STRUCTURE AND VISCOSITY OF MOLTEN BORATES AND PHOSPHATES

by

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INTRODUCTION

PURPOSE

The primary purpose of this study was to compare experimental viscosity results, as a function of composition, with the theory of Toop and Samis (1,2) of the structure of liquid silicates. The secondary objectives were to construct and operate a high-temperature viscometer suitable for corrosive oxide melts, and to measure the viscosity of some liquid borates and phosphates, since few values for such systems were available in the literature.

A viscometer of the Margules type was constructed and found, together with the furnace, to operate in a satisfactory manner. Viscosity was measured in several binary oxide systems. Results appeared to be in agreement with the predictions of Toop and Samis' theory.

ACKNOWLEDGEMENTS

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THEORETICAL CONSIDERATIONS

BACKGROUND

Accurate knowledge of the structure of liquid slags is of considerable importance if a better understanding of the function of slags in process metallurgy is to be realized. A structural model is of particular importance in the interpretation of physical properties and of slag-metal reactions. In the past, investigations of physical properties and structure have often been concerned with complex melts similar in composition to those encountered in metallurgical slags, or in glass-making processes. But it is evident that until the structures of binary melts are understood, little true progress is possible by consideration of multi-component, technologically important systems.

The slags used in metallurgical practice are, virtually without exception, mixtures of oxides, as are most inorganic glasses (3,4). In structural terms, the ionic nature of molten oxides has become widely accepted (5); physicochemical evidence includes electrical conductivity, electrolysis, transport numbers, e.m.f., surface tension, viscosity, density, and expansivity (5-12). If one constituent in a binary melt is an acid, or oxygen-accepting, oxide, such as SiO_2, B_2O_3, or P_2O_5, and the second is a basic or oxygen-donating oxide, such as CaO, Na_2O, or PbO, the nature of the melt is different for different compositions. The basic oxides ionize in the liquid to form metal cations and oxygen anions, but boron and phosphorus, like silicon, are complexing agents. In combination

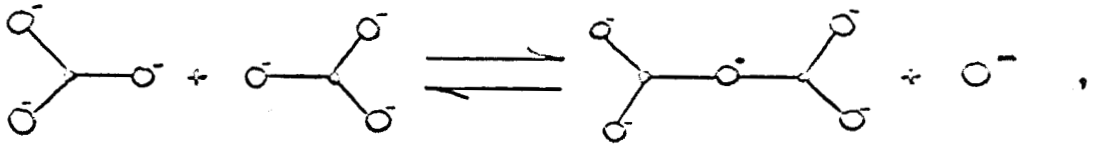
with oxygen, they form chain, ring, or branched anions of varying sizes, depending upon the proportions of the constituents.

Reorganization readily occurs in borate (13,14) and phosphate (11,15,16) melts, making possible a dynamic equilibrium among various possible structures. Similarly, organic polyesters readily undergo reorganization in the liquid. It is thus natural to regard borate, phosphate, or silicate melts as liquid polymers. The degree of polymerization in silicate melts, as a function of composition, has been characterized by Toop and Samis (1,2) in terms of thermodynamic equilibrium in the melt between singly-bonded oxygen (O^-), doubly-bonded oxygen (O^o), and free oxygen anions ($O^=$). This result has been extended to borate and phosphate melts (17), in which complex anions similar to those found in silicate melts are known to exist (16,18-20).

It is to be expected that as the anion size (degree of polymerization) of such melts changes, the viscosity will also change; available experimental evidence generally confirms this (7,11,14). It was the primary purpose of this work to compare experimental viscosity versus composition data for binary borate and phosphate systems with predicted structure versus composition curves derived from the model of Toop and Samis (1,2).

SUMMARY OF THE THEORY OF TOOP AND SAMIS

It may be valuable to elaborate briefly on some aspects of Toop and Samis' theory. As mentioned above, equilibrium among the ionic species in the melt may be described in terms of the oxygen atoms, since neither the metal cations (Na^+, Pb^{++}) nor the "acid atoms" (B^{+3}, P^{+5}) undergo changes. For the case of two BO_3^{-3} ions reacting to form a single $B_2O_5^{-4}$ ion, one can indicate the reaction schematically as



or, for the oxygen ions alone, one can write $6\ O^- \rightleftharpoons 4\ O^- + O^\circ + O^=$. This reduces to

$$2\ O^- \rightleftharpoons O^\circ + O^= \quad . \qquad (1)$$

For the reaction of Equation 1, one can also write an equilibrium constant,

$$k = (O^\circ)\ (O^=)\ /\ (O^-)^2 \quad .$$

An equation relating k to ΔG° (of any compound in the relevant phase diagram) has been given by Toop and Samis (1,2); with ΔG° data, therefore, one can obtain values of k. Now Toop and Samis have illustrated that for silicates, this constant is generally non-zero. But on the basis of the ΔG° data which are available, it can be suggested that for borates and phosphates of the type investigated, the value of k is generally so small (e.g. 1×10^{-7}) as to be essentially zero.

The consequences of a zero value of k for Equation 1 must be emphasized. A zero value of k means that Equation 1 will go to virtual completion to the left as written, thus implying that in borate and phosphate systems, the ions present will be small as the availability of free oxygen anions ($O^{=}$) will permit. If the equilibrium constant is then postulated to be identically zero, one can readily construct diagrams such as Figures 1 and 2, which show the amounts of each oxygen atom present at various values of the mole fraction of acid oxide (N_B or N_P). It may be noted that these diagrams differ somewhat from those drawn by Henrikson (17) for borate and phosphate systems with a non-zero value of k. Such figures enable one to relate the mole fraction N_B or N_P to the composition parameter of Toop and Samis, which is the (O^-) fraction: $O^- /(O^- + O^o + B^{+3})$ or $O^- /(O^- + O^o + P^{+5})$.

Toop and Samis have postulated (1,2) that silicate melts should exhibit a "melt line", which passes through the envelope of possible ions on a graph of the number of silicon atoms per ion (written as Si* in this paper) versus composition, $O^- /(O^- + O^o + Si^{+4})$. Such a graph, for borates, is reproduced here as Figure 3. The points in this diagram represent individual ions: chains, single rings, and single rings joined at one, two, or more places. The position of the dashed line is hypothetical. However, one would expect from entropy considera- that this line would tend toward the lower limit of the envelope. Entropy is maximized by a maximum number of particles,

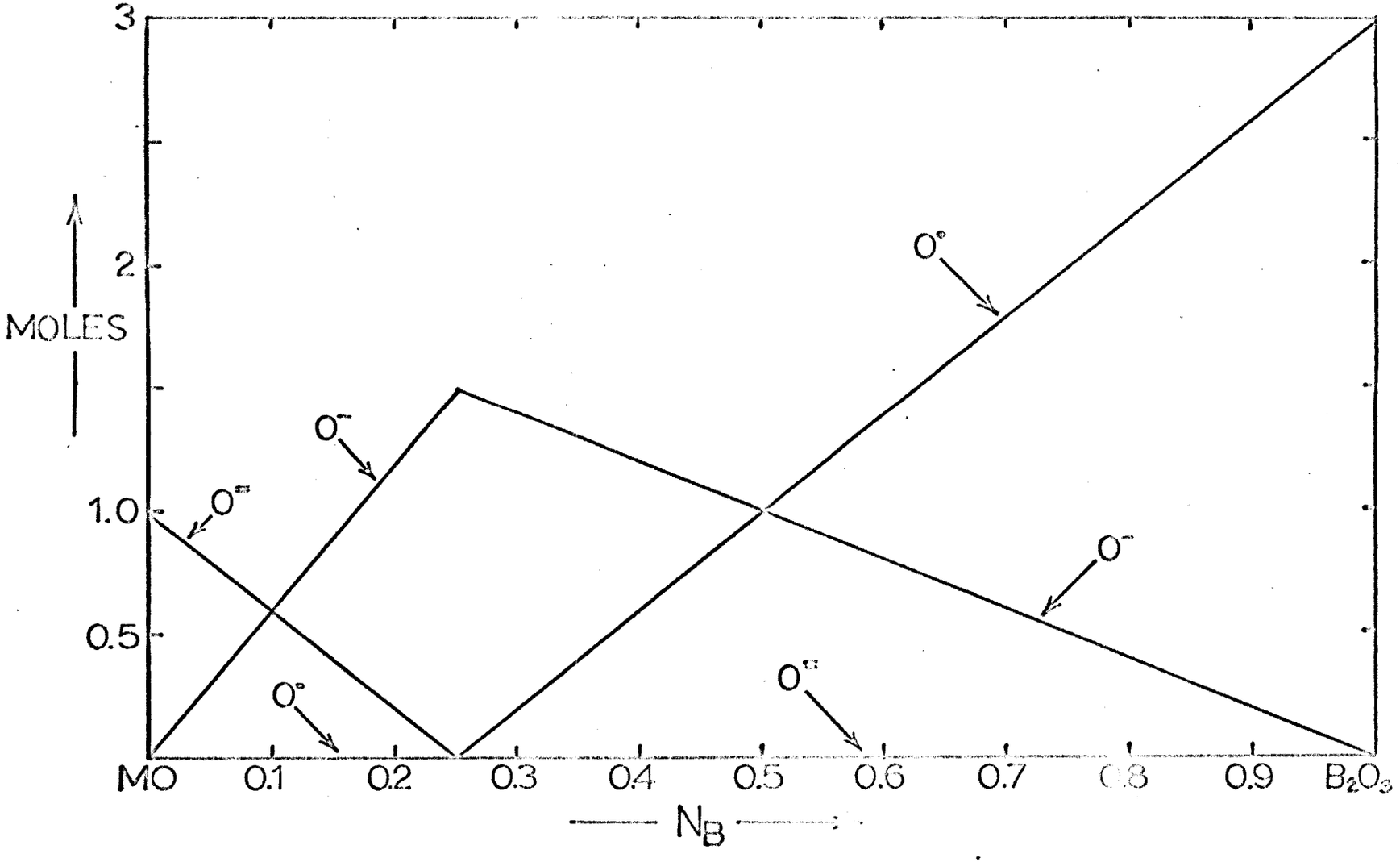


FIGURE 1. NUMBER OF MOLES OF OXYGEN SPECIES IN A BORATE SYSTEM WITH k=0.

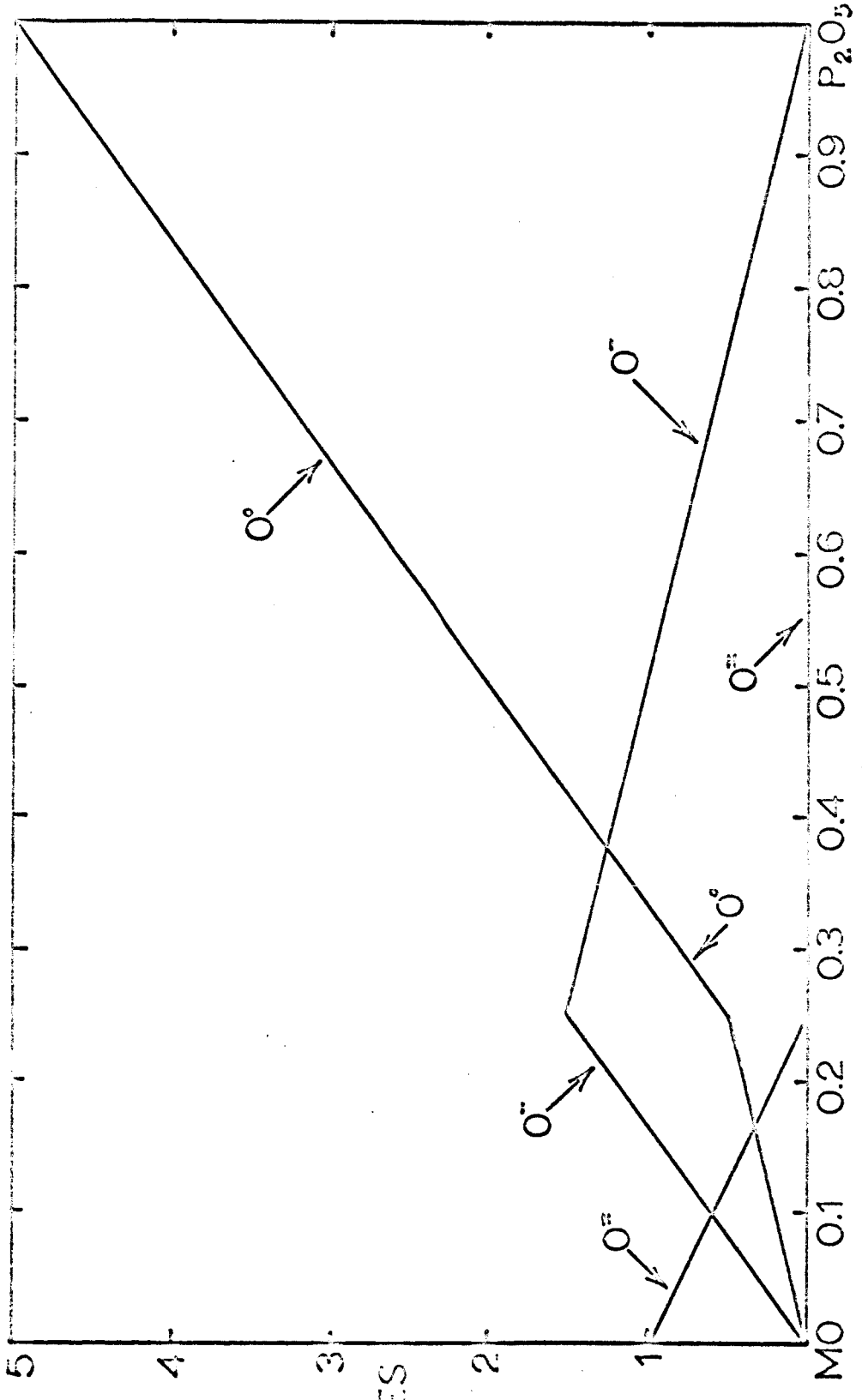


FIGURE 2. NUMBER OF MOLES OF OXYGEN SPECIES IN A PHOSPHATE SYSTEM WITH K=0.

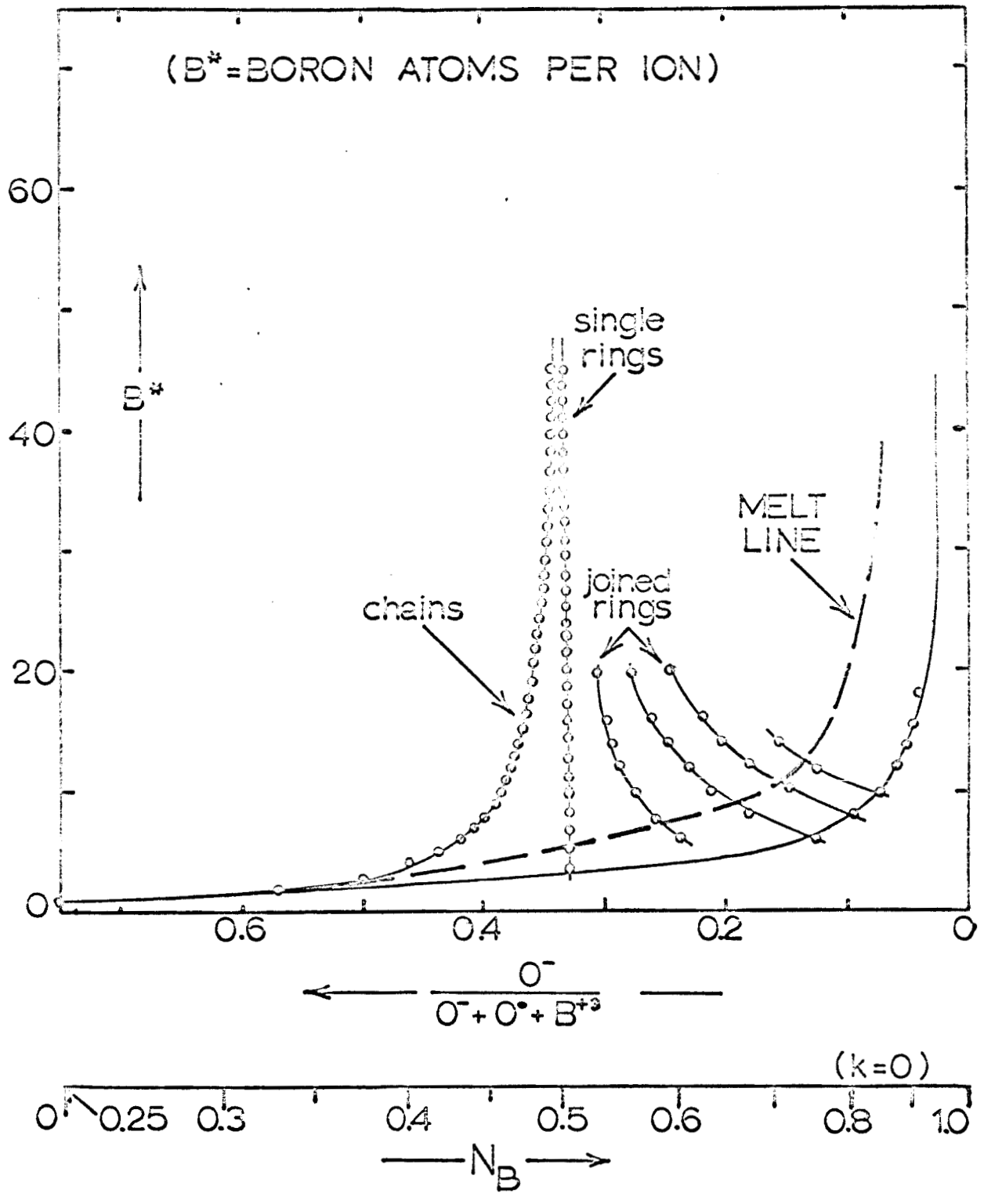


FIGURE 3. BORON ATOMS PER ION VERSUS COMPOSITION.

i.e. many small ions rather than a few large ones at a given composition. Therefore, the melt line has been given the approximate shape of the lower envelope limit.

One would intuitively expect the viscosity of a complex silicate, borate, or phosphate melt to be a strong function of ion size. Size is of course not the only factor, but it should exert a considerable influence. If this is so, a graph of viscosity versus composition should bear a strong resemblance to the melt line in a graph of ion size (e.g. B^*) versus composition. Thus, the theory of Toop and Samis predicts the general shape of the viscosity versus composition curve, and this shape is given by the melt line in Figure 3 for the case of a borate melt.

DERIVATION OF THE VISCOSITY EQUATION

Newton's analysis of viscosity, based upon concentric cylinders, concluded that the shear stress developed in a fluid is proportional to the rate of shear at any point (21) or that

$$\tau = k\ (-\ dv/dr) \quad ,$$

where τ = shear stress and k = coefficient of proportionality. If the coefficient of proportionality is a constant for a given fluid, the fluid is called Newtonian. The coefficient is then written as η, often referred to as simply the viscosity, and usually measured in units of dyne-sec./cm.^{2}, or poises. The viscosity relation becomes, for this case,

$$\tau = \eta\,(-\ dv/dr) = \eta\,(-r\ d\omega/dr) \quad , \qquad (2)$$

where ω = angular velocity in the fluid.

The apparatus geometry which was adopted for this work was essentially that Margules (22) and others (see Experimental Procedure). The apparatus consisted of an inner cylinder, or bob, rotating with angular velocity Ω in a concentric cylinder, or crucible (see Figure 4). For this geometry, it may readily be shown (neglecting end effects) that the stress τ is related to the torque T at any radius r by the relation

$$\tau = T\ /\ 2\pi\ r^2\ h \quad , \qquad (3)$$

where h = depth of immersion. Substituting Equation 3 into Equation 2 leads to the differential equation

$$d\omega = -\ (T\ /\ 2\pi\ h\eta)\ dr/r^3 \quad . \qquad (4)$$

For the condition that there be no slippage at the cylindrical

surfaces, $\omega = 0$ at the crucible wall and $\omega = \Omega$ at the bob surface; thus 0 and Ω are the integration limits of $d\omega$. The radius r varies from the crucible radius R_C to the bob radius R_B. Therefore Equation 4 becomes

$$\int_0^{\Omega} d\omega = - T / 2\pi h\eta \int_{R_C}^{R_B} dr/r^3 \quad ,$$

which may be integrated and solved for η to give the well-known Margules equation,

$$\eta = \frac{T}{4\pi h \Omega} \left(1/R_B^2 - 1/R_C^2 \right) \quad . \qquad (5)$$

Equation 5 may be expressed with a constant which includes the experimental geometry, as

$$\eta = K \left(T / h\Omega \right) \quad , \qquad (6)$$

where

$$K = \frac{1}{4\pi} \left(1/ R_B^2 - 1/ R_C^2 \right) \quad . \qquad (7)$$

The above relations neglect end effects, which arise from the shear developed between the bottom of the bob and the crucible bottom. Such effects increase the total torque produced over that due to h alone, and may be included in Equation 6 as an additional "effective height", h_0. Replacing h by h', where $h' = h + h_0$,

$$\eta = K \left(T /(h+h_0) \Omega \right) = K \left(T / h'\Omega \right) \quad . \qquad (8)$$

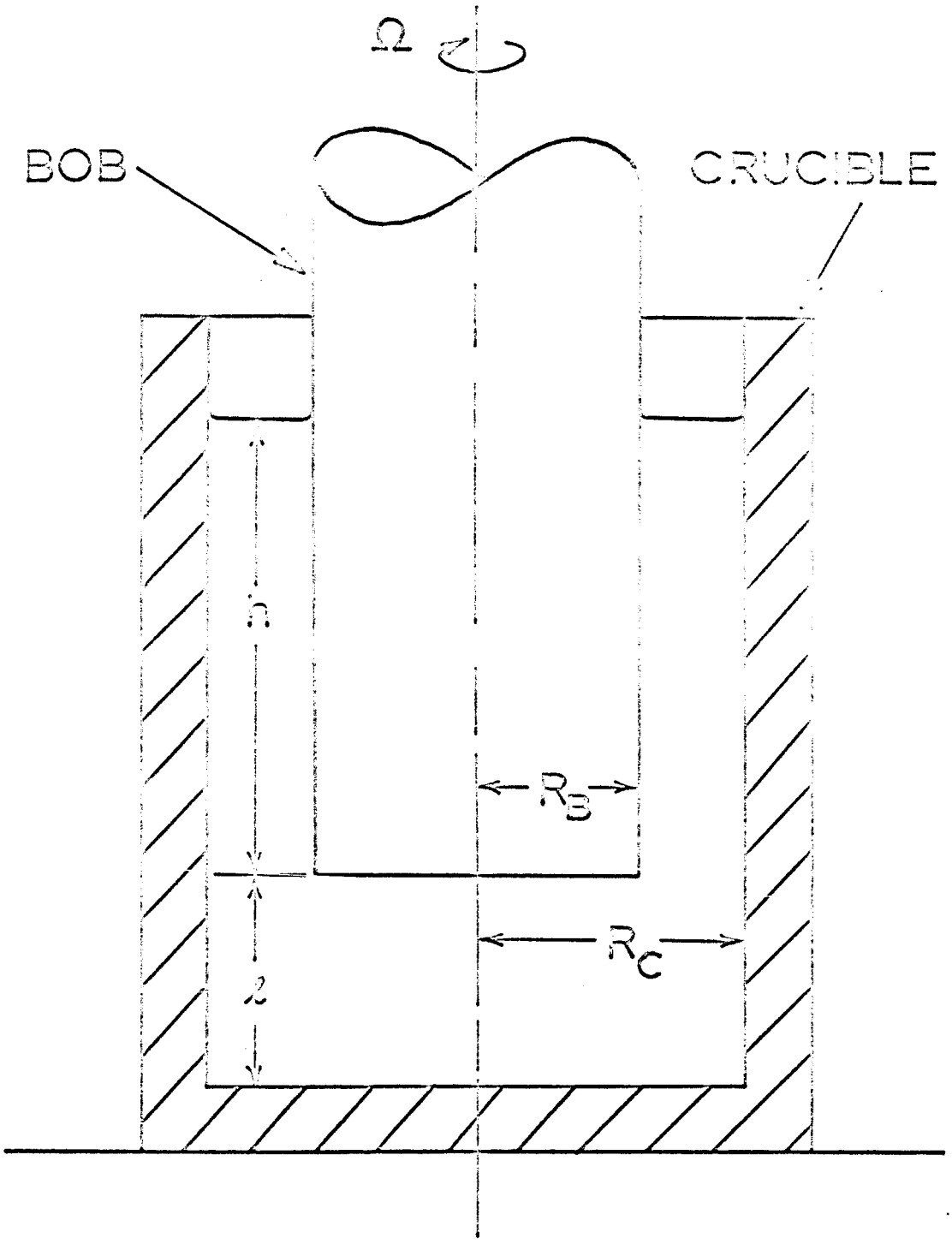


FIGURE 4. SCHEMATIC OF EXPERIMENTAL GEOMETRY.

For h_0 to be a true constant, certain limits must be observed, as pointed out by Lindsley and Fischer (23). This subject is more fully discussed under Experimental Procedure; as explained there, care was taken to accomodate each of Lindsley and Fischer's criteria for constant h_0, thus insuring the validity of Equation 8.

EXPERIMENTAL PROCEDURE

Six binary systems were chosen for investigation: oxides of sodium and lead with B_2O_3, and oxides of sodium, lead, potassium and calcium with P_2O_5. The temperatures and compositions investigated were chosen with reference to published phase diagrams (24); wherever possible, similar values of these variables were selected to allow comparison among binaries. In all cases, temperatures were above the liquidus, but in order to maximize viscosity values, the temperatures were kept as low as possible.

SAMPLE PREPARATION

The mixtures to be melted were prepared in two ways. Either a suitable compound was mixed with the necessary amount of acid oxide (e.g. $Na_2B_4O_7$ and B_2O_3), or the metal carbonate was mixed with the acid oxide (e.g. $PbCO_3$ and B_2O_3). In a few cases, these methods were combined in a single melt. Reagent grade chemicals were used throughout. The majority of these were obtained from the J. T. Baker Co. Some P_2O_5 was obtained from the Allied Chemical Co., and $Pb_3(PO_4)_2$ was obtained from Matheson, Coleman and Bell. Considerable care was taken in calculation of weights and in weighing, and the compositions are believed accurate to ± 0.2 mole %.

The majority of the chemicals used (and some glasses obtained) were hygroscopic to varying degrees. In order to avoid inaccuracies in composition due to weighing errors, as well as water contamination of the melts to be measured, chem-

icals were stored and weighed in a sealed glove box in which P_2O_5 powder was liberally exposed to the air. Accordingly, water pick-up is considered to have been negligible.

Since the volume of crystalline chemicals considerably exceeded the volume of melted glass in most cases, several successive melting runs were required for most compositions. In every case, care was taken that the temperature did not exceed that at which the melt was to be measured. McKinnis and Sutton have suggested (25) that heating viscous glasses above the measurement temperature may significantly affect the viscosity value subsequently observed. This "melting history" concept will be discussed further in the section Discussion of Results.

It has been observed that small amounts of absorbed water may remain in borate (6,26) and phosphate (11) melts, even at high temperatures, unless a vacuum is utilized. This retained water can significantly affect viscosity. Accordingly, most melts (particularly those with large N_B or N_P) were removed from the furnace in the molten state on the last pre-measurement melt, quickly placed in a vacuum dessicator, and the dessicator pumped out. Appreciable bubbling of the melts was generally observed while pumping. The crucibles were then allowed to cool under dynamic vacuum (mechanical pump only). It may be noted in passing that the stirring action of the out-gassing is believed beneficial for homogenization of viscous melts (3).

Melts were not analyzed for constancy of composition after measurement. However, the charge weights remained constant within ± 0.1 gram (of a total of 300-6-- grams) before and after measurement in all cases. It may also be noted that previous investigators have not detected composition changes in borate (6,7) or phosphate (11) melts under similar conditions of temperature, pressure, composition, etc.

FURNACE AND VISCOMETER

A "Globar" resistance furnace was constructed of suitable insulating firebrick. The working zone was about 5 x 5 x 8 in., which was not too large in view of the external size of the crucibles, 2 1/2 in. diam. x 4 in. All furnace components were designed for temperatures of at least 1400° C.

As mentioned under Theoretical Considerations, the viscometer was of the Margules type, which has been used by many investigators.* Several design details and dimensions were adopted from the apparatus of Rait and Hay (30,31). The greatest change from their arrangement was in the method of measurement. In the present case, measurements were made of the torque required to turn the bob at a fixed speed. The ceramic bob was connected to the pulley by a carbon rod, as shown in Figures 5 and 6. Heat conduction up this rod, and the attendant heating of the pulley and main pulley bearing, were alleviated by

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*See, for example, Mackenzie's discussion (Ref. 27, pp. 313-314); or that by Tiede (28) or Van Wazer, et al. (29).

cooling the pulley with dry ice. Two synchronous motors were available, of 10 and 400 RPM output; a wide selection of gears, together with the appropriate motor, permitted rotation speeds of 1 RPM to 75 RPM.

Furnace temperature was controlled by a Wheelco Model 402-P controller reading a thermocouple placed above and behind the crucible. This thermocouple was thus subject to greater temperature fluctations during the controller's high-low cycle than was the measurement couple (see below), but in no instance did it cycle more than 3° C. from the set point. A continuous flow of tank nitrogen was blown into the furnace to reduce oxidation of the carbon parts, as the furnace was not gastight. The temperature was measured by means of a Pt / Pt-13%RH thermocouple, a 0° C. reference junction, and a potentiometer. This thermocouple passed through a refractory block and was in contact with the crucible wall while surrounded by the block. It is believed that this gave temperature values within 2° C. of the melt temperature. No temperature fluctuations during controller cycles could be detected through this thermocouple.

The depth h (Figure 4) was obtained by means of a rigid mullite thermocouple sheath containing two separate platinum wires connected at the upper (cold) end to an ohmmeter, and moved vertically by a screw device. When the lower ends of these wires just touched the melt surface, a circuit was established and a finite reading abruptly observed on the meter. With suitable dimensional calibration, this proved an excellent measuring device, being both accurate and reproducible.

A discussion of the factor h_0 is given in Theoretical Considerations. For Equation 8 to hold, certain limits must be observed, as has been indicated by Lindsley and Fischer (23). They showed that h_0 is not a function of η, for η greater than about 1 poise; that h_0 is not a strong function of ℓ, for ℓ greater than about R_B; and that h_0 is not a function of the quantity $(R_C - R_B)$, provided suitable dimensions are maintained. In their investigation, h_0 was a constant for R_B = 1.57 cm. and $(R_C - R_B)$ 0.95 cm. These conditions were fulfilled in the present experiments, where R_B = 1.505 cm., R_C = 2.540 cm., and ℓ = 2.00 cm. The value of h_0 was determined by measuring h and T at fixed values of Ω in standard viscosity oils obtained from the National Bureau of Standards. A water-jacketed copper crucible and an aluminum bob of the above dimensions were used for this determination. The value obtained was 0.21 cm., which is similar to single-bob values obtained by Lindsley and Fischer (23).

The crucibles and bobs were of either high-density mullite or 99% alumina obtained from the McDanel Co. Careful investigation of these parts after use revealed little or no corrosive attack. Most of the glasses, when broken out of the crucible, separated cleanly from the crucible wall. Bobs which had been used with water-soluble melts and subsequently cleaned, experienced changes in diameter (if any) of less than 0.001 in. Slight grooving at the melt surface line in the most basic melts was observed, but it is felt that the corresponding changes in

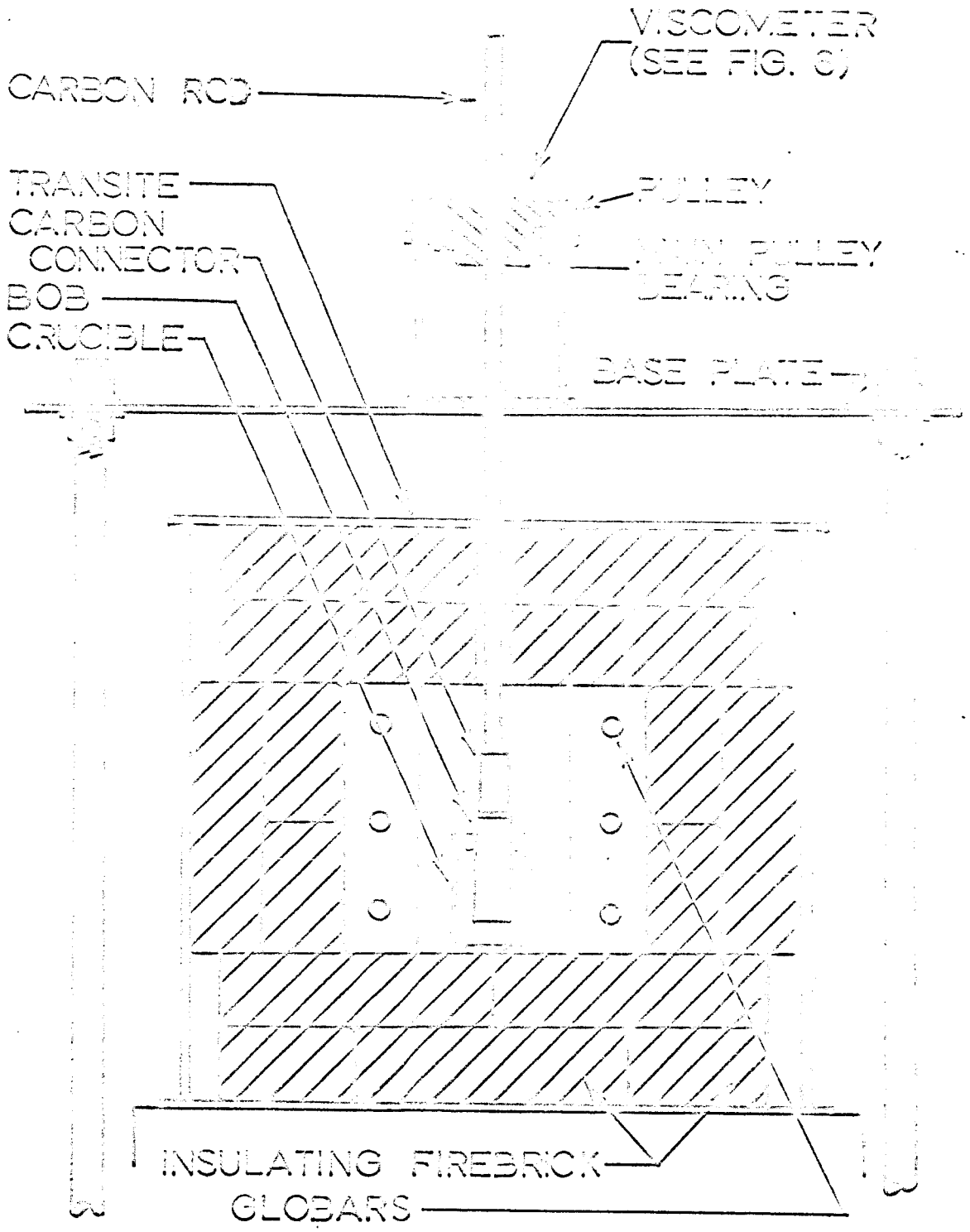

FIGURE 5. SCHEMATIC APPARATUS SECTION

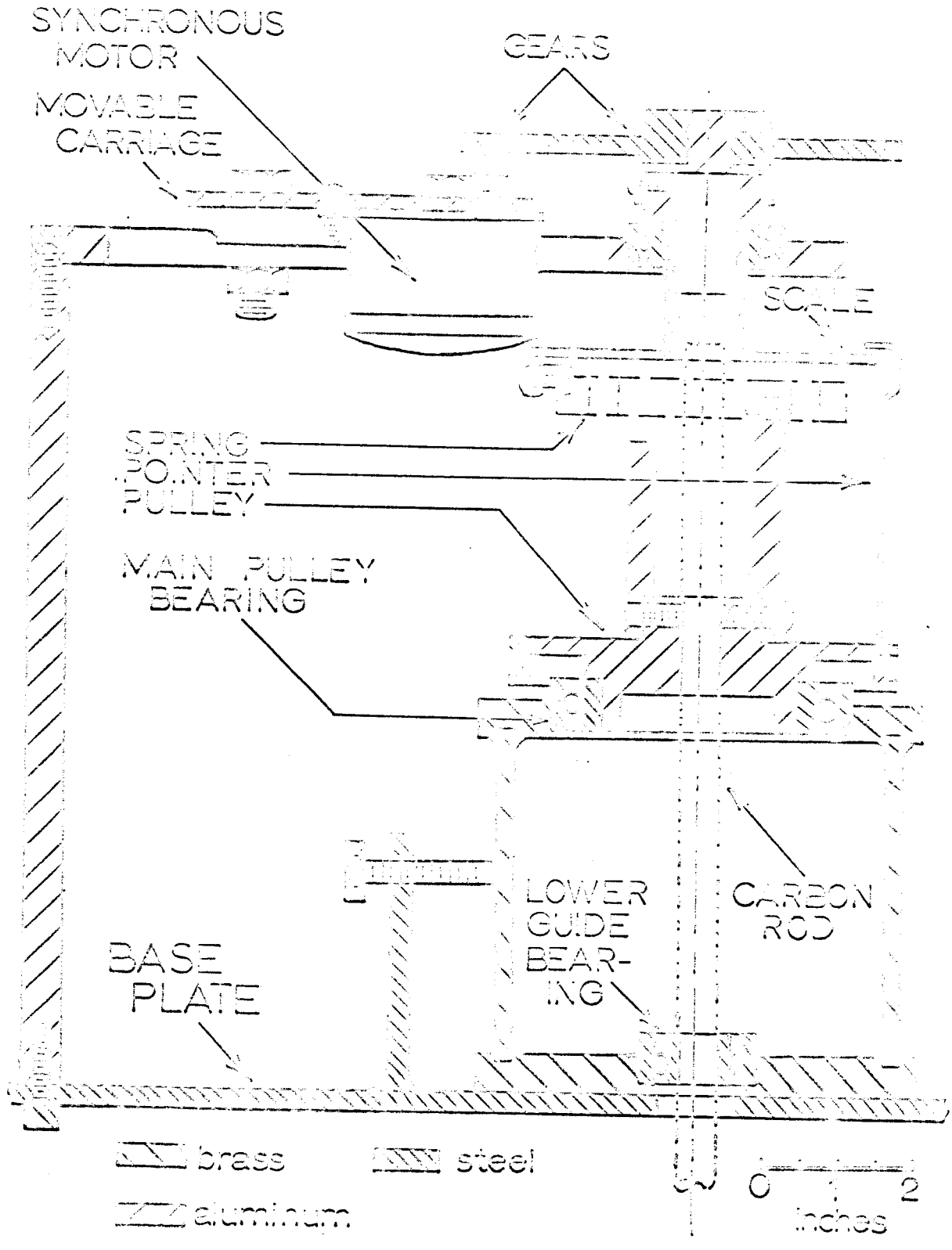

FIGURE 3. NEPHELOMETER DETAIL.

system geometry and melt purity were negligibly small.

The experiments of Rait and Hay (30,31) on the magnitude of various geometrical errors were repeated in part, and results obtained were generally similar to theirs. For example, the error due to various amounts of non-concentric rotation of the bob was measured. For geometry alone, the product of the maximum errors from all sources was about 2%, the most probable error less than 1%.

Both Mackenzie (27) and Van Wazer *et al.* (29) have given equivalent formulae for the Reynolds number applicable to the geometry used in this work. Mackenzie's equation may be written with the notation used here as

$$R = \Omega R_B (R_B - R_C) \rho / \eta \quad , \qquad (9)$$

where ρ = density of the liquid. The largest value of R for which laminar flow obtains, i.e. the critical Reynolds number R_{crit}, was given in c.g.s. units for this geometry by Van Wazer *et al.* (29). It may readily be shown for these experiments that $R_{crit} = 64.7$, and that the maximum values of Ω and ρ, and minimum values of η encountered in this investigation give $R = 15.4$ It may be seen in Equation 9 that this is a maximum value of R. Thus, since $R \ll R_{crit}$, it was concluded that laminar flow was realized in all cases.

MEASUREMENTS

Before each run, the bob to be used was screwed to the carbon connector and rod and lowered into an empty crucible until it touched bottom. It was then raised exactly 2.00 cm.

and a reference mark made at the top of the rod. This established the value of l. The crucible containing the melt to be measured was then centered on the bob by means of special gauge blocks. Since some eccentricity of rotation of the bob was usually observed, this centering was done with the bob rotating. When necessary, the corrections for eccentricity described by Rait and Hay were used (30,31).

When the melt reached measurement temperature, it was held at least 30 minutes to insure equilibrium. Where appropriate, this time was extended according to the rule of thumb suggested by Van Wazer (11). This rule states that in liquids of about one poise viscosity, reorganizational equilibrium is reached in fractions of a second; each order of magnitude increase in viscosity corresponds to an increase of two orders of magnitude in the time to reach equilibrium. For example, a 100-poise liquid should equilibrate in about 20 minutes. The depth was then measured, followed by rotation of the bob in the melt for 15-30 minutes (depending on expected viscosity) before readings were taken. For melts which were measured at more than one temperature (i.e. lead phosphate), the above equilibration sequence was followed at each new temperature.

The principle of measurement employed was that the torque required to turn the bob in a melt was equal to the torque required to produce a given deformation of the spring. For a properly selected spring, the initial rotation of the drive shaft deformed the spring, moving the scale relative to the pointer (see Figure 6), but did not move the pulley, until the

until the torque required to further deform the spring exactly equalled that to move the pulley, rod and bob. At that point, the pulley and scale began to rotate together. Comparison of angular readings (on an arbitrary scale) between the situation with the bob in the melt, and not in the melt, gave a difference, or deflection. This value was converted to the equivalent torque by calibration curves, which were obtained by raising weights on the pulley. The value of torque T could then be put into Equation 8 to calculate the viscosity.

Since angles read on the scale were not perfectly reproducible, at least 25 readings were taken for every measurement, and the mean used as the true value. Such a procedure of course assumes that the individual values are part of a normal, or Gaussian, distribution if the usual statistical formulae are used (32). Large samples (200-500 readings) were collected during calibration and the distribution of values about the mean was found to be Gaussian. The standard deviation of the mean was computed for every measurement sample. This was in all cases less than 0.20°, compared to deflections which ranged from 5 to 40°. All viscosity values were the result of at least two sets of readings, a set being 25 readings with the bob in the melt, followed by 25 readings as soon as it was withdrawn. The bob was re-inserted for successive sets. It should be noted that the use of blank readings at the time of the measurement insured that changes in the bearings, spring length, lubricant, or other factors were taken into account.

OBSERVATIONS AND RESULTS

BORATE VISCOSITIES

The results for the two borate binaries, $Na_2O - B_2O_3$, and $PbO - B_2O_3$, at 800° C. are given in Table I. Note that the two sodium borate compositions were each measured on separate occasions, and hence are reported as two separate values. The same results are also plotted in Figure 7, together with the data of Mackenzie (33) for pure B_2O_3 and of Shartsis *et al.* (7) for sodium borates. The several features of this diagram will be discussed below.

PHOSPHATE VISCOSITIES

The general results for phosphates are presented in Table II. Note that, with the exception of lead phosphate, only one measurement was made in each binary. The reasons the program was curtailed are as follows. First, it has been reported by Van Wazer (11) that above $N_P = 0.53$, a significant vapor pressure of P_2O_5 was observed. This will of course lead to variations in composition, as well as depositing hygroscopic P_2O_5 on the working parts of the furnace. In addition, Van Wazer reported that such melts are themselves hygroscopic while molten. Second, in the direction of the basic oxide end of these binaries, one commonly encounters liquidus lines ascending sharply in temperature toward the metal oxide melting points (24). A high temperature must then be chosen to permit investigation of appreciable different compositions. The combination of increasing temperature and increasing melt basicity

TABLE I

VISCOSITY OF BORATES

COMPOSITION (In B_2O_3)			METAL OXIDE	TEMP. (°C.)	VISCOSITY (POISES)	PUBLISHED VALUE (POISES)
N_B	X_B*	$\frac{O^-}{O^- + O^\circ + O^+}$				
0.667	0.693	0.183	Na_2O	803	12.10	12.75**
				800	14.21	
0.900	0.911	0.044	Na_2O	804	59.9	37.1**
				801	49.2	
0.500	0.238	0.333	PbO	800	39.2	---
0.590	0.310	0.244	PbO	802	53.3	---
0.680	0.399	0.178	PbO	800	67.6	---
0.810	0.571	0.090	PbO	802	124.2	---

* X_B = weight fraction of B_2O_3

** Ref. 7

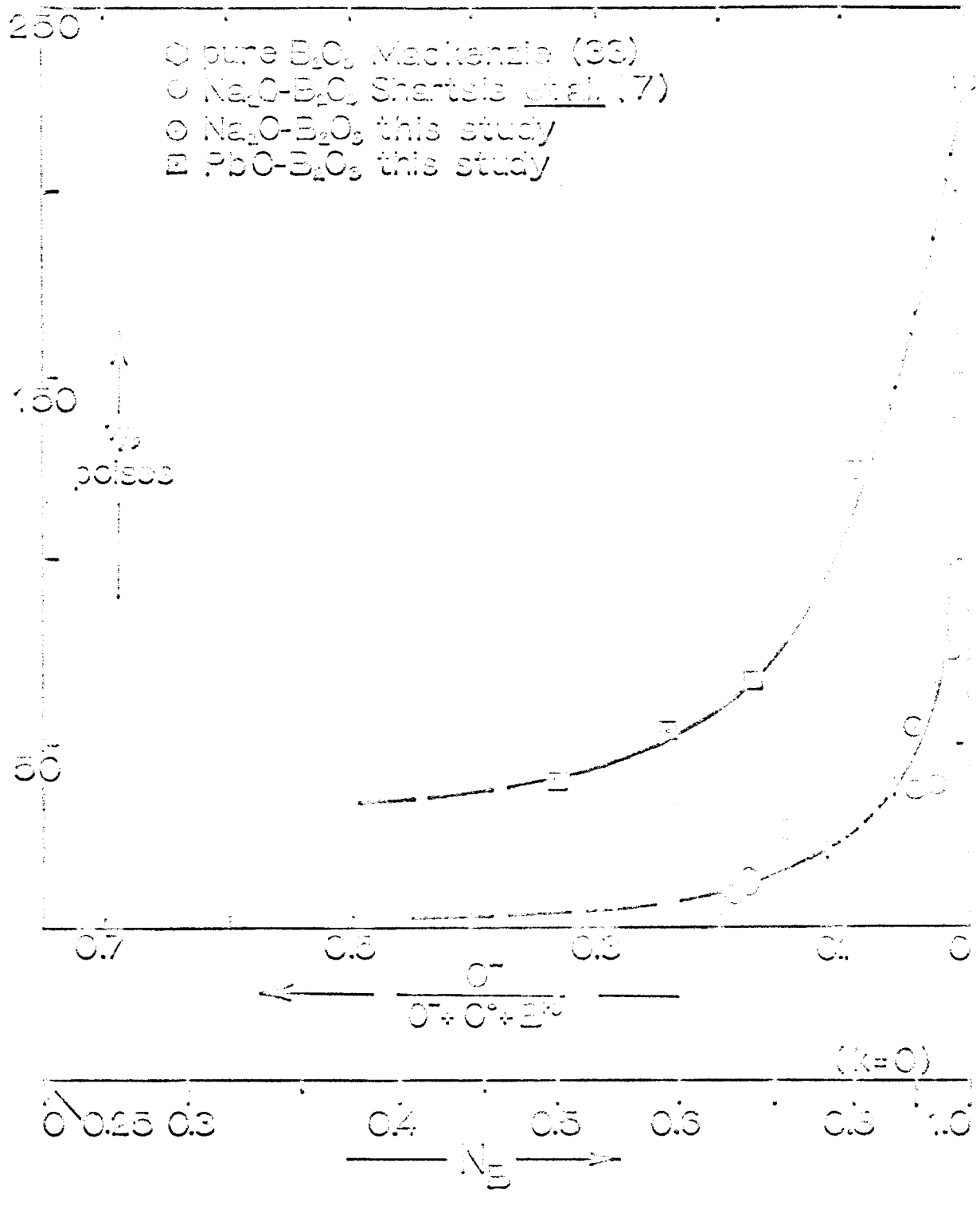

FIGURE 7. BORATE VISCOSITY VERSUS COMPOSITION AT 900° C.

TABLE II

VISCOSITY OF PHOSPHATES

COMPOSITION (In P_2O_5)			METAL OXIDE	TEMP. (°C.)	VISCOSITY (POISES)	PUBLISHED VALUE (POISES)
N_P	X_P*	$\frac{O^-}{O^-+O^o+P^5}$				
0.500	0.695	0.250	Na_2O	702	8.47	7.0**
0.500	0.601	0.250	K_2O	851	29.55	---
0.500	0.717	0.250	CaO	1000	17.49	---
0.333	0.241	0.444	PbO	850	29.99	---
0.393	0.291	0.360	PbO	852	19.51	---
0.481	0.371	0.267	PbO	703 850	50.8 24.1	---

*X_p = Weight fraction of P_2O_5.

**Read from graph, Ref. 34.

has the effect of greatly increasing melt corrosiveness. Therefore, only the system PbO - P_2O_5, which has a relatively low liquidus between $N_P = 0.3$ and $N_P = 0.5$ (see Ref. 24), was widely investigated.

The data for lead and potassium phosphates are plotted in Figure 8. In Figure 9, the published data of Callis et al. (34) on sodium phosphates are plotted with the value measured in this study, and the lead phosphate value measured at the same temperature.

DENSITIES

Since a fairly accurate measure of melt depth, and hence of melt volume, was required in these experiments, and since charge weights were known, an estimate of density at the measurement temperature can be made. For purposes of the viscosity measurement, the meniscus volumes are irrelevant, since they take no part in the viscosity phenomenon. But they are quite relevant for densities, and unfortunately are not measurable by the technique used for this work. Therefore, these data must be regarded as estimates, which will in general be biased in the sense of large values, i.e. the true densities are somewhat lower than those reported here. The data as measured are presented in Tables III and IV.

If the meniscus dimensions observed in the solid glasses are used, an estimate of the additional volume can be made, and a partial correction applied to the measured data. Such corrected values appear in Tables III and IV; note that the meniscus

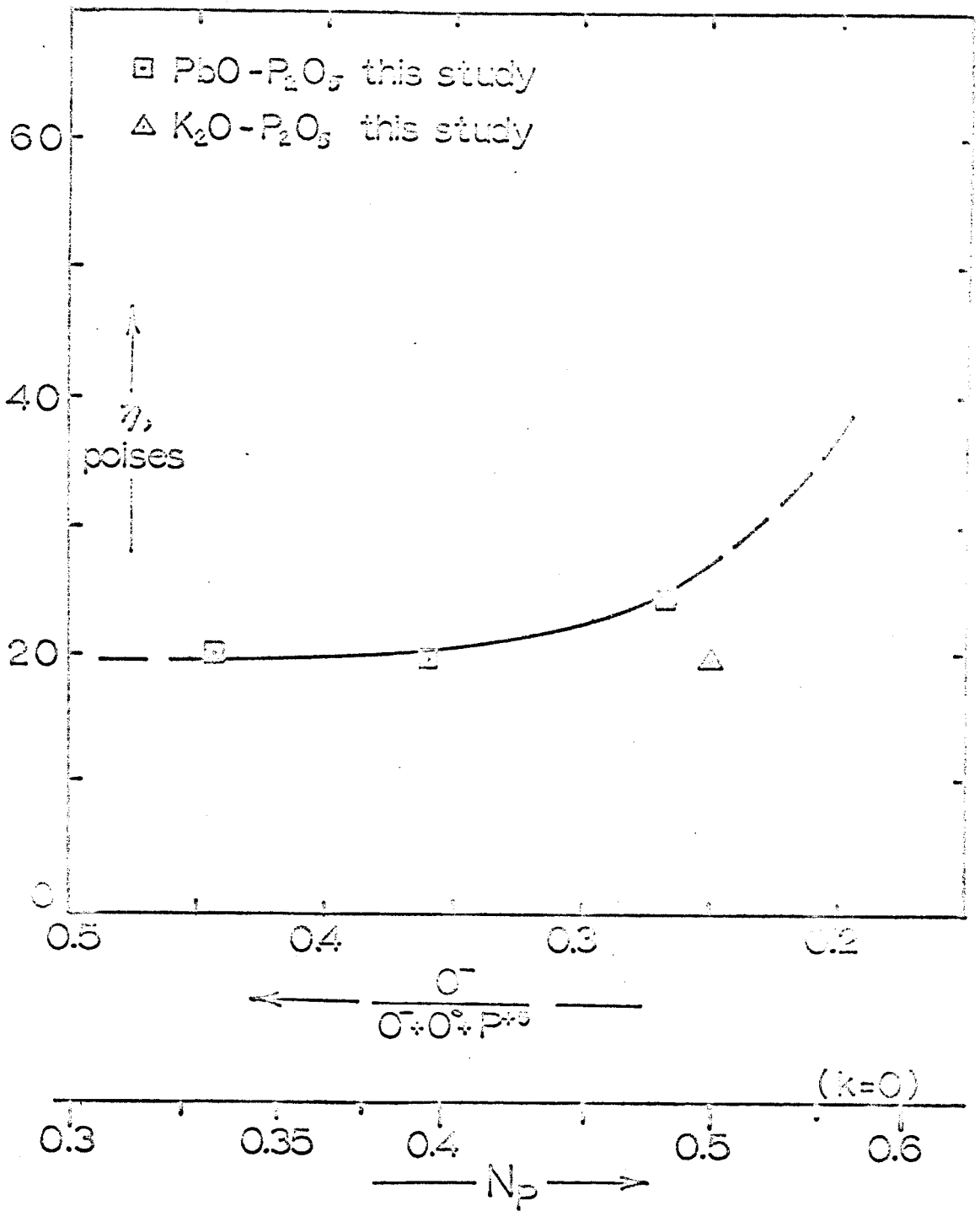

FIGURE 8. PHOSPHATE VISCOSITY VERSUS COMPOSITION AT 850° C.

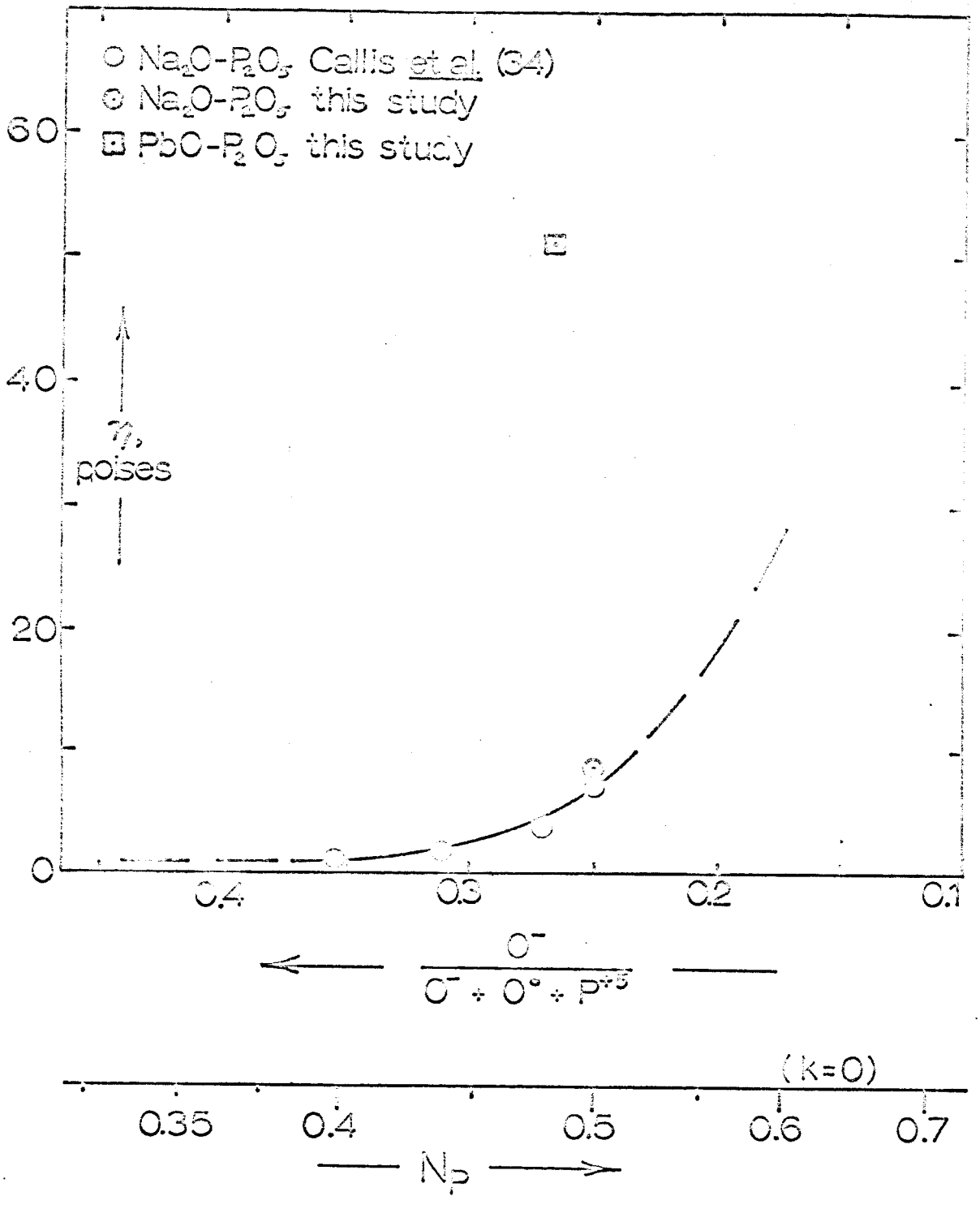

FIGURE 9. PHOSPHATE VISCOSITY VERSUS COMPOSITION AT 700° C.

TABLE III

BORATE DENSITIES

N_B	METAL OXIDE	TEMP., °C	DENSITY, gm/cm^3	CORRECTED* DENSITY, gm/cm^3	PUBLISHED** DENSITY, gm/cm^3
0.667	Na_2O	797	2.14	2.12	2.092
0.900	Na_2O	804	1.63	1.62	1.805
0.500	PbO	800	5.31	5.30	---
0.590	PbO	802	3.65	3.64	---
0.680	PbO	800	3.44	3.43	---
0.810	PbO	802	2.73	2.72	---

*See text

**Ref. 6

TABLE IV

PHOSPHATE DENSITIES

N_3	METAL OXIDE	TEMP., °C	DENSITY gm./cm.^{3}	CORRELATED DENSITY * gm/cm.^{3}	PUBLISHED ** DENSITY, gm/cm.^{3}
0.500	Na_2O	702	2.03	2.02	2.224
0.500	K_2O	851	1.91	1.90	---
0.500	CaO	1000	2.69	2.67	---
0.333	PbO	850	5.39	5.37	---
0.393	PbO	852	5.00	4.97	---
0.481	PbO	703 850	4.52	4.51	---

*See text

**Calculated from equation, Ref. 35.

volume was quite small.

OTHER RESULTS

Physical behavior of the glasses measured was in general as might be expected from the literature (5-7,10-12, 36-39). In all cases, glasses were clear and appeared homogeneous on cooling; no devitrification was encountered in any of the compositions used, except possibly sodium phosphate. Most of the glasses were colorless, although lead borate glasses showed a yellow coloration tending to a very light green as the B_2O_3 fraction increased, and lead phosphate glasses displayed a pale pinkish-purple color, which became more distinct as the P_2O_5 fraction increased.

As mentioned in Experimental Procedure, all melts to which vacuum was applied showed evidence of outgassing to varying degrees. Some difficulty was encountered in making up the lead phosphate melts high in P_2O_5. Sublimation of the pure P_2O_5 evidently caused the vaporization losses which were observed.

The problem of melt corrosion was not great, as explained in Experimental Procedure. The suggestion of Eitel (36), that acid glasses should not affect dense ceramic refractories too much, was thus verified. The reason for the observed melt surface line attack is not clear, although it is a common occurrence in glassmaking. It is possible that increased diffusion along the surface allowed any crucible-melt reaction or dissolution to proceed at a faster rate than would have been possible if such a process were limited by the slow diffusion rates in these viscous liquids.

The analysis of viscosity presented in Theoretical Considerations, and indeed the very process of describing viscosity by a single parameter, assumes that the liquid under consideration is actually Newtonian. An effort was made to verify this assumption for the melts measured. Pure single-phase liquids, as these melts are believed to have been, commonly exhibit Newtonian behavior (3,29,36). But when the constituent ions or molecules in a liquid exceed 1000 atoms in chain length, non-Newtonian behavior may be observed (11,29), and in fact such effects have been reported for very acid phosphate (11) and titanate (36) glasses. Although it was believed that the chain length did not exceed even 100 atoms in any of the compositions measured, nonetheless the most acid melt (sodium borate, with $N_B = 0.90$) was measured at several different shear rates in an effort to examine the Newtonian assumption. The experimental values of torque T were used in Equation 3 to give shear stress τ, and Equation 2 was then used to obtain (dv/dr). The results are presented in Figure 10.

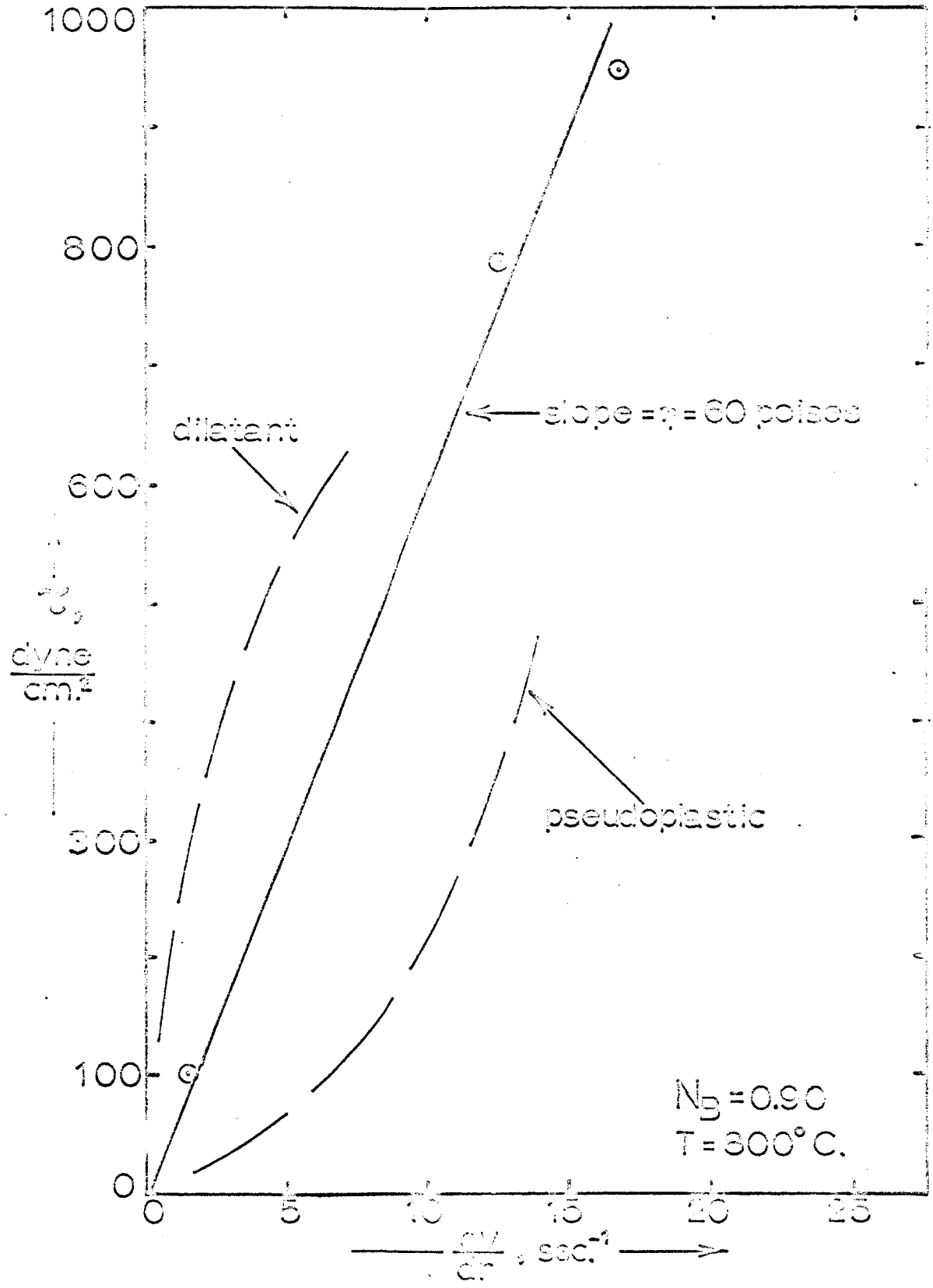

FIGURE 10. RHEOLOGICAL BEHAVIOR OF SODIUM BORATE.

DISCUSSION OF RESULTS

One aspect of the results which deserves notice is the good agreement with published results, as shown in Tables I and II. This is of particular note in a measurement such as viscosity, which is notorious in its variability from laboratory to laboratory, and even from run to individual run. The densities are in less good agreement. As explained in Observations and Results, these are definitely to be regarded as estimates, but the reason for the discrepancy being of the opposite sign than what was expected is not known. In any case, the values obtained in this study were precise to ± 0.01 gm./cm.^{3}, and were quite reproducible.

In Figures 7, 8 and 9, the dashed lines are the probable extensions of the measured regions. Particularly in Figures 8 and 9, in which no value for pure P_2O_5 was available, the dashed portion must be regarded as entirely hypothetical. However, especially in the borate case (Figure 7), the general shape of these lines is quite evident. They are markedly similar to the melt line shown in Figure 3, and as such constitute agreement with the predictions of the theory of Toop and Samis (see Theoretical Considerations).

In Figure 7, the sodium borate curve contains a portion drawn in short dashes. At 800° C., the dashed composition range includes the two-phase regions on either side of a congruently melting compound (24). Since it is impossible to be certain that a melt remains entirely single-phase in such a region, measurements might well be non-representative of the

temperature, non-reproducible, and almost surely non-Newtonian. Accordingly, no measurements were attempted in this region. Shartsis et al. (7) did not similarly limit themselves, and obtained viscosities across this region which showed a sharp increase in viscosity, followed by a sharp decrease as N_B decreased. As pointed out by Bradbury and Williams (12) and by Mackenzie (40), such values are meaningless. They certainly cannot be interpreted in terms of the "boron anomaly", as Shartsis et al. attempted to do. There is evidence that this anomaly, or coordination change of boron, is a real effect (41,42), but unequivocal evidence in the form of viscosity measurements has not been published (cf. Refs. 22, 24). Therefore, the data of Shartsis et al. in the two-phase regions were not plotted in Figure 7, and the data in this study have been used throughout on the assumption of three-coordinated boron in the liquids. Similar limitations do not apply to the system PbO - B_2O_3, since it is a single-phase liquid at all the temperatures and compositions considered (24).

It may be noted in Table I and Figure 7 that the data point for $N_B = 0.90$ is somewhat higher than that reported by Shartsis et al. (7). It is believed that this difference may be related to the "melting history" concept of McKinnis and Sutton (25), which was mentioned in Experimental Procedure. McKinnis and Sutton found that heating a viscous glass above the measurement temperature and then cooling to that temperature produced a lower measured viscosity than if the glass had been held very long times at measurement temperature and no higher.

In the borosilicate glasses they examined, such effects persisted as much as 300° C. above the liquidus, and near the liquidus, the discrepancy was quite large. Shartsis et al. did not describe their heating sequence in detail, but they made measurements at several temperatures in descending order for each composition. For $N_B = 0.90$, two higher temperatures (than 800° C.) were used. McKinnis and Sutton's concept might not seem fully applicable to borates, since the equilibration rate of borates is probably greater than that of silicates (and the viscosity much less), but the possibility of a "history" effect cannot be discounted without explicit contrary evidence. Thus, it is felt that the discrepancy between present data and that of Shartsis et al. (7) may be due to technique.

A striking feature of Figure 7 is that the lead borate curve lies substantially above that for sodium borate. The reason for this may be sought in the suggestion of Mackenzie (5,40), that a divalent cation (Pb^{++}) can simultaneously form coulombic interactions with two adjacent anions, creating a tenuous, momentary connection between the anions. A monovalent cation such as Na^+ obviously cannot do this. Such a quasi-bond in the liquid would not be equivalent to a normal covalent bond within an ion, but on a time-average basis would increase the ion sizes, and thereby the viscosity. Mackenzie (5,40) has shown a graph of activation energy for viscous flow versus composition in silicates, in which the values for monovalent cations (Li^+, Na^+, K^+) lie on a distinct curve lower than the

values for divalent cations (Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}). This is taken as evidence for the above hypothesis. The data point for potassium phosphate at 850° C. lies below the lead phosphate curve (Figure 8), and the data point for lead phosphate at 700° C. (Figure 9) lies well above the sodium phosphate curve. If these points are indicative of the location of the complete curves, they correspond to Figure 7 and to Mackenzie's suggestion.

The phosphate curves in Figures 8 and 9 are much less complete than those for the borates. Less data are available in the literature for phosphate systems, and as explained in Observations and Results, it was not possible to take as many measurements in phosphates as had originally been planned. Also, the curves shown lie rather far toward the basic oxide end of the diagram, which is of less interest with regard to the exact curve shape for comparison with a melt line. Nevertheless, the shapes which do appear are of the predicted kind, and do not contradict the predictions of the theory.

The illustration of Newtonian behavior, Figure 10, is quite explicit: the data points fall reasonably well on a straight line, the slope of which is the Newtonian viscosity. A rheologist might argue that the points could be more exactly fitted by a curve of the dilatant type (see Figure 10). However, it is known that when liquids deviate from Newtonian behavior by reason of the chain length becoming very great, they generally exhibit pseudoplastic behavior (29). It is

obvious from Figure 10 that a pseudoplastic curve would be difficult to fit to these points. Therefore it is felt that Newtonian behavior was observed in this melt, the most acid which was measured. As indicated by Figure 3, all melts of a lower acidity should have had a lesser chain length, and presumably exhibited Newtonian behavior also.

Since the above borate and phosphate data are not as complete as one might wish, a few viscosity data for sodium silicate were obtained (43). These data were taken from smoothed curves which represented a compilation of data from many investigators; they are plotted in Figure 11. Note that it was necessary to plot log viscosity rather than linear viscosity on account of the very great range of values in this system. Although this change of scale somewhat affects the detailed curve shape, the overall features are preserved, as was verified by making linear plots over a restricted range. The dashed portion of the curve is the region beyond the cristobalite liquidus in this system. As discussed above, viscosities in such a two-phase region cannot be compared with data from a single-phase region. As with the earlier results (Figures 7-9), the shape is similar to, and in agreement with, the melt line predicted by the theory of Toop and Samis.

It should be emphasized again that Toop and Samis' theory does not predict a specific, quantitatively-detailed curve, for the relation between viscosity and ion size is not known in a quantitative way. But it does predict a characteristic shape,

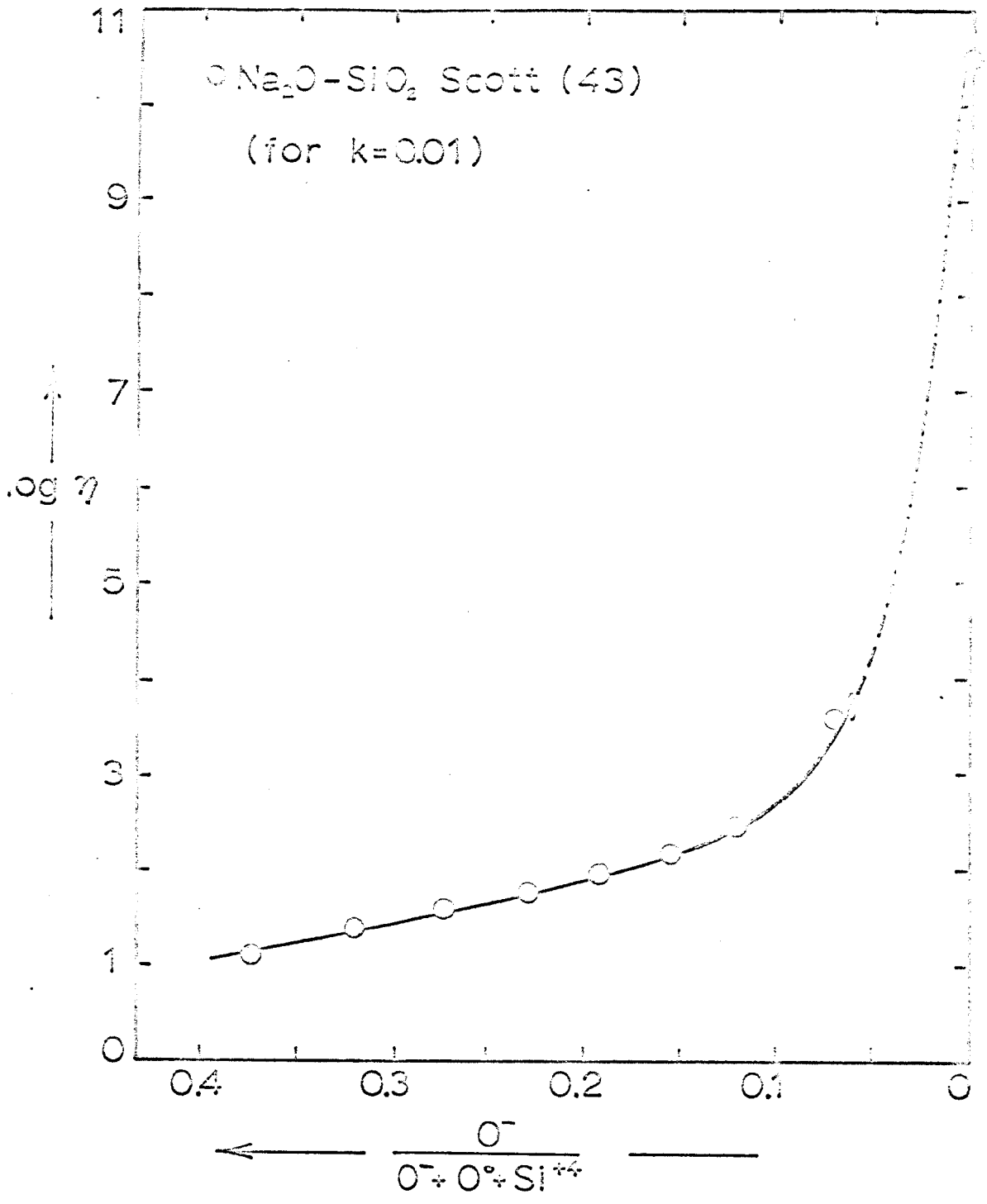

FIGURE 11. SILICATE VISCOSITY VERSUS COMPOSITION AT 1400° C.

and such a shape has been found in the borate, phosphate and silicate systems examined in this study. It is felt, therefore, that the above results are in agreement with the theory.

SUMMARY AND CONCLUSIONS

A viscometer suitable for high-temperature measurements on corrosive melts was found to operate in a satisfactory manner. Care was taken that difficulties characteristic of such an apparatus were minimized or eliminated. Viscosity was measured in the following binary systems: sodium and lead borate, and sodium, lead, potassium and calcium phosphate. Data obtained were reproducible and in agreement with published values. Published data for sodium silicate were also analyzed. The Newtonian behavior of the melts investigated was tested, and it was concluded that such behavior was observed.

The results obtained were all in agreement with the predictions of the thory of Toop and Samis. Although these qualitative results are not an absolute confirmation of the theory itself, it is felt that they constitute as good agreement as is possible without an explicit relation between ion size and viscosity.

SUGGESTIONS FOR FUTURE WORK

Two kinds of suggestions may be made, those concerning the apparatus, and those with respect to future experiments.

There are two portions of the apparatus which could undergo significant improvement. The first is the furnace. If it were surrounded by a gastight case with appropriate inlets and outlets, atmosphere control would be fully possible. In the limit, it might be made tight enough so that a mechanical vacuum pump could be attached. Vacuums of the order obtainable with a mechanical pump alone would significantly aid in dehydration of hygroscopic melts, especially phosphates (11). It probably would not be possible to make measurements under vacuum, but an evacuated and backfilled furnace would be a considerable improvement over the present situation, and atmospheres of hydrogen, nitrogen, argon, etc. could be used routinely. A second furnace addition might be a muffle. Alumina plates (or a tube) set vertically between the heating elements and the specimen zone would greatly increase the temperature stability of the crucible, and in addition would permit more accurate control.

Improvements in the viscometer components could also be made. The main pulley bearing might be replaced with a bearing which would turn more freely at the load levels encountered. Alternatively, an effort could be made to use more appropriate lubricants. Either change should result in appreciable improvements in both the accuracy and precision of measurements and might make possible the routine observation of viscosity values as low as one poise. A more major modification would be

the substitution of a stainless steel rod for the present carbon rod; this would be contingent upon the atmosphere control mentioned above. If a larger diameter rod than the present 1/2 inch were used, it would be possible to provide a water-cooling passage part-way down the rod axis. This would virtually eliminate heat flow up the rod, provided that suitable rotating seals could be devised. Confidence in high-temperature readings would thereby be increased, together with stability of the viscometer.

Several types of future experiments can be suggested. One type would be to extend the present data to more compositions and temperatures in the binaries studied, or to investigate other borate, phosphate or silicate binaries, or even to pursue measurements in ternary systems. These experiments would be of intrinsic value and would not represent too great an extrapolation of the present technique. A second type of experiment would be to study binaries based on other acid oxides such as GeO_2, As_2O_3, MnO_2, VO_2, TiO_2, SnO_2 or Sb_2O_3 (Ref. 36, p. 1288); this would be a useful extension of the known data, and would provide a broader test of Toop and Samis' theory (1,2).

A third area of investigation might include experiments on the so-called "model glasses". For instance, BeF_2 behaves very much like SiO_2, and in fact forms "siliceous" glasses with metal fluorides (36); a sample experiment might be a viscosity measurement in the binary BeF_2-NaF, which is entirely analogous to SiO_2-CaO (e.g. see Ref. 44). Other glassforming

systems include carbonates (e.g. K_2CO_3-$MgCO_3$), sulfates ($KHSO_4$), nitrates (e.g. those of Na, Ca, K), sulfides (GeS_2, As_2S_3), and some halides ($ZnCl_2$ or BeF_2). The fluoroberyllates are probably the most interesting of the group.* A fourth type of investigation could include organic glasses; polymeric hydrocarbons, e.g. polyisobutylene, are non-polar and have distinct glassforming tendencies (Ref. 36, p. 302). Other candidates for study include polystyrene and the polyorganosiloxanes, especially polymethylsiloxane (36). The advantage in studying organic glasses lies in the extensive theoretical and experimental knowledge of molecular structures and size distributions which is available. Should the theory of Toop and Samis prove applicable to melts based on such diverse species as SiO_2, GeO_2, BeF_2 and polymethylsiloxane, it would be a very cogent indication of validity.

Aside from studies such as the above, aimed at broader applications of Toop and Samis' theory, another class of experiments can also be suggested. For example, it could prove extremely interesting to measure and interpret the viscosity of several compositions in a borate binary, where the compositions are chosen in the range $N_B = 0.98 - 1.00$. This is the composition region in which relatively few boron-oxygen bonds are being broken, yet a very large change in viscosity is observed.

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*Discussion of some of these systems may be found in Eitel (36), pp. 85-88,117,256,338. Others are discussed in Mackenzie (40), Tokeuchi and Furudawa (13), and Jones (3).

Another example: one could attempt to directly relate η to B^*, P^*, or Si^* by chromatography (cf. Ref. 16 and others of Westman's papers; or Ref. 20) to determine the distribution of ions in glasses quenched from the temperature of investigation. It might also be possible to directly compare results calculated from Toop and Samis' theory with Flory's reorganization theory (for a discussion, see Ref. 11) or with Eyring's reaction rate theory (45). This latter treatment is of special interest, inasmuch as it relates to kinetic processes; viscosity certainly should be amenable to analysis of this kind.

REFERENCES

1. Toop, G.W. and Samis, C.S., "Some New Ionic Concepts of Silicate Slags", Can. Met. Quarterly, 1 129 (1962).
2. Toop, G.W. and Samis, C.S., "Activities of Ions in Silicate Melts", Trans. Met. Soc. A.I.M.E., 224 878 (1962).
3. Jones, G.O., Glass, Methuen and Co., London, 1956.
4. Elliott, J.F., Gleiser, M., and Ramakrishna, V., Thermochemistry for Steelmaking (Vol. II), Addison-Wesley Publ. Co., Reading, Mass., 1963.
5. Mackenzie, J.D., "The Physical Chemistry of Simple Molten Glasses", Chem. Reviews, 56 455 (1956).
6. Shartsis, L., Capps, W., and Spinner, S., "Density and Expansivity of Alkali Borates and Density Characteristics of some other Binary Glasses", J. Am. Ceramic Soc., 36 35 (1953).
7. Shartsis, L., Capps, W., and Spinner, S., "Viscosity and Electrical Resistivity of Molten Alkali Borates", J. Am. Ceramic Soc., 36 319 (1953).
8. Shartsis, L., and Shermer, H.F., "Surface Tension, Density, Viscosity and Electrical Resistivity of Molten Alkaline-Earth Borates", J. Am. Ceramic Soc., 37 544
9. Bockris, J. O'M., Tomlinson, J.W., and White, J.L., "The Structure of Liquid Silicates", Trans. Faraday Soc., 52 299 (1956).
10. Coughanour, L.W., Shartsis, L., and Shermer, H.F., "Viscosity, Density, and Electrical Resistivity of Molten Alkaline-Earth Borate Glasses with 3 mole % of Potas-

sium Oxide", J. Am. Ceramic Soc., 41 324 (1958).

11. Van Wazer, J.R., Phosphorus and Its Compounds (Vol. I: Chemistry), Interscience Publishers, New York, 1958.

12. Bradbury, B.T. and Williams, D.T., "Physical Properties and Constitution of Liquid Slags", Metallurgia, 62 235 (1960); ibid., 63 19 (1961).

13. Takeuchi, S., and Furukawa, K., "Structure Analysis of Some Fused Salts and Oxides by X-Ray Diffraction", Physical Chemistry of Process Metallurgy, Part I (G.R. St. Pierre, Ed.), Interscience Publishers, New York, 1960, p. 133.

14. Eipeltauer, E. and Schaden, K., "Interrelation between Viscosity and Composition of Binary Sodium Borate Glasses", Glastech. Berichte, 35 505 (1962); Chem. Abstracts, 58 7697h (1963).

15. Westman, A.E.R. and Crowther, J.P., "Constitution of Soluble Phosphate Glasses", J. Am. Ceramic Soc., 37 420 (1954).

16. Westman, A.E.R., "Phosphate Glass Structure - A Review of Recent Work", J. Can. Ceramic Soc., 27 87 (1954)

17. Henrikson, H.W., "Theory of Ionic Structure of Borates and Phosphates", Thesis, University of Washington, June 1964.

18. Kemp, P.H., The Chemistry of Borates, Part I, Borax Consolidated Ltd., London, 1956.

19. Westman, A.E.R. and Cartaganis, P.A., "Constitution of Sodium, Potassium and Lithium Phosphate Glasses", J. Am. Ceramic Soc., 40 293 (1957).

20. Meadowcroft, T.R., "Some Structural and Thermodynamic Aspects of Phosphate Slags", Ph.D. Thesis, University of London, March 1962.

21. Newton, I.S., The Mathematical Principles of Natural Philosophy, 3rd Ed. (Trans. by Andrew Motte), printed for B. Motte, London, 1729, Book II, Section IX ff.

22. Margules, M., "Über die Bestimmung des Reibungs und Gleitungs Coefficienten aus ebenen Bewegungen einer Flüssigkeit", Sitzber. Akad., Wiss. Wien, 83 (part II) 588 (1881).

23. Lindsley, C.H. and Fischer, E.K., "End-effect in Rotational Viscometers", J. Appl. Phys., 18 988 (1947).

24. Levin, E.M., Robbins, C.R., and McMurdie, H.F., Phase Diagrams for Ceramists, American Ceramic Society, Columbus, Ohio, 1964.

25. McKinnis, C.L. and Sutton, J.W., "The Glassmelting Process: I, Theory of Nature of Silicate Melts and of their Interaction with Silica", J. Am. Ceramic Soc., 42 194 (1959); "II, Glass Structure and Effects of 'Melting History' on Glass Properties", op. cit., 42 250 (1959).

26. Everstyn, F.C., Stevels, J.M., and Waterman, H.I., "Density, Refractive Index, and Specific Refraction of Vitreous Boron Oxide and of Sodium Borate

Glasses as Functions of Composition, Method of Preparation, and Rate of Cooling", Phys. and Chem. Glasses, 1 123 (1960); Chem. Abstracts, 55 4907f (1961).

27. Mackenzie, J.D., "Viscometry", Physico-chemical Measurements at High Temperatures (J. O'M. Bockris, J.D. Mackenzie, and J.L. White, Eds.), Academic Press Inc., New York, 1959, pp. 313-333.

28. Tiede, R.L., "Improved Apparatus for Rapid Measurement of Viscosity of Glass at High Temperatures" J. Am. Ceramic Soc., 42 537 (1959).

29. Van Wazer, J.R., Lyonds, J.W., Kim, K.Y., and Colwell, R.E., Viscosity and Flow Measurement, Interscience Publishers, New York, 1963.

30. Rait, J.R. and Hay, R., "Viscosity Determination of Slag Systems", J. Royal Tech. College (Glasgow), 4 252 (1938).

31. Rait, J.R., McMillan, Q.C., and Hay, R., "Viscosity Determinations of Slag Systems", J. Royal Tech. College (Glasgow), 4 449 (1939).

32. Bowker, J.R. and Lieberman, G.J., Engineering Statistics, Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1959.

33. Mackenzie, J.D., "The Viscosity, Molar Volume and Electrical Conductivity of Liquid Boron Trioxide", Trans. Faraday Soc., 52 1564 (1956).

34. Callis, J.F., Van Wazer, J.R., and Metcalf, J.S.,

"Structure and Properties of the Condensed Phosphates. IX. Viscosity of Molten Sodium Phosphates", J. Am. Chem. Soc., 77 1471 (1955).

35. Callis, C.F., Van Wazer, J.R., and Metcalf, J.S., "Structure and Properties of the Condensed Phosphates. VIII. Density and Surface Tension of Molten Sodium Phosphates", J. Am. Chem. Soc., 77 1468 (1955).

36. Eitel, W., The Physical Chemistry of the Silicates, 3rd English edition, University of Chicago Press, Chicago, 1954.

37. Krog-Moe, J., "Electron Microscope Studies of Borate Glasses", Arkiv för Kemi, 14 1 (1959).

38. Krogh-Moe, J., "The Relation of Structure to some Physical Properties of Vitreous and Molten Borates", Arkiv för Kemi, 14 553 (1959).

39. Krogh-Moe, J., "An X-Ray Study of Lithium Borate Glasses", Arkiv för Kemi, 14 31 (1959).

40. Mackenzie, J.D., "Some Structues of Some Inorganic Glasses from High Temperature Studies", Modern Aspects of the Vitreous State (J.D. Mackenzie, Ed.) Butterworths Publishers, London, 1960, p. 188.

41. Bray, P.J. and O"Keefe, J.G., "Nuclear Magnetic Resonance Investigations of the Structure of Alkali Borate Glasses", Phys. and Chem. Glasses, 4 37 (1963); Chem. Abstracts, 46 240i-G (1963).

42. Bray, P.J., Leventhal, M, and Hooper, H.O., "Nuclear

Magnetic Resonance Investigations of the Structure of Lead Borate Glasses", Phys. and Chem. Glasses, 4 47 (1963); Chem. Abstracts, 46 2414a (1963).

43. Professor William D. Scott, University of Washington, private communication, 1965.

44. Roy, D.M., Roy, R., and Osborn, E.F., "Fluoride Model Systems: III, The System NaF - BeF_2 and the Polymorphism of Na_2BeF_4 and BeF_2", J. Am. Ceramic Soc., 36 185 (1953).

45. Glasstone, S., Laidler, K.J., and Eyring, H., The Theory of Rate Processes, McGraw-Hill Book Co., New York, 1941, Chapter 9.