ANALYSIS OF RECENT MEASUREMENTS OF THE VISCOSITY OF GLASSES

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ABSTRACT

Viscosity of Simple Soda-Silicate Glasses, 500° to 1400°C

Comparison of the results given by English with those of Washburn, Shelton and Libman, indicates a discrepancy in the absolute values of $\log_{10}$ viscosity amounting to 0.6, those of Washburn *et al.*, being relatively too high. If correction for this is made, the isothermal curves of $\log_{10}$ viscosity as a function of soda content are smooth up to 50% Na_2O, showing no inflection. The observations as a function of temperature T are all represented within accidental error by an equation of the type

$$\log_{10} \eta = -A + B \times 10^3 / (T - T_0)$$

where all three constants vary regularly with the composition.

Change of Viscosity of Glass ($6SiO_2$, $2Na_2O$) due to Molecular Substitution of CaO, MgO and Al_2O_3 for Na_2O

The effect is clearly brought out by plotting (from the results of English) the change of $\log_{10} \eta$ due to the substitution as a function of temperature. The curves each show a sharp bend at a temperature between 840° and 1050°C, which is designated the aggregation temperature T_a. If we divide these curves by the corresponding percentage substituted, we get curves for each oxide which are straight and parallel below the aggregation temperatures, the slopes (increase of change of $\log_{10} \eta$ per 100°C) being -0.056 (CaO), -0.055 (MgO), -0.018 (Al_2O_3) per per cent oxide substituted. For substitution of $^1/_2$ molecule the slopes are -0.325 (CaO), -0.23 (MgO) and -0.18 (Al_2O_3) per 100°. At the aggregation temperature the change of $\log_{10} \eta$ per per cent is a minimum, 0.03 to 0.06 for CaO, 0.12 for MgO, 0.07 for Al_2O_3.

Evidence of Aggregation in Glasses, from Viscosity Measurements

The sharp bends in the plots of change of $\log_{10} \eta$ due to substitution of an oxide for Na_2O, suggest the beginning of molecular aggregation at these temperatures. These aggregation temperatures are close to the devitrification temperatures, but the effect on the viscosity curves cannot be due to actual devitrification since it does not change with time. Taking the aggregation temperatures as equal to devitrification temperatures, additional isotherms are roughly sketched into the *equilibrium triangle of the system* $Na_2O–CaO–SiO_2$.

Change of Viscosity of Glass ($4SiO_2$, $2Na_2O$) due to Substitution of B_2O_3 for SiO_2

The change of $\log_{10} \eta$ (from the results of English) is plotted as a function of temperature, and also the change of $\log_{10} \eta$ per per cent B_2O_3. The curves are more complex than for the substitution for Na_2O.

Introduction

To the glassmaker the viscosity of his glass, particularly at the higher temperatures, is of the greatest importance. The refining of glass depends on the rate at which the gas bubbles rise and this varies with the viscosity; the weight of the gather, the size of the gob fed through an orifice,

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[1] Recd. March 20, 1925.

the distribution obtained in a blown article, the sharpness with which the glass takes the form of the mold, and the rate of annealing, each depend upon the viscosity of the glass through the corresponding range of temperature. Nevertheless until recently no accurate measurements have been made. During the past year, however, the results of two extensive, systematic and carefully made investigations have been published. S. English[1] studied the viscosity of several series of soda-lime, soda-magnesia and soda-boric oxide glasses at temperatures from 500° to 1400°C. Just previously Washburn, Shelton and Libman[2] obtained values for a series of soda-lime glasses for the range 800° to 1500°C. It seemed worth while to subject the data to a graphical analysis in order to correlate and compare the results of the two investigations and to get as much information as possible from them as to the variation of viscosity with temperature and with composition.

The method of measurement used in the two investigations is the same in principle. In both cases the glass was melted to a definite depth in a porcelain crucible held at the desired temperature by means of an electric resistance furnace, and the viscosity was measured by the rate at which a given torque, applied by means of a weight hung on a silk thread, rotated a rod mounted on ball bearings which carried a stirrer which was carefully centered and immersed to a definite depth in the glass. The furnaces were somewhat different, that of English having been relatively quite long while that of Washburn *et al.*, closely fitted the crucible and was supplied with independent heating wires in the lid as well as on the sides and bottom and was controlled by means of three thermocouples, while English used only one. The stirrer used by English was cylindrical and covered with an iridio-platinum sheath, while Washburn *et al.* used a carefully formed porcelain stirrer with a relatively small neck where it passed through the surface of the glass. Both pieces of apparatus appear to have been carefully calibrated and the precision obtained in each case seems to be about the same. A careful reading of both articles did not suggest any definite reason why the results obtained in the two investigations should not be given equal weight.

For temperatures from 500° to 750°C, it is impossible to use the above method, so English obtained values for the viscosity from measurements of the rate of elongation of a rod or thread under a given applied load.

In the following analysis, the various glasses will be designated by the authors' numbers, followed by an E or a W, to indicate English or Washburn *et al.*

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[1] S. English, *J. Soc. Glass Tech. Trans.*, **7**, 25 (1923) and **8**, 205 (September, 1924).

[2] E. W. Washburn, G. R. Shelton and E. E. Libman, Univ. of Illinois Eng. Exp. Station, *Bull.* **140,** 74 pp. (April, 1924).

1. Sodium Silicate Glasses

Results are given for the following glasses:

Glass	Na_2O, per cent	R_2O_3, per cent	RO, per cent	Loss ($H_2O + CO_2$), per cent	Ratio of Na_2O to SiO_2
2W	17.0	0.46	0.0	0.8	0.207 = 1/4.84
600E	19.46	.80	.1	?	.244 = 1/4.1
1E	25.34	.42	.2	?	.342 = 1/2.93
3W	29.5	1 (about)	.1	?	.43 = 1/2.32
4W	39.3	1 (about)	.1	?	.67 = 1/1.5
1W	49.4	0.6 to 1.8	.1	2.5	1.03 = 1/0.97

The data for 1E extend from 485° to 1310°C. When log η (η = viscosity) is plotted as a function of temperature (see English, Fig. 6) a curve concave upward is obtained, log η decreasing less rapidly the higher the temperature. Let us change the variables so as to get as near a straight line plot as possible. If log η is plotted as a function of $1/T$, where T is absolute temperature centigrade, a curve concave upward is still obtained. The concavity is less if $1/T^2$ is used, and it was found that log η plotted as a function of $(1/T)^{7/3}$ gave practically straight lines both for 600E and 1E (see Fig. 1).[1] Therefore

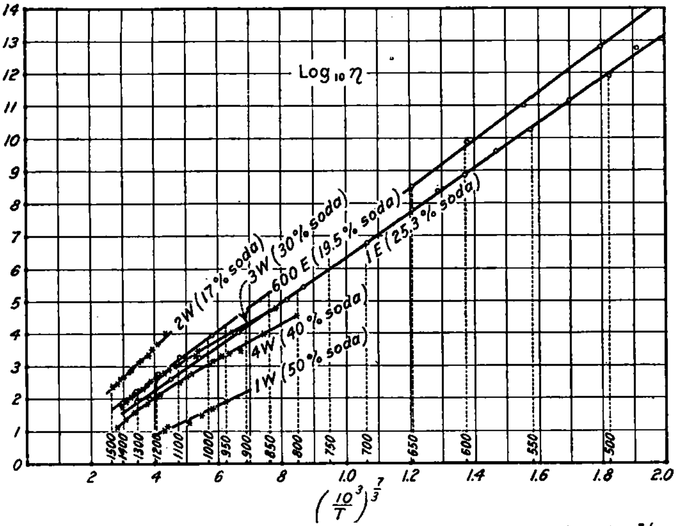

FIG. 1.—Observed values of $\log_{10} \eta$ as a function of $(10^3/T)^{7/3}$. Smooth curves drawn through experimental points.

$$\log \eta = -a + b\,(10^3/T)^{7/3}. \qquad (1)$$

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[1] Slightly better agreement with a linear relation is obtained if we assume that there is a jog of 0.17 between the line through the points below 700° obtained by the elongation method, and the line through the points above 700°. If we subtract 0.17 from the values for the lower temperature the data for 1E are represented within experimental error (±0.03) by the equation (1E) $\log_{10} \eta = -0.40 + 6.66(10^3/T)^{7/3}$.

In Fig. 1 the results for glasses 1W, 2W, 3W or 4W have also been plotted and full lines have been drawn through the observations so as to represent them as closely as possible. The curves for 3W and 4W are definitely concave downward. But the most interesting fact brought out in this figure is the marked discrepancy between the E and W curves, not so much in the shape as in the absolute values. The 3W curve for 30% soda crosses the 1E curve (25.3% soda) at 850° and nearly touches the 600E curve (19.5% soda) at 1400°, while the 2W curve (17% soda) is farther above the 600E curve (19.5% soda) than the 4W curve (40% soda) is below it. If the results for a certain temperature, say 1200°, are plotted as a function of the ratio of soda to silica r, an irregular curve is obtained, as shown in Fig. 2*A* by the dotted line *abcde*.

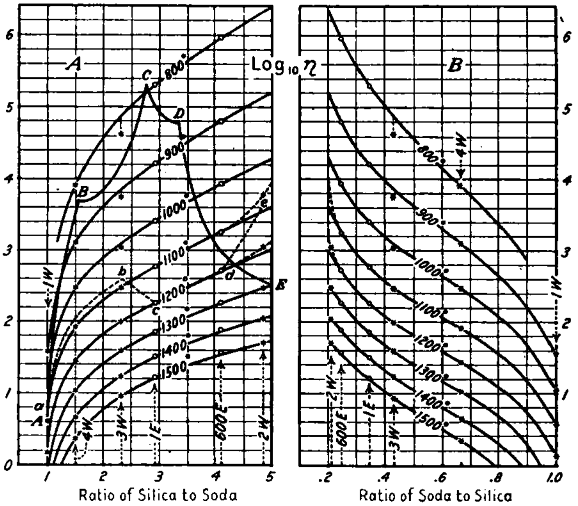

FIG. 2.—Value of $\log_{10}\eta$ as a function of composition for various temperatures.

Now it is possible, of course, that this dotted curve represents the real relation between viscosity and composition. The only other evidence we have is by Morey and Bowen[1] who recently determined the equilibrium diagram for soda and silica. The devitrification curve given by them shows corners at compositions 23, 26.5 and 39.2 per cent soda corresponding to ratios r = 3.34, 2.77 and 1.55. On Fig. 2 the curve *ABCDE* shows log η at the devitrification temperature as a function of r.

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[1] Morey and Bowen, *J. Phys. Chem.*, **28**, 1174 (November, 1924). The devitrification temperatures plotted in Fig. 2 are as follows:

r =	0.97	1.55	1.94	2.77	3.03	3.34	4.85
T_d =	1088°	840°	874°	793°	842°	870°	1280°

There is no relation evident between curves *abcde* and *ABCDE*, and we must conclude that the viscosities of the sodium silicates are not influenced by any tendency to devitrification. Therefore until measurements on more compositions have been made we must assume that the curve showing the relation between log η and r is a smooth one.

Returning to curve *abcde*, it is evident that the two E values are relatively too low to fit in with the W values. It was found that when 0.6 is subtracted from each of the latter, all the values lie on the smooth curves shown of the full lines in Fig. 2, except the values for 2W for 1200° and below, which seem too high, indicating devitrification, and the values for 3W for 1000° and below which seem too low.

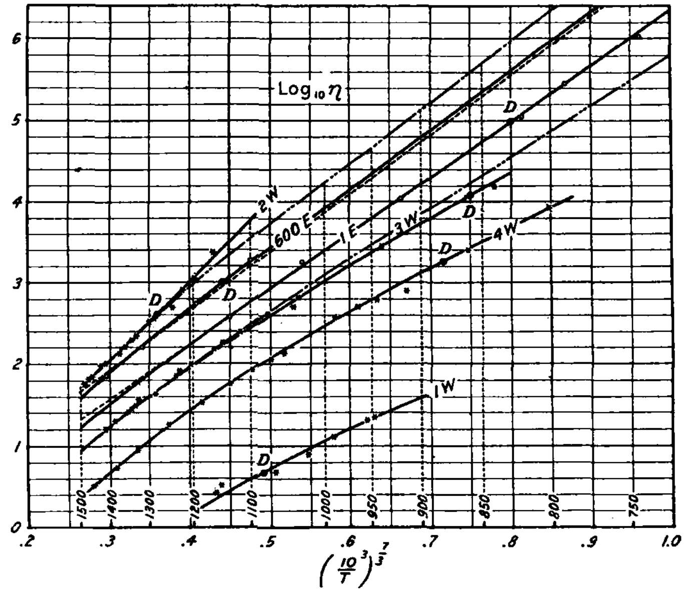

FIG. 3.—Values of $\log_{10} \eta$ as a function $(10^3/T)^{7/3}$ with values for W curves decreased by 0.60.

Figure 3 shows the same curves as Fig. 1, for temperatures above 750°, with the W curves displaced downward 0.6. The curves drawn with lines and dashes represent the smoothed values from Fig. 2 where these differ from the full line values. The dotted lines represent the straight lines as drawn in Fig. 1 for 600E and 1E.

It is of interest to note that the viscosity curves for both E and W glasses extend to temperatures below that at which they should begin to devitrify, without showing any bending, except 2W. (The devitrification parts are marked by *D* on Fig. 3.)

From the curves in Figs. 2 and 3, the relative values of the viscosity of any two sodium silicates between 800° and 1500° and for *r* between 1 and 5 may be determined as accurately as the values upon which these curves are based, are known. But even if our curves give the relative values correctly, the absolute values are still uncertain because of the apparent discrepancy of 0.60 between the results of the two investigations. Since 0.60 is the logarithm of 4, this discrepancy means that the W viscosities are four times too large or the E values are four times too small or there are errors in both sets such that the ratio of the required correction factors is 4, for instance $^1/_2$ and 2. This conclusion emphasizes the importance of developing a reliable method of calibrating high temperature viscosity apparatus. If the absolute values for a standard glass at high temperatures were known, this glass could then be used in calibrating all such apparatus. It is suggested that future experimenters make a few runs with glasses having compositions approaching closely those of 1E, 600E and 3W so as to enable their results to be compared with those discussed in this paper.

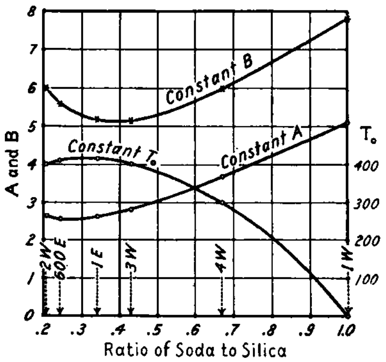

FIG. 4.—Constants in equation $\log_{10}\eta = -A + B \times 10^3/(T - T_0)$, as a function of ratio of soda to silica.

As to the mathematical representation of the curves, the data plotted in Fig. 3 indicate that the curves are not straight for temperatures above 1000° but bend downward; that is, above 100° log η varies inversely as some higher power of the temperature than $^7/_3$. Equations of the form

$$\log\eta = A - B/T + C/T^2 \qquad (2)$$
$$\log\eta = -A + BT + C/T^2 \qquad (3)$$
$$\log\eta = -A + B\log T + C/T^2 \qquad (4)$$
$$\log\eta = -A + B/(T - T_0)^2 \qquad (5)$$

may be made to represent the results more or less closely but the three constant equation which seems to fit the results best is of the form

$$\log\eta = -A + B \times 10^3/(T - T_0) \qquad (6)$$

This equation with the values of the constants given in Table II fits the experimental results for both 1E and 600E (corrected by subtracting 0.17 from the values for below 750°) within the accidental errors. For the other glasses the range of temperature is too small to determine T_0 accurately so values of T_0 were chosen which give values of log η for 500°C consistent with the values for the E glasses. The constants were also adjusted so as to vary continuously with the soda-silica ratio (see Fig. 4).

TABLE II

CONSTANTS IN THE EMPIRICAL EQUATION (6) FOR SODA-SILICA GLASSES[1]

Glass	Soda/silica	A	B	T_0	Log η at 500° (calc.)
2W	0.207	2.64	6.00	400°	13.45
600E	.244	2.56	5.60	410	12.87
1E	.342	2.63	5.20	415	11.89
3W	.43	2.81	5.15	400	11.0
4W	.67	3.68	6.00	300	9.0
1W	1.03	5.08	7.80	0	5.0

In Fig. 5 are plotted the values of log η as a function of $10^3/(T-T_0)$. The observed values are indicated only for 1E, 600E and 2W; but for all the glasses the straight lines represent the smoothed values on the curves of Fig. 2 quite accurately. In the case of 2W the observed viscosity evidently increases too rapidly with decreasing temperature below 900°. This is probably due to crystallization.

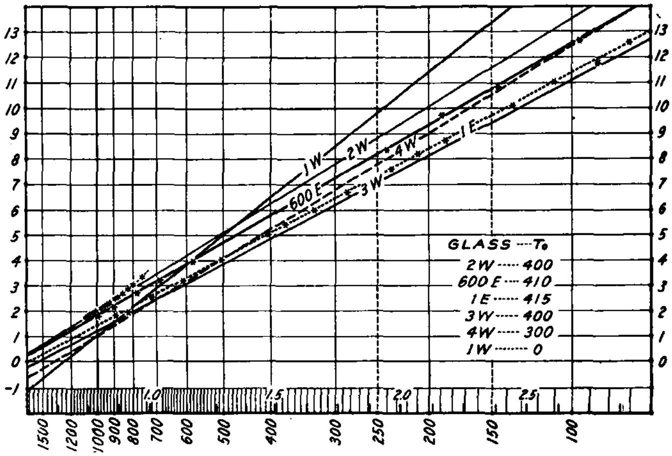

FIG. 5.—$\text{Log}_{10}\,\eta$ function of $10^3/(T-T_0)$.

Whether or not equations (1) and (6) have any physical significance, they are evidently useful for plotting in order to compare the results for different glasses or those obtained by different observers.

In two recent papers[2] LeChatelier states that when log (log η) is plotted as a function of T, two straight lines meeting at an obtuse angle are obtained for each glass. While such a plot may be convenient for interpola-

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[1] The empirical equations correspond to the observed values of log η corrected by subtracting 0.60 from all the W values and 0.17 from the E values obtained by the elongation method (below 750°).

[2] Henri LeChatelier, *Compt. rend.*, **1924**, pp. 517 and 718 (referred to in *Nature*, **114**, p. 731, November 15, 1924); *J. Soc. Glass Tech.*, **9**, 12 (March, 1925).

tion purposes, it should be evident that this equation is unlike that of any of the ordinary physical equations in that the shape of the curve obtained depends not only on the base of the logarithms used (e or 10) but also on the units in which η is expressed. For instance if the values of $\log_e (\log_e \eta)$ for temperatures 1000°, 1200° and 1400° are 2.130, 1.780 and 1.430 (approximately the values for 3W) the curve is a straight line; but the values of $\log_e(\log_e e^2\eta)$ are 2.3433, 2.0707 and 1.8212, the middle value being 0.0115 less than it should be if the relation is linear, corresponding to a difference of 9.6 per cent in η. The plot of $\log_e(\log_e \eta/e^2)$ curves the other way; the middle value is greater than it should be for a linear relation, the difference of 0.191 in $\log_e \eta/e^2$ corresponding to a difference of 21% in η. Any linear relation obtained in such a plot is therefore purely accidental and can have no physical significance. The positions of the inflections reported by LeChatelier would also shift more or less with the units employed, the shift being greater the nearer the angle of inflection is to 180°. The curves plotted in Fig. 5, however, show no indications of inflection. In the case of 1E the viscosity changes in the ratio of 1 to 10^{11}, yet the results are represented within accidental error by the single straight line.

2. Soda-Lime-Silica Glasses

English investigated the series of glasses whose percentage compositions are given in Table III. Starting with the soda tri-silicate 1E (Na_2O, $3SiO_2$), CaO was substituted for Na_2O molecularly in steps of about 0.1 molecule up to (Na_2O, CaO, $6SiO_2$).

TABLE III

PERCENTAGE COMPOSITION OF SODA-LIME-SILICA GLASSES (ENGLISH)

Glass	CaO	Na_2O	($CaO+Na_2O$)	Equiv. Na_2O	SiO_2	Minor	Total
1E	0.21	25.34	25.55	25.57	74.05	0.38	99.98
3E	2.61	23.00	25.61	25.80	74.08	0.37	100.05
4E	3.81	21.50	25.31	25.59	74.07	0.42	99.80
5E	4.50	20.78	25.28	25.61	73.78	0.72	99.78
6E	6.26	19.38	25.64	26.00	73.18	1.40	100.22
7E	7.45	17.20	24.65	25.21	74.41	0.94	100.00
8E	8.16	16.00	24.16	24.77	74.99	0.66	99.81
9E	9.36	14.88	24.24	24.94	74.96	0.86	100.06
10E	10.38	14.22	24.60	25.37	74.59	0.96	100.15
11E	11.68	13.02	24.70	25.57	74.93	0.86	100.49

Percentage Substitution of CaO for Na_2O

Since the percentage of SiO_2 is practically constant we may consider these a series of glasses with about 74.5% SiO_2 in which CaO is substituted for Na_2O, per cent for per cent. To bring out the effect of this substitution, the *change of* $\log_{10} \eta$ *due to substitution* is plotted in Fig. 6 as a function of the temperature for each of the glasses

3E to 11E. In getting these values correction was made for the variation of percentage of (CaO + Na_2O) by comparing with the results for a simple soda glass having a percentage of soda equal to the percentage of (CaO + Na_2O) (obtained by interpolation between 1E and 600E curves). The observed changes of $\log_{10} \eta$ are indicated by points connected by dashed lines. Although these dashed curves are somewhat irregular, they each show unmistakably a sudden bend at about 900° to 1000°C. Above this temperature, the change in $\log \eta$ due to the substitution does not vary much with temperature though it shows a tendency to decrease with decreasing temperature. Below this temperature, however, the change in $\log \eta$ increases approximately linearly with decreasing temperature. The full line curves were drawn with the aid of a plot of the change of $\log_{10} \eta$ at certain fixed temperatures as a function of the per cent CaO, so that they represent the results smoothed with respect to CaO variation as well as to temperature variation.

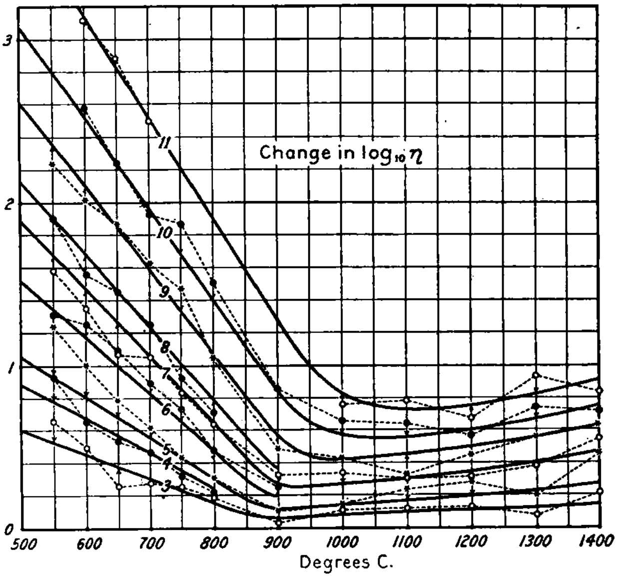

FIG. 6.—Δ $\log_{10} \eta$ for various lime glasses as a function of temperature.

It is evident that the slopes of the low temperature parts of the curves of Fig. 6 increase with the percentage of CaO. If we divide each of the full line curves of Fig. 6 by the corresponding per cent CaO we obtain the curves of Fig. 7 which therefore give the *change in* $\log_{10} \eta$ *per per cent CaO substituted.* The low temperature parts are now parallel. While the observations are not accurate enough to prove that these curves must be exactly parallel, yet the best smooth curves drawn through the observations lead to lines which are remarkably close to being parallel.

Now as to the physical interpretation of this result. Evidently as the soda-lime glass cools, at a temperature varying from 860° (for 2% CaO) to 1010°C (for 12% CaO) some process of molecular rearrangement must start which increases the rate at which the viscosity changes with decreasing temperature. It is natural to suppose that this is a process of molecular aggregation so we shall call the temperature at which this starts the *aggregation temperature*. These temperatures will be shown to be about those at which devitrification is to be expected. Devitrification was actually observed only in the case of glasses 10E and 11E and none of the recorded points (except perhaps 750–900° for 10E) relate to devitrified glass. When visible devitrification sets in, crystals grow steadily so that consistent readings cannot be taken. The molecular aggregations responsible for the change of slope of the viscosity curves of Fig. 6 must, therefore, be sub-crystalline, for while they begin to form at a temperature at which devitrification is to be expected, yet they seem to be in equilibrium (for less than 10 per cent CaO) and to give a definite viscosity at each temperature. The fact that the curves giving change of log η per per cent CaO are parallel below 850° means that the *increase per degree of the change of logη due to the substitution of CaO is proportional to the per cent of CaO substituted;* the shift of the line to the right with increasing per cent CaO is due to the shift of the aggregation temperature to higher values.

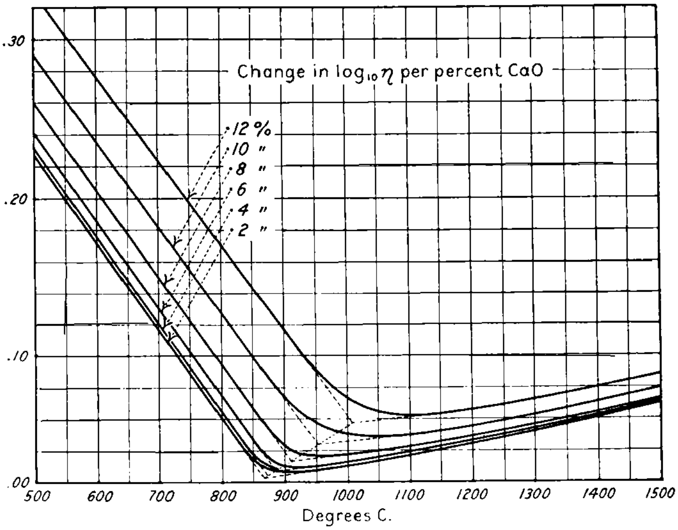

FIG. 7A —Percentage substitution of CaO for Na_2O.

Molecular Substitution of CaO for Na_2O

The curves of Fig. 7A are for substitution of CaO for Na_2O, per cent for per cent, in a sodium silicate with about 74.5% SiO_2. In case of molecular substitution, since 56 gm. of CaO are molecularly equivalent to 62 gm. of Na_2O, the silica content does not remain constant but increases slightly, in fact from 74.05 for ($6SiO_2$, $2Na_2O$) to 74.93 for ($6SiO_2$, $1Na_2O$, $1CaO$). Since increasing the silica content increases the viscosity, the changes in $\log_{10} \eta$ due to molecular substitution are somewhat greater than for percentage substitution. The smoothed results for the change of $\log_{10} \eta$ per per cent CaO for substitution of 0.2, 0.4, 0.6, 0.8 and 1 molecule of CaO in the soda-tri-silicate ($6SiO_2$, $2Na_2O$) are shown in Fig. 7B.[1]

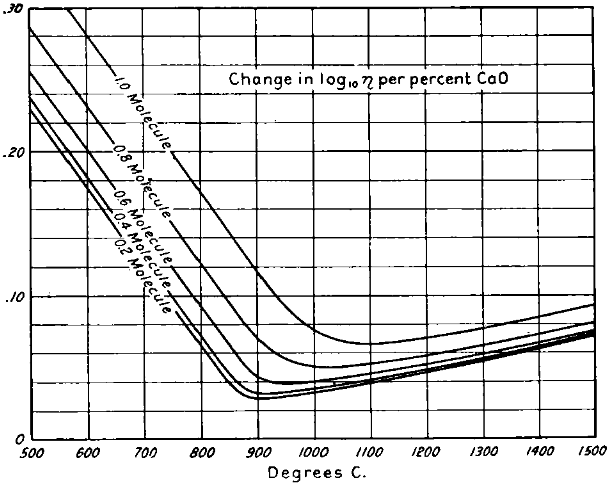

FIG. 7B.—Change in $\log_{10} \eta$ per per cent CaO, for molecular substitution of 0.2 to 1 molecule for Na_2O.

The compositions of the corresponding glasses are given in Table IV.

The variation of the aggregation temperature with per cent CaO is shown in Fig. 8, for 25% (Na_2O + CaO). The devitrification temperature for pure sodium-silicate with 25% Na_2O is about 838° according to the curve of Morey and Bowen[2] while the value for the aggregation tempera-

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[1] As shown in Table III, the equivalent Na_2O (which is the amount of soda in the simple soda-silicate in which molecular substitution of a certain percentage of CaO will give a glass of the composition of the actual glass, and therefore determines the composition of the simple soda-silicate with which the actual glass is to be compared as to viscosity) is practically constant, as was intended in making up the glasses. The slight corrections necessary were made so as to reduce all to 25.34% equivalent Na_2O. The formula for equivalent per cent Na_2O is $N' = (KC + N)/[100 + (K-1)C]$, where C is per cent Na_2O, and K is ratio of molecular weights of Na_2O to CaO.

[2] *Loc. cit.*

TABLE IV

Glass	SiO_2, per cent	Na_2O, per cent	CaO, per cent
$6SiO_2$, $2Na_2O$	74.05	25.34	0
$6SiO_2$, 1.8 Na_2O, 2CaO	74.23	22.85	2.3
$6SiO_2$, 1.6 Na_2O, 4CaO	74.40	20.4	4.61
$6SiO_2$, 1.4 Na_2O, 6CaO	74.58	17.9	6.93
$6SiO_2$, 1.2 Na_2O, 8CaO	74.75	15.4	9.26
$6SiO_2$, 1.0 Na_2O, 1CaO	74.93	12.8	11.63

ture from these viscosity measurements is 860°. The agreement is so close that one is inclined to attribute the small difference to the impurities present or to uncertainty in the determination of the aggregation temperature. The devitrification temperature of pure calcium silicate with 25% CaO is 1540° according to G. A. Rankine.[1] This point also seems to lie on the aggregation temperature curve extrapolated from 12% CaO. We may therefore conclude that the aggregate temperature given by the viscosity curve is the same as the devitrification temperature or slightly above it. However, it should be emphasized that aggregation does not seem to be the same as devitrification. It occurs promptly and reaches a limit which is a definite function of the CaO content whereas devitrification for low content of CaO, especially when alumina is present as impurity, may not occur unless the glass is held at the proper temperature for a long time and when it starts it increases with time so that successive viscosity measurements are not the same.

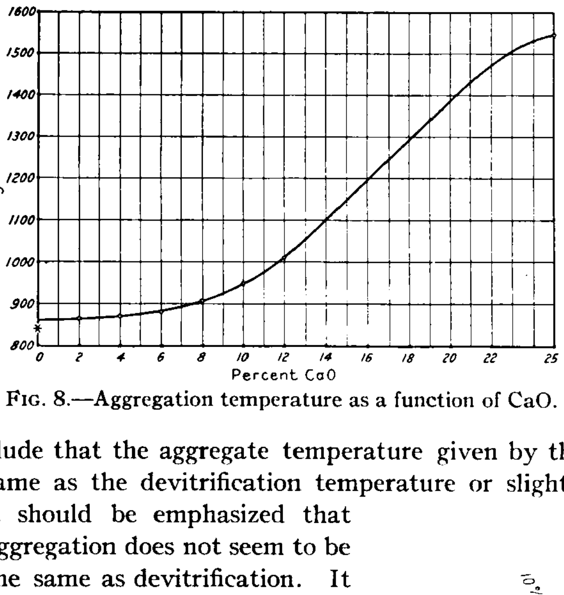

FIG. 8.—Aggregation temperature as a function of CaO.

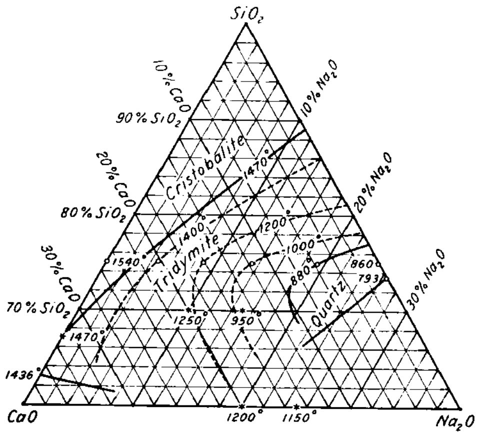

FIG. 9.—Equilibrium triangle for system $CaO-Na_2O-SiO_2$.

Part of the equilibrium tri-

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[1] G. A. Rankine, *Amer. Jour. Sci.*, **39**, 5 (1915).

angle for the system Na_2O–CaO–SiO_2 is given in Fig. 9. The limits of the cristobalite and tridymite regions have been determined for calcium silicates and for sodium silicates but nothing is known about the interior of the triangle. Assuming that the aggregation temperatures given by the viscosity curves are the same as the devitrification temperatures, we have now for 75% SiO_2 points on the isothermal curves for 880° (boundary between quartz and tridymite), 1000° and 1200°. Also the points for 1400° and 1470° (boundary between tridymite and cristobalite) may be taken from Fig. 8. This allows us to sketch in roughly the isotherms as shown in Fig. 9.[1] Two points for 70% SiO_2 obtained from the curves of Washburn *et al.* (see Fig. 11 below) are also used in drawing these curves. The two points for 60% SiO_2, also obtained from Washburn *et al.*, probably lie outside the tridymite regions. This figure shows how viscosity and similar measurements may help in the determination of the isothermals of such systems.

Washburn *et al.* also determined the viscosity curves of a number of soda-lime silicates. Their results for the change of $\log_{10} \eta$ due to substitution of 10% and 20% CaO for Na_2O in glasses with 60, 65, 70 and 75% SiO_2, are shown in Fig. 10. The dashed curves are for actual glasses, the full line curves are from the smoothed isotherm plots. It should be noted that since the change of $\log_{10} \eta$ is obtained by subtracting the value of $\log_{10} \eta$ for the sodium-silicate glass from that for the soda-lime-silica glass, this change is independent of the absolute values and is the same whether we subtract 0.60 from all the W values or not.

In Fig. 10A the curve obtained by English for 10% CaO and 75% SiO_2 is given for comparison. The corresponding W curve is evidently quite different, showing a maximum where the E curve has a minimum. Each of the W curves for 10% CaO except that for 70% SiO_2 shows no indication of a bend upward but rather a tendency to decrease with decreasing temperature below 100°. However in Fig. 10B, the curves for substitution of 20% CaO show bends corresponding to those of the E curves. The corresponding aggregation temperatures are indicated on the equilibrium triangle Fig. 9.

In Fig. 11 are plotted some W values for the change of $\log_{10} \eta$ per per cent CaO, together with the E curve for 10% CaO from Fig. 7. It is remarkable that the left hand straight parts of the curves for 70% SiO_2, 20%

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[1] Note added May 1. Dr. Morey has recently shown me an equilibrium diagram he has prepared on the basis of determinations of the devitrification temperatures of many pure soda-lime silicates. The results will be ready for publication soon. His curve corresponding to Fig. 8 is below mine for less than 10 per cent CaO and above mine for higher percentages. The difference may be due to impurities present in the glasses used for viscosity measurements. Fig. 9 is found to be only a rough approximation, as was to have been expected.

CaO; 60% SiO_2, 20% CaO; 60% SiO_2, 15% CaO and 75% SiO_2, 10% CaO (English) all have about the same slope. The curve for 65% SiO_2, 20% CaO is anomalous. The increase of the change of $\log_{10} \eta$ per degree decrease of temperature seems then not only proportional to the per cent of CaO substituted but independent of the per cent SiO_2.

A striking difference between the E and W results, as shown in Fig. 11, is that above the aggregation temperatures the E curves slope up whereas the W curves slope down, so that at 1400° C the effect per per cent CaO of substituting 10% CaO is .07 according to English (75% SiO_2) and only .004 (70% SiO_2) according to Washburn *et al.* The W results also indicate that the effect at 1400° of substituting lime decreases with decreasing percentage of SiO_2 until for 60% SiO_2 it is practically zero.

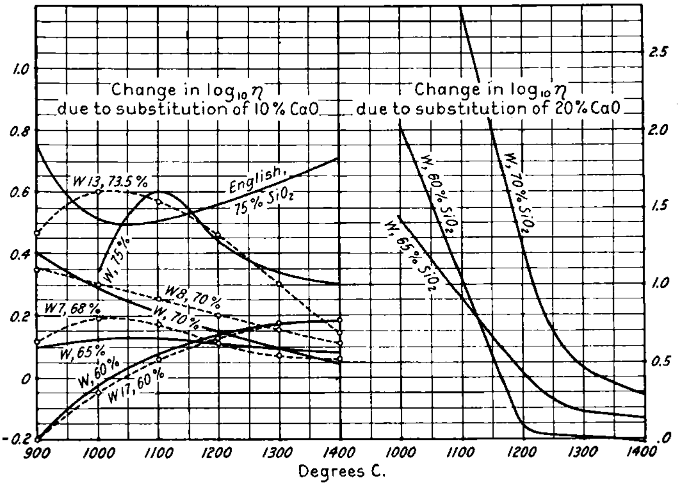

FIG. 10.—Percentage substitution of CaO for Na_2O.

3. Soda-Magnesia-Silica Glasses

English studied four glasses derived from the soda-tri-silicate 1E by molecular substitution of about 0.3, 0.6, 0.9 and 1.1 molecule of MgO for Na_2O. The percentage compositions are given in Table V.

TABLE V

Glass	MgO, per cent	Na_2O, per cent	Equiv. Na_2O, per cent	SiO_2, per cent	Fe_2O_3, Al_2O_3 and CaO, per cent	Total, per cent
1E	0	25.34	25.34	74.05	0.59	99.98
26E	2.49	22.12	25.61	75.00	.26	99.87
329E	5.09	18.26	25.39	76.30	.74	100.39
32E	7.46	14.55	24.98	78.66	.93	99.80
390E	9.30	11.76	24.80	78.28	.91	100.25

Correcting for the slight variation of the values of the equivalent per cent Na_2O (shown in the fourth column) from that for 1E, the *changes of* $\log_{10} \eta$ *due to molecular substitution of MgO and* Na_2O for the various percentages of MgO were determined. These are plotted in Fig. 12A. The full line curves correspond to the curves of Fig. 12B for the change of $\log_{10} \eta$ per per cent MgO. The curves of Fig. 12B show the same type of bend at the aggregation temperature, the same increase of aggregate temperature with per cent substituted and the same constancy of slope below the aggregate temperatures, as the corresponding CaO curves. The experimental results are more irregular, however, and leave us in doubt as to whether the curves for temperatures above the aggregation temperature rise or fall with increasing temperature, and also whether the lines continue straight below 700° or curve down as indicated.

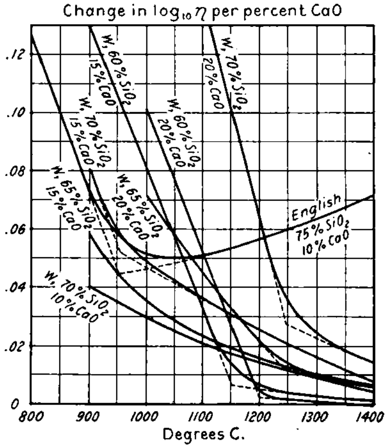

FIG. 11.—Substitution of CaO.

4. Soda-Alumina-Silica Glasses

The two glasses investigated by English had the compositions given in Table VI, being approximately produced by the substitution of .34 and .63 molecule of Al_2O_3 for Na_2O in glass 1E.

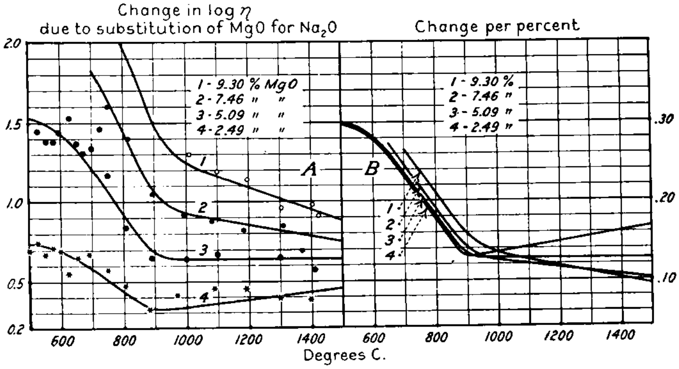

FIG. 12.—Molecular substitution of MgO for Na_2O.

TABLE VI

Glass	Al_2O_3, per cent	Na_2O, per cent	Equiv. Na_2O, per cent	SiO_2, per cent	CaO and Fe_2O_3, per cent	Total, per cent
1E	0.24	25.34	25.48	74.05	0.35	99.98
443E	6.85	20.62	25.52	72.05	.20	99.72
446E	12.69	15.28	24.39	71.56	.31	99.84

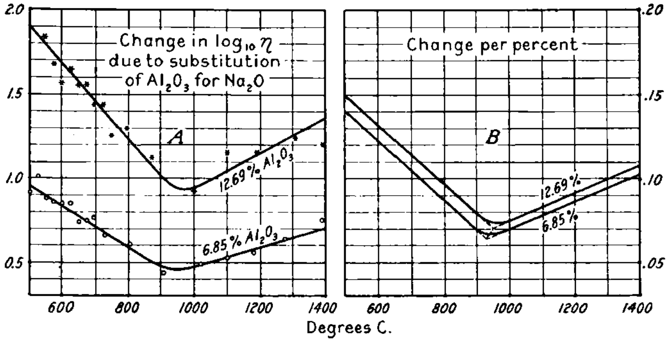

FIG. 13.—Molecular substitution of Al_2O_3.

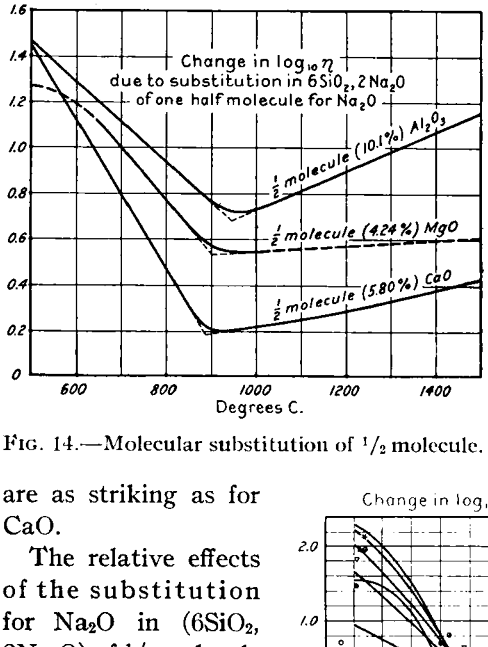

FIG. 14.—Molecular substitution of $^1/_2$ molecule.

The observed changes of $\log_{10} \eta$ due to molecular substitution of Al_2O_3 for Na_2O, corrected for the variation of equivalent Na_2O, are plotted in Fig. 13A. The full line curves correspond to the curves of Fig. 13B for the change of $\log_{10} \eta$ per per cent Al_2O_3. These curves of 13B are evidently similar to the corresponding curves for CaO and MgO. The straightness of the curves of Fig. 13A below 900° and the equality of slope of the curves of Fig. 13B below 900° are as striking as for CaO.

The relative effects of the substitution for Na_2O in ($6SiO_2$, $2Na_2O$) of $^1/_2$ molecule of CaO, MgO and Al_2O_3 are shown in Fig. 14. The three curves are strikingly similar. The Al_2O_3 produces the greatest change of $\log_{10} \eta$ at all temperatures, the CaO produces the greatest increase in rate of set-

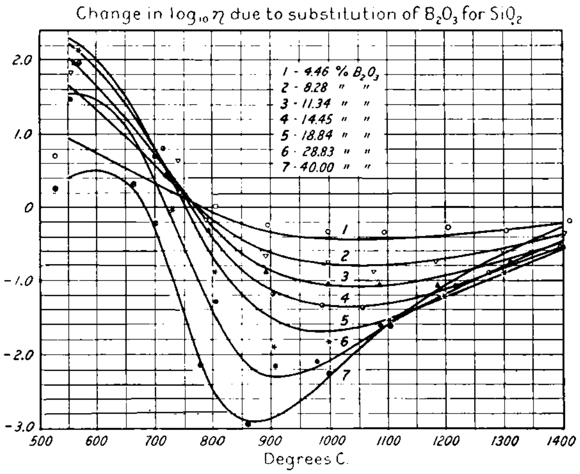

FIG. 15.—Substitution of B_2O_3.

ting at low temperatures, while the effect of MgO is intermediate in both respects. The slopes below 850° are 0.325 (CaO), 0.235 (MgO) and 0.178 (Al_2O_3) per 100°.

5. Soda-Boric Oxide-Silica Glasses

The seven glasses investigated by English were derived from the soda-silicate 600E ($4SiO_2$, $2Na_2O$) by the percentage substitution of boric oxide for silica—not for soda as in previous series—since boric oxide is acidic in character. The compositions are given in Table VII.

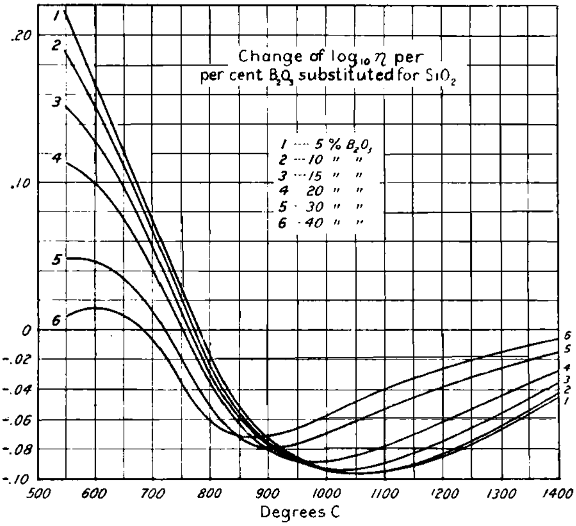

FIG. 16.—Change per per cent due to substitution of B_2O_3.

The change of $\log_{10} \eta$ due to substitution of B_2O_3 for SiO_2 is plotted in Fig. 15 for the seven glasses. The curves are quite different from those for substitution for Na_2O. Above 800° the change is a decrease. Figure 16 gives the change of $\log_{10} \eta$ per per cent B_2O_3 for 5, 10, 15, 20, 30 and 40% B_2O_3. These all show bends at 800° to 1000°, but these are not as sharp as in the case of substitution of Na_2O. The curves below 800° for 5 and 10% B_2O_3 are straight and parallel, but the curve for the higher percentage is on the low temperature side. Perhaps if molecular substitution had been adopted instead of percentage, the curves might have been more similar to each other and to those for molecular substitution of Na_2O.

TABLE VII

Glass	B_2O_3, per cent	SiO_2, per cent	(B_2O_3 + SiO_2), per cent	Na_2O, per cent	Minor per cent	Total per cent
600E	0	79.84	79.84	19.46	0.92	100.22
601E	4.46	74.22	78.68	19.78	1.21	99.67
602E	8.28	71.56	79.84	18.76	1.18	99.78
603E	11.34	68.39	79.73	18.92	1.22	99.87
604E	14.45	64.72	79.17	19.95	0.92	100.04
605E	18.84	61.28	80.12	18.93	0.93	99.98
606E	28.83	50.04	78.87	20.36	0.91	100.14
607E	39.99	35.22	75.21	23.71	1.07	99.99

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