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VISCOSITIES OF MAGMATIC SILICATE LIQUIDS: AN EMPIRICAL METHOD OF PREDICTION*

H. R. SHAW

U.S. Geological Survey, Washington, D.C. 20242

ABSTRACT. Based on the compilations and calculations of Bottinga and Weil (1972), it has been discovered that viscosities of multicomponent anhydrous silicate liquids can be estimated more rapidly and with equal precision using only four partia molar coefficients of SiO_2. The addition of a fifth coefficient extends the method to hydrous compositions with somewhat less precision. Comparisons with experimenta data are illustrated for viscosities ranging from the order of one poise to 10^{13} poise and compositions ranging from "lunar basalt" to terrestrial rhyolites and "hydrous granites of ternary minimum composition". The method does not explicitly consider halogens, or other "volatile" or minor constituents, but semiquantitative effects can probably be estimated; the empirical coefficients can easily be expanded in number or refined in value if need is indicated by experimental or other evidence.

INTRODUCTION

The recent paper by Bottinga and Weill (1972) should be read as an introduction to the present discussion, with one additional comment. The question of "mixing laws" for the physical properties of silicate liquids has been an intermittent subject of study in this laboratory for some years. However, various attempts at viscosity prediction had been only crudely successful, until the systematic studies by Bottinga and Weill (1970, 1972) revealed important simplicities in multicomponent silicate mixtures of rock forming compositions. The present paper uses their work to show that even greater simplicities exist for magmatic liquids. The starting point of the discussion is given by the mixing relationship used by Bottinga and Weill.

ADDITIVITY RULES FOR VISCOSITIES OF LIQUID MIXTURES

It has been known for a long time that the viscosities of some simple liquid mixtures can be estimated fairly well by what is sometimes called the Arrhenius mixture rule (Bondi, 1967, p. 76)

$$\ln \overline{\eta} = \sum_{i=1}^{n} X_i \ln \eta_i \qquad (1)$$

where $\overline{\eta}$ is the viscosity of the mixture, and η_i is some characteristic viscosity contribution of component i of mole fraction X_i.

The results tabulated by Bottinga and Weill essentially show that this approximation adequately describes the behavior of silicate liquids within certain ranges of composition, if the constituents are suitably chosen. More importantly, however, they also show that the contributions of these constituents can be determined by averaging the behavior shown by synthetic systems of relatively few constituents compared with magmatic systems.

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On closer inspection, the additivity of viscosity values (ln η_i), can also be expressed in terms of the additivity of parameters describing the temperature dependence of viscosity. For silicate liquids the viscosity is known to be approximated fairly well by the Arrhenius relation

$$\eta = \eta_o \exp (E^*/RT) \tag{2}$$

where η_o and E^* are constants usually called the "pre-exponential constant" and "activation energy" respectively, and R is the gas constant. These constants are given by the intercept and slope of a line on a plot of ln η versus 1/T (K), so that η_o can be viewed as a hypothetical viscosity limit at infinite temperature. Equation (2) re-expressed in the form

$$\ln \eta = \ln \eta_o + (E^*/R)(1/T) \tag{2A}$$

shows that the Arrhenius mixture rule might be expanded in terms of additivity rules for ln η_o and E^*.

Additivity relations for ln η_o and E^* were under investigation by the author when the present results of Bottinga and Weill were announced. The initial approach had been to attempt fitting the viscosity data for rock compositions using methods of multiple regression analysis. Bottinga and Weill, however, found that it is easier to build up the relations from synthetic systems than it is to reduce analytically the magmatic systems, largely because of the relative abundances of data. This conclusion was used to test a relationship that had been noted in the author's experimental studies of the temperature and composition dependence of silicate viscosities (Shaw, 1963, 1969, unpub. data).

STRATEGY OF PREDICTION

The success of correlation schemes for physical and chemical properties of matter rests on some form of normalization that is found to reveal similarities in the behavior of one system in a given class of systems (that is, systems consisting of a gas, a liquid, a coexisting gas and liquid, et cetera) relative to that of other systems in the class. This is the strategy of the "reference substance principle" developed by Othmer and coworkers (see Othmer and Chen, 1968) and of the principle of corresponding states; in the latter case there is also the aim of finding a set of universal constants to describe the class. Although these techniques have been used with some success for viscosity correlations (see Bondi, 1967; Othmer and Chen, 1968, p. 119), they often rely on data of types not available for silicate systems. For example, viscosities of silicate liquids might be generalized, if the temperature could be expressed relative to the glass transition and critical temperatures (compare Bondi, 1967), but data on these characteristic temperatures for silicates are meager.

However, inspection of graphs of ln η versus 1/T for silicate liquids suggests a simple pattern. Particularly conspicuous is the convergence between viscosity curves for silicate mixtures and the viscosity curve for

liquid SiO_2 at high temperatures and the tendency for regular variation of slope with composition (compare Shaw, 1963, 1965; Bottinga and Weill, 1972; Hofmaier and Urbain, 1968); there are also conspicuous contradictions (see Euler and Winkler, 1957). Tentatively ignoring the exceptions, it was decided to test these two observations against the data of Bottinga and Weill, compared with data for SiO_2 as reference substance. As a first try, only binary systems were considered, and viscosities were calculated from the coefficients of Bottinga and Weill (1972, table 3). Surprisingly, nothing more was required to predict nearly all measured viscosities of magmatic liquids within a factor of two in most cases.

Graphs of ln η versus 1/T for binary silicate liquids.—Figure 1 shows several graphs for *calculated* binary viscosities as examples of convergence at high temperatures. Although there is much scatter, behavior resembles the pattern of convergence shown by the system Li_2O–SiO_2. At least some of the scatter relates to uncertainty of slopes based on narrow temperature ranges of measurement. Few measurements are at temperatures above $10^4/T = 5$, and many individual sets of measurements cover

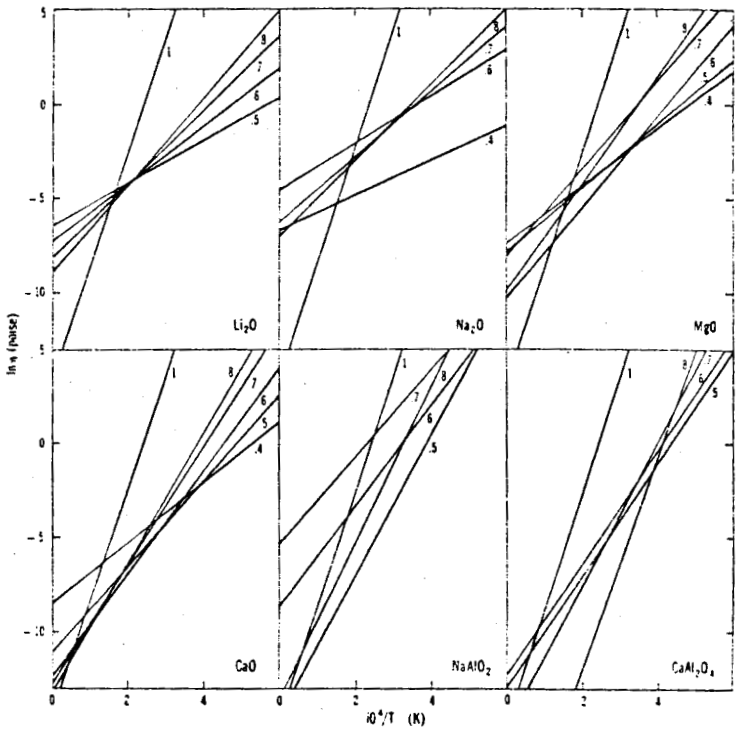


Fig. 1. Arrhenius plots of pseudobinary viscosity data for liquid mixtures of SiO_2 plus the indicated oxides calculated from coefficients of Bottinga and Weill (1972, table 3). Numbers are the approximate mole fractions of SiO_2 taken at the midpoint of ranges indicated by Bottinga and Weill.

than unit change in $10^4/T$, and one or two decades change in vis-
ity (that is, a few units of ln η; see fig. 8).

It is emphasized that the lines in figure 1 *do not represent best fits the binary data.* They are derived from the coefficients of Bottinga and
:ill that are based on averaging the effects of the different oxides in
ıthetic systems of 2 to 6 constituents (see Bottinga and Weill, 1972,
ɔle 1); the lines are calculated from binary pairs of the tabulated co-
ıcients. That is, it is assumed that if multicomponent systems demon-
ate some systematic average behavior, then the calculated values for
e binary pairs may indicate the form of this behavior, even though
perimental data for the binary systems considered individually may
viate significantly from the average model. In this sense the dia-
ams can be thought of as "pseudobinary" or as being derived by pro-
cting best fits of all data for the synthetic systems to the binary joins.

The first of two principal assumptions used to define an empirical
odel of average behavior is that viscosity curves for multicomponent
licate liquids tend to intersect the reference curve for SiO_2 liquid at a
ıaracteristic temperature and a characiteristic viscosity suggested by
ıe averages of the binary intersections. Mathematically, the consequence
f this assumption is that values of ln η_0 in equation (2A) are fixed by
ne value of slope. Physically, of course, this also implies a systematic
elationship between ln η_0 and E^* (a theoretical meaning for such a
elationship is discussed later). By this assumption viscosities are given
ɔy an equation of the form

$$\ln \eta = s(10^4/T) - c_T s + c_\eta \qquad (3)$$

vhere s is a characteristic slope for a given multicomponent mixture,
ınd c_T and c_η are coordinates of the point of intersection. This assumed
elationship is shown graphically in figure 2. From equation (3) it is
vident that E^* and ln η_0 are given by

$$E^* = 10^4\, sR = 19.87\, s \text{ (kcal mole}^{-1}\text{)}$$
$$\ln \eta_0 = c_\eta - c_T s \text{ (natural log viscosity, poise)}$$

The coordinates c_η and c_T were chosen by taking the arithmetic means
f the apparent intersections in figure 1. However, this value also de-
ɔends on the data used for SiO_2 liquid. The means are $c_\eta \cong -6.6$,
$_T \cong 1.3$ for the data of Hofmaier and Urbain (1968), and $c_\eta \cong -4.9$,
$_T \cong 1.9$ for the data of Bockris, MacKenzie, and Kitchener (1955).
ater comparison with multicomponent data led to adoption of the
eighted means

$$c_\eta = -6.40$$
$$c_T = 1.50$$

Variation of E with composition.*—The general form of composition
ependence of E^* is also indicated by the Arrhenius plots of figure 1.
lopes derived from some of the calculated binary viscosities are illus-

trated in figure 3A. Here inconsistencies are also apparent, but again there is a hint of pattern. For compositions ranging from about 0.4 to 0.8 mole fraction of SiO_2, the variation of slope with composition tends to be linear; above mole fractions of 0.8, of course, the slopes increase rapidly to intersect the value for SiO_2 liquid. Extrapolation of the estimated trends to unit mole fraction of added oxide gives an intercept at a small value relative to the intercept for pure SiO_2.

In a plot of mean molar quantities versus mole fractions in binary systems, the ordinate intercepts of tangents to the mean molar curve are the partial molar quantities of the components. Figure 3A essentially portrays

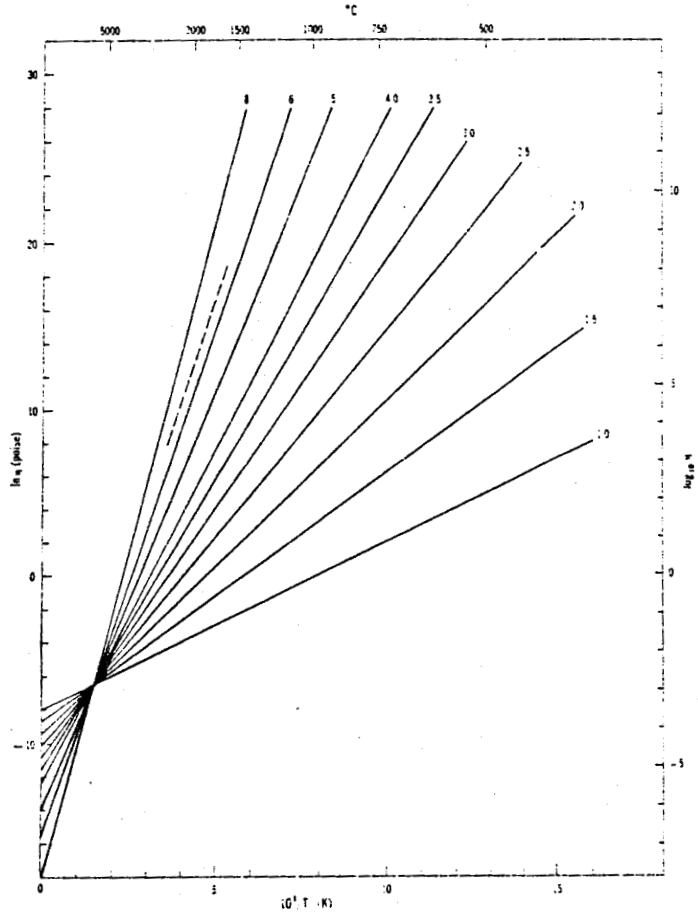


Fig. 2. Generalized graph of Arrhenius slopes, d ln η/d(10^4/T), for multicomponent silicate liquids relative to a *postulated* average inversion point at ln η = −6.40, (10^4/T) = 1.50. The dashed line gives the range of measurements for SiO_2 liquids at high temperatures by Hofmaier and Urbain (1968). This graph represents a reference grid for viscosity estimates only in the range of temperatures discussed in the text.

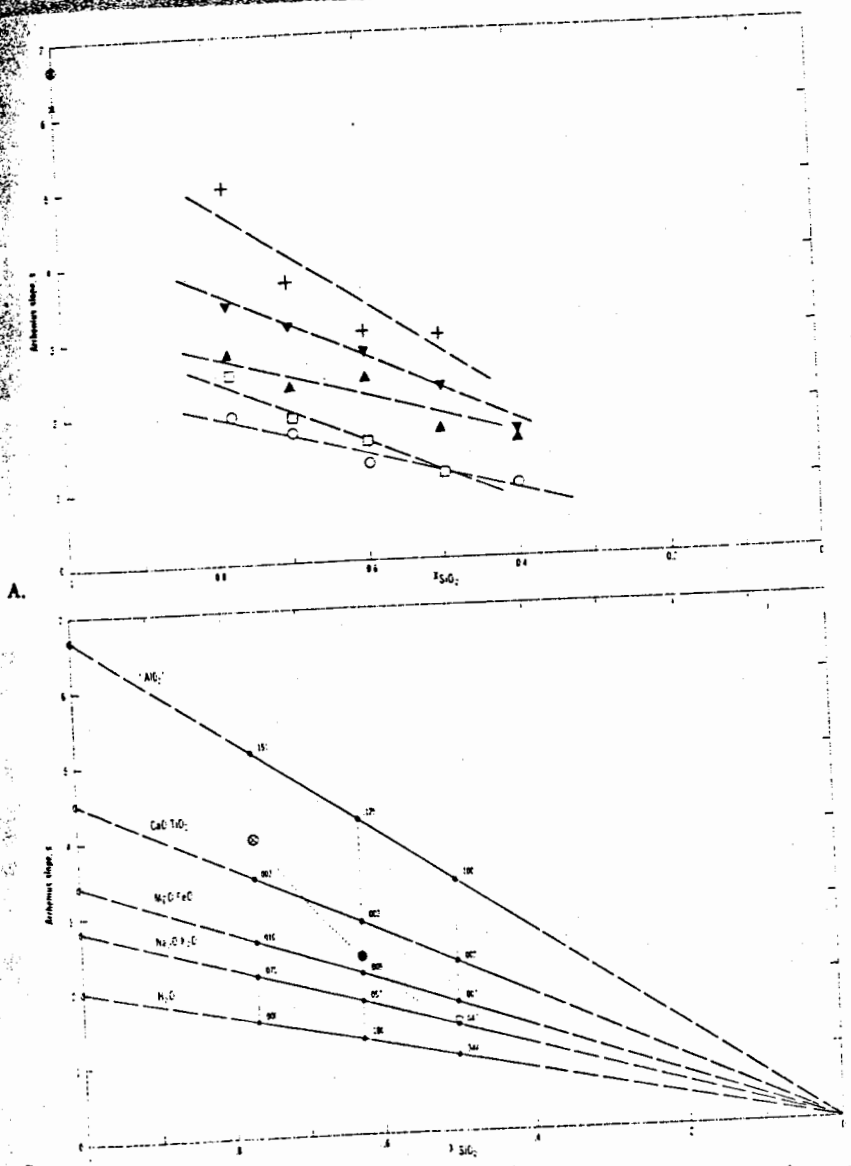


Fig. 8. Composition dependence of Arrhenius slopes for silicate liquid mixtures.

A. Values calculated from binary data of figure 1: Na_2O–open circle; Li_2O–square; MgO–triangle; CaO–inverted triangle; $CaAl_2O_4$–cross. Points are not plotted for FeO or $NaAlO_2$ because there is too much scatter to see a trend, but the average values fall, respectively, near that for MgO and somewhat below that for $CaAl_2O_4$. Values for "pure" SiO_2 are based on data of Bockris, MacKenzie, and Kitchener (1955)–circled X, and Hofmaier and Urbain (1968)–X; see footnote 2, table 1.

B. Postulated composition dependence based on data in (A). Intercept values are listed in table 1. Mean molar values are illustrated for an obsidian composition varying only in H_2O content, where the numbers on the curves at constant X_{SiO_2} are mole fractions of the other oxides : anhydrous–circled X; 6.2 percent H_2O by weight–bold dot (see table 2); 12 percent H_2O by weight–square. These points are the arithmetic means of the values shown by the small solid circles proportioned according to the indicated mole fractions. Values for other granitic compositions fall near the light dashed line. Note that the trend of this line is almost directly away from a value near that for pure SiO_2 (the "AlO_2" intercept), showing how alumina pulls the activation energies toward those of framework compositions at high silica contents.

mean molar values of E* (that is, of $s = E^*/10^4R$), and therefore the intercepts can be considered "partial molar activation energies" of the binary components. The right hand intercepts near zero simply imply that the mean molar activation energy is mainly controlled by the partial molar activation energies of SiO_2 in the intermediate range of compositions ($0.4 \leq X \leq 0.8$). At very low concentrations of SiO_2, presumably near the orthosilicate ratio ($X = 0.33$), the mean molar curves may show entirely different trends.

Accordingly, the second major assumption of the model is that at intermediate compositions the mean activation energy of multicomponent mixtures is given by the average of characteristic partial molar activation energies of SiO_2 in the pseudobinary systems, without considering any contribution of partial molar activation energies of the added oxides. This assumption is represented by figure 3B, where the intercepts at $X = 1$ are the characteristic binary values designated $s_i°$. Other simplifications were introduced by assuming that FeO–MgO and the alkali oxides are each represented by a single intercept value and by noting that the uncertain values of intercepts for $NaAlO_2$–SiO_2 and $CaAl_2O_4$–SiO_2 mixtures could be approximated just as well by averaging $s_i°$ values for either Na_2O or CaO with an intercept in an imaginary system "AlO_2"–SiO_2 which has the same value as the molar activation energy of SiO_2 (however, see footnote 2, table 1). The alumina constituent is indicated by the shorthand "AlO_2" partly to emphasize a role closer to that of SiO_2 (and lack of charge balance) but mainly to emphasize the formula basis for computing mole fractions (the convention is equivalent to using gram atomic proportions of the metals except for the alkalies, H_2, et cetera). The postulated partial molar activation energies of SiO_2 characteristic of given oxide-silica pairs are listed in table 1 (the basis for the pair H_2O–SiO_2 is discussed later).

Although the arbitrary convention for alumina has no strict basis in terms of models of silicate structure, the viscosity data suggest an inherent "preference" for computing the mole fractions on the basis of twice the number of moles of Al_2O_3. Possible implications are briefly discussed in the concluding section.

PROCEDURE FOR CALCULATING VISCOSITIES

The operations required to test and apply the empirical model are simply: (A) convert the chemical analysis to a value for the mean slope s, and (B) derive viscosity versus temperature either by interpolation from figure 2 or by using equation 3. The first operation involves the following steps: (1) convert the chemical analysis to moles of the appropriate oxides in table 1 and calculate the corresponding mole fractions, (2) multiply the values of $s_i°$ in table 1 by the mole fraction of SiO_2, (3) multiply these values by the total mole fraction of each $s_i°$ category, (4) sum the products and divide by $(1 - X_{SiO_2})$, giving the mean value of the slope.

A numerical example of the calculation is given in table 2. It can be seen that this procedure simply finds an average value for the contributions of the various slopes in figure 3B at a characteristic mole fraction of SiO_2. This form of normalization is equivalent to expressing the composition as a linear mixture of hypothetical binary pairs, each having the same ratio of SiO_2 to the added oxide.

Table 3 lists calculated values of slope for a number of rock compositions. For convenience, intercepts at $10^4/T = 0$ and $10^4/T = 10$ are indicated so that viscosity curves for these compositions can be drawn directly. In calculating the slopes, Fe_2O_3 was converted to "FeO", as was done by Bottinga and Weill (1972). No systematic error could be detected in this procedure, even though the oxidation state must have varied widely in the various viscosity measurements. The amounts of minor constituents like MnO, SrO, BaO, Cr_2O_3, P_2O_5, S, F, and Cl are too small in these analyses to affect the mean slope significantly, if they have values of $s_i°$ at all similar to the intercepts in figure 3. This conclusion is supported by later comparisons with viscosity data for the compositions of table 3, where minor elements were ignored. However, some magmatic compositions may be exceptionally rich in one or more of the "minor" elements, and independent tests of more specific effects are needed. The role of H_2O sheds some light on the magnitudes to be expected for exceptionally effective network modifiers. The role of F may be similar, since on a molar basis fluoride ions could modify an equal number of Si–O bonds. In both cases the large effect is amplified by the low formula weight as well as the low value of $s_i°$.

TABLE 1

First approximation of partial molar activation energies of SiO_2 in binary systems based on values shown in figure 3

Metal oxide–silica pairs*	Slope intercept $s_i°$	Equivalent partial molar activation energy, kcal mole^{-1}
H_2O-	2.0	40
K_2O, Na_2O-, Li_2O-	2.8	56
MgO-, FeO-	3.4	68
CaO-, TiO_2-	4.5	89
"AlO_2"-	6.7	134**

* The hyphen after the oxide refers to binary mixtures of the given component with mole fractions of SiO_2 between about 0.4 and 0.8. The H_2O-SiO_2 value was obtained by inference from the other values and data of Shaw (1963).

** The original choice for this value was based on the data of Bockris, Mackenzie, and Kitchener (1955) for SiO_2 liquids. More recent measurements by Hofmaier and Urbain (1968) indicate that a better value is 123 ± 2 kcal mole^{-1}. Interestingly, however, adjusting the slope intercept of "AlO_2"-SiO_2 to fit this value worsens the agreement of calculated and observed viscosities of magmatic compositions. Therefore, the empirical slope intercept is retained as stated. Comparison of viscosity data for SiO_2 liquids and glasses shows order of magnitude differences between measurements by different laboratories or between different samples by the same laboratory. This appears to reflect differences in the techniques for preparing and stabilizing "pure" SiO_2 glasses more than it indicates instrumental errors; see data comparisons of Hofmaier and Urbain (1968, figs. 2 and 3) and data of Hetherington, Jack, and Kennedy (1964).

COMPARISON OF CALCULATED AND MEASURED VISCOSITIES

Exhaustive comparisons with published measurements on magmati compositions are not attempted because Bottinga and Weill (1972) r view much of the data, and the present calculations can be tested b comparison with their results. Therefore, discussion is limited to selecte data for magmatic systems and to a few examples from simpler system: Some of the examples were chosen to show where the method can be use with confidence, and others were chosen to indicate its limitations an the ways experimental measurements might test deviations and thei structural implications.

Anhydrous magmatic compositions; viscosities below 10^6 poises.— Figure 4 illustrates the calculated and measured viscosities from a fe of the key sources considered by Bottinga and Weill. The sets of measure ments by Carron (1969), Shaw (1969), and Murase and McBirney (1970 are seen to be remarkably consistent with the calculated curves. Thi agreement partly reflects the fact that these data sets were used to adjus the mean for the reference coordinates in figure 2 and equation 3. How ever, numerical comparisons given in table 4 suggest that the presen method gives as good a fit to the data as does the method of Bottinga and Weill. It appears that both methods tend to deviate more often toward higher values than the measured viscosities, although the mean difference for all comparisons is nearly zero by the present method. The precision is about the same if the calculated values are all adjusted by the amounts of the mean differences.

TABLE 2

Example of conversion of a chemical analysis to the calculated slope of a viscosity curve on the Arrhenius plot illustrated in figure 2. The chemical data are from Shaw (1968). Numbers are given to slide rule accuracy.

Constituent	Wt %*	Moles	x	s_i	$s_i \cdot X_{SiO_2}$	$X_i(s_i \cdot X_{SiO_2})$
SiO_2	71.9	1.195	0.627			
Al_2O_3	12.1	0.238**	0.125	6.7	4.20	0.53
Fe_2O_3	0.57	0.007**	0.004			
FeO	0.52	0.007	0.004	3.4	2.13	0.02
MgO	0.04	0.001	0.001			
CaO	0.27	0.005	0.003	4.5	2.82	0.01
TiO_2	0.09	0.001	0.001			
Na_2O	3.94	0.064	0.033	2.8	1.75	0.10
K_2O	4.32	0.046	0.024			
H_2O	6.20	0.344	0.180	2.0	1.25	0.23
Sum	99.95	1.908				0.89

Mean slope:

$$s = \Sigma X_i(s_i \cdot X_{SiO_2}) \div (1 - X_{SiO_2}) = 2.39$$

* Analysis DC-2 in table 1 of Shaw (1968) recalculated to 100 percent on the basis of 6.2 percent H_2O.

** These values are twice the number of gram formula weights of the stated oxides. They are the number of gram atoms of the respective elements Al and Fe or the number of moles of the hypothetical constituents "AlO_2" and "FeO" (see text).

The agreement with data of Euler and Winkler (1957), shown in figure 4B, is not as good as the agreement in figure 4A, but as illustrated by Bottinga and Weill (1972, fig. 9), there are some features of their data that suggest the possibility of experimental error. This remains an open question that should be rechecked experimentally. However, the mean difference between calculated and measured viscosities represented by figure 4B and other data of Euler and Winkler (1957) is small (but negative rather than positive as in table 4). The deviations of calculated values by Bottinga and Weill are apparently similar.

Anhydrous magmatic liquids and glasses; viscosities above 10^6 poises. —Reproducible measurements are difficult at high viscosities because increasingly important "memory" effects are related to decreasing rates

TABLE 3

Values of mean slope calculated from the chemical analysis (see table 2)

Identification*	Slope(s)	$10^4/T = 0$†	$10^4/T = 10$
BW22; Shaw (1969)	2.23	− 9.73	12.57
BW23; Carron (1969)	3.76	−12.04	25.56
BW24; Murase and McBirney (1970)	1.91	− 9.26	9.84
BW25; Murase and McBirney (1970)	2.40	−10.00	14.00
BW26; Murase and McBirney (1970)	3.02	−10.93	19.27
BW13; Euler and Winkler (1957)	3.00	−10.90	19.10
BW14; Euler and Winkler (1957)	2.95	−10.83	18.67
BW15; Euler and Winkler (1957)	2.70	−10.45	16.55
BW16; Euler and Winkler (1957)	2.25	− 9.77	12.73
BW17; Euler and Winkler (1957)	2.32	− 9.88	13.32
BW19; Euler and Winkler (1957)	2.04	− 9.46	10.94
BW20; Euler and Winkler (1957)	1.95	− 9.32	10.18
"Lipari"; Carron (1969)	3.95	−12.33	27.17
"Arkansas"; Carron (1969)	3.88	−12.22	26.58
"Islande"; Carron (1969)	3.85	−12.18	26.32
Rhyolite, anhydrous; Friedman, Long, and Smith (1963)**	4.11	−12.56	28.54
Rhyolite + 0.5% H_2O; Friedman, Long, and Smith (1963)	3.84	−12.16	26.24
Obsidian, anhydrous; Shaw (1963)	4.04	−12.46	27.94
Obsidian + 6.2% H_2O; Shaw (1963)	2.39	−10.00	14.00
"Spruce Pine" + 8.8% H_2O; Burnham (1967)	2.01	− 9.42	10.68

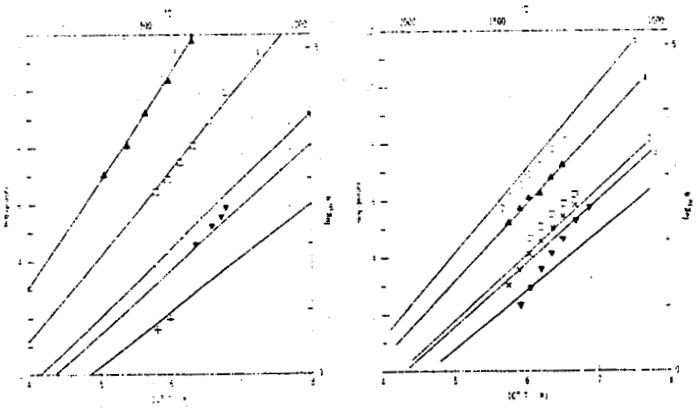
* The analyses prefixed by BW are in table 6 of Bottinga and Weill (1972), from the original sources indicated. Other compositions are identified by characteristic names for which the analysis is easily found in the references cited, except for the rhyolite of Friedman, Long, and Smith (1963).

** A composition for this rhyolite was supplied by Robert L. Smith (written commun., 1971); following are the major oxides in weight percent: SiO_2–74.16, Al_2O_3–12.02, Fe_2O_3–0.93, FeO–0.38, MgO–0.08, CaO–0.35, Na_2O–3.73, K_2O–4.77, TiO_2–0.07, P_2O_5–0.02, MnO–0.05, sum–96.56. The remainder is mainly H_2O which was not included in calculating the slope on the anhydrous basis. F and Cl were also indicated at roughly the 0.2 percent level, but they were not taken into account in calculating the indicated values of slopes.

† This column gives the intercept values of ln η, showing the value of the pre-exponential constant computed from equation 3. The next column gives the corresponding values at $10^4/T = 10$, so that viscosities are graphed either by drawing a straight line through these coordinates or more simply by drawing a line between the reference point of figure 2 and the value of ln η at $10^4/T = 10$.

of adjustment to different conditions of internal equilibrium. This is a complicated problem that requires consideration of changes during transformation between the liquid and the glassy state where thermodynamic properties such as heat capacity and thermal expansion coefficients resemble those in crystals. Although this transition on cooling is usually associated with a viscosity of about 10^{13} poises (see discussion by Bottinga and Weill, 1972), ambiguous states at somewhat lower viscosities can give different results at the same temperature depending on the previous sample history (see Tool, 1946; Macedo and Weiler, 1969). For example, Hetherington, Jack, and Kennedy (1964) show that at viscosities as low as about 10^9 poises measured values for "vitreous silica" can differ by an order of magnitude or more depending on previous annealing temperatures. In these cases, the temperature dependence of viscosity for individual specimens deviates strongly from the Arrhenius relation.

For the above reasons it would not be expected that the simple correlations used in this paper would be valid, because they assume a unique temperature-viscosity function depending only on composition. However, the prediction might relate more closely to some limiting



A. B.

Fig. 4. Comparison of calculated and measured viscosities for anhydrous magmatic liquids. Calculated values are from data in table 3.

A. Data sets from three different laboratories chosen on the basis of good mutual agreement. Solid lines are calculated values and the data points are measurements as listed by Bottinga and Weill (1972, table 5) where the number prefixed BW is the analysis in their table 6: (1) "lunar basalt" of Murase and McBirney (1970), BW 24–cross; (2) Hawaiian tholeiite of Shaw (1969), BW 22–inverted triangle; (3) Columbia River basalt of Murase and McBirney (1970), BW 25–circle; (4) Mount Hood andesite of Murase and McBirney (1970), BW 26–square; (5) "Vulcano" obsidian of Carron (1969), BW 23–triangle.

B. Data of Euler and Winkler (1957) as listed by Bottinga and Weill (1972, table 5) with rock names as given by Euler and Winkler: (1) "olivine basalt," BW 19–inverted triangle; (2) "basalt", BW 17–cross; (3) "tephrite", BW 16–square; (4) "kersantite", BW 15–triangle; (5) "andesite", BW 13–circle. Some additional data were not plotted because of overlap. The numbering of lines 2 and 3 is reversed to emphasize the reversed sequence of calculated versus measured values and poor agreement with the data for "tephrite".

TABLE 4

*Comparison of selected experimental data with calculated viscosities by the methods of Bottinga and Weill and of this paper**

T (°C)	$10^4/T$ (°K^{-1})	Measured η (ln η)	Calc η-Shaw** (ln η)	Calc η-BW (ln η)	Slope (Δ ln η/ Δ $10^4/T$)	Composition (analysis: table 6, BW)	Reference
1298	6.365	11.70	11.92 (+0.22)	12.22 (+0.52)	3.76	23	Carron (1969)
1400	5.977	10.31	10.49 (+0.18)	10.70 (+0.39)			
1491	5.669	9.16	9.32 (+0.16)	9.49 (+0.33)			
1587	5.376	8.04	8.25 (+0.21)	8.34 (+0.30)			
1700	5.068	7.00	7.09 (+0.09)	7.13 (+0.13)			
1200	6.789	9.84	9.56 (−0.28)	9.33 (−0.51)	3.02	26	Murase and McBirney (1970)
1250	6.566	8.90	8.87 (−0.03)	8.71 (−0.19)			
1300	6.357	8.17	8.25 (+0.08)	8.13 (−0.04)			
1350	6.161	7.43	7.65 (+0.22)	7.59 (+0.16)			
1400	5.977	6.85	7.10 (+0.25)	7.08 (+0.23)			
1450	5.804	6.39	6.55 (+0.16)	6.60 (+0.21)			
1250	6.566	6.01	5.80 (−0.21)	6.14 (+0.13)	2.40	25	Murase and McBirney (1970)
1300	6.357	5.46	5.29 (−0.17)	5.55 (+0.09)			
1350	6.161	4.84	4.82 (−0.02)	5.00 (+0.16)			
1400	5.977	4.26	4.38 (+0.12)	4.49 (+0.23)			
1450	5.804	3.80	3.94 (+0.14)	4.00 (+0.20)			
1200	6.789	5.77	5.42 (−0.35)	6.12 (+0.35)	2.23	22	Shaw (1969)
1210	6.743	5.48	5.31 (−0.17)	5.99 (+0.51)			
1220	6.698	5.42	5.22 (−0.20)	5.86 (+0.44)			
1235	6.631	5.30	5.10 (−0.20)	5.68 (+0.38)			
1300	6.357	4.55	4.48 (−0.07)	4.92 (+0.37)			
1395	5.995	1.96	2.21 (+0.25)	1.88 (−0.08)	1.91	24	Murase and McBirney (1970)
1450	5.804	1.61	1.82 (+0.21)	1.34 (−0.27)			
Algebraic sum of differences			+0.59	+4.04			
Mean of differences			+0.026	+0.176			

* These examples are chosen as representative of mutually consistent data on different rock compositions obtained by three different laboratories. Additional comparisons are not shown to avoid duplication of table 5 in Bottinga and Weill (1972).

** The values in parentheses are ln η (calc) − ln η (measured). The calculated values in this column were read from expanded graphs of the calculated curves; the second decimal place is interpolated.

viscosity curve representing both stable and metastable ("supercooled") liquids under conditions of internal equilibrium. This possibility is compared in figure 5 with some measurements by Carron (1969) on obsidian compositions. Predicted values are generally lower than the measured values, although there is remarkably close agreement with Carron's data for compositions designated "Vulcano" and "Lipari". The calculated curves for compositions designated "Islande" and "Arkansas" are near that for "Lipari" and obviously underestimate the experimental viscosities. These deviations are consistent in magnitude and direction with possible differences in thermal history of the different samples. Since the sample designated "Vulcano" apparently had the same thermal history as material used for the high temperature measurements shown in

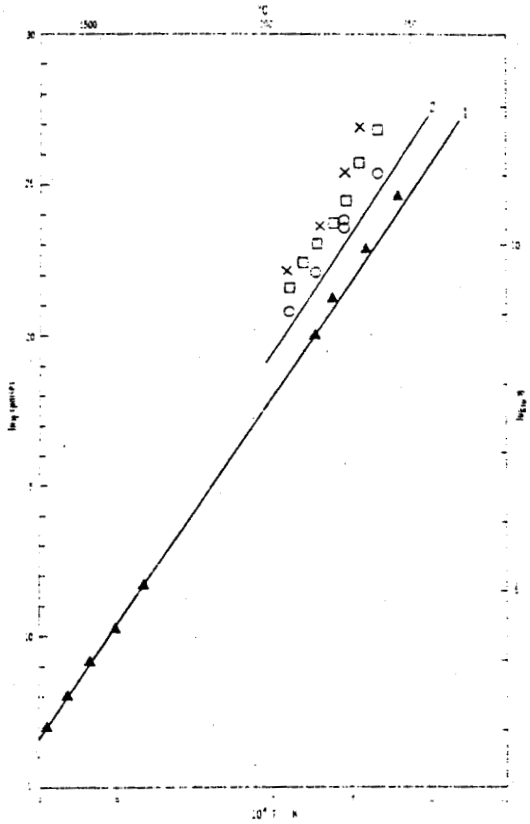


Fig. 5. Comparison of calculated and measured viscosities for anhydrous obsidian compositions of Carron (1969). Data points are: "Vulcano"–triangle; "Lipari"–circle. "Arkansas"–square; Islande–cross. Solid lines are calculated from table 3: (1) "Vulcano". (2) "Lipari". The other compositions give calculated lines near that for "Lipari". Since the "Vulcano" composition was also measured at high temperatures these data may be closest to equilibrium values (see text for discussion of the large deviation of other compositions).

figure 4A (see Carron, 1969, p. 22), the agreement of the calculations with data for this composition is consistent with the possibility of memory effects in other samples not similarly annealed.

At present it can only be concluded that predicted viscosities may not reproduce experimental data at viscosities above about 10^6 poises; the calculated values may be too low in many cases. However, it is also clear that predictions must inevitably fail unless they are referred to a limiting equilibrium condition or take special account of sample history. This is a problem of great experimental, theoretical, and practical interest.

Magmatic liquids containing H_2O.—The characteristic value of $s^\circ_{H_2O}$ was chosen by calculating mean slopes for the obsidian of Shaw (1963) containing 4.3 and 6.2 percent H_2O (by weight) using the other values of s_i° from table 1 and then assigning a value for H_2O–SiO_2 that reproduced the measured viscosities. Predictions using $s^\circ_{H_2O} = 2.0$ are compared with other measurements in figure 6. Unfortunately, data are insufficient for a rigorous test of precision. Excluding the data of Shaw (1963), which automatically agree fairly well because of the above manipulation, the principal tests are given by the data of Friedman, Long, and Smith (1963), Burnham (1964), and Carron (1969).

The viscosities given by Friedman, Long, and Smith (1963) were obtained from experiments designed primarily to demonstrate mechanisms of compaction in ash flow sheets, and this method gives too much unavoidable scatter of viscosity values to indicate more than rough agreement with the calculations (these measurements also represent conditions of high viscosity where sample history could be a source of variation in results for different experimental runs). The data of Burnham (1964) are in serious disagreement with the calculated viscosities. The fact that these viscosities at 8.8 percent H_2O (by weight) are not much lower than the values of Shaw (1963) at 6.2 percent H_2O suggests the possibility of errors in the viscosities and/or H_2O contents in one or both of these studies. However, Carron (1969, p. 51) gives measurements at two different H_2O contents for two alkali aluminosilicate liquids that differ considerably in the proportions of other major oxides. Calculated viscosities for these compositions agree very closely with the measurements, although there is only one measured value in each case. A remaining possibility is that the higher pressures of Burnham's experiments increase viscosities more than we had previously expected (Shaw, 1963, 1965; Burnham, 1967).

It is concluded that the calculated viscosities of figure 6 are consistent with the measurements, within known probabilities of experimental error, except for the data of Burnham (1964). Thus the assumptions of the model may not be valid at such high H_2O contents and pressures, and therefore the method is not recommended for exceptionally H_2O-rich "pegmatitic" fluids or for pressures greater than a few kilobars. It is evident that there is great need for further study of pressure dependence

at constant composition, especially for silica poor compositions, to pressures of the order of 20 kb.

Summary of comparisons with experiment for magmatic compositions.—Figure 7 summarizes the deviations discussed above for comparison with figure 8 of Bottinga and Weill (1972). If figure 7 were taken to represent a homogeneous set of similar data, one might be

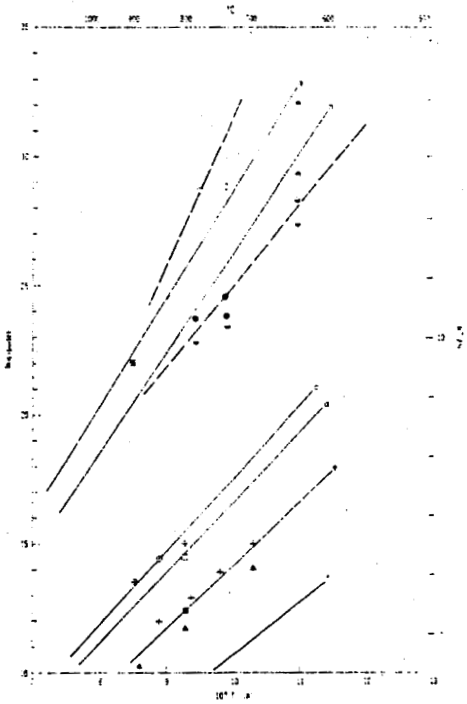


Fig. 6. Comparison of calculated and measured viscosities for granitic compositions containing H_2O (percentages are by weight). Calculated curves and corresponding data points are: (A) rhyolite of Friedman, Long, and Smith (1963) containing less than 0.1 percent H_2O–open circle (the square with cross is an unpub. measurement by Shaw) (B) rhyolite of Friedman, Long, and Smith (1963, table 2) with about a half percent H_2O–circle filled at top (0.4 percent), solid circle (0.5 percent), circle filled at bottom (0.6 percent); (C) obsidian of Shaw (1963) with 4.3 percent H_2O–circle with cross; (D) "Verre No. 1" of Carron (1969) with 4.5 percent H_2O–open square; (E) obsidian of Shaw (1963) with 6.2 percent H_2O–cross, and "Verre No. 2" of Carron (1969) with 5.2 percent H_2O–solid square; (F) "Spruce Pine" pegmatite of Burnham (1964, 1967) containing 8.8 percent H_2O–solid triangle.

The dashed lines are from figure 10 of Friedman, Long, and Smith (1963) for the above compositions. Systematic deviations of these lines from the calculated curves may partly reflect experimental uncertainty, because H_2O contents of experimental runs were inferred from independent measurements, and viscosities were obtained by interpretation of compaction curves where rates are variable during a run (note that agreement is best for viscosities near liquidus temperatures). The agreement of the calculated viscosities of curve E with measured values for glasses of two different H_2O contents (that is 6.2 and 5.2 percent) is because the synthetic glass "Verre No. 2" of Carron (1969) is relatively much richer in total alkalies.

tempted to conclude that some of the measurements of Carron (1969) at high viscosities and those of Burnham (1964) are systematically in error. However, it is emphasized that this is not a valid conclusion for the reasons mentioned before. Every composition and set of conditions must be examined to see if any possible unique factors exist that are not represented in those data on which the predictions are based. Within such guidelines, fair confidence is indicated for predictions within a factor of two at viscosities to about 10^8 poises and for equilibrium values

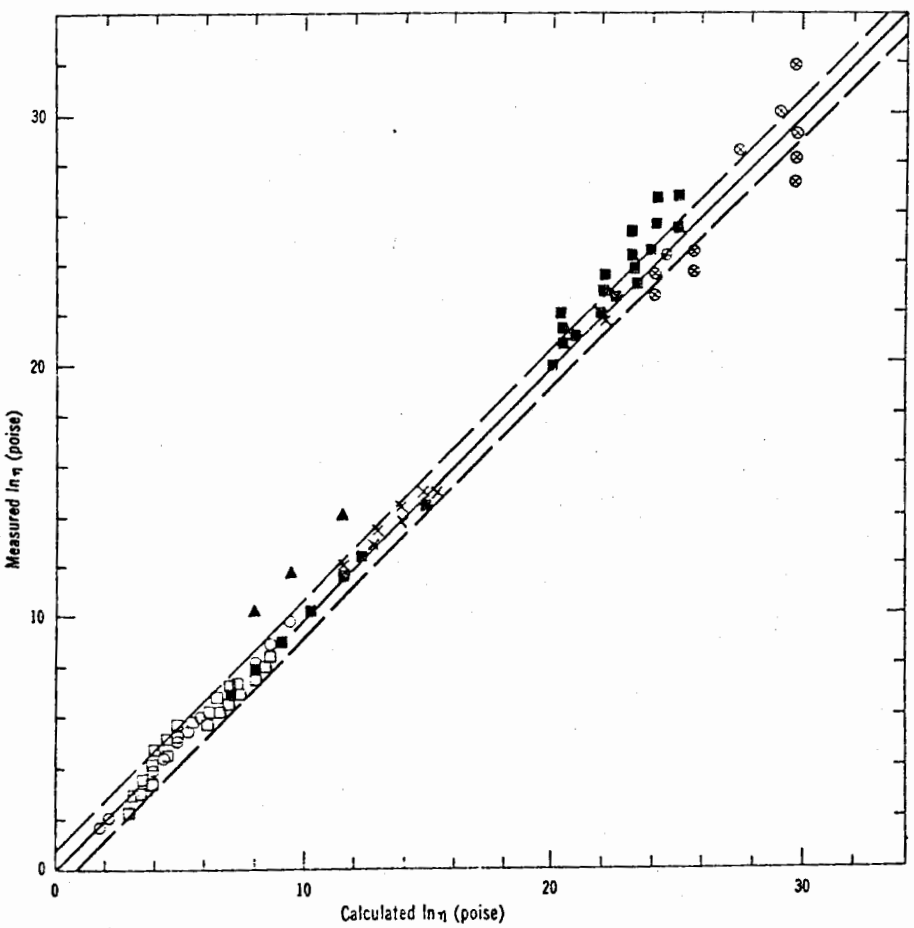


Fig. 7. Correlation between calculated and measured viscosities. Dashed lines define an envelope within which the calculated viscosities range between one half and twice the measured values. The number of points from each source is given in parentheses after each symbol given below (in the low viscosity range some overlapping points have been omitted for clarity). Data sources are:

Murase and McBirney (1970)–open circle (10); Euler and Winkler (1957)–open square (39); Shaw (1963, 1969, unpub.)–cross (11); Burnham (1964)–solid triangle (3); Friedman, Long, and Smith (1963)–circled cross (11); Carron (1969)–solid square (25).

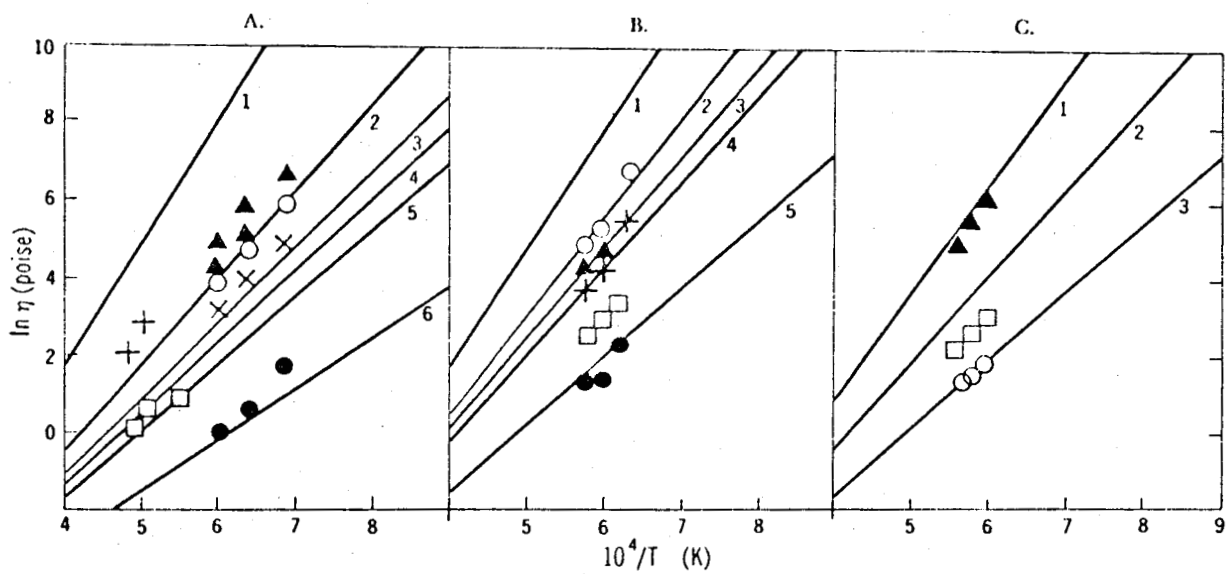


Fig. 8. Comparison of measured and calculated viscosities for synthetic liquids of few constituents. Data and original sources are given in table 2 of Bottinga and Weill (1972). Compositions are given below as mole fractions in parentheses following the oxide; in each case the remainder is SiO_2. Numbers on the figure identify the calculated curve corresponding to the symbol listed after each number below. Note that the sequence of lines does not necessarily correspond to sequence of symbols.

A. *Binary liquids*: (1) CaO (0.305)–plus sign; (2) Na_2O (0.20)– solid triangle; (3) Li_2O (0.30)–cross; (4) K_2O (0.33)–open circle; (5) MgO (0.50)–open square; (6) FeO (0.61)–solid circle.

B. *Ternary liquids*: (1) CaO (0.26) "AlO_2" (0.17)–open circle; (2) CaO (0.31) "AlO_2" (0.23)–plus sign; (3) MgO (0.32) "AlO_2" (0.15)–solid triangle; (4) CaO (0.25) MgO (0.21)– open square; (5) CaO (0.39) MgO (0.20)–solid circle.

C. *Quaternary liquids*: (1) CaO (0.10) MgO (0.13) "AlO_2" (0.22)–solid triangle; (2) CaO (0.35) MgO (0.07) "AlO_2" (0.11)–open square; (3) CaO (0.45) MgO (0.07) "AlO_2" (0.11) open circle.

of stable or metastable liquids at higher viscosities. Confidence weakens for predicting very high viscosities, because of uncertainties in the sample states for which data are available (see earlier discussion and footnote 2, table 1).

Bottinga and Weill (1972, fig. 8) did not test their calculations at the highest viscosities shown in figure 7, but for the sets of data at lower viscosities the correlations are very similar, as expected. Surprisingly, however, the much simpler scheme of the present paper gives a slightly tighter grouping of points, and the general trend is closer to the line of 1:1 correlation. This conclusion is reached mainly because of the differences in our calculated values for the numerous points of Euler and Winkler (1957). Some of the older data are not included in figure 7 (see Bottinga and Weill, 1972, fig. 8), but deviations from these data would be similar to those shown by Bottinga and Weill.

It may seem puzzling that the results are similar to those of Bottinga and Weill, even though no special recognition was given to the apparent discontinuities in viscosity versus composition, at constant temperature, shown by the binary data (see their figs. 1 through 3). Evidently these discontinuities are either averaged out by addition of other constituents, or they are not as sharp as the trend lines in their diagrams would suggest. The present method avoided the designation of composition ranges by first fitting the viscosity to a temperature function which was then fitted to composition. Apparently a very crude fit of the data on this basis gives as good discrimination as more elaborate fitting of the composition variations of viscosity.

Synthetic systems of few constituents.—The purpose of testing predictions against "simpler" systems is to emphasize the averaging effects that apparently provide the key to prediction of the multicomponent data. Figure 8 shows comparisons with the data of binary, ternary, and quaternary compositions in table 2 of Bottinga and Weill (1972). For the binary and ternary compositions deviations are larger than those for magmatic liquids, and there seem to be systematic errors associated with specific constituents. For example, predictions are almost always too high for binary and ternary compositions containing CaO. With the addition of one more constituent, however, this deviation is apparently weakened. In the magmatic compositions considered earlier CaO varies from 0.90 percent (by weight) for the "Vulcano" composition of Carron (1969) to about 11 percent for the Hawaiian tholeiite of Shaw (1969). In both cases the viscosities deviate only about 20 percent from the calculated values, and the composition richer in CaO deviates in the opposite sense from the comparisons of figure 8 (see fig. 4A and table 4).

Evidently, the deviations between measured and calculated viscosities in systems of a few constituents cannot be used individually to adjust the estimates for multicomponent compositions. The comparisons for magmatic compositions could be attributed to a fortuitous compensation of errors, but the odds against such a chance correlation seem very

large. It is hard to avoid the conclusion that the model reflects a general rule. Apparently in multicomponent mixtures every pairing of a specific constituent with SiO_2 is so modified by all other constituents that the pair behaves similarly despite wide variations in proportions of the additional constituents.

Judging from composition effects such as those in figure 3, the above conclusion would seem to be limited to compositions having mole fractions of SiO_2 less than about 0.8. Since this composition can be identified structurally with the onset of rapidly increasing linkage between Si–O tetrahedra at higher mole fractions, it might also be assumed that the composition limit should be given by the proportion of oxygen bonded to the sum of the tetrahedral cations (such as silicon and aluminum). However, on this basis many quartzo-feldspathic compositions would be out of bounds (that is, too highly coordinated for the assumptions of the model), whereas there is excellent agreement of calculated viscosities for the well documented composition from Vulcano (Carron, 1969) and reasonable agreement in other cases. Aluminum apparently cannot be simply categorized as a "network former", even in compositions undersaturated in Al_2O_3 according to the normative scheme of Bottinga and Weill (1972, see their discussion of studies on aluminosilicate compositions). The present method assumes that the "binary pair" "AlO_2"–SiO_2 behaves in a manner similar to other pairs without specifying proportions of tetrahedral and octahedral occupancy. For magmatic liquids this assumption appears to work as well or better than more detailed classifications.

Figure 9 indicates that the above assumption is not valid for compositions of feldspar stoichiometry, even though it appears to fit data for feldspar-silica mixtures (see figs. 5 and 6). Therefore, a study of transport properties in liquids of feldspar compositions and their mixtures with SiO_2 might greatly advance the understanding of liquid aluminosilicate structures, particularly in the light of structural and thermodynamic data for the crystalline phases. However, effects relating to sample history will require careful evaluation.

COMMENTS ON PHYSICAL INTERPRETATION OF VISCOSITY CORRELATIONS

At present, it is not entirely clear why the assumptions represented by figures 2 and 3 should give such consistent results as indicated by figure 7. Therefore the paper is concluded with some rather speculative remarks intended to suggest directions in which a better understanding might be sought.

Thermodynamic components and transport properties.—In general, any extensive property of a phase in a multicomponent system of n components is described by n partial molar coefficients, so that the quantity is summed according to proportions that vary in a hyperspace of n–1 dimensions. In polyphase systems, the number of compositional degrees of freedom can be tested by compatibility with the phase rule.

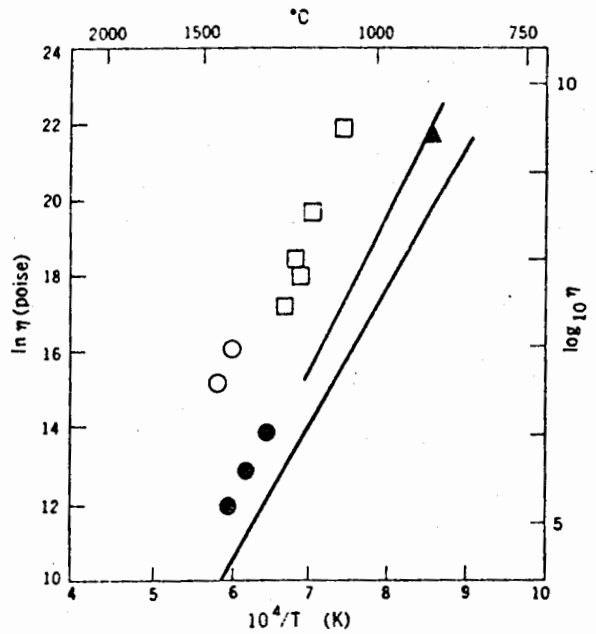


Fig. 9. Liquids in systems $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2. Lines are calculated from s_1^* values in table 1; that is, no distinction is made between Na and K: the lower line is for pure alkali feldspar stoichiometry, and the upper line is for a "ternary minimum" composition (based on the chemical analysis in table 2 renormalized on the anhydrous basis). Data points are: triangle–anhydrous obsidian of Shaw (1963; the viscosity value is from an unpublished measurement); square–$KAlSi_2O_6$ (Shaw, unpub. data); open circle–$KAlSi_3O_8$ (data of Kani, as published in Clark, 1966, table 12·6); solid circle–$NaAlSi_3O_8$ (data of Kani).

However, since this definition of components according to the phase rule depends on criteria of heterogeneous equilibrium, there is no obvious way to choose the "proper" number of composition variables to describe internal properties of an isolated homogeneous phase; the number could be arbitrarily expanded without limit. Silicate phases afford notorious examples of this problem, and contrasts in possible choices are shown by the different variables used by Bottinga and Weill (1972) and in this paper. In the first case, composition variables were highly subdivided, reflecting the fact that a different set of coefficients is normally required to describe any mean molar property of a mixture at each point of composition space. Alternatively, the method of this paper attempts to find the *minimum* number of composition variables consistent with experimental knowledge of the mean molar property. In this sense, the method of choosing composition variables vaguely resembles the definition of thermodynamic components for heterogeneous systems.

In an assemblage of heterogeneous phases, each of fixed composition and at constant temperature and pressure, an extensive property of the system, such as the Gibbs free energy, is given by values characteristic

of each phase summed according to the total mass of each phase, regardless of their relative proportions. For a homogeneous phase, however, the summation is more complicated, because entities of fixed properties generally do not exist. Some "excess" energy of mixing (reflecting internal reactions or other changes in local energy densities) is found relative to the additivity of energies according to proportions of "pure end members".

By the above analogy, the calculation of mean molar activation energies in this paper resembles the additivity relations for heterogeneous systems. Such an interpretation applied to the idealized relation in figure 3 suggests that there may be complexes of SiO_2 that maintain a certain level of activation energy characteristic of a given type of modifying cation which is simply "diluted" by adding more of the same modifying constituent. Such a relation would exist if there were discrete microheterogeneous "phases" of a few types that control the mean activation energy by simple summations of their respective amounts. Since the mean activation energy is normally expected to be influenced by energies of mixing (Bondi, 1967, p. 70), this is also equivalent to saying that these energies are small relative to viscosity variations of the precision represented by figure 7.

The reaction rate theory (or "relaxation theory") of transport properties developed by Eyring and coworkers (see Ree and Eyring, 1958; Bondi, 1967) showed that the viscosities of many simple liquids could be correlated by an expression analogous to the Arrhenius equation, given by

$$\eta = (h/v) \exp (\Delta E_v/2.45\ RT) \qquad (4)$$

where ΔE_v is the energy of vaporization, v is the molecular volume, and h is Planck's constant. In simplest terms, such expressions relate the preexponential constant of equation 2 to dimensions of molecular structure and relate the activation energy to some measure of the "volatility" of structural units. According to this idea the postulated relationships of figures 2 and 3 correspond to a continuous variation of some characteristic "molecular" size from very large values for pure SiO_2 to smaller sizes with the addition of modifying constituents. The analogous vaporization energy decreases proportional to E^*, thus with decreasing size according to the assumption of figure 2 as interpreted by equation 4. Furthermore, at a given mole fraction of SiO_2 (on the basis specified earlier) there would be a similar variation as a function of the type of modifying constituent; that is, the apparent molecular size and vaporization energy increase upward in figure 3.

Liquid silicate solution theories.—Shaw (1964, p. 616) suggested that concepts of polymeric reactions in silicate liquid mixtures might be tested by viscosity data. Although this has not been accomplished directly, it is instructive to compare the above ideas to ionic models of silicate structure. Recently, Hess (1971) has shown that there is a high

probability of forming an infinitely branching network in binary silicate liquids when a third of the oxygens singly bonded to silicon became doubly bonded by two silicon atoms. Following Flory (1953) he calls this the "gel point" and notes that for cations of low field strength this occurs at a mole fraction of SiO_2 close to 0.44. This is also approximately the lower limit of the "intermediate" composition range as outlined in the present paper. Interestingly, it was earlier found by A. C. Lasaga and M. Sato (written commun., 1968) that this composition region is correlated with a minimum in the "alpha function" of Darken and Gurry (1953), which Lasaga and Sato explained by a maximum in the coulombic attractions between cations and polymeric anions of silicate mixtures. These observations emphasize the earlier admonition that the assumed linearity of figure 3 cannot be extrapolated to mole fractions of SiO_2 lower than about 0.4.

Hess (1971) points out that cations of high field strength form the most highly coordinated melts at a given silica concentration. The field strength is given by Z/a^2 where Z is the cation charge and a is the sum of the ionic radii of the cation and oxygen. This hierarchy is analogous to the relationship suggested by the partial molar activation energies of figure 3 and their dimensional implications discussed in the preceding section.

Liquid immiscibility at high silica concentrations is also correlated with the polymerization reactions as modified by the field strength of cation-oxygen bonding (Charles, 1969; Hess, 1971). Cations of high field strength favor coordination with "free oxygen ions" (that is, those not bonded to silicon). Consequently, under some conditions it is possible to minimize the Gibbs free energy by formation of a nearly pure SiO_2 phase and a cation-rich phase. Because this free energy difference is small, the distinction between macroscopic phase separation and a microheterogeneous solution is ambiguous. In the "silica-rich" region of binary systems (that is, at compositions comparable to the range considered in this paper), the solution is considered to be structurally inhomogeneous consisting of gel and sol portions (Hess, 1971, p. 302).

The above picture is quite similar to the interpretation of the additivity relations for activation energies discussed in the last section. The correlations between relaxation theories, solution theories, and transport properties for silicate liquids of magmatic composition seem to show a consistency that holds some promise for even greater systematic classification in the future.

Incidental observations and reservations.—The possible correlations of polymeric structure with ionic strength and partial molar activation energies of "components" in microheterogeneous mixtures suggest a correlation with thermal expansion coefficients. These coefficients for oxide constituents given by Bottinga and Weill (1970) for the same composition ranges show variations roughly inverse to those of s_i° in figure 3, as might be expected. However, as in the case of ionic strength,

the order of values for CaO, MgO, and FeO do not agree with the sequence shown by the activation energies. Nevertheless, such lines of comparison may lead to a much better understanding of interaction potentials in silicate liquids.

The coordinate system for temperature and viscosity in figure 2 can only be considered as a tentative reference grid to illustrate the model; it may have no physical meaning at temperatures near the point of convergence. Hypothetically, however, the common intersection represents a point of inversion where the composition dependence of viscosity at constant temperature changes sign. Conceivably, this sort of behavior could relate to a change from liquidlike to gaslike behavior of the multicomponent mixtures. Certainly, the vapor pressures would be quite high at such a temperature (roughly 6000 K), although the variety of actual chemical species at this temperature would be quite different from those present in the liquids.

A closing comment returns to the bases for expressing silicate compositions. The basis chosen here (see table 2) seemed the simplest expedient consistent with definitions of the partial molar activation energies. It was found that expressing aluminum on the Al_2O_3 basis or on the various aluminate formula bases either gave poor values of mean activation energy or required the use of more coefficients. Obviously, since the mole fraction of SiO_2 is different on each different basis, it has no unique value for a given composition. The apparent success of the "AlO_2" convention seems to relate to its dual role. That is, defining mole fractions in this way gives contributions to the activation energy resembling those of pure SiO_2 at high silica concentrations, but at low silica concentrations alumina is considered to "dilute" the network in a manner more like the other oxides. This effect may be related to a systematic variation of aluminum coordinations relative to polymeric and free oxygens and to its effective field strength considered as a modifying cation. In any attempts to refine or give a theoretical interpretation of relationships proposed here, it may be more profitable to compute compositions in terms of ionic species referred to the total number of oxygen ions. For the present purpose, however, this was not practical because of analytical uncertainties in the oxygen content and uncertainties in assigning structural occupancies.

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