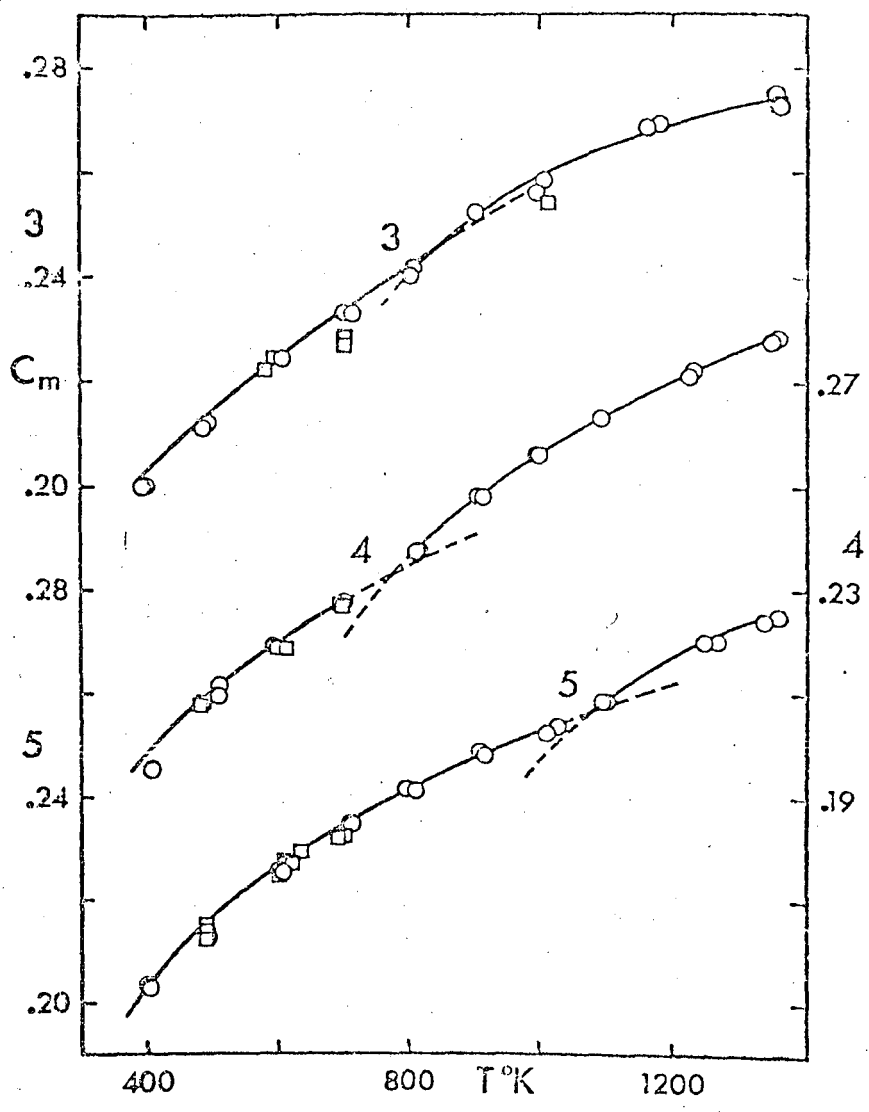


Fig. 2

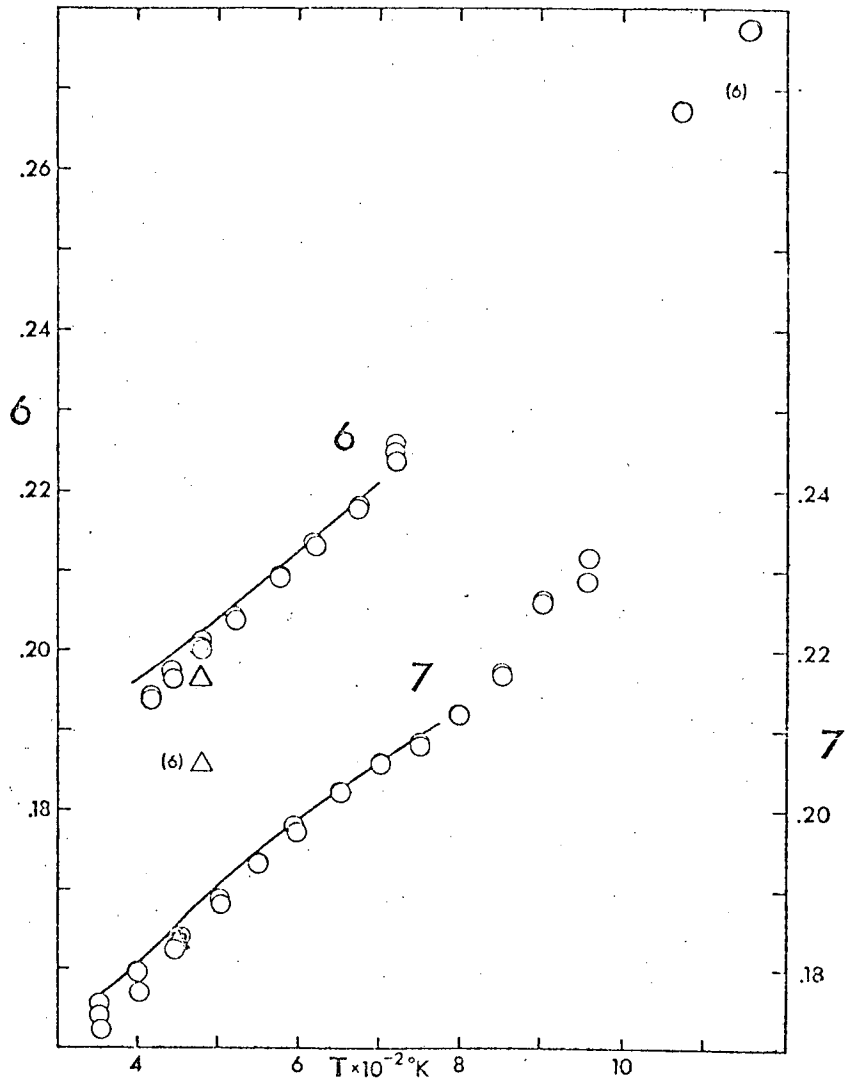


Fig. 3

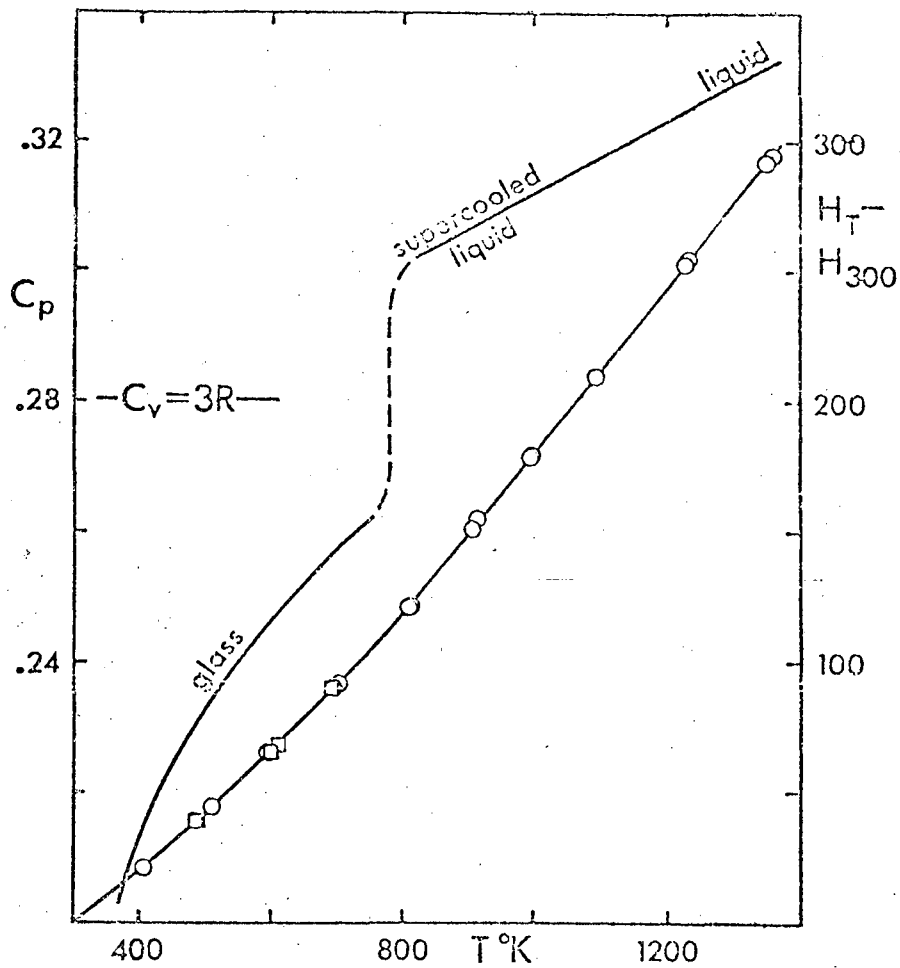


Fig. 4

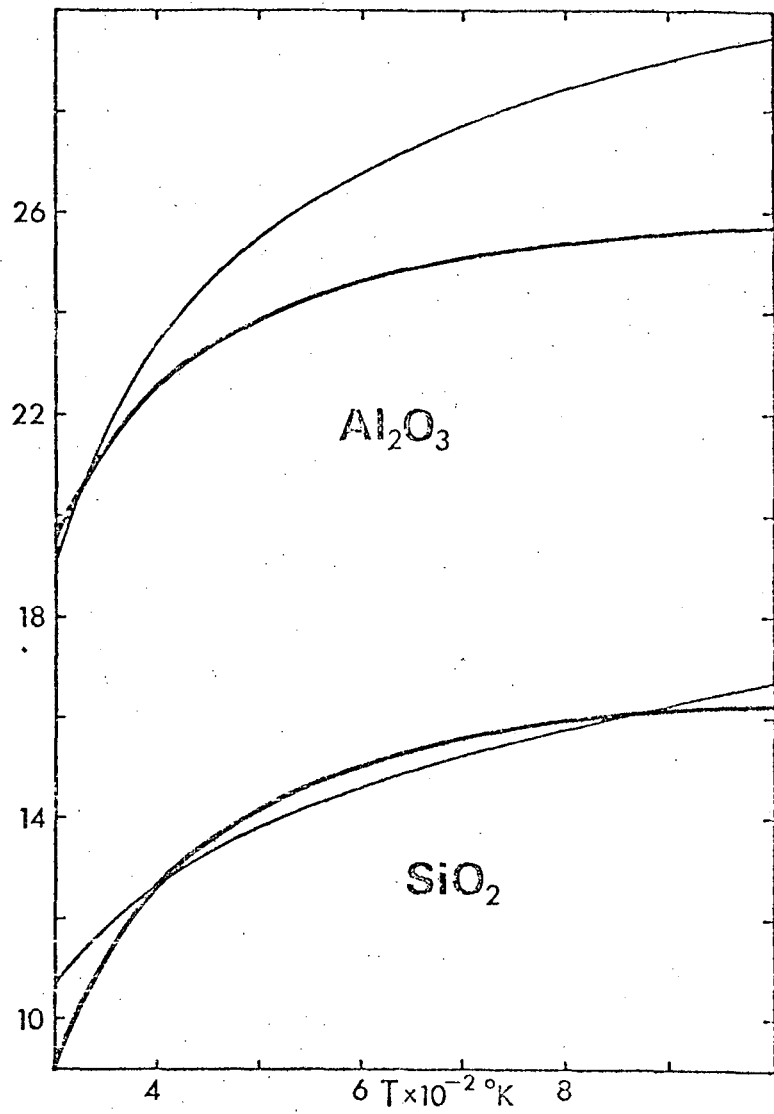


Fig. 5

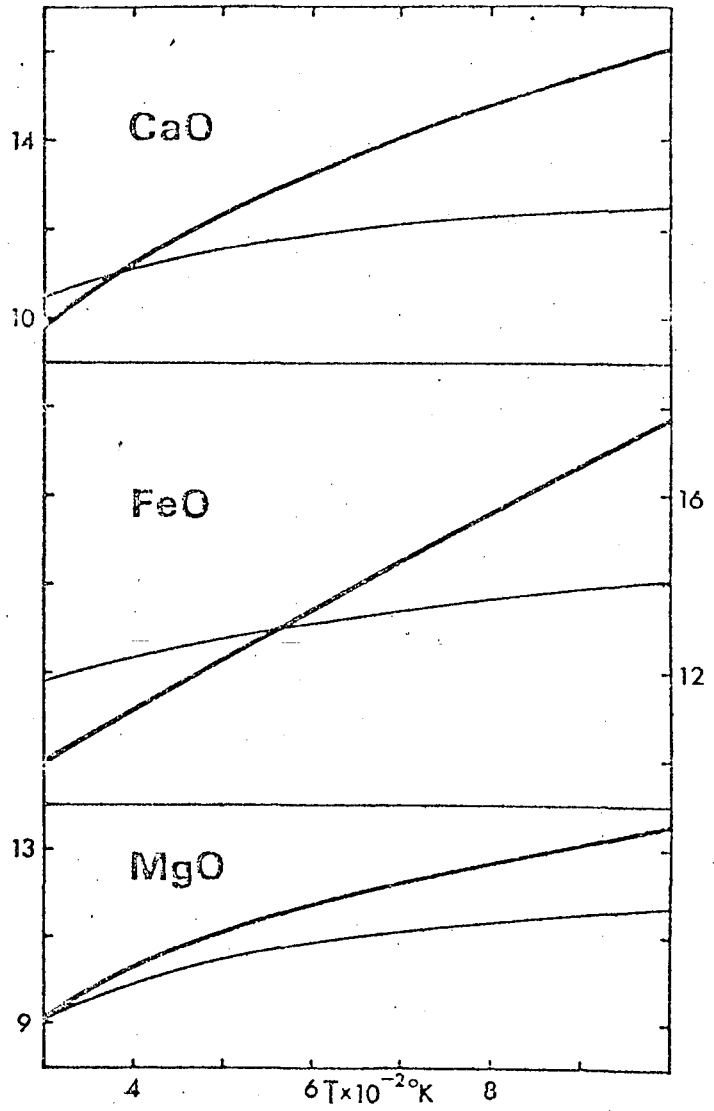


Fig. 6

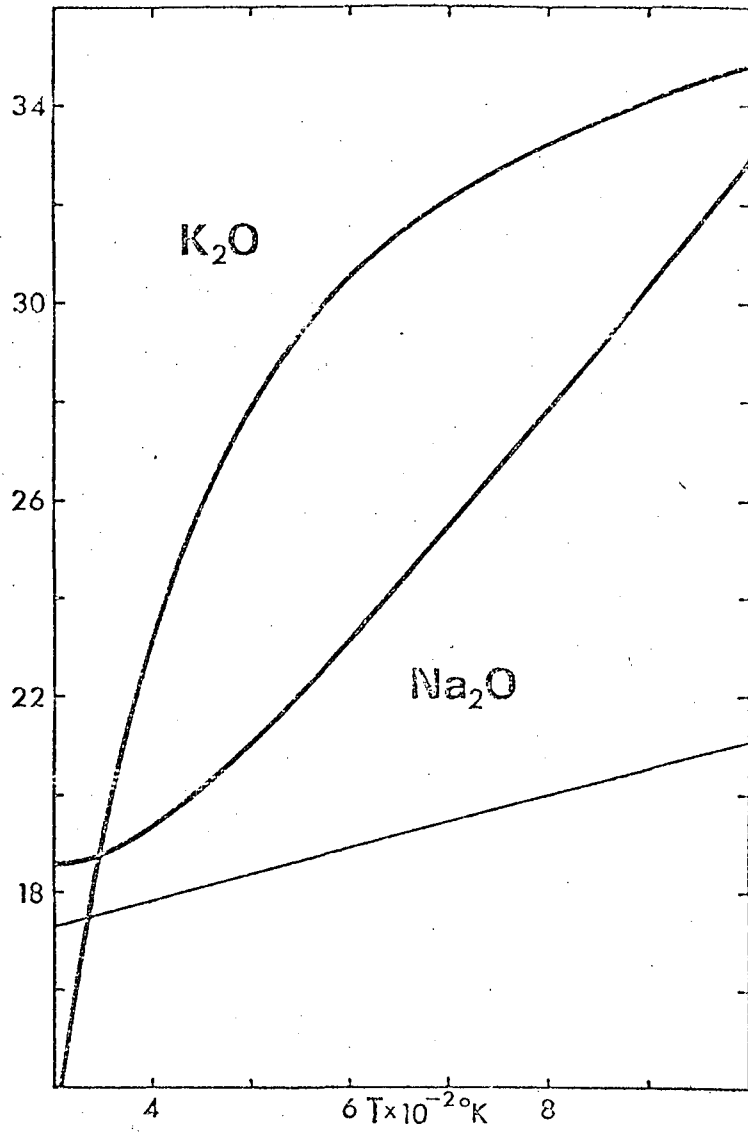


Fig. 7

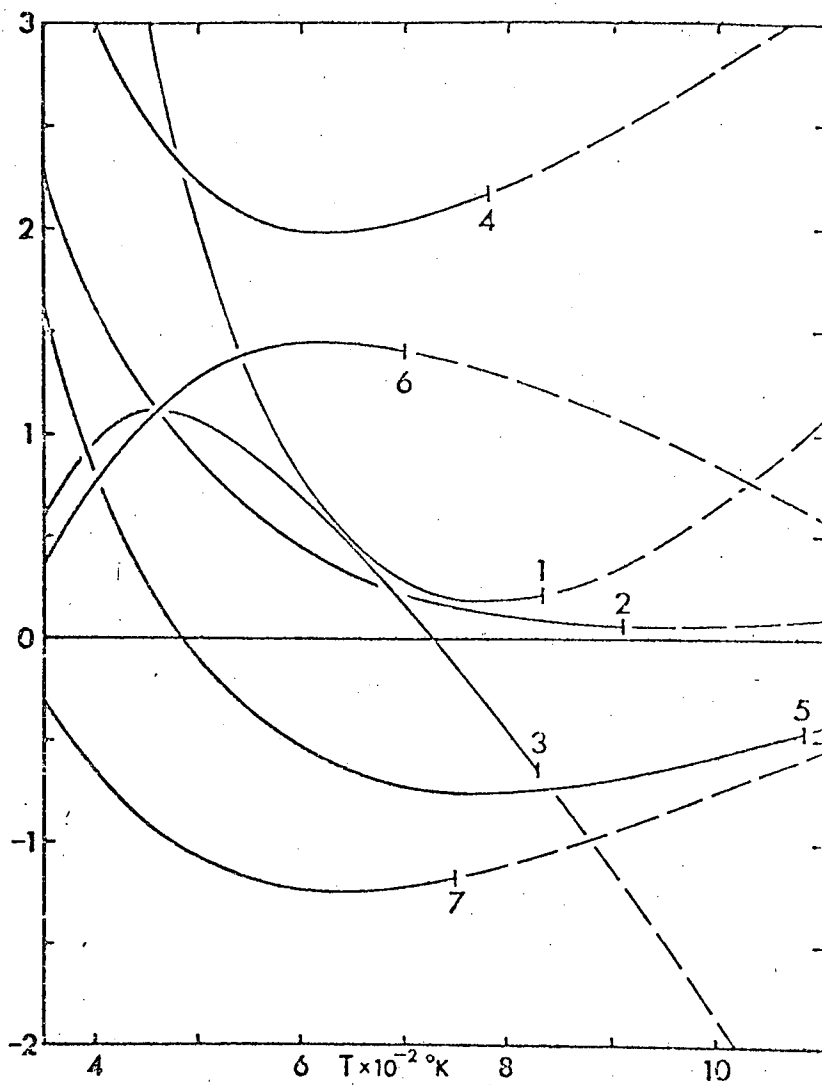


Fig. 8

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