

VISCOSITY-COMPOSITION RELATION-SHIPS WITH APPLICATION TO GLASSES FOR ELECTRIC INDUSTRIES GLASS FORMING PROPERTIES

Viscosity-Composition Relation-Ship

BY

Prof. Dr. Abd El-Hady Nasser ; Prof. Dr. Soad M. Serage
Dr. Lotfy Louis Seffin and Eng. Mohamed M. Gadou

ABSTRACT :

In this paper the properties of Soda-lime glasses are determined by using linear multi-variate regression. The technique was applied to a specific glass composition range for Soda-lime glasses used in electrical appliances. By using this technique it was possible to find a linear formula for the most important physical properties which affects the application of glass and it was possible to express viscosity as function of glass forming oxides thus both forming and end product properties could be fore-cost. The technique was applied by many other researches but it is applied for the first time for this composition range which is of prime importance for the industrial Soda-lime glasses in the Egyptian Industry.

Key words : Forming properties, Linear Multi-variate regression, Density, Thermal Expansion and Viscosity.

INTRODUCTION :

The main properties which should be controlled for glass in glass-making industries are mainly the density, thermal expansion and specially viscosity.

As we are interested finally to control the forming process and costs for glass it was necessary for our

glass composition range to establish a relationship between these properties and the glass forming oxides.

The paper is to determine the regression constants for these main properties in the formula

$$P = \sum a_i x_i + E$$

where :

- P - Property,
- a_i - Regression constant for oxide (i),
- x_i - Composition of oxide (i),
- E - Regression error.

It was possible in this paper to find the regression constants by using least-square fit. The source of data was the published properties of glass by previous researchers and the analysis of glasses and properties available from the Philips research laboratories.

For glass samples specially prepared by the authors for the composition range of glasses for electric industries.

For viscosity as it is the main properties for glass forming technology we developed a new mathematic approach to express the viscosity of glass as a linear function of the oxides concentration specially for the glasses used in electrical industries (e.g) lamps and electronic valves.

GLASS FORMING PROPERTIES RELATION-SHIPS

I. COMPOSITION-DENSITY RELATIONSHIPS :

In an investigation of the properties of glasses of various compositions the data may conveniently be expressed as a table or matrix, in which each row represents observations on one glass and each column observations of one variable. Many problems in this field may then be approached by carrying out mathematical operations (in particular, matrix operations) on this data set. Several such studies have been published, concerned with the relationship between changes in additive factors and features of the appropriate phase diagram, the design of an information retrieval system, the calculation of glass viscosity, and the classification of glass forming systems.

Additive factors are the coefficients (a_i) in an equation of the form :

$$P = a_1 X_1 + a_2 X_2 + a_3 X_3 + \dots \quad (1)$$

where :

P represents the value of a physical property and the X_i the relative abundances of the various components of the glass, preferably as molar percent of the component oxides.

Several sets of additive factors for a variety of properties have been published, however, such factors generally do not apply beyond the composition range for which they were calculated, and this can present a problem to those interested of new, possibly unusual, compositions. This paper describes statistical analysis of published density data for several binary and ternary systems.

The problems of using data from the literature are well known, particularly in glass science⁽²⁾. Ideally

the data should cover as wide a range of compositions as possible, and the distribution of points should be fairly uniform. Experiments may be planned to provide optimum use of statistical analysis but much of the older published information is unsuitable for these techniques. ⁽¹⁾ Where possible the data analysed in this investigation were checked against other sources and also checked for internal consistency. A few points were discarded because the published density measurements were varying from those for neighbouring compositions. In no case were data from different experimenters combined, so it is hoped that within each system the effects of thermal history may be ignored.

The goodness of fit of the various equations was measured by calculating a statistic similar to a standard deviation, (Δ_{rms}),

$$(\Delta_{rms})^2 = \frac{\sum (X_o - X_c)^2}{n}$$

where :

(X_o) and (X_c) are the measured and calculated values respectively and (n) is the number of points. An exception to this occurs in Table (2) and is explained when describing Equation (4)

Although in some instances the square of this value has been used to calculate a variance ratio, (F) to indicate the statistical significance of the differences between the goodness of fit of equations, this procedure is of limited applicability. In particular such comparisons should be limited to the same set of data and not used for comparing the application of the same equation to different sets of data :

N a₂O - CaO - SiO₂ data :

Using the 176 data points of the following equation was obtained on the assumption that there was a linear relationship between (V_s) and the molar percent of the oxides :

$$V_s = 0.4371 - 0.001011 (\text{Na}_2\text{O}) - 0.001783 (\text{CaO}) \quad \dots (2)$$

with a Δ_{rms} of 0.004. The error associated with one point was ten times larger than the other errors and this point was therefore deleted and the remaining 175 points used to fit equations of the form :

$$V_s = b(\text{Na}_2\text{O}) + \sum_{i=v}^n a_i (\text{SiO}_2)^i \quad \dots (3)$$

The results are summarised in Table (1) and the (Δ_{rms}) value obtained for Equation (3), 0.001, indicates a significantly better fit than the Δ_{rms} of 0.004 obtained for Equation (2).

Table (1) : Specific Volumes Calculated from Equation (3) using 175 points, the first Calculation Below is for Comparison , with Equation (1) :

n	V_B	Δ_{rms}
1	$0.4373 - 1.012 \times 10^{-3} (Na_2O) - 1.803 \times 10^{-3} (CaO)$	0.0034
2	$0.3290 + 8.276 \times 10^{-4} (Na_2O) - 5.295 \times 10^{-4} (S_iO_2) + 1.805 \times 10^{-5} (S_iO_2)^2$	0.0010
3	$0.3244 + 8.276 \times 10^{-4} (Na_2O) - 3.244 \times 10^{-4} (S_iO_2) + 1.504 \times 10^{-5} (S_iO_2)^2 + 1.481 \times 10^{-8} (S_iO_2)^3$	0.0010
4	$0.5019 + 8.269 \times 10^{-4} (Na_2O) - 1.069 \times 10^{-2} (S_iO_2) + 2.426 \times 10^{-4} (S_iO_2)^2 - 2.165 \times 10^{-6} (S_iO_2)^3 + 7.510 \times 10^{-9} (S_iO_2)^4$	0.0030

Table (3): Equations fitted to $Na_2O - CaO - S_iO_2$ data 68 Points :
 $P = Na_2O, q = CaO, r = S_iO_2$ (mol %); $S = P + q + 2r$:

Equ. No.	V_B	Δ_{rms}
1	$0.4429 - 0.001169 (P) - 0.001938 (q)$	0.0036
2	$0.4542 - 0.002587 (P) - 0.003075 (q) + 0.06544 (P/r) + 0.04568 (q/r)$	0.0009
3	$0.4545 - 0.003034 (P) - 0.002782 (q) - 0.01643 (P/r)^2 + 0.01972 (q/r) + 0.01011 (q/r)^2 + 0.1029 (P/r)$	0.0003
4	$0.4555 - 0.003891 (P) - 0.001923 (q) + 0.1717 (P/r) - 0.03968 (P/r)^2 - 0.003926 (P/r)^3 - 0.06126 (q/r) + 0.06378 (q/r)^2 - 0.0162 (q/r)^3$	0.0006
5	$0.4561 - 0.004046 (P) - 0.003380 (q) + 0.1837 (P/r) - 0.04829 (P/r)^2 + 0.063211 (q/r) - 0.004621 (q/r)^2 - 0.04790 (Pq/r^2)$	0.0006
6	$0.4559 - 0.004619 (P) - 0.004780 (q) + 0.495 (P/S) + 0.3890 (q/S)$	0.0008

Table (2): Coefficients For Use With Equation (4)

n	a ₀	a ₁	a ₂	a ₃ × 10 ⁴	a ₄ × 10 ⁶	a ₅ × 10 ⁷	Δ _{rms}
<u>Section 1-20 Points</u>							
2	760.4	-23.62	0.1787				6.86
3	857.0	-27.75	0.2360	-2.589			6.70
4	677.6	-13.88	-0.1257	36.690	-0.1529		6.62
5	-91.82	18.77	-0.4155	-7.947	0.7097	- 3.775	8.12
<u>Section 2-11 Points</u>							
2	784.9	-26.14	0.2078				4.41
3	101.6	-36.85	0.3697	-7.978			4.12
4	602.6	- 0.03351	-0.7260	126.400	-0.5846		4.01
5	677.4	-13.73	0.1318	21.850	0.2210	- 2.243	4.43
<u>Section 3-11 Points</u>							
2	539.1	-17.91	0.1433				10.03
3	1558	-61.88	0.7545	-27.43			3.39
4	1086	-30.07	-0.01020	51.07	-0.2924		4.62
5	-1837	92.48	-0.4559	- 0.02514	4.161	-18.300	52.77
<u>Section 4-16 Points</u>							
2	679.4	-21.82	0.1689				9.61
3	1656	-63.49	0.7442	-25.76			4.89
4	1114	-31.85	0.06614	37.58	-0.2181		4.50
5	-1564	106.60	-2.252	137.00	0.6049	- 6.190	11.95
<u>Section 5-12 Points</u>							
2	709.9	-22.26	0.1685				5.55
3	354.8	- 5.028	-0.1042	14.14			5.36
4	318.4	- 5.254	-0.03739	0.8375	0.07536		5.32
5	-987.2	63.13	-1.238	- 6.797	1.785	-10.69	6.84

The variation of the specific volume may now be investigated using equations of the following form.

$$\Delta V_s \times 10^4 = \sum_{i=0}^n a_i (S_i O_2)^i \quad (4)$$

Where: (ΔV_s) is the difference between the observed values and the calculated values using Equation (2). Equation (4) is thus only estimating the nonlinear variation of V_s.

The results are summarised in Table(2), the(Δ_{rms}) values are now an order of magnitude smaller and, in addition, there is considerable scatter in these values.

Table (4): Equations fitted to binary data, $P = R_2^0$
 or R_0 , $r = S_1 O_2$ (mol %), $S = P + 2 r$.

Equ. No.	V_s	Δ_{rms}
<u>$Na_2O - SiO_2 - 36$ Points.</u>		
1	$0.4529 - 0.002418 (P) + 0.05870 (P/r)$	0.0007
2	$0.4613 - 0.006876 (P) - 0.4306 \exp(-P/r) - 1$	0.0003
3	$0.4559 - 0.004463 (P) + 0.4724 (P/S)$	0.0005
<u>$Na_2O - SiO_2 - 21$ Points.</u>		
1	$0.4539 - 0.002524 (P) + 0.06621 (P/r)$	0.0009
2	$0.4558 - 0.005697 (P) - 0.3447 \exp(-P/r) - 1$	0.0007
3	$0.4549 - 0.004365 (P) + 0.4587 (P/S)$	0.0007
<u>$K_2O - SiO_2 - 10$ Points.</u>		
1	$0.4539 - 0.003651 (P) + 0.1465 (P/r)$	0.0007
2	$0.4541 - 0.007115 (P) - 0.4781 \exp(-P/r) - 1$	0.0007
3	$0.4540 - 0.006342 (P) + 0.8132 (P/S)$	0.0006
<u>$Ca_2O - SiO_2 - 6$ Points.</u>		
1	$0.4540 - 0.003049 (P) + 0.04422 (P/r)$	0.0006
2	$0.4539 - 0.007161 (P) - 0.3973 \exp(-P/r) - 1$	0.0015
3	$0.4540 - 0.004783 (P) + 0.3940 (P/S)$	0.0009

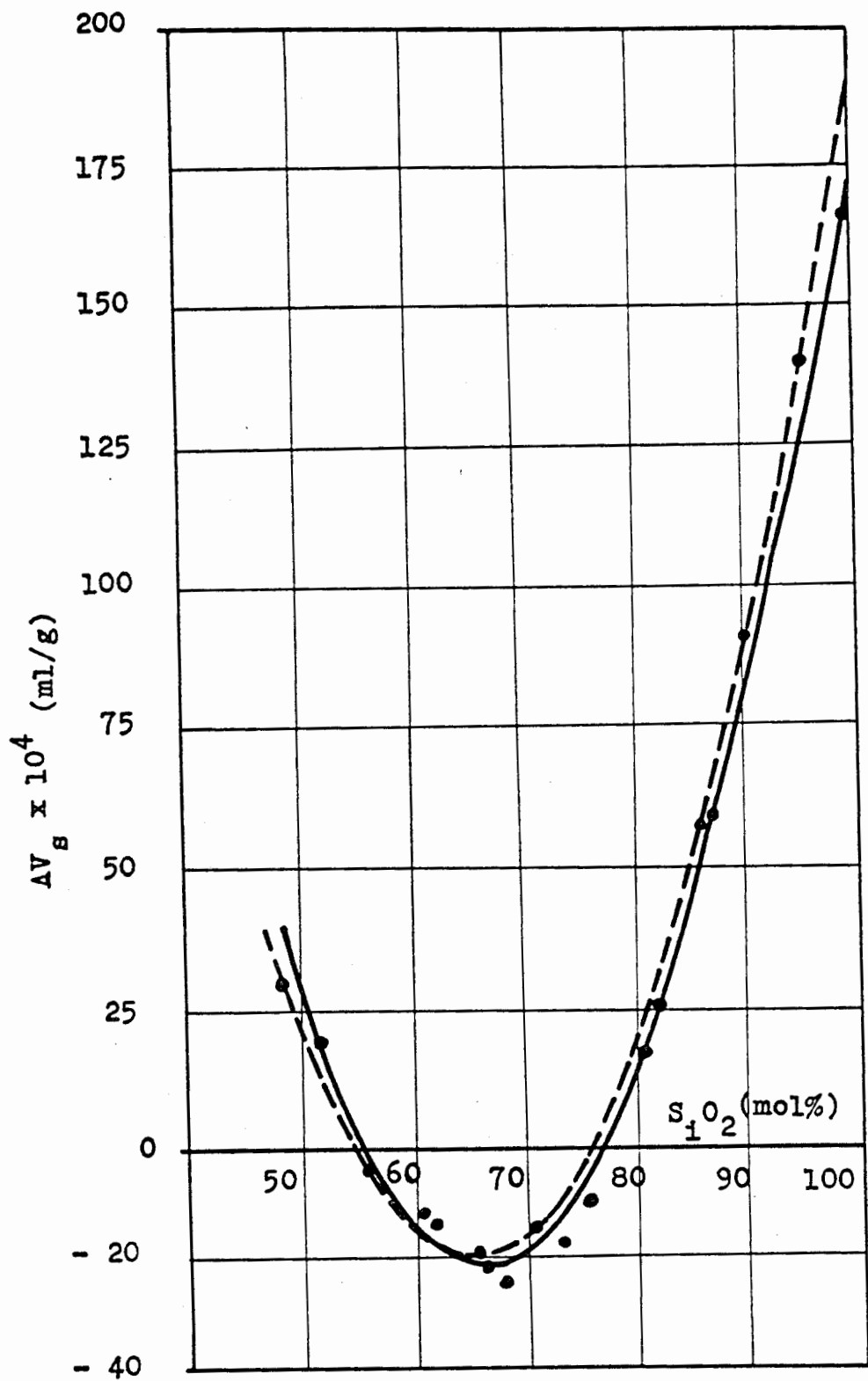


FIG.(1): Plot of results from Section 1 of Table(2)

————— $n = 4$

----- $n = 2$

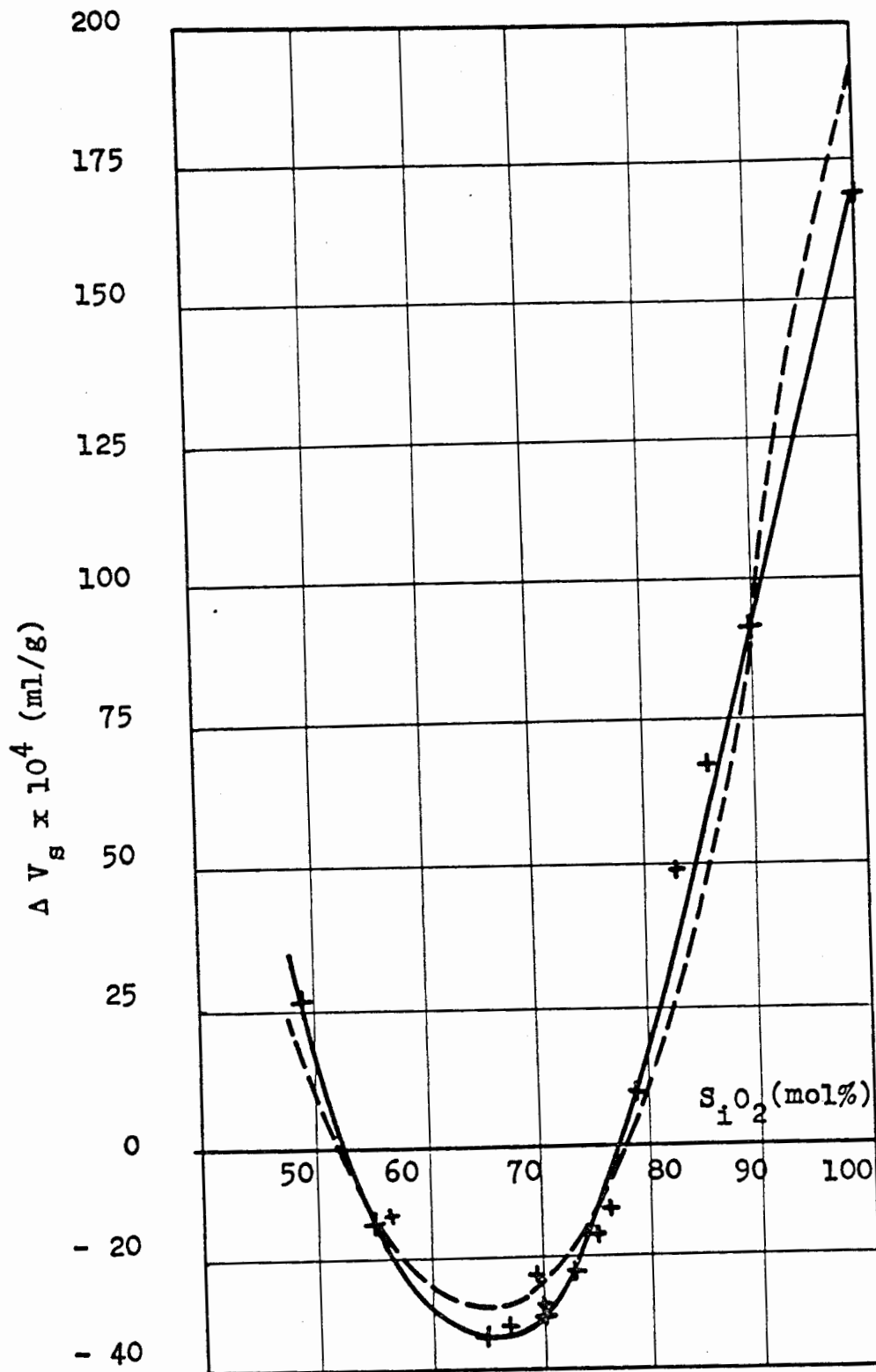


FIG.(2): Plot of results from Section 4 of Table (2)

————— $n = 4$ - - - - - $n = 2$

II. COMPOSITION-THERMAL EXPANSION RELATIONSHIPS MATHEMATICAL METHODS :

Miller & White have used an expression

$$V = a_0 + \sum_i (a_i X_i + f_i [X_i (S_i O_2)]) \quad (1)$$

Where : X_i are molar percentages of oxides other than silica, to relate density and composition and this paper describes the use of computerised statistical analysis to fit equations of the same general form to thermal expansion data.

Silicate Glasses ($R_2O-R'_2O-S_iO_2$ and $Na_2O-R_2O-S_iO_2$)

Data for the systems ($Li_2O - Ma_2O - S_iO_2$), ($Li_2O - K_2O - S_iO_2$), and ($Na_2O - K_2O - S_iO_2$) were obtained by Shebany and the additive factors calculated from these data are given in Table (1). For the ($Li_2O - Na_2O - S_iO_2$) system Shebany reported devitrification of the three glasses with 85 mol % S_iO_2 , so these results should be treated with caution. As only nine points are given for each system the data are barely adequate for this type of analysis.

The ($Na_2O - BaO - S_iO_2$) data were obtained by Yasuhara and taken for this investigation from karkhanavala. The first set of factors in Table (1) was obtained using all the data, while the second was computed after the points with the largest values of $\Delta = [(\alpha_{obs.} - \alpha_{calc.}) \times 10^7]$ had been omitted. The results are still unsatisfactory, as it has not been possible to check the original references these result should be treated with caution.

The ($Na_2O - BeO - S_iO_2$) data were obtained by Rencker, The additive factors calculated from these data are also given in Table (1), the first set being calculated from ternary data only and the second including data for five binary soda-silica glasses. The ($Na_2O - CaO - S_iO_2$) data

were obtained by Schmidt, Finn & Young again, the first set of factors was computed from ternary data only while the second set includes data on binary Soda-Silica glasses.

For each set of data the values of Δ were plotted against composition on a ternary diagram, in no case was it possible to identify regions in which the thermal expansion coefficient was a strictly linear function of composition. This suggested the use of nonlinear equations, similar to Equation (1), and for each set of data coefficients were obtained for two such equations. For a glass of composition $[pR_2O. q(R'_2O \text{ or } R' O). r S_iO_2]$, where (p,q) and (r) represent the molar percentages of the oxides, these equations are : $(\alpha \times 10^7 = a_0 + a_1p + a_2q + a'_1p/r + a'_2q/r..(2)$ and $(\alpha \times 10^7 = b_0 + b_1p + b_2q + b'_1 p/S + b'_2 q/S(3)$ where $(S = p + q + 2 r)$ represents the total oxygen content of the glass and the constant terms (a_0) and (b_0) represent the extrapolated thermal expansion coefficient of vitreous silica.

The results of these analyses are summarised in Table (2) and (3). In each case the first set of $(Na_2O - BeO - S_iO_2)$ results was computed from ternary data only while binary soda-silica data were included for the second set. For the $(Na_2O - CaO - S_iO_2)$ system both binary and ternary data were used. In all the systems the Δ_{rms} values were lower than the linear ones and in most cases this was statistically significant.

Table(1) : Additive factors for silicate glasses.

Components	Composition range (mol %)	Additive factors	Temperature range (deg C)	Δ rms
Li_2O	4 - 26	2.98		
Na_2O	4 - 26	4.31	10 - 300	5.3
SiO_2	65 - 85	0.14		9 points
Li_2O	4 - 26	2.74		
Na_2O	4 - 26	4.51	10 - 300	2.8
SiO_2	65 - 85	0.17		6 points
Li_2O	4 - 26	4.23		
Na_2O	4 - 26	4.69	10 - 300	3.6
SiO_2	65 - 85	0.23		9 points
Li_2O	6 - 28	3.80		
Na_2O	6 - 29	0.64	20 - 100	3.0
SiO_2	49 - 83	0.18		20 points
Li_2O	6 - 38	3.82		
Na_2O	0 - 29	0.61	20 - 100	2.7
SiO_2	49 - 83	0.18		15 points
Li_2O	11 - 48	4.34		
Na_2O	0 - 23	1.46	25 - 400	3 - 1
SiO_2	51 - 84	0.22		30 points
Li_2O	11 - 37	4.28		
Na_2O	3 - 23	1.56	25 - 400	3 - 2
SiO_2	51 - 81	0.22		49 points
Li_2O	5 - 36	3.06		
Na_2O	2 - 25	2.54	50 - 300	7.8
SiO_2	61 - 81	0.35		49 points
Li_2O	5 - 31	2.99		
Na_2O	2 - 25	2.64	50 - 300	4.3
SiO_2	61 - 81	0.34		26 points

Table (2) Coefficients for Equation (2)

Equ. No.	System	$\alpha \times 10^7 =$	Δ_{rms} .	Temperature range (deg C)
1	a $Li_2O \cdot b Na_2O \cdot r Si_2O_2$	- 31.2 + 9.81a + 13.2b - 37 a/r - 513 b/r	1.4	10 - 300
2	a $Li_2O \cdot c K_2O \cdot r Si_2O_2$	5.1 + 2.29a + 8.86c + 49.9 a/r - 285 c/r	1.0	10 - 300
3	b $Na_2O \cdot c K_2O \cdot r Si_2O_2$	- 5.8 + 7.19b + 11.3c - 149 b/r - 404 c/r	0.5	10 - 300
4	b $Na_2O \cdot d BeO \cdot r Si_2O_2$	7.9 + 5.82b - 0.03d - 124 b/r + 51.4 d/r	2.2	20 - 100
5	b $Na_2O \cdot d BeO \cdot r Si_2O_2$	6.9 + 5.15b + 0.80d - 78.0 b/r - 0.12 d/r	2.3	20 - 100
6	b $Na_2O \cdot e CaO \cdot r Si_2O_2$	10.6 + 5.28b + 2.41e - 51.1 b/r - 54.2 e/r	2.8	25 - 400
7	b $Na_2O \cdot e CaO \cdot r Si_2O_2$	10.3 + 5.36b + 2.52e - 55.9 b/r - 60.7 e/r	2.6	25 - 400

Table (3): Coefficients for Equation (3) :

Equ. No.	System	$\alpha \times 10^7 =$	Δ_{rms}	Temperature range (degC)
1	a $Li_2O \cdot b Na_2O \cdot r Si_2O_2$	- 38.1 + 19.2a + 25.0b - 246 a/S - 322 b/S	1.4	10 - 300
2	a $Li_2O \cdot c K_2O \cdot r Si_2O_2$	3.3 + 1.82a + 14.9c + 2.11a/S - 172 c/S	1.0	10 - 300
3	b $Na_2O \cdot c K_2O \cdot r Si_2O_2$	-10.1 + 11.4b + 20.3c - 106 b/S - 249 c/S	0.5	10 - 300
4	b $Na_2O \cdot d BeO \cdot r Si_2O_2$	6.0 + 9.33b - 0.94d - 886 b/S + 293 d/S	2.2	20 - 100
5	b $Na_2O \cdot d BeO \cdot r Si_2O_2$	4.7 + 7.40b + 1.35d - 559 b/S - 88.2d/S	2.3	20 - 100
6	b $Na_2O \cdot e CaO \cdot r Si_2O_2$	6.9 + 7.38b + 4.53e - 459 b/S - 470 e/S	2.6	25 - 400

III. CALCULATION OF THE VISCOSITY-TEMPERATURE RELATION

The viscosity-temperature relation is expressed by the Fulcher equation.

$$\text{Log } \eta = -A + \frac{B}{T-T_0} \quad \text{or} \quad T = T_0 + \frac{B}{\text{log } \eta + A}$$

where : $\text{Log } \eta = \text{Log}_{10}$ viscosity in poises,
 T = the temperature in °C

$T_0, B,$ and A are constants.

The Fulcher equation was optimised for minimum temperature deviations by least squares techniques, as the deviations of log viscosities are not normally distributed. There is no direct method to optimise this form of an equation, and the Fulcher equation was first transformed into the form

$$T_0 \cdot \text{Log } \eta - A \cdot T + A \cdot T_0 + B = T \cdot \text{log } \eta .$$

with multiple regression analysis techniques for two independent variables, the values for $A, T_0,$ and B could be calculated.

The equation corresponds to the general form

$$a_0 + a_1 x_1 + a_2 x_2 = y$$

where: $a_1 = T_0, a_2 = A, a_0 = A \cdot T_0, x_1 = \text{log } \eta, x_2 = T,$
 and $Y = T \cdot \text{log } \eta$. The solution gives values for the constants $A, T_0,$ and B which in many cases are accurate enough for practical industrial use, but does not give the best fit to the curve. In the second step, different values for A were put into the equation :

$$T = T_0 + B \frac{1}{\text{Log } \eta + A}$$

which corresponds with the general form $[y = a_0 + a_1 \cdot x]$

where : $y = T, a_0 = T_0, a_1 = B$ and $x = 1/\text{Log } \eta + A$.

The value of A was changed until a minimum residual variance was achieved. The value was then determined to three decimals, and this procedure usually needs

8 - 10 runs with different values of A. The time needed for this calculation depends on the equipment available, but with a Hewlett-Packard 9100 B programmable desk calculator a complete calculation could be finished in about one hour.

The Fulcher equation gives a very good description of the viscosity-temperature relations in spite of certain limitations. The curve of deviations shows a systematic S-shaped form, independent of measuring techniques, apparatus, or viscosity-range. This indicates that the real viscosity-temperature function is not identical with the curve described by the Fulcher equation, and the Fulcher equation was discussed by Mecrlender. A cubic equation of the form

$$T = a_0 + a_1 \left(\frac{1}{\log \eta} \right) + a_2 \left(\frac{1}{\text{Log } \eta} \right)^2 + a_3 \left(\frac{1}{\text{Log } \eta} \right)^3$$

gives standard deviations one - half to one - third of the Fulcher equation. Despite this it was decided to use the Fulcher equation because of its simplicity and general acceptance. A linearised viscosity-temperature function for a typical glass is shown on Figure (3) .

The standard deviations for the present measurements in the high temperature region were less than 1 deg C, usually 0.7 - 0.8 deg C, and were approximately 1.0 - 1.5 deg C for the complete viscosity curve from 10^2 to 10^3 poise. As this accuracy is fully satisfactory for determining the viscosity - temperature relations of a glass, there is no need for more accurate formulae.

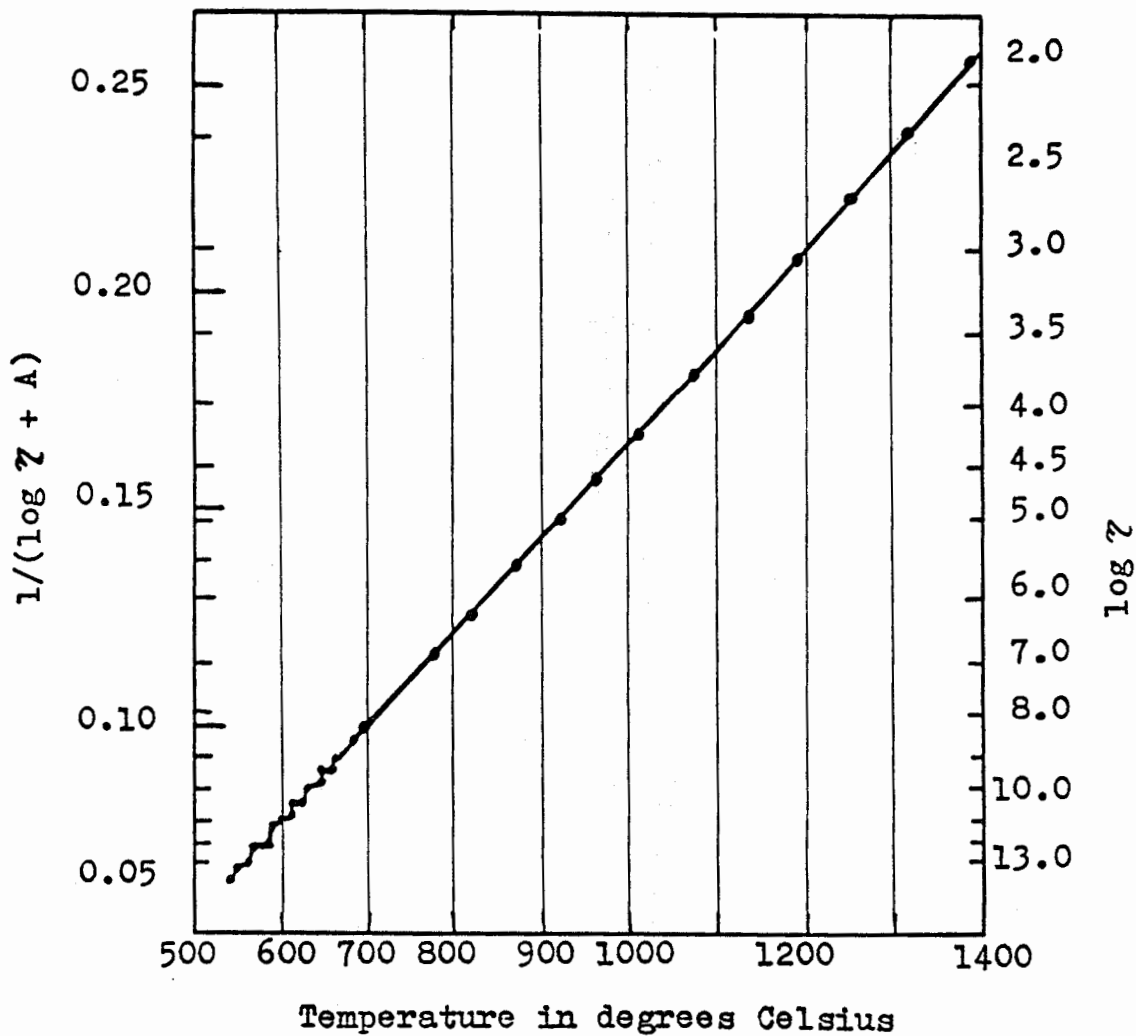


FIG.(3): Linearised viscosity-temperature function for glass 4; standard deviation = 1.16 °C.

VI. "COMPARATIVE ANALYSIS OF SAME INDUSTRIAL GLASS FOR
ELECTRICAL INDUSTRIAL"

Table For The Industrial Glass Properties

Table (1) : Constants and coefficient for the effect of
glass oxides.

Oxide	strain	Density	Viscosity					Anneal- ing temp. $t_k/100$ $^{\circ}C$
			L.o.t. $^{\circ}C$	H.o.t $^{\circ}C$	Ph.v.t $^{\circ}C$	Am.v.t $^{\circ}C$	W.t $^{\circ}C$	
Na ₂ O	270	0.0180	- 9.0	- 9.9	-10.8	-15.7	-29.0	- 3.4
K ₂ O	226	0.0140	- 6.9	- 7.7	- 8.4	-12.3	-19.3	4.1
CaO	- 9	0.0272	8.3	8.0	7.6	5.5	- 9.1	12.9
PbO	50	0.0335	-0.8	-1.1	-1.3	-2.7	- 3.2	1.2
AL ₂ O ₃	- 90	0.0025	9.0	9.5	9.5	11.2	17.0	0.6
B ₂ O ₃	- 56	0.0178	14.2	12.4	10.9	3.1	-17.8	3.0
C	-4288	1.9034	516.6	560.6	600.9	862.6	1468.7	280.5
S _g	83	0.0055	9.5	9.4	9.3	13.1	7.5	14.0

where : L.o.t. = Low operating temp.
H.o.t. = Hight operating temp.
Ph.v.t. = Philips viscosity temp.
Pm.v.t. = American viscosity temp.
W.t. = Work temp., $t_k/100$ = Annealing temp.

Table (2): Standard analysis of physical property

Standard deviation		standard deviation of Measured property		Standard error of the Measured property				
Oxide	S_{pi}	Property	(S_w)	calculated (Ss0)	sample (Ss1)	01-Glass (Ss2)	78-Glass (Ss3)	291-Gla. (Ss4)
SiO ₂	0.06	strain	10	20	83	22	16	19
Na ₂ O	0.05	Density	0.002	0.004	0.0055	0.005	0.003	1
K ₂ O	0.04	L.o.t.	2°	2°	9.5°	-	-	1
CaO	0.04	H.o.t.	2°	2°	9.4°	-	-	1
MnO	0.002	Ph.v.t.	1.5°	2°	9.3°	-	-	1
PbO	0.08	Am.v.t.	1.5°	2°	13.1°	-	-	1
Al ₂ O ₃	0.007	working temp.	2.5°	3°	7.5°	-	-	1
Sb ₂ O ₃	0.002	tk 100	3°	3°	14.0°	-	-	1
Fe ₂ O ₃	0.002							

Table (3) : Results of standard deviation and physical properties :-

Physical property	S_E	S_w
strain	15	10
Density	0.003	0.002
L.o.t. $b_{ij}Z = 10^{14.6}$	0.600	2.000
H.o.t. $b_{ij}Z = 10^{13.4}$	0.700	2.000
Ph.v.t. $b_{ij}Z = 10^{12.4}$	0.700	1.500
Am.v.t. $b_{ij}Z = 10^{7.6}$	1.000	1.500
work temp. $b_{ij}Z = 10^{4.0}$	1.800	2.500
Annealing Temp. $t_k/100$	0.700	3.000

$$E = C + \sum_{i=1}^{n-1} f_i \cdot P_i \quad \dots(1)$$

where

E = physical property.

C = constant, P_i = Percentage of oxide (i)

n = No. of components

f_i = effect of oxide (i)

$$S_s^2 = \sum (f_i \cdot S_{pi})^2 + S_w^2 \quad \dots(2)$$

where

S_s = standard deviation of error.

S_{pi} = standard deviation of the analysis of element

S_w = standard deviation of the physical property.

$$\bar{\Delta} = \frac{\sum (E - w)}{n} \quad \dots(3)$$

where:

$\bar{\Delta}$ = mean deviation

W = physical property "reel"

E = Physical property "Calculated"

n = No. of components.

$$S_{s1}^2 = \frac{\sum \Delta^2 - (\sum \Delta)^2 / n}{n_i - 1} \quad \dots(4)$$

where :

S_{s1} = standard deviation of sample.

Δ = deviation.

n_i = no. of reading for oxide (i)

n = no. of components.

$$S_E^2 = \sum (f_i \cdot S_{pi})^2 \quad \dots(5)$$

where :

S_E = Total standard deviation.

f_i = effect of oxide (i)

S_{pi} = standard deviation of the analysis of element.

$$\text{Log } \eta = A + \frac{B}{T - T_0} \quad \dots (6)$$

where:

Log η = log poise viscosity

A, B = constants.

T = temperature in °C.

T₀ = temp. constant.

$$A_i = \frac{100 C_i}{100 + \sum \alpha_{ij} (C_j - \bar{C}_j)} \quad \dots (7)$$

$$A_i = a + b R_i \quad , \quad A_i = K C_i$$

$$K = \frac{100}{100 + \sum \alpha_{ij} (C_j - \bar{C}_j)}$$

where :

A_i = concentration as linear function of R_i

C_i = constant for oxide (i)

R_i = Intensity ratio

\bar{C}_j = constant

α_{ij} = Influence factor of element(i) on element(j).

a, b = constants

k = factor for element.

Example for sample = No. (1) - Table (4), Table (5) for Na₂O the (K) factor is :

$$K = \frac{100}{100 + \sum \alpha_{ij} (C_j - \bar{C}_j)}$$

from Table (4, 5)

$$\begin{aligned} \sum \alpha_{ij} (C_j - \bar{C}_j) &= -0.287 (1.88-5) + 0.167 (9.87-10) + \\ &\quad + 0.827 (35.95 - 35) \end{aligned}$$

$$= 0.395 - 0.022 + 0.786 = 1.659$$

$$K = 100 / (100 + 1.659) = 0.98368.$$

$$A_i = a + b R_i \quad \text{and} \quad C_i = a + b R_i$$

where :

r = correlation factor

S_Y/x = standard deviation

$$S_N = \sqrt{\frac{\sum (C_N - C_i)^2}{(n-1)}}$$

C_N = Average .

n = No. of samples.

a, b = constants .

R_i = Intensity ratio.

Table (4) : Composition of samples

No.	Fe ₂ O ₃	P ₂ O ₅	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	SiO ₂	Sb ₂ O ₃	M _n O
1	0.035	35.95	3.35	1.88	9.87	1.98	46.40	0.345	0.225
2	0.043	24.65	3.15	1.80	6.02	1.85	61.90	0.340	0.260
3	0.036	27.50	2.94	1.62	7.25	1.64	58.50	0.360	0.140
4	0.033	49.00	3.56	1.70	15.03	2.26	27.80	0.365	0.225
5	0.033	47.50	3.81	2.17	13.60	2.30	29.90	0.335	0.275
6	0.036	40.52	3.68	2.02	11.00	2.72	39.50	0.340	0.200
7	-	28.60	0.97	8.05	4.33	-	57.70	0.330	-
8	-	28.75	0.96	4.24	4.36	-	61.40	0.320	-
9	-	29.00	0.96	6.20	4.24	-	59.30	0.320	-
10	-	28.70	0.93	10.10	4.27	-	55.70	0.290	-
11	-	28.85	0.95	8.20	2.38	-	59.30	0.300	-
12	-	28.83	0.94	8.15	6.30	-	55.50	0.280	-
13	-	28.50	0.94	8.11	8.12	-	54.00	0.280	-
14	-	28.60	0.91	10.30	2.38	-	57.50	0.280	-
15	-	28.85	0.93	6.27	6.29	-	57.30	0.320	-
16	-	28.60	0.92	4.36	8.14	-	57.70	0.300	-
17	-	26.80	0.91	8.14	4.30	-	59.50	0.320	-
18	-	30.45	0.92	8.21	4.37	-	55.70	0.340	-
19	-	28.70	0.28	8.17	4.37	-	58.20	0.280	-
20	-	28.90	1.56	8.23	4.36	-	56.60	0.340	-

Table (5): Coefficients "Results":

Element	$\alpha_{i,j}$		
	Na ₂ O, $\bar{C}_j=5\%$	K O, $\bar{C}_j=10\%$	P _b O, $\bar{C}_j=35\%$
Na K	- 0.287	+0.167	+ 0.827
Al K	+ 0.981	+0.198	+ 1.057
Si K	+ 0.323	+0.131	+ 1.033
K K	- 0.141	-0.078	+ 1.490
Ca K	- 0.115	+0.871	+ 1.488
Mn K	—	—	—
S _b K	- 0.104	+0.780	+ 1.590
P _b M	- 0.280	-0.584	+ 0.197
Fe K	- 0.105	+0.770	+ 1.632

Table (6) Table of Factor (K) :

No.	Fe ₂ O ₃	PbO	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	SiO ₂	Sb ₂ O ₃
1	0.98253	0.98876	1.02127	0.98368	0.98169	0.98368	1.01630	0.98296
2	1.24409	0.98832	1.17463	1.09058	1.17178	1.22698	1.16072	1.23805
3	1.16283	0.98937	1.13363	1.06035	1.11712	1.15163	1.12220	1.59000
4	0.78698	0.99261	0.88844	0.88211	0.82690	0.79623	0.88964	0.79035
5	0.80992	0.98861	0.89969	0.89485	0.84215	0.81926	0.90045	0.81316
6	0.90834	0.98680	0.96985	0.94703	0.92109	0.91385	0.96730	0.91019
7	1.17829	0.98813	1.05147	1.07660	1.10526	1.17388	1.05090	1.17531
8	1.16908	0.97775	1.09252	1.06261	1.09608	1.16448	1.08484	1.16628
9	1.16759	0.98188	1.06730	1.06687	1.09481	1.16391	1.06343	1.16493
10	1.17965	0.99327	1.02871	1.08261	1.10692	1.17580	1.03158	1.17670
11	1.19389	0.97711	1.05119	1.07848	1.09915	1.19269	1.04651	1.19125
12	1.15229	0.99933	1.04322	1.07066	1.10277	1.14565	1.04433	1.14932
13	1.14132	1.01065	1.04375	1.07046	1.11083	1.13208	1.04604	1.13798
14	1.20292	0.98323	1.03172	1.08768	1.10728	1.20146	1.03357	1.20006
15	1.14978	0.99404	1.06371	1.06462	1.09954	1.14323	1.06150	1.14685
16	1.13361	0.99995	1.08414	1.05730	1.10254	1.12448	1.07970	1.13071
17	1.22102	0.99173	1.07199	1.09450	1.13916	1.21252	1.07104	1.21670
18	1.13763	0.98629	1.02854	1.05960	1.07288	1.13692	1.02876	1.13984
19	1.17577	0.98854	1.04892	1.07596	1.10369	1.17155	1.04862	1.17286
20	1.17147	0.98826	1.04598	1.07427	1.10016	1.16769	1.04583	1.16869

Table (7) Table of $A_i = K C_i$

No.	Fe ₂ O ₃	P _b O	AL ₂ O ₃	Na ₂ O	K ₂ O	CaO	SiO ₂	S _b 2O ₃
1	0.034	35.546	3.421	1.846	9.689	1.948	47.156	0.334
2	0.053	24.362	3.700	1.963	7.054	2.270	71.848	0.421
3	0.042	27.208	3.333	1.718	8.099	1.889	65.649	0.394
4	0.026	48.638	3.163	1.500	12.428	1.799	24.732	0.289
5	0.027	46.959	3.428	1.942	11.453	1.884	26.924	0.358
6	0.033	39.985	3.569	1.913	10.132	2.486	38.208	0.309
7		28.262	1.020	8.667	4.786		60.637	0.388
8		28.110	1.049	4.505	4.779		66.609	0.373
9		28.474	1.025	6.615	4.642		63.062	0.373
10		28.507	0.957	10.934	4.727		57.459	0.341
11		28.190	0.999	8.844	2.616		62.236	0.357
12		28.831	0.981	8.727	6.947		57.961	0.322
13		28.803	0.981	8.681	9.020		56.486	0.319
14		28.120	0.939	11.206	2.635		59.430	0.336
15		28.678	0.968	6.675	6.916		60.824	0.367
16		28.599	0.997	4.610	8.975		62.299	0.339
17		26.578	0.976	8.909	4.898		63.727	0.389
18		30.002	0.946	8.699	4.688		57.302	0.386
19		28.371	0.294	8.791	4.823		61.030	0.328
20		28.561	1.632	8.841	4.797		59.194	0.397

Table (8): $C_i = a + bR_i$ - concentration as linear function

Oxide	r	a	b	$\frac{S_y/x}{X}$	S_N
Fe_2O_3					
P_bO	0.9988	0.240	33.9516	0.341	0.583
AL_2O_3	0.9882	-0.041	3.4542	0.188	0.123
Na_2D	0.9995	-0.153	2.1280	0.102	0.107
K_2O	0.9769	-1.347	12.1497	0.768	0.646
CaO	0.9681	-0.007	2.0769	0.262	0.447
SiO_2	0.9956	10.506	37.1267	0.944	0.681
Sb_2O_3	0.5733	0.1502	0.1869	0.031	0.028

Table (8) $A_i = a + bR_i$

Fe_2O_3					
P_bO	0.9994	0.2010	33.6399	0.241	0.210
AL_2O_3	0.9997	0.0074	3.4380	0.030	0.027
Na_2O	0.9997	-0.414	2.3549	0.085	0.076
K_2O	0.9991	0.179	10.0416	0.122	0.140
CaO	0.9931	-0.018	2.0340	0.115	0.220
SiO_2	0.9975	1.465	47.2448	0.903	0.350
Sb_2O_3	0.5794	0.191	0.1785	0.029	0.029

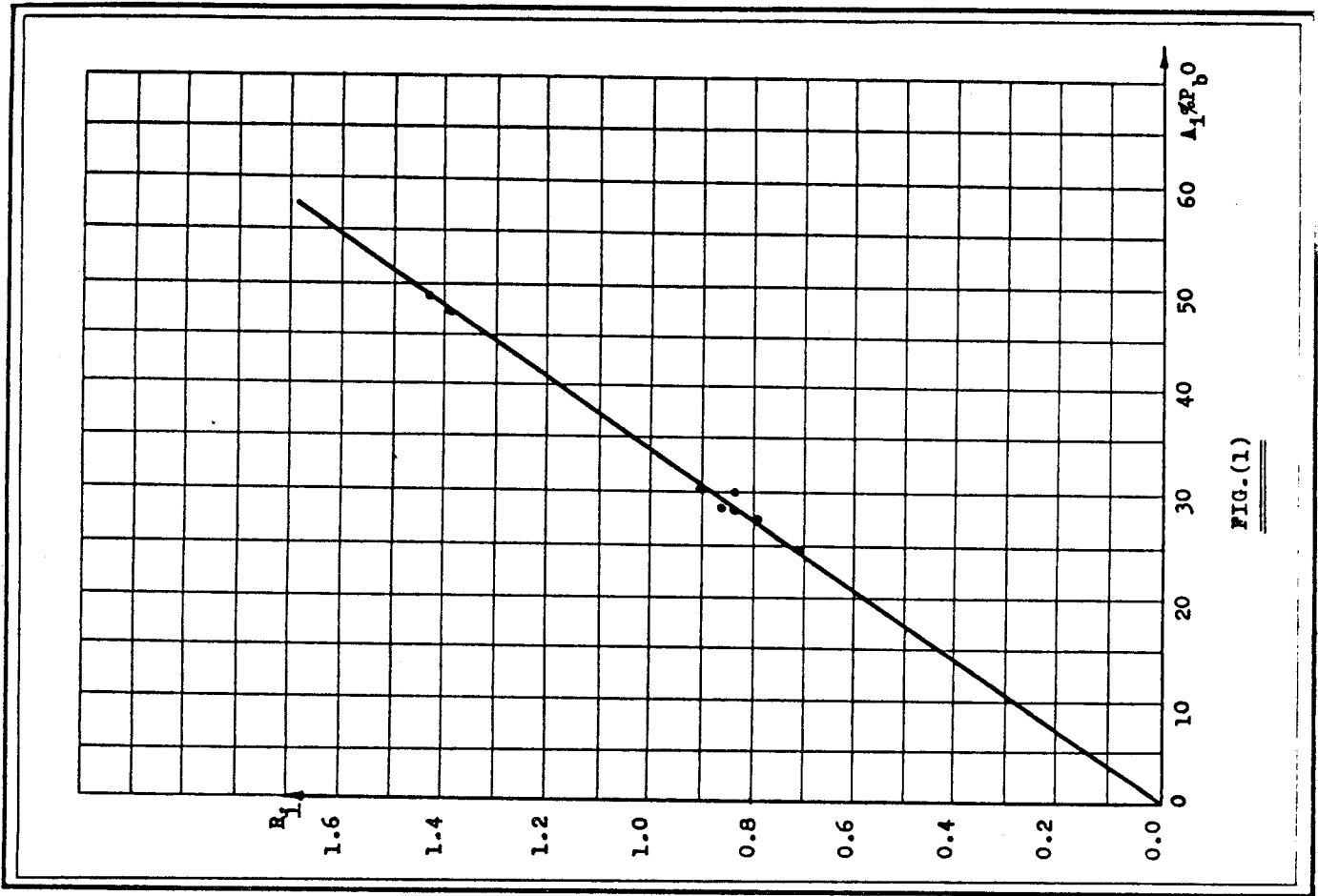
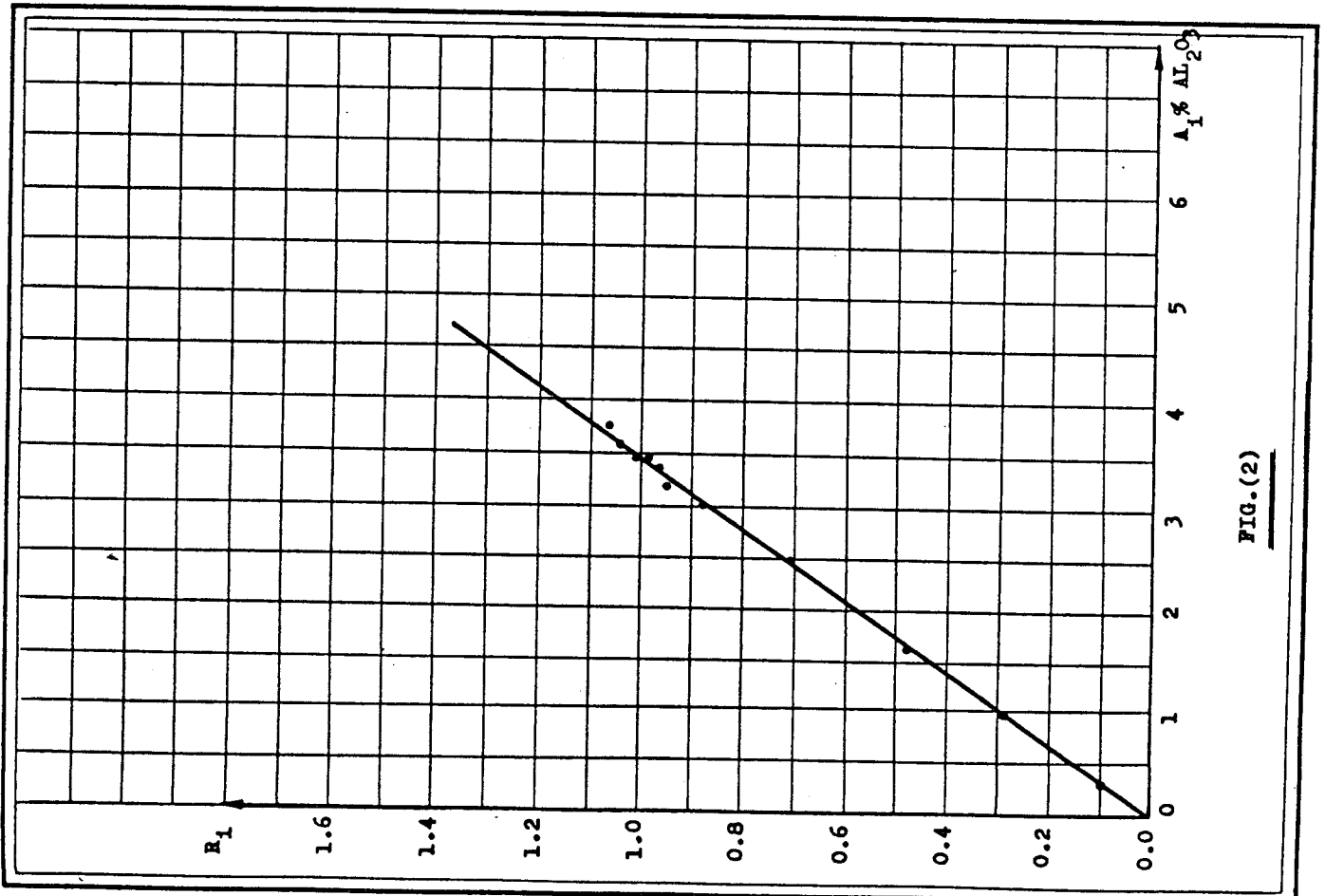
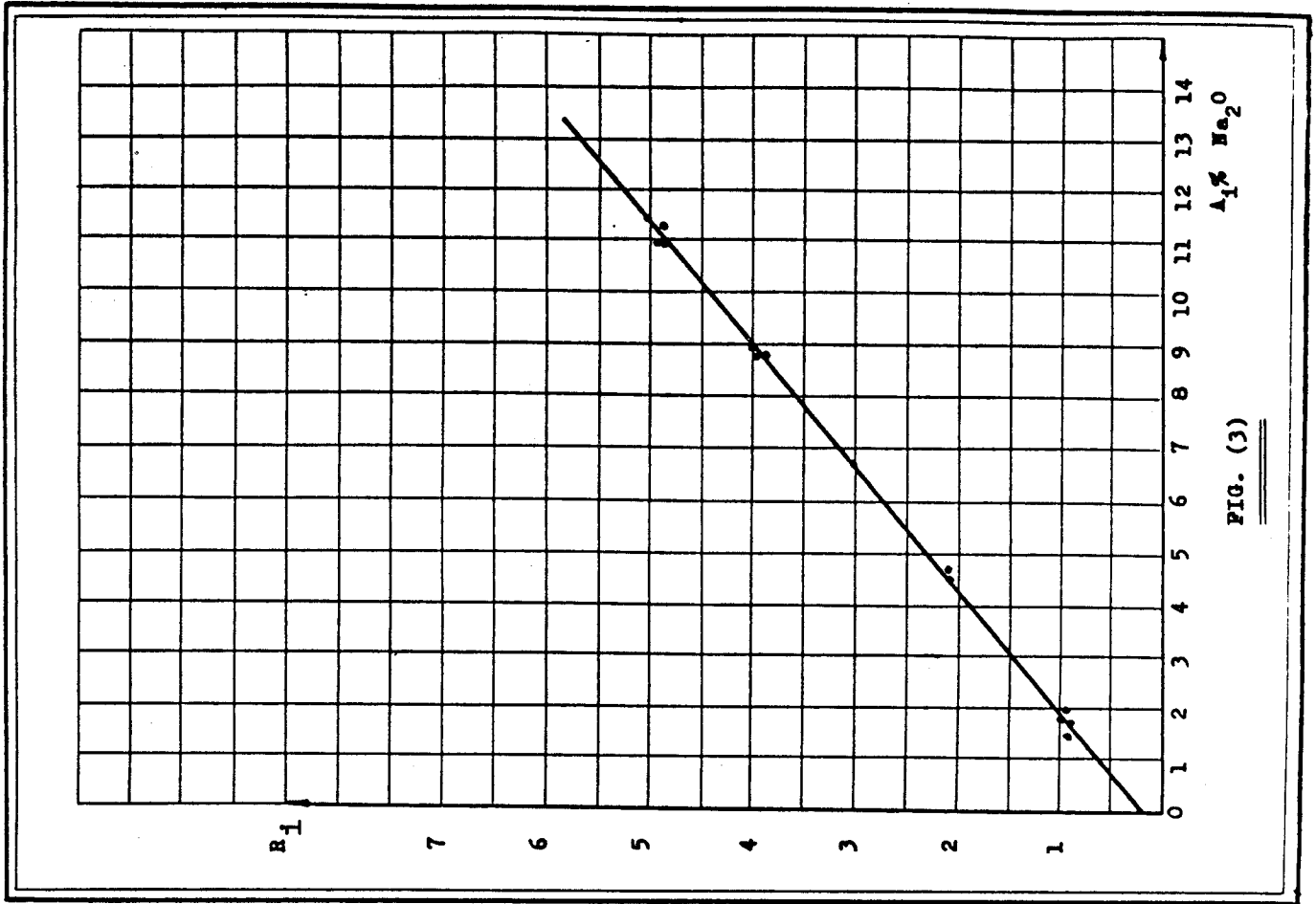


FIG. (1)

FIGURES INDICATING LINEAR
RELATIONS BETWEEN PHYSICAL
PROPERTIES AND CHEMICAL
COMPOSITIONS OF GLASS.

Figures (1) : (7)



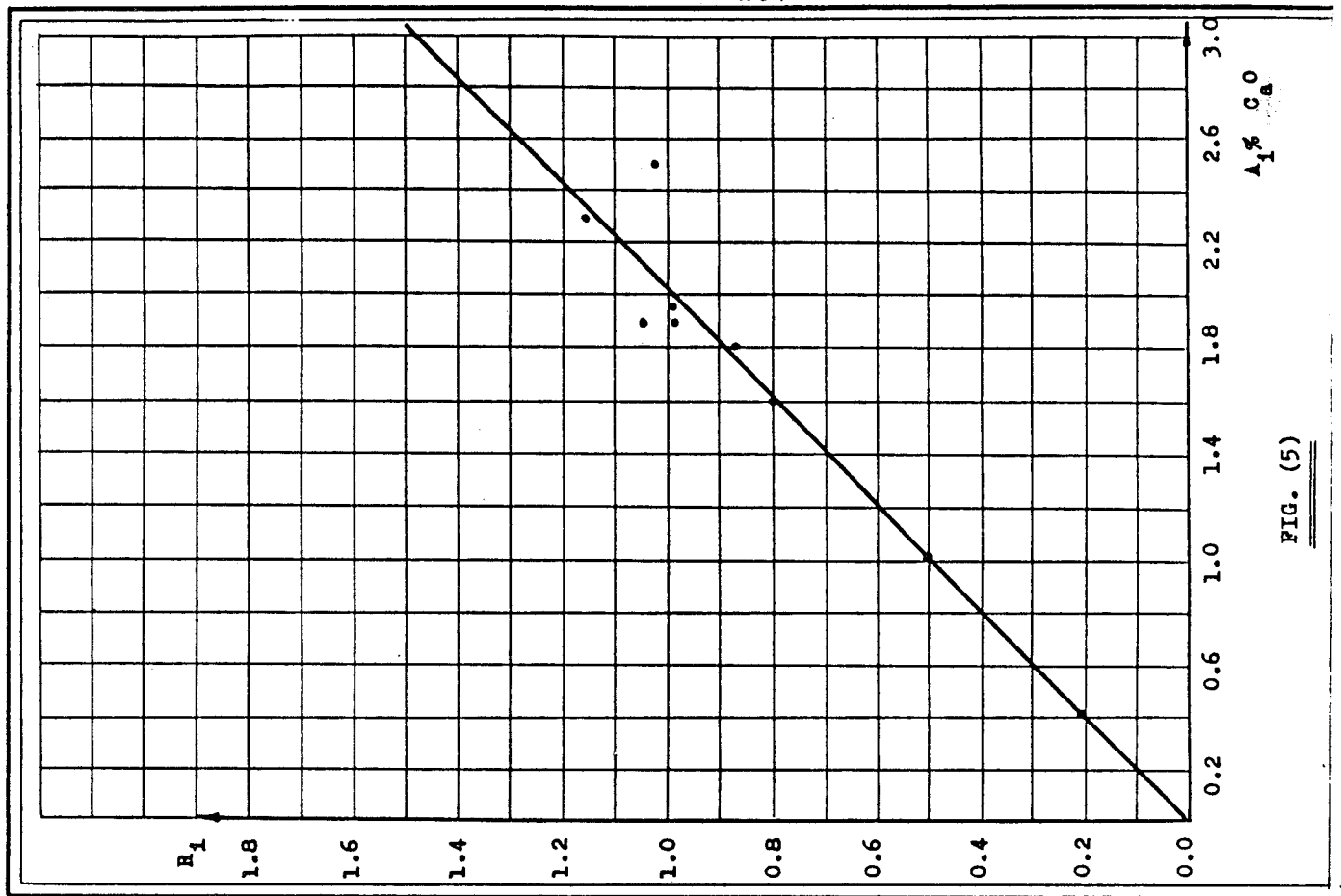


FIG. (5)

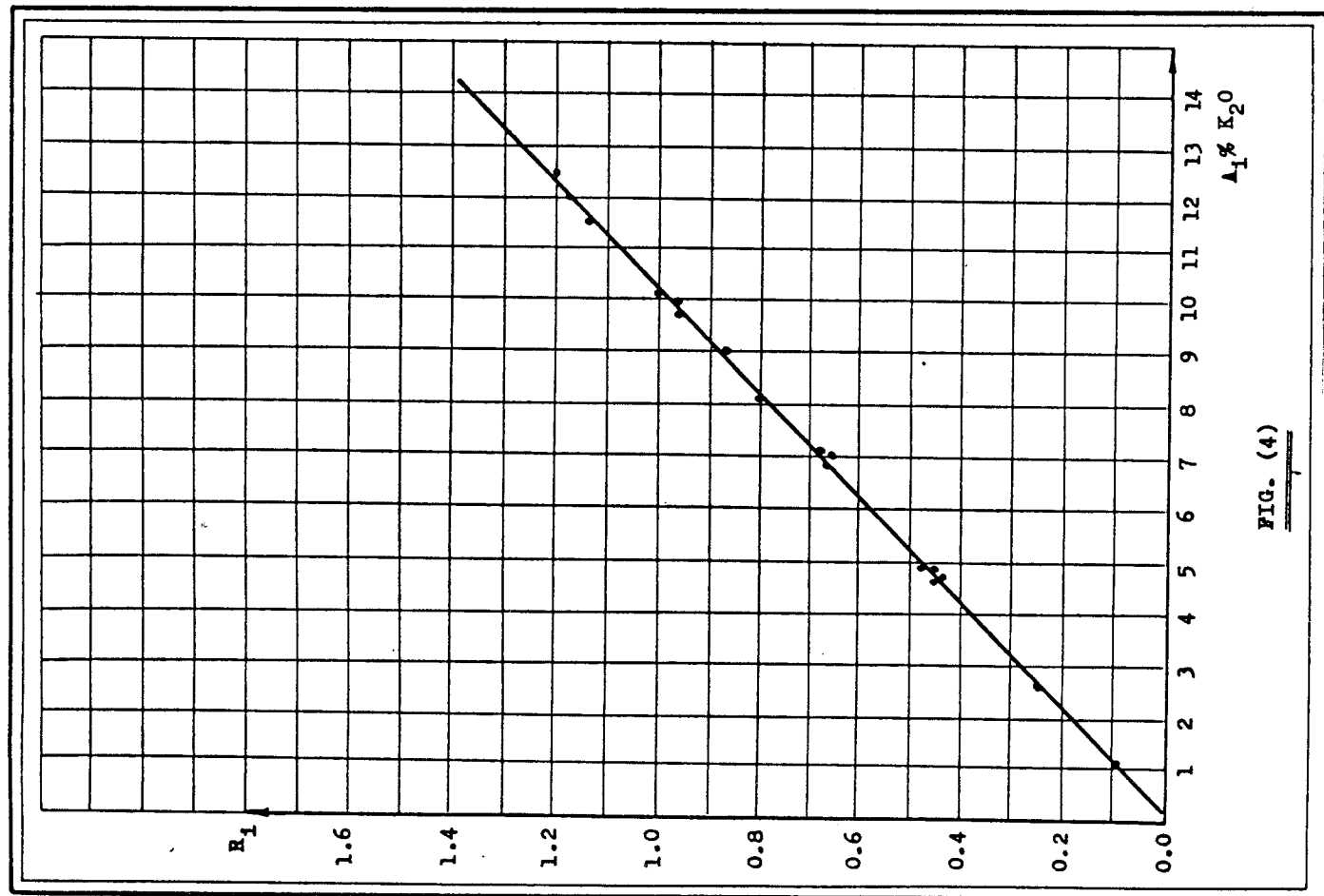


FIG. (4)

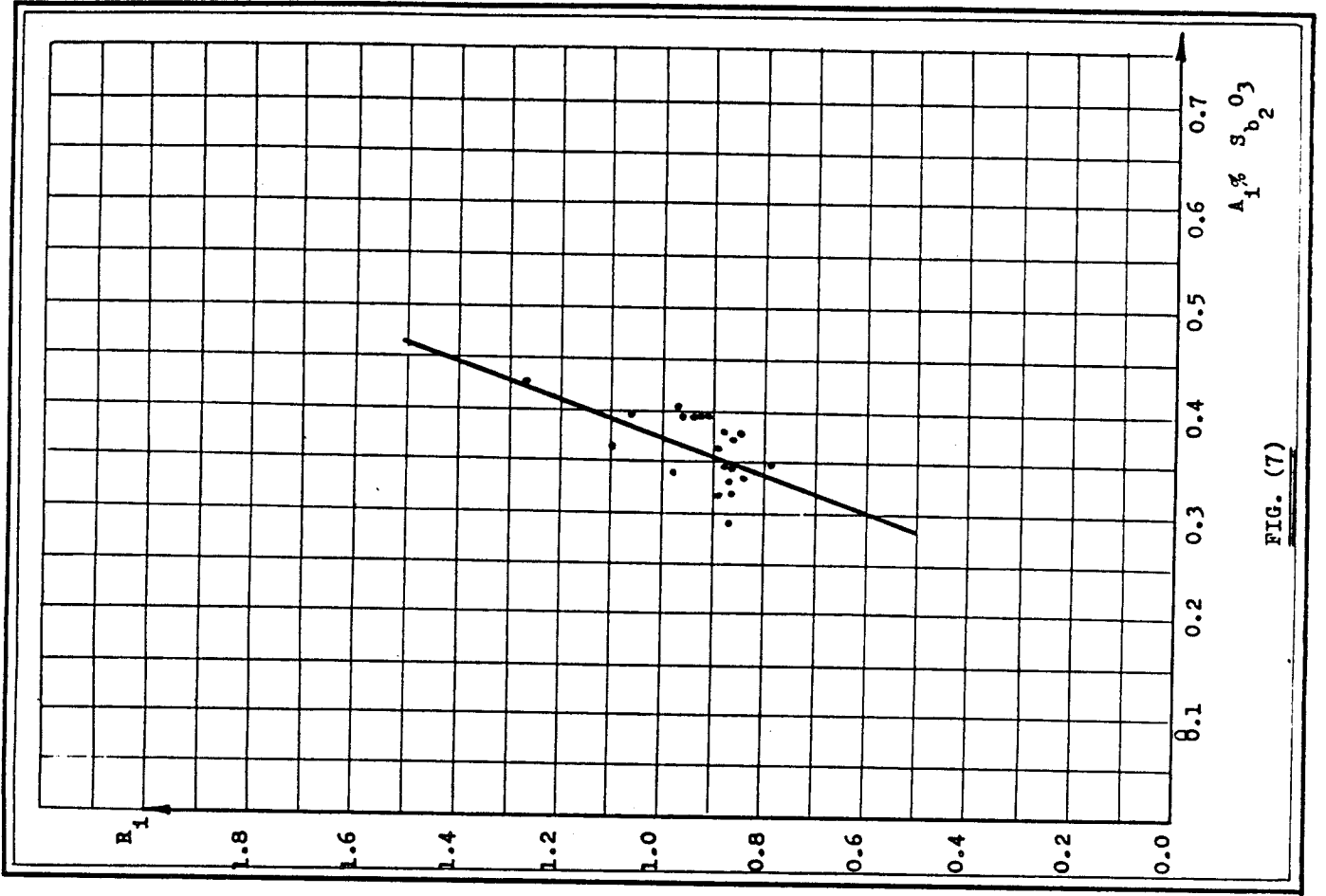


FIG. (7)

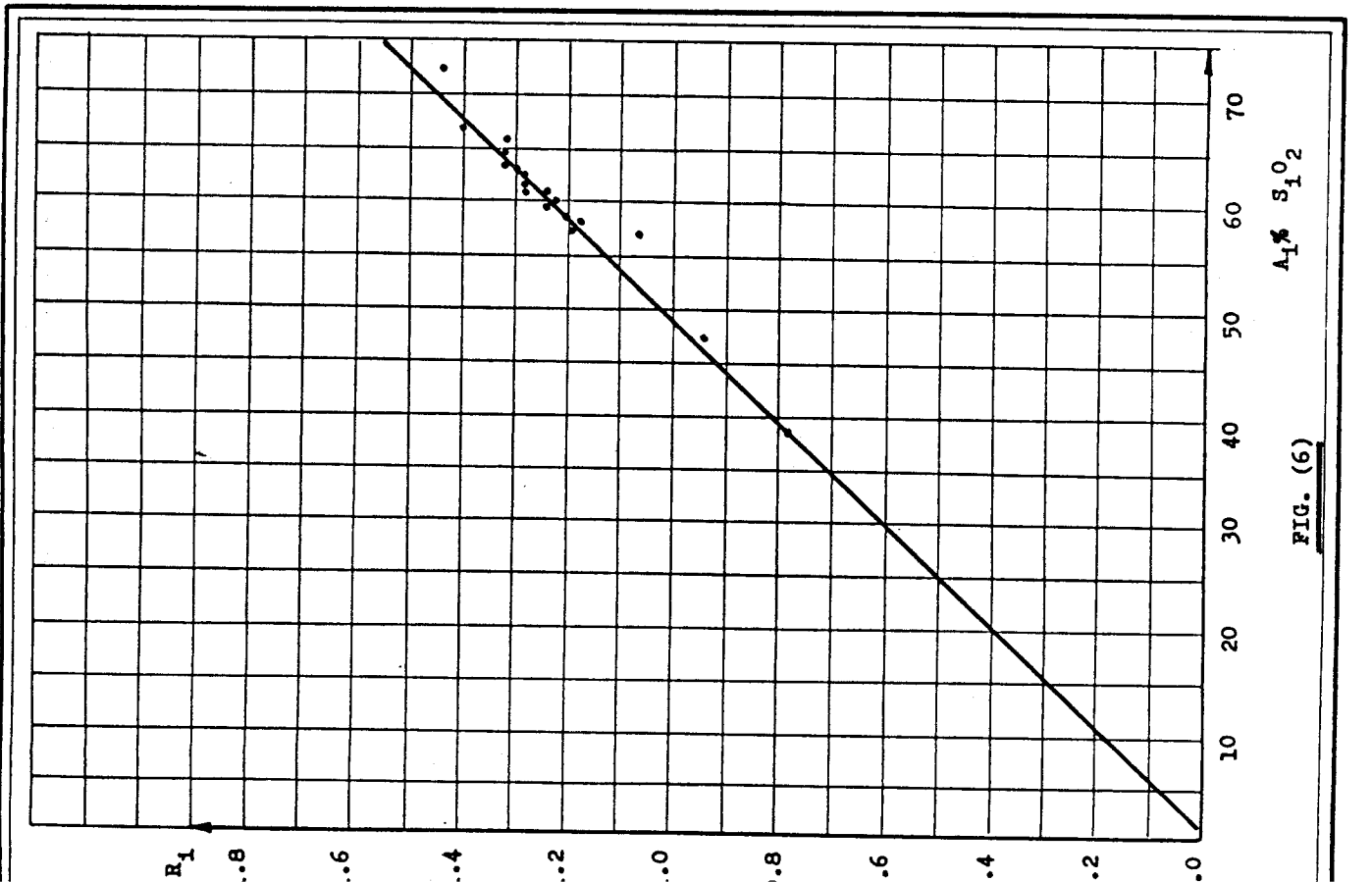


FIG. (6)

APPENDIX

Viscosity measurements at low temperatures :

Viscosities at low temperatures were measured by the beam bending method, described by Hagy in the viscosity range $10^8 - 10^{13}$ poise.

The apparatus is shown diagrammatically in Figure(1) viscosity was determined by measuring the midpoint deflection of a glass beam supported at each end and was calculated from the equation.

$$\eta = \frac{g \cdot L^3}{2.4 \times I_c \cdot v} \left[M + \frac{v \cdot A \cdot L}{1.6} \right] \text{ poise}$$

where (g) is the constant of gravitation in cm/sec².

(L) is the support span in cm,

(I_c) is the cross-section moment of inertia of the test beam in Cm⁴.

(v) is the speed of deflection in cm/min,

(M) is the applied load in grames,

(v) is the specific weight of the glass in g/cm³

(A) is the cross-section area of the beam in cm².

For rectangular beams

$$I_c = a \cdot b^3 / 12 \text{ cm}^4$$

where : (a) is the width and (b) is the height of the beam in cm, while for cylindrical beams,

$$I_c = \pi d^4 / 64 \text{ cm}^4$$

where : (d) is the diameter of the beam in cm.

By the use of different beams and loads, viscosities could be measured in the range of $10^8 - 10^{13}$ poise, but higher viscosities need very long times, several hours for stabilisation.

Rectangular beams with $a = 7$ mm and $b = 2$ mm, cylindrical beams = 7 mm diameter and cylindrical beams = 13 mm diameter were used. Loads of 40, 140, 510 grams were applied and these included the weight, of the loading rod, the transformer core, and the weight support. The temperature measured near the midpoint of the beam and the output of the transformer were recorded on a two channel recorder : with zero suppression and 1 mv/250 mm sensitivity, the temperatures were recorded with an accuracy of 0.2 deg. C and deflection rates were measured accurately by choosing the sensitivity and paper speed of the recorder to give a line of nearly 45, As this method gives absolute viscosity values, no calibration is necessary and a smooth transition between the low and high temperature curves is an effective control for the accuracy of the measurements.

The glasses for low temperature determinations were remelted in a platinum 2% rhodium crucible of 160 ml volume, stirred for 2h, held overnight at 1400 - 1425 °C and cooled in the crucible.

Several rods of 7 and 13 mm diameter were drilled out directly from the crucible with diamond core drills, and some 7 mm rods were ground down to 2 mm.

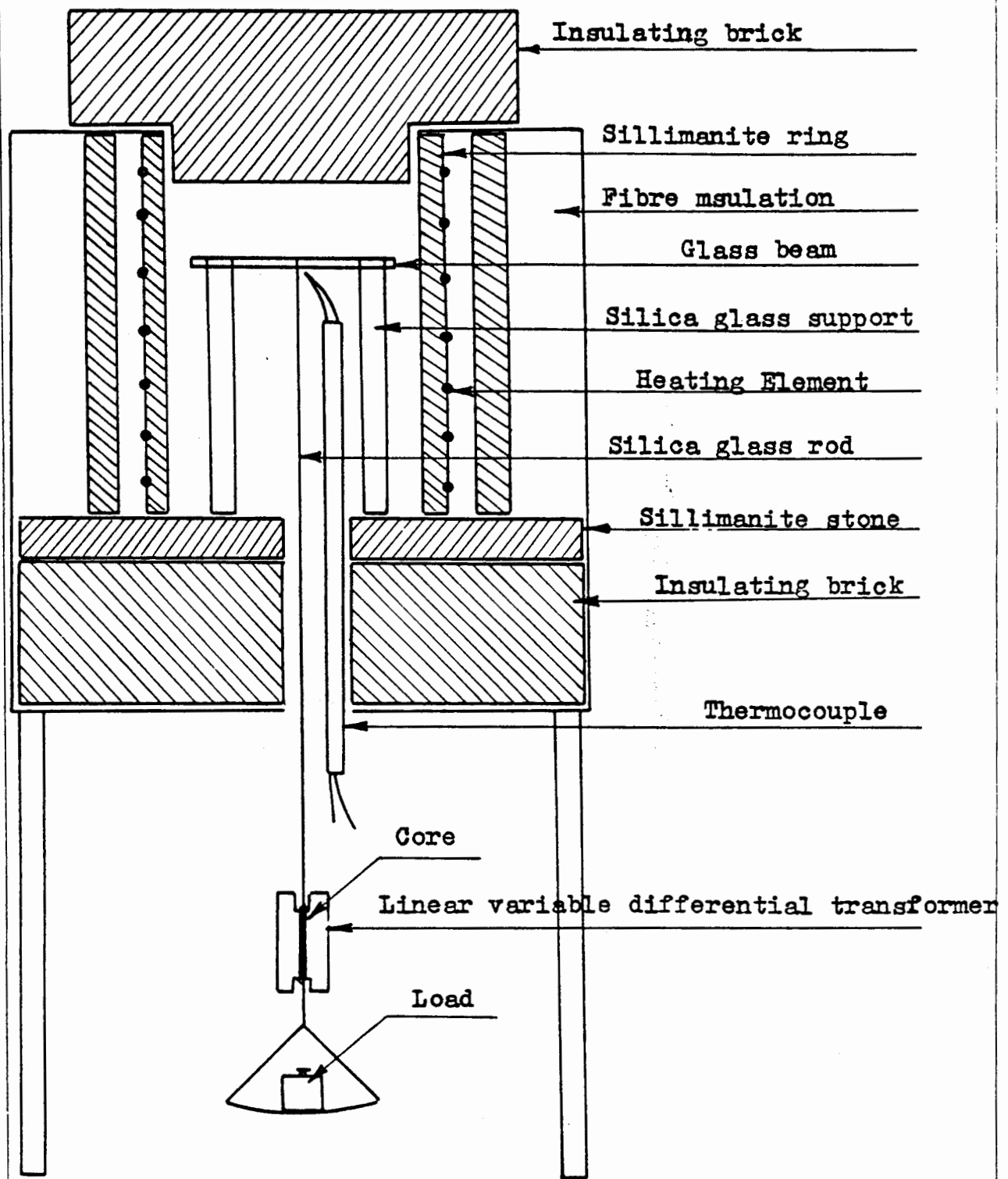


FIG.(1): Viscometer for measuring viscosity
at low temperatures.

CONCLUSION

It has been proved that its possible to forecast the important properties of glass for the production and process engineer as linear function of the oxides composing its structure.

We strongly recommend our Egyptian industries of glass making to encourage research in this area so that the control of final product specification could be controlled by proper control of the glass-Mix.

REFERENCES

- 1] Hald "Statistical Analysis with Industrial Application"
- 2] Morey "The properties of glass" 1964.
- 3] Lacy, E.D. "Physics and Chem. glasses" No. 4 pp. 234.
- 4] Babcock, C.L. (1968). J.Am. Ceram. Soc. 51, 163.
- 5] Huff, N.T. & Call, A.D. (1973). J.Am. Ceram. Soc. 56, 55.
- 6] Lakatos, T., Johansson, L.G. & Simmingskold, B. (1972)
- 7] Knott, P. (1971), Mon-Bull-Glass Ind. Nos. 432-8, C.E. Ramsiden & Ramsden & Co. Ltd., Stoke on Trent.
- 8] Huggins, M.L. & Stevels, J.M. (1964). J.Am. Ceram. Soc. 37, 474.
- 9] Williamson, J. & Glasser, F.P. (1965). Science 148, 1589.
- 10] Miller, G.H. & White, D. (1977) Glass Technol. 18, 72.
- 11] Karkhanavala, M.D. (1964). Glass Ind. 33, 403, 458.
- 12] Miberg, M.E. (1972): Physics Chem. Glasses. 13, 79.
- 13] Miller, G.H. & White, D. (1977) Glass Technol. 18, 113.
- 14] Vargin, V.V. (1967): Technology of enamels. Trans. K. Shaw, Maclaren, London.