The Physical Properties of Glasses. The Relationship to Chemical Composition and Mode of Preparation.

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PART I.

COMMERCIAL glasses cover a range of compositions comparable in variety with the industrial metallic alloys; and in respect of the number of components present they are usually much more complex than the alloys. The simplest commercial glass is fused silica. Glasses composed of two component oxides have occasional use, such as lead borate and zinc borate, for sealing-in purposes. For the most part, however, the number of major constituents is at least three, and in some cases may be as many as twelve or more.

In practice the glasses are prepared by the high-temperature fusion of the component or components. In the case of silica a temperature of at least 1800° is needed and is obtained electrically. In other cases the fusion of one or more of the acidic oxides, silica, boric oxide, phosphoric oxide, arsenious and arsenic oxides and antimony oxide, with two or more basic oxides, or, more frequently, with metallic salts, is involved. In practice, the oxide itself is employed in the case of lead oxide and, sometimes, of lime. The alkalis are most frequently introduced as carbonates, but also as nitrates, sulphates and borates. The carbonates are more frequently employed than any other salts, this being the usual form in which calcium, barium, magnesium, sodium, potassium and zinc are added.

In discussing the properties of glasses, however, compositions are invariably referred to the proportion of the oxide constituents present. This is the outcome of two causes, the chief of which is the usual method of presenting the results of analysis of a glass; this method in turn is based on the fact that even now our knowledge of the constitution of glasses, and of the particular chemical compounds which are present, is in a very elementary state. In these circumstances it is safer to adopt the plan of describing a glass in terms of its constituent oxides; for example, one containing the elements silicon, sodium and calcium is best described, not as a sodium calcium silicate, but as a soda–lime–silica glass.

As already stated, the number of oxides entering into the composition of a glass may be very considerable. Even in the earliest Egyptian glasses, the composition of which is well authenticated (Table I), namely, those discovered by Flinders Petrie at Tell el

Amarna, as many as thirteen oxides were present in some and eleven or twelve in several of the glasses.

TABLE I.

Composition of Egyptian Glasses from Tell el Amarna * (ca. 1400 *B.C*).

	Opaque.			Transparent.
	Dark blue.	Leaf-green.	Turkish blue.	Colourless.
SiO_2	61·7	62·44	62·58	63·86
Al_2O_3	2·45	1·00	0·82	0·65
Fe_2O_3	0·72	0·84	0·58	0·67
MnO	0·47	—	—	Trace.
CaO	10·05	9·23	9·33	7·86
MgO	5·14	3·05	4·37	4·18
Na_2O	17·63	18·08	18·19	22·66
K_2O	1·58	2·76	2·75	0·80
CuO	0·32	2·00	0·52	—
Cu_2O	—	—	—	—
PbO	—	0·47	—	—
SnO_2	—	—	0·47	—
SO_3	—	0·72	0·45	—

* Neumann, *Z. angew. Chem.*, 1925, **38**, 776.

No doubt the presence of some of these oxides is more or less accidental, due to the composition of the mineral constituents employed. This applies probably to alumina and lead oxide, but it is quite likely that even at that early date the colouring powers of certain minerals, such as those containing iron oxide, manganese oxide, and the oxides of copper and tin, were understood.

During the next 1400 years, so far as we know, there was no addition of other oxides to the glass-maker's list, although some doubt may be admitted in regard to cobalt oxide. Thompson in his recent "Chemistry of the Ancient Assyrians" refers to the use of arsenic in the glass-making processes of the 7th century B.C.; but I know of no analysis which indicates the presence of such a constituent in any glass of that date. Again, between the first year of the Christian era and 1600 A.D., the only new oxides utilised appear to be those of antimony and phosphorus, but metallic gold was also introduced. Between 1600 and 1800 there were certainly used the oxides of arsenic, lead, boron and cobalt, and of these lead oxide was the most important. In the next 75 years (1800—1875) the list of glass-making constituents tested underwent great expansion. Thus, Fraunhofer introduced bismuth oxide, and Döbereiner strontia and baryta; zinc oxide appears to have been first used by Maes in 1851, whilst Lamy, in 1866, experimented with thallium oxide. Vernon Harcourt's studies (1834—1870) on the effect of chemical composition on the properties of glass included the oxides of lithium, cadmium magnesium, beryllium, titanium, vanadium, chromium, molybdenum, tungsten, uranium and nickel, and the element fluorine as fluoride. The last fifty years have seen further expansion, and possible constituents now include the oxides of zirconium, germanium, cerium, didymium and other rare-earth elements, as well as the elements carbon, selenium, tellurium, sulphur and chlorine. The work of Schott was largely concerned with bringing to successful commercial application in glasses fluorides and such oxides as alumina, baryta, boric oxide, phosphoric oxide, and zinc oxide.

The study of glasses has therefore come down to the question of the relationship of the effect of the component oxides (or elements) on the physical properties. The list of properties studied is a long one, and includes representatives of the colligative, constitutive, and additive types.

One good instance of a colligative property is the rate of change of mobility in the neighbourhood of the softening temperature. Twyman [1] came to the conclusion that a general relationship existed represented by the equation $M = k \,.\, 2^{\theta/8}$. The researches of English [2] on the mobility and viscosity of glass have shown that this relationship holds good for a large number of glasses of differing composition, except for the slight modification that the 8° should be replaced by 9°. In other words the mobility is either doubled or halved according as the temperature rises or falls by each 9°. Gray and Dobbie [3] had previously observed that the specific conductivity of a number of glasses was doubled for each 9° rise in temperature.

The constitutive properties include the viscosity, the annealing temperature (which depends directly on the viscosity), light absorption and transmission, both general and selective, the electrical conductivity, and—what is to be regarded partly as a chemical process, since it usually involves hydration and hydrolysis—the resistance of glass to the action of water, aqueous solutions, acid solutions, and the alkalis. It is necessary in a lecture of limited scope to make a choice of subjects, and the plan which I decided to adopt was to discuss those properties of glass which have been the subject of investigations during the past few years and are more or less directly of interest to the chemist.

In connexion with the subject of light transmission and absorption I will content myself with reference to a number of problems of a definitely chemical character which still await solution. It is known, for example, that slightly tarnished camera lenses, owing to the reduction of the amount of light lost by reflection, are " faster " than when the surface is freshly polished. Wright and Ferguson [4] have confirmed this fact and found that suitable modification of the surface can be brought about by the action of solutions of many salts, but in different degrees. Sodium dihydrogen phosphate in 1% aqueous solution acting for 18 hours at 80° is one of the most successful. A satisfactory theory of the action is yet wanting. The study of the changes in colour associated with the process of decolorising glass presents another very interesting field awaiting more thorough cultivation. A small fraction of 1% of iron oxide in the ferrous condition imparts a greenish tint to glass, sufficient to be detected in a thickness of about 2 cm. when as little as 0·02% is present. For use in table glassware and general domestic purposes, this tint is corrected (decolorised) partly by the use of oxidising agents, such as nitrates, to convert the green lower oxide into the straw-coloured ferric condition, and partly by the addition of some constituent, such as manganese dioxide, nickel oxide or selenium, which provides a tint complementary to that due to the iron oxide present. The decolorised state is not permanent and colour changes may subsequently occur which indicate the occurrence of slow chemical changes involving oxidation and reduction in a medium so immobile as glass. Thus, exposure to strong sunlight gradually turns purple those glasses decolorised at an earlier stage by manganese dioxide, whilst glasses decolorised by selenium or by arsenious oxide —itself a decolorising agent of not definitely-known function—turn yellow. Even the bright greenish tint in glass to which no decolorising agent has been added turns yellowish-green on long exposure to light and it may be remarked that soda glasses are more difficult to decolorise than those containing potash, probably because of the greater viscosity of potash glasses as the result of which the dissociation of ferric into ferrous oxide with liberation of oxygen is retarded.[5]

The other four properties mentioned have certain aspects in common, but it will be of interest to refer to each separately before indicating their inter-relationships.

The viscosity of glass is a property of the greatest importance to the glass-maker. Until quite recently the attempts to determine the viscosity of glass had been few and unsystematic, but in the last three years three groups of investigations have widely extended our information on this subject: Washburn, Shelton and Libman [6] in America, Stott,[7] and Stott, Irvine and D. Turner,[8] at the National Physical Laboratory, and English [9] at Sheffield, have been responsible for these investigations. All the investigators have covered somewhat similar ground, but as the work of English deals with a greater range of oxides it will be made the basis of a few remarks on this subject.

The range of variation of viscosity varies greatly between the temperature at which the glass is present in the furnace and that at which it becomes too stiff for manipulation. Thus, a glass containing 75% SiO_2, 16% Na_2O, 8·16% CaO, which is typical of much commercial soda–lime–silica glass, has a viscosity at 1392° of $1{\cdot}54 \times 10^2$ *C.G.S.* units, whilst at 726° it is $4{\cdot}3 \times 10^7$, a difference of more than 200,000 times. At a temperature which is suitable for the annealing of this glass, namely, 550°, the viscosity is in the neighbourhood of 10^{13} *C.G.S.* units. By the study of a series of glasses in which silica and soda were constituents, and in which the third constituent was lime, magnesia, alumina or boric oxide, it has been found that the viscosity of the glass increases in the order lime, magnesia, alumina. Glasses containing boric oxide are comparatively fluid. The rate of change of viscosity, however, takes place in the inverse order, the alumina-containing glasses setting most slowly and the lime-containing most quickly when comparing the three oxides. The fluid boric oxide-containing glasses likewise set with increasing rapidity as the boric oxide content is increased.

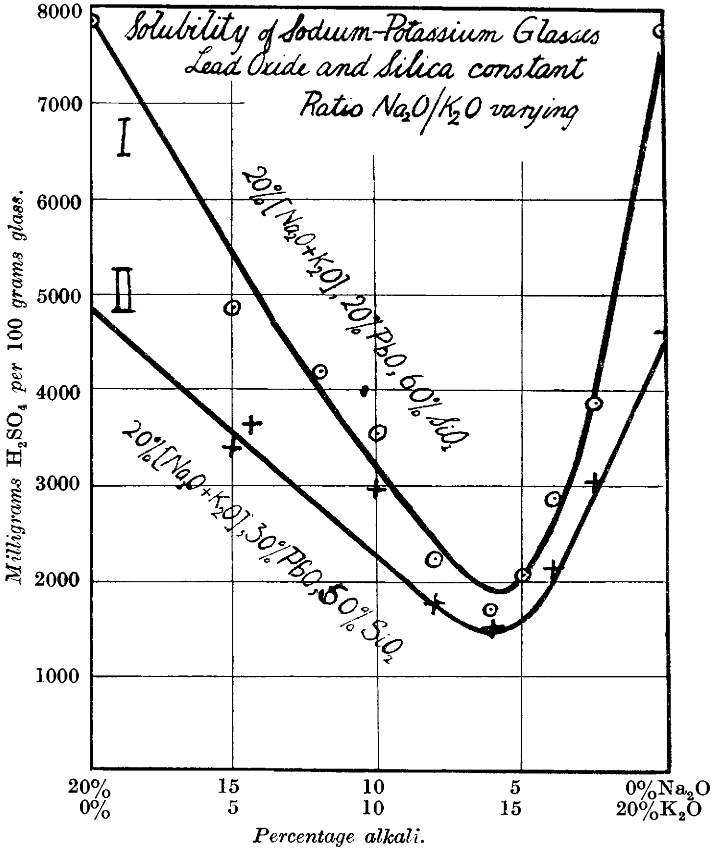
The viscosity of glass controls the rate of diffusion and also the ease with which the glass can be manipulated and worked into objects. The high viscosity accounts for the slow rate of diffusion and for the existence of inhomogeneities such as are seen in their gross form as cords and waves, and in their finer form as striæ. The former marred a good deal of the earliest chemical ware produced in this country. Most of the glasses prepared for this purpose contained between 5 and 10% of alumina, as well as other oxides such as that of zinc, which produce glasses of high viscosity. Mechanical stirring is essential in order to promote homogeneity when the glass is prepared for optical purposes. If the inhomogeneity revealed in waves, cords, and stripes is considerable, then, because each portion has its own viscosity and rate of setting, as well as its corresponding thermal expansion and mechanical properties, stresses are set up which cannot be removed by the annealing process, whilst if the article passes successfully through the annealing furnace it will often fracture spontaneously shortly afterwards.

The annealing temperature is directly connected with the viscosity, since removal of stresses can only take place when the glass possesses sufficient mobility. English and Turner [10] and Sheen and Turner [11] have published the results of annealing temperature measurements as related to the composition of glass containing the oxides SiO_2, Na_2O, CaO, MgO, Al_2O_3, B_2O_3, TiO_2, ZnO, BaO, ZrO_2, and English has subsequently shown that the determined annealing temperatures actually correspond to the temperature at which the logarithm of the viscosity of the glass is approximately 12·75.

The electrical conductivity of glass within the range in which it is still rigid has been the subject of recent investigations by Ambronn [12] and still more recently by Gehlhoff and Thomas.[13] The electrical conductivity of glass is electrolytic in character and the form of the curves showing the relationship between electrical conductivity and temperature for similar series of glasses bears a

FIG. 1.

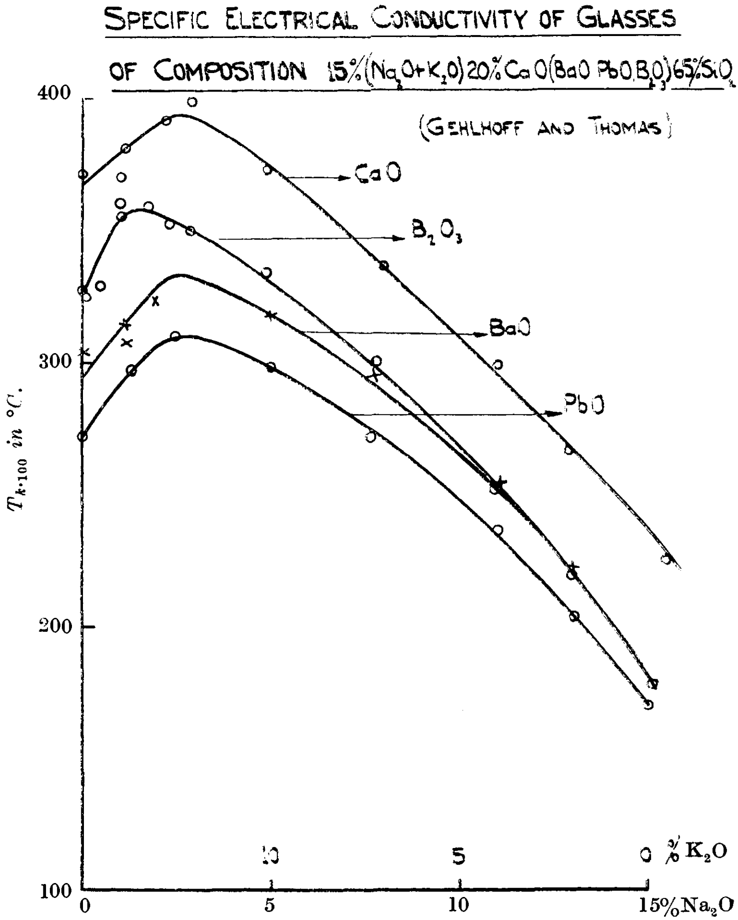
Alkali extracted by water at 80° from finely powdered soda–potash–lead oxide–silica glasses.
(*C. J. Peddle.*)



distinct resemblance to the mobility curves. The governing factor in the conductivity of glass, especially at the lower temperatures, thus appears to be the viscosity of the medium.

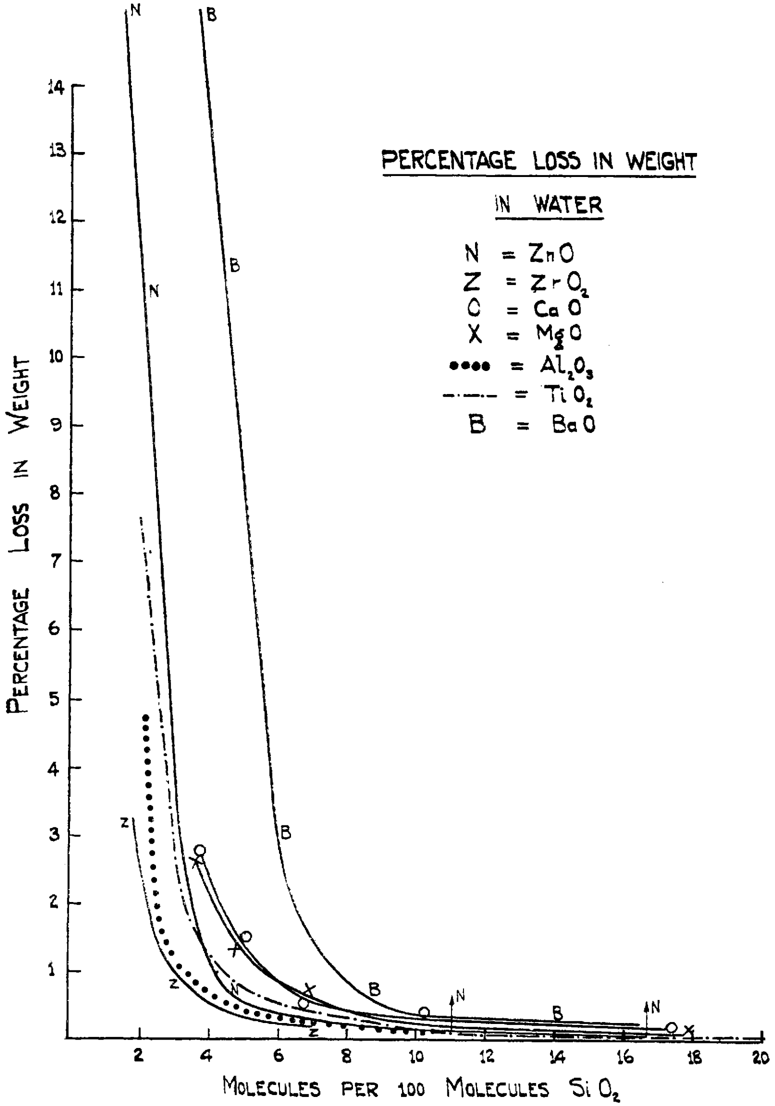
It was pointed out by Kohlrausch that the insulating properties of a glass were dependent on its power of resisting the action of water—in other words, on its chemical durability. This relationship was strikingly confirmed by Gehlhoff and Thomas in connexion with glasses containing both soda and potash as alkaline constituents. It had previously been shown by Peddle [14] that, in alkali–lead oxide–silica glasses containing both soda and potash, the maximum resistance to the attack by water was reached when the ratio of the potash to the soda was in the proportion of 7 to 3, in parts by weight (Fig. 1), and that generally speaking the resistance was greater for the glass containing the mixed alkalis than when only one of these oxides was present. Gehlhoff and Thomas found a similar relationship in that the specific resistance also reached a maximum corresponding to the maximum resistance to the attack by water.

Fig. 2.



This fact the authors set out graphically (Fig. 2) by plotting against the percentages of soda and potash the value of the temperature (T_{k100}) at which each glass had the same electrical conductivity, *viz.*, 100 × 10^{-10} mho per cm. The higher the

Fig. 3.



temperature the greater must be the electrical resistance of the glass.

The resistance of glass to water and chemical reagents is of first-class importance to the chemist. A very great deal of work on this subject has been carried out at Sheffield, and the results may be set out very briefly. Comparison of the durability of glasses has been made in various ways, but one of them has been exploited by us fairly fully. In this particular series of investigations (not hitherto published), a parent glass corresponding to the approximate formula $6SiO_2,2Na_2O$ was prepared, and for the soda were substituted, stage by stage, lime, magnesia, alumina, titania, zirconia, zinc oxide, and barium oxide, providing for test some sixty glasses in this series alone. The effect of boric oxide will be referred to at a later stage.

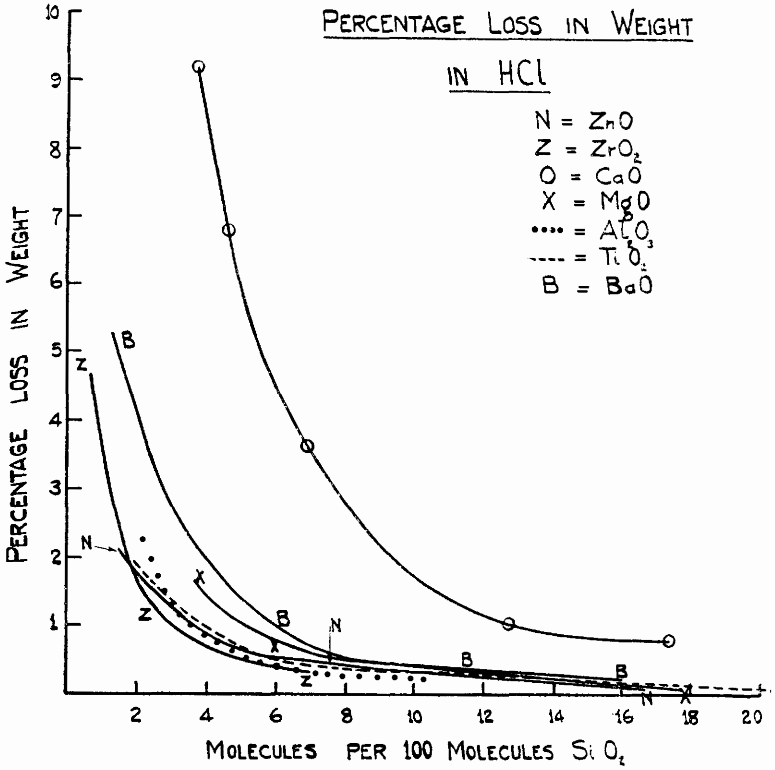
In Fig. 3 the resistant power, determined by the percentage loss in weight sustained on boiling in water for 1 hour a fixed weight of the glass in the form of powder of definite grain size, is set out to show the variation with chemical composition. The comparison is made on the basis of molecular composition. It will be seen that in each case replacement of the sodium oxide by a small amount of one of the other oxides mentioned results in a rapid increase of resistant power. The resistance, as shown by the curves, appears to increase in the order barium oxide, lime, magnesia, titania, zinc oxide, alumina and zirconia. If we bear in mind that the glasses rich in the alkali oxides soda and potash are very readily attacked by water, and that the glasses rich in silica are highly resistant, we shall see that a very rough and ready rule exists, namely, that the glass is all the more resistant as the soda is replaced progressively by an oxide of very low solubility in water; thus barium oxide, calcium oxide and magnesia have a distinct solubility in water, diminishing in the order stated, whilst at the other end alumina, zirconia and silica are practically insoluble.

The action of neutral salt solutions is, generally speaking, practically that of water itself. The same remark holds good for a number of dilute acids such as nitric and sulphuric, and concentrated sulphuric acid has been found in some cases to have a smaller corrosive action than pure water. Hydrofluoric acid reacts with silicate glasses, as also does phosphoric oxide above 400°. Of the commonly used acids, hydrochloric acid apparently provides the most searching test of a glass in regard to resistance to acids. For test purposes at Sheffield we have selected hydrochloric acid of 20·24% strength as a standard reagent. Fig. 4 shows the relative resistance of the glasses to this acid.

In the case of alkaline solutions, whether those of alkaline salts or of caustic alkali, the corrosion is usually very much greater than is caused by water or acids. This is not unexpected in view of the fact that most commercial glasses contain 70% of silica or other acidic oxides.

The third group of properties is that in which additive relationships exist. The first of the properties for which Winkelmann and Schott found this type of relationship is thermal expansion, and the result of studies at Jena of other physical properties of glasses disclosed a number of similar character. The equation which is made to fit the results in all cases contains the same number of terms as the number of oxides present in the glass. Thus, the cubical thermal expansion coefficient of glass can be calculated by the equation devised by Winkelmann and Schott, namely, $3\alpha = ap_1 + bp_2 + cp_3 + \ldots$, in which p_1, p_2, p_3, etc., represent the percentages by weight of the various constituent oxides in the glass, and a, b, c, etc., are constants depending on the nature of the oxide. The constant

FIG. 4.



in question is the contribution which each 1% of the constituent oxide makes to the total cubical expansion of the glass.

A similar linear relationship exists for the specific volume, and the density may be calculated from the formula $100/D = p_1/d_1 + p_2/d_2 + p_3/d_3 +$ etc., in which D represents the density of the glass, p_1, p_2, p_3, etc., the percentage of each oxide, and d_1, d_2, d_3, etc., the constants for the individual oxides.

Like formulæ have been derived to express the data obtained in the case of the thermal conductivity, the tensile strength, the compressibility, specific heat, Young's modulus of elasticity, and hardness.

On some of these properties very little systematic work has been carried out since that of Winkelmann and Schott, and further reference will be confined to the thermal expansion, density and refractive index which have been the subject of many recent investigations. It may, however, be mentioned in passing that two recent investigations on glasses and silicate rocks, namely, one by Adams and Williamson [15] and the other by Bridgman,[16] have shown the general additive character of the relation between compression strength and composition.

The thermal expansion, which is an important element in the thermal endurance of chemical and heat-resisting glass, has been the subject of systematic investigation at Sheffield. Winkelmann and Schott's work was based on glasses of very varying composition. At Sheffield we have studied series of glasses of similar molecular composition, namely, those based on the formula $6SiO_2,(2-x)Na_2O,xRO$ (R_2O_3 or RO_2), and the results, summarised in Fig. 5, for glasses containing lime, magnesia, alumina, zinc oxide, barium oxide and zirconia indicate the existence of a definite linear relationship over a considerable range of composition as sodium oxide in the parent glass is replaced step by step by one of the oxides mentioned. We have found that a number of Winkelmann and Schott's constants are in error : that for silica, for example, appeared to be distinctly high. The basis of the calculation by these two workers was empirical. We have set out on the assumption that in the above glasses silica exercises its own thermal expansion, and the comparative values ($\times 10^9$) are summarised in Table II, those of Winkelmann and Schott being denoted by W. & S. and those of English and Turner by E.& T. The value for ZnO must be regarded as provisional.

TABLE II.

Constants for Calculating Cubical Thermal Expansion.

	SiO_2.	Na_2O.	CaO.	MgO.	ZnO.	Al_2O_3.	ZrO_2.
W. & S.	80	1000	500	100	180	500	—
E. & T.	16	1300	490	135	(20)	40	70

FIG. 5.

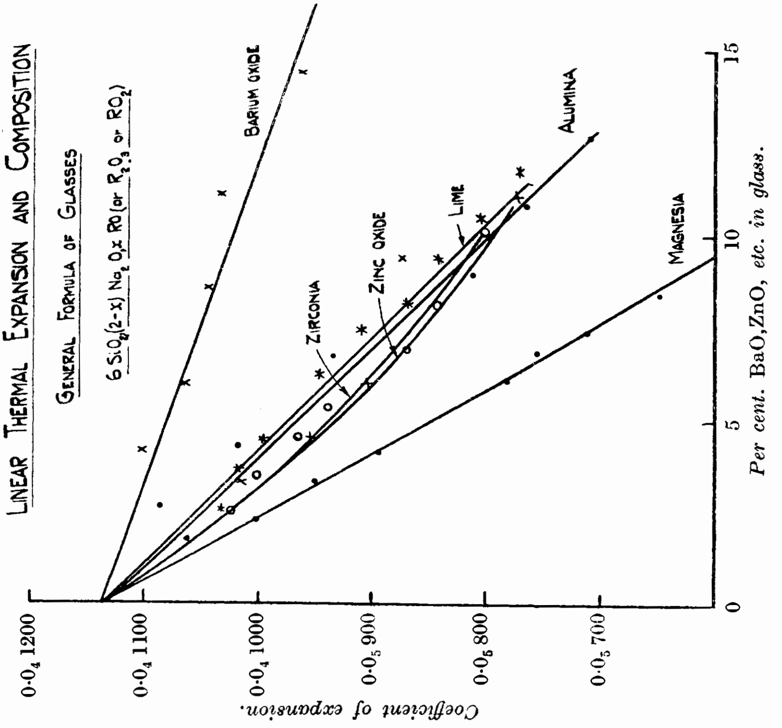
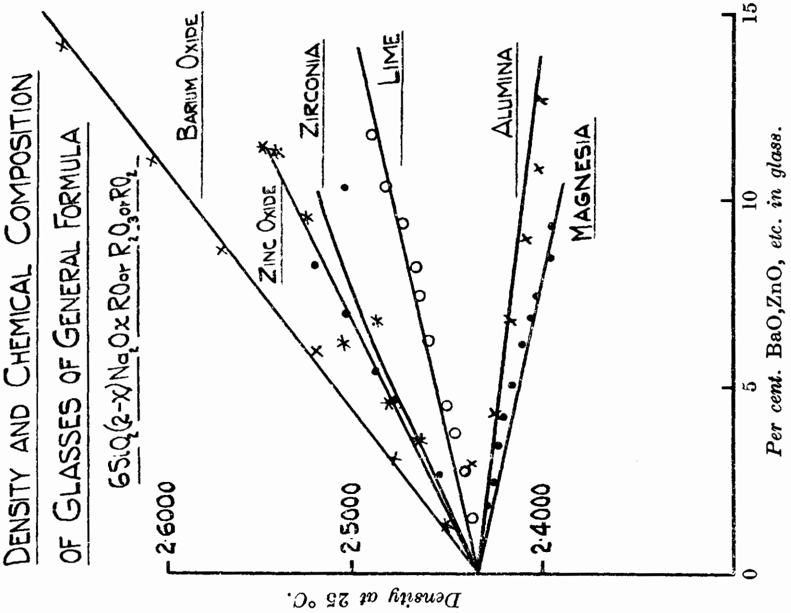

LINEAR THERMAL EXPANSION AND COMPOSITION
GENERAL FORMULA OF GLASSES
6 SiO₂,(2-x) Na₂O,x RO (or R₂O₃ or RO₂)
BARIUM OXIDE
ZIRCONIA
ZINC OXIDE
LIME
ALUMINA
MAGNESIA
0·0₄ 1200
0·0₄ 1100
0·0₄ 1000
0·0₅ 900
0·0₅ 800
0·0₅ 700
Coefficient of expansion.
0
5
10
15
Per cent. BaO,ZnO, etc. in glass.

FIG. 6.


DENSITY AND CHEMICAL COMPOSITION
OF GLASSES OF GENERAL FORMULA
6SiO₂(2-X)Na₂O X RO or R₂O₃ or RO₂
BARIUM OXIDE
ZIRCONIA
LIME
ZINC OXIDE
ALUMINA
MAGNESIA
2·6000
2·5000
2·4000
Density at 25 °C.
0
5
10
15
Per cent. BaO,ZnO, etc. in glass.

Saltpeter,[17] referring to Winkelmann and Schott's constants, pointed out that the oxides of high value, like soda and potash, contain elements which occupy peaks on the atomic volume curves, whilst those of low value contain elements which occupy the depressions. On this basis, some of the constants, such as those of zinc oxide and alumina, needed revision. Our own constants are more in keeping with the generalisation.

The relationship between density and composition has also been investigated at Sheffield and the results are summarised in Fig. 6. Again the general linear relationship holds good. Constants are likewise available for the calculation of density. We have not yet provided a completely revised set but those worked out by Baillie [18] can be used satisfactorily for the purpose of approximate density calculations.

The refractive index and dispersion are also largely additive in character. This appears to be the case for glasses of the general series $6SiO_2,(2-x)Na_2O,xRO$ (see, for example, Clarke and Turner,[19] for the soda–lime–silica glasses). Peddle has made comprehensive measurements of the relationship between refractive index and composition and the additive character revealed may be illustrated by reference to Fig. 7 for potash–lime–silica glasses.

The simplicity of these relationships in practice, whatever they mean in theory, makes it possible to prepare glasses of approximately known properties by bringing together suitable oxides in the requisite proportions. For example, the preparation of optical glasses of specified refractive index is rendered easier by the general additive relationships subsisting. The development of heat-resisting glasses in practice has largely resulted from a study of the thermal expansion constants combined with improvement in the melting capacity of furnaces so as to make it possible to use as components of the glasses those oxides of high melting point, particularly silica, which contribute only slightly to the total thermal expansion. In this connexion the alkaline oxides soda and potash are to be avoided wherever possible. They are the controlling factors in the thermal expansion as well as in the action of water and chemical agents on glasses containing them. The special virtue of these oxides lies in the greater ease of melting which they impart to glasses: but so far as chemical durability and physical properties are concerned their influence is generally detrimental.

The bearing of the facts which have been related on chemical resistance glass can be very well illustrated by reference to Table III containing the compositions determined by analysis, of the latest types of chemical resistance glasses available. The analyses are our own where no other source of information is quoted.

Fig. 7.

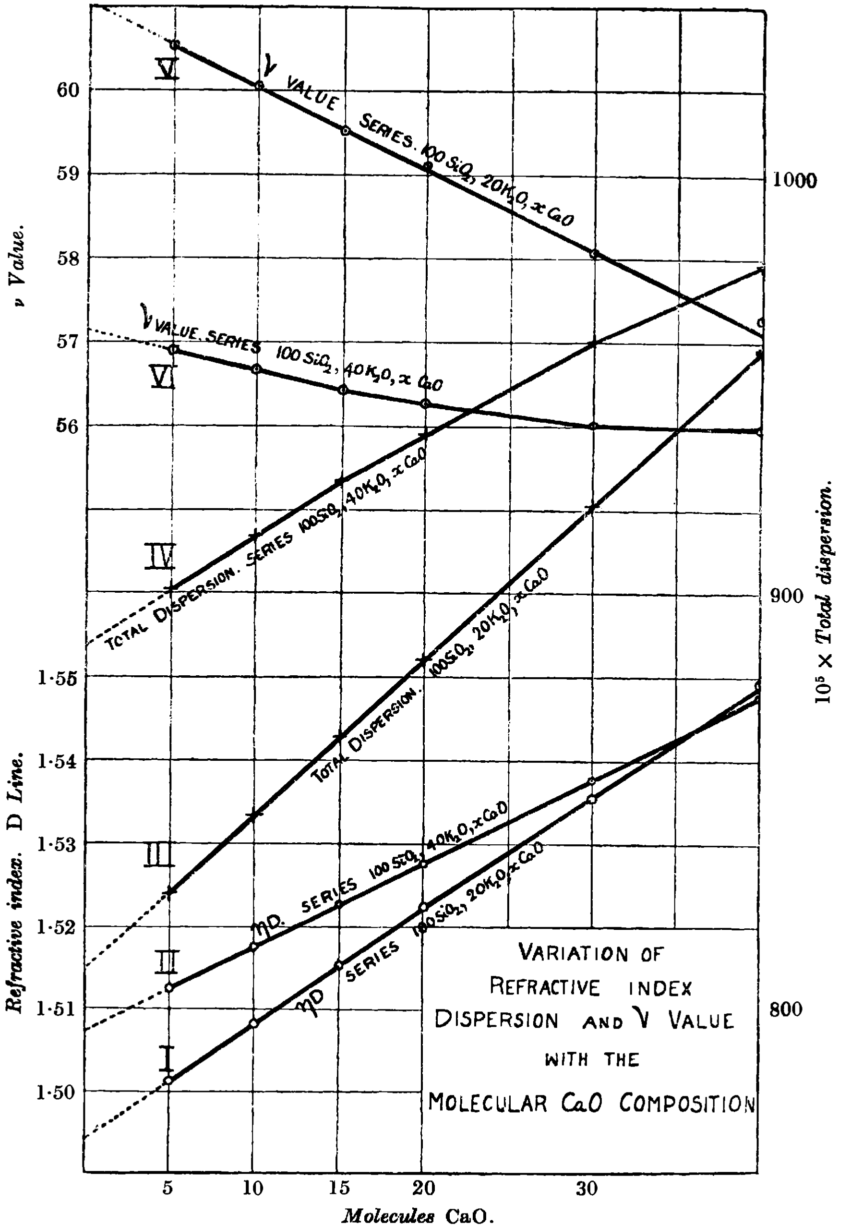

ν Value.
60
59
58
57
56
1·55
1·54
1·53
1·52
1·51
1·50
Refractive index. D Line.
1000
900
800
10⁵ × Total dispersion.
5
10
15
20
30
Molecules CaO.
V
ν Value Series. 100 SiO₂, 20K₂O, x CaO
VI
ν Value. Series 100 SiO₂, 40K₂O, x CaO
IV
Total Dispersion. Series 100SiO₂, 40K₂O, x CaO
III
Total Dispersion. 100SiO₂, 20K₂O, x CaO
II
ηD. Series 100 SiO₂, 40K₂O, x CaO
I
ηD Series 100SiO₂, 20K₂O, x CaO
Variation of Refractive index Dispersion and ν Value with the Molecular CaO Composition

TABLE III.

Chemical Composition of Some Modern Resistant Glasses.

	SiO_2.	B_2O_3.	As_2O_5.	Sb_2O_3.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	ZnO.	BaO.	K_2O.	Na_2O.
Chance Bros.* (1924)	71·2	12·0	—	3·4	3·5	0·1	1·3	—	—	—	—	8·6
Duroglass (1916)...	66·5	1·6	—	—	6·7	0·1	4·3	0·3	3·6	—	2·6	11·5
Durosil (1923)	72·3	12·6	—	—	4·2	0·1	0·5	0·1	3·3	—	1·4	5·0
Jena † (1920)	74·5	4·6	—	—	8·5	—	0·8	0·1	—	3·9	—	7·7
Moncrieff (1916) ...	66·4	6·9	—	—	6·6	0·1	0·5	0·1	8·7	—	1·1	10·0
Moncrieff-Monax * (1926)	75·3	11·3	—	—	3·0	—	0·5	—	2·8	—	1·2	6·3
Pyrex (1917)	80·6	11·9	0·7	—	2·0	0·1	0·2	0·2	—	—	0·6	3·8
Resista ‡ (1923) ...	81·4	10·6	—	—	2·0	—	0·7	—	—	—	1·1	4·4
Resista ‡ (1925) ...	75·3	15·8	—	1·3	2·5	—	—	—	—	—	1·0	3·4
Sv Resistance (1925)	81·3	10·1	—	—	3·9	0·1	—	—	—	—	0·4	4·2
Wood Bros.* (1926)	59·3	9·6	—	—	7·6	—	5·0	1·7	5·2	—	2·9	8·8

* Private communications.

† Keppeler, *Z. Verein. deutsch. Ing.*, 1923, **26**, 509.

‡ Thiene, *Glas u. Apparat*, 1924, **5**, 1; *Z. angew. Chem.*, 1926, **39**, 193.

It will be noticed from this table that the silica content with three exceptions exceeds 70% and the total of the acidic oxides, mainly silica and boric oxide, generally runs high. The Jena glass of 1911 and the glasses of the war-time period, both in this country and in America, in most cases had a silica content between 64·5 and 68%. The total proportion of basic oxides, except in the case of Pyrex glass, was accordingly distinctly higher. As glass for chemical purposes may have to withstand the action of water and of acids and alkalis, some sort of compromise has to be effected for the simple reason that a glass may be expected to be all the more readily attacked by alkalis the richer it is in acid oxide constituents. In the last few years, the tendency has been to sacrifice something of the resistance towards alkaline solutions and to concentrate on improving the resistance towards water and acid solutions. Silica is eminently suitable for this purpose, and in the case of the action of water, the presence of boric oxide within certain limits is also advantageous. Hence, the most recent glasses contain silica, boric oxide, and alumina as three of the chief components, and only such proportions of alkaline and other oxides as may be desirable to produce fairly ready melting. It will be noticed how closely a number of recent glasses are attempts to copy Pyrex glass, which was brought out in 1915.

Whilst sacrificing a little of the resistance towards alkaline reagents, the use of a high percentage of silica, and, within limits, of boric oxide, reduces substantially the thermal expansion of the glass and renders it increasingly immune from sudden changes of temperature. In fact, the glasses which most readily furnish resistance to the action of water and acids are also those which are the best heat-resisting glasses.

PART II.

Up to this stage our account of the properties of glass has been descriptive and on the whole the impression probably given is that of comparatively simple relationships. Even in properties described as constitutive the mass factor operates; that is to say, there is a more or less continuous variation in the viscosity or electrical conductivity or resistance to chemical reagents as the proportion of a specific oxide in the glass is increased. The existence of so many additive relationships suggests a comparatively simple constitution for glasses. There are some workers, indeed, for example, Sosman [20] and Tammann,[21] who suggest that in glasses the oxides are in a state of dissociation. This presents possibly no greater anomaly than the case of aqueous or other solutions. The suggestion of Sosman is that possibly compounds are only definitely established at the moment of their separation in the form of crystals from the glass. The specific-volume curve for mixtures of magnesium and calcium silicate shows a definite break for the crystalline mixtures, but not for the glasses containing the same components in the same proportions. Definite evidence of the existence of compounds in glasses has yet generally to be established. In the simple system sodium oxide–silica, when the specific volume and also the specific refraction are plotted against the composition, a definite break occurs in each case at a point corresponding to $Na_2O,2SiO_2$.[22] This particular compound was first isolated from melts and characterised by Morey and Bowen [23] only in 1924. The systematic investigation of the constitution of glasses through a study of the variation of physical properties is only just being taken up.

A large number of silicates have been isolated from silicate fusions containing the oxides employed in making commercial glasses. Thus, by suitable thermal treatment of fusions of soda–lime–silica, deposition has been obtained not only of the simple silicates Na_2O,SiO_2; $Na_2O,2SiO_2$; CaO,SiO_2; and $2CaO,SiO_2$, but also of a series of complex compounds, namely, $2Na_2O,CaO,3SiO_2$; $Na_2O,2CaO,3SiO_2$; and $Na_2O,3CaO,6SiO_2$, each characterised by extensive dissociation when liquefied.[24]

The examination of glasses by X-rays has not yet revealed any marked structure, although Wyckoff and Morey in 1925, in a study of the X-ray diffraction patterns of the soda–lime–silica glasses, found both broad bands and in some cases lines, the precise interpretation of which has yet to be made.

If we bear in mind the number of the components which Morey and Bowen have already shown to be capable of existence in the system soda-lime–silica, and if, further, we assume that some or all of them exist in the glass, we shall be better able to appreciate the possibility of some of the anomalous results which will presently be referred to as having in very recent years been observed to exist in certain properties of glasses.

Before passing on to this subject, however, and while the subject of the constitution of glass is being considered, reference may be made to the similarity in the behaviour of certain glasses to zeolites such as heulandite and desmine. These zeolites are characterised by their power of parting with a considerable proportion of their water without loss of structure or optical properties. Moreover, it is possible by means of concentrated hydrochloric acid to withdraw the whole of the basic constituents, leaving the residual silica as a skeleton in which the original structure is preserved. It is a striking fact that samples of ancient glass, on treatment with hydrochloric acid, frequently behave in a very similar way, the basic constituents being withdrawn and a silica skeleton remaining. This, however, is true not only of ancient glass, but also of certain newly melted glasses which are readily attacked by water and by hydrochloric acid. Thus, we have found it possible in the case of a sample of glass tubing of percentage composition, SiO_2 49·5, B_2O_3 25·7, CaO 9·08, Na_2O 7·0, and K_2O 7·5, to extract by means of hot hydrochloric acid of strength not less than 20·24% all other constituents from the glass except the silica, the latter retaining the form of the original tube.[25] The silica at no stage appears to exist in the gelatinous form. Whatever bearing this may have on the constitution of glass, it is at least a reasonable surmise that the zeolites were probably glasses which through weathering action have been so modified as to render their constituents easily capable of extraction or substitution, the silica in the meantime having slowly developed a lattice accompanied by definite optical properties and crystalline form.

I now wish briefly to direct attention to three factors influencing the properties of glass, namely, the influence of concentration and specific composition, the effect of the mode of preparation, and finally the influence of heat treatment.

1. *The Effect of Concentration and of Specific Oxides.*

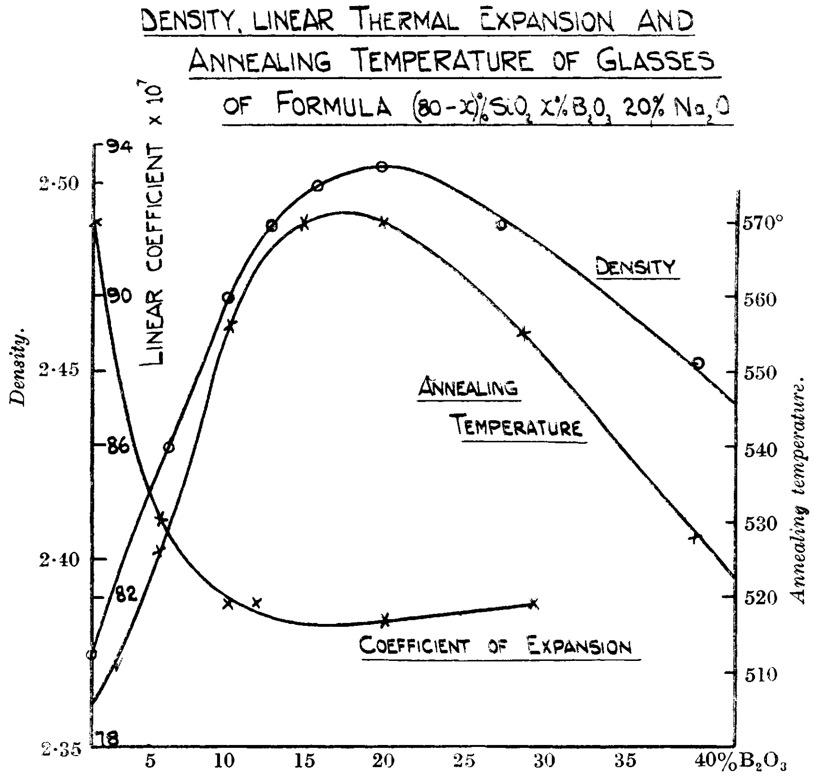
In the case of the basic constituents of glass, as also of silica in silicate glasses, our present information shows that there is continuous variation of the physical property directly with the variation of composition and frequently in an additive manner. For the system of glasses Na_2O–SiO_2, the curve showing the variation of thermal expansion with composition is nearly straight over a considerable range, so straight over such a length as to suggest that silica in these glasses exercises the thermal expansion it possesses in the free vitreous state.[26] The refractive index and density curves for mixtures of albite and anorthite, as well as for magnesium silicate and calcium silicate, over the whole range from 0 to 100% of each are either rectilinear or nearly so.[27]

In some series of glasses the graphs show a marked tendency to be concave or convex to either axis. Instances occur in the thermal expansion curve for titania-containing glasses [28] and in the refractive index curves of some series examined by Peddle.

Finally, the occurrence of inversion points has already been referred to in the physical properties of glasses containing mixtures of sodium oxide and potassium oxide. Thus, the resistance to the action of water attains a maximum at a certain ratio of potash to soda, namely, 7 : 3, whilst the specific resistance similarly reaches a corresponding maximum. It is also of interest to note that the after-contraction which takes place in glass, especially as revealed in thermometer bulbs, is greatest when both alkaline oxides are present and the after-contraction can only be made more or less negligible by using a glass containing one alkali oxide only. The precise ratio of soda to potash which gives the maximum after-contraction has not been generally determined. It may prove to coincide with the maxima on the water-resistance and the electrical-resistance curves.

Boric oxide is another constituent which does not follow additive relationships over a wide range of concentration. Great value has been attached to this oxide as a constituent for chemical and heat-resisting glass and almost all modern glasses of these types contain it. During lengthy investigations at Sheffield 8 to 9 years ago on the subject of chemical glassware we came to the conclusion that it was a constituent of limited usefulness and especially in the case of glasses intended to resist hydrochloric acid. Further researches between 1923 and 1925 showed that this limit definitely exists. Fig. 8 shows the influence of boric oxide on the density, the annealing temperature, and thermal expansion of glasses of the system soda–boric oxide–silica in which the sodium oxide content is approximately 20% throughout the series. It will be seen that a minimum occurs in the thermal expansion curve and maxima in the other two cases. Moreover, a maximum occurs in the resistance to the action of water, after which the glass breaks down rapidly. In Fig. 9 we have precisely similar results in the case of a series of glasses based on Kavalier's chemical glass, the silica being progressively replaced by boric oxide. The refractive-index curve also shows a maximum but the point of its occurrence is displaced compared with the curves of the other properties. In the case of the chemical durability no advantage at any stage was found by substituting boric oxide for silica, the resistance to water and hydrochloric acid remaining constant for a certain concentration and thereafter rapidly breaking down. This reversal may possibly be due to the formation, in the early stages of the substitution of boric oxide for silica, of silicates in which part of the silica is replaced by boric oxide. Further experimental work on this subject is in hand to endeavour to trace the cause satisfactorily.

Fig. 8.



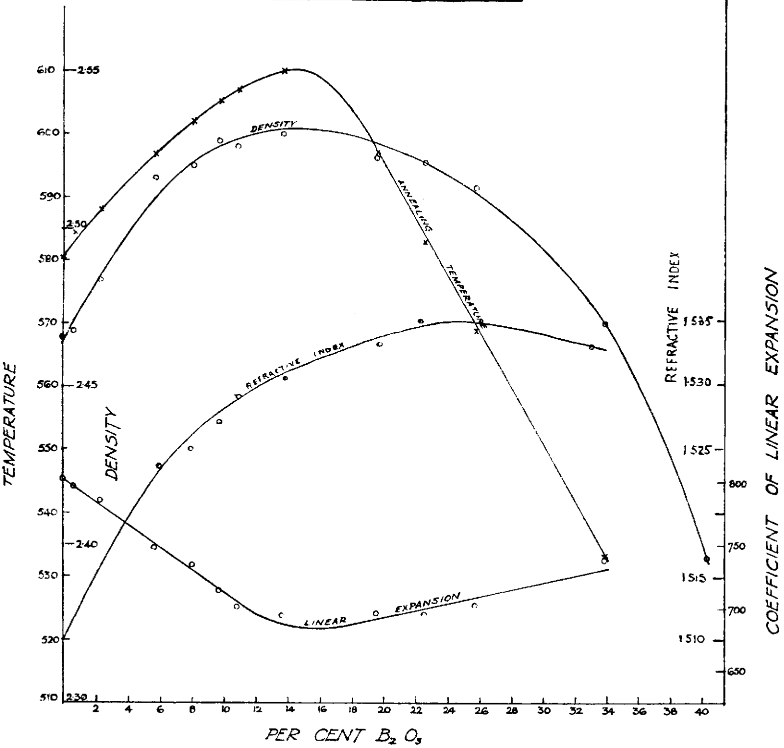
2. *The Influence of the Mode of Preparation of the Glass.*

The mode of preparation of the glass also has an influence on at least some of its physical properties. The prosecution of this problem by refined physical methods is only just beginning, but the facts now appear to admit of no doubt.

A particular glass may be produced by the melting of different substances, many of which can be introduced in alternative forms. The alkaline elements may be introduced as carbonates or nitrates, for example. The alumina may be introduced as calcined alumina, hydrated alumina or through some mineral of known composition such as China clay, felspar, etc. One would expect the reactions on fusion to proceed to the same end. Chemical analysis, generally

FIG. 9.

REFRACTIVE INDEX, ANNEALING TEMPERATURE, DENSITY, AND LINEAR EXPANSION CURVES.



speaking, shows that this is the case. We have found, however, that when glass is worked from the pot and drawn into tubing its working range (which depends on the rate of change of viscosity) is, in some cases, appreciably different according to the constituents from which the glass has been prepared. We have not yet detected such differences when simple salts serve as the basis for the glass mixture, except in so far as chlorides and sulphates almost invariably leave residues which influence the working properties. A distinct difference is observed according as alumina is introduced in the simple form or as a mineral containing it. It is conceivable that when a mineral is employed a longer period is required to reach equilibrium, and this view is strengthened by the proof by Morey and Bowen [29] that orthoclase has an incongruent melting point and is slowly converted into leucite.

The presence of considerable amounts of water in the ingredients used in the glass-making mixture also has a definite effect on the working properties of the resulting glass. A soda–lime–silica or a potash–lead oxide–silica glass which has been melted from a wet batch mixture, that is, one containing 7, 8, 10 or more % of moisture, invariably sets more quickly than one produced from a dry batch mixture, although the composition of the resulting glass gives no clue to any difference of composition, and it has definitely been shown by us at Sheffield that in such cases the amount of water retained in the glass cannot exceed 0·05%. The influence of such factors was at first a matter of some surprise. Several investigations in which these influences were found to operate were reported to a Research Committee of the Glass Research Association and the results were regarded with some scepticism. I myself for a time was in doubt that the idiosyncrasies of the workman were not sufficient to account for this phenomenon. Becoming convinced, however, of the reality of these influences, I finally persuaded my colleagues on the Committee to accept them on the basis of further results obtained by putting the glass-worker through an examination in which pairs of glasses—in one or two cases the same, in other cases either of different composition or with one prepared from dry mixtures, the other from wet, and so on—were prepared, and the glass-maker only allowed to come into contact or have any knowledge whatever of the operation at the moment the glass was ready for manipulation. He was then asked to draw up a report on the working character of the glasses and to make suggestions as to the mixtures from which they had been made. His report, based entirely on the general manipulation of the glass, set out with astonishing accuracy the conditions under which the glasses had been prepared.

The remelting of glass is also accompanied by a shortening of its working range. At each melting it sets slightly more rapidly and becomes more brittle. There is no change in chemical composition to account for this quite marked change in viscosity or plasticity. In a series of glasses, made by us from mixtures of raw materials and previously melted glass, the working range of which was progressively shortened as the proportion of remelted glass in the mixture was increased, the extreme variation in the silica content was about

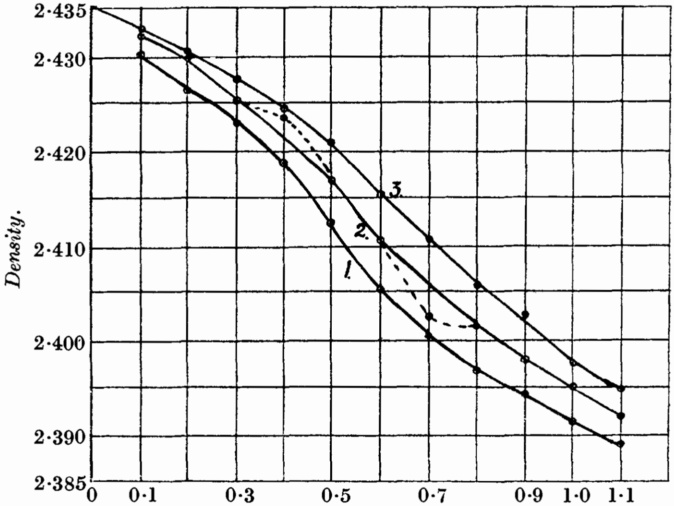
0·5 throughout the series, in the alumina 0·3, iron oxide 0·04, lime 0·3, and in the sodium oxide 0·36. Such variations make no difference which is observable when the glasses are melted from ordinary normally dry batch materials.

3. *The Influence of Heat Treatment.*

The subject of the heat treatment of glass has been one of the most interesting fields cultivated in the last few years. For example, we know that the state of annealing of glass influences the value of the physical property. The density of strained glass is lower than that of annealed glass. Fig. 10 shows the results of experiments made by us[29a] on a series of soda–magnesia–silica glasses, the curve (3) representing the density when the glasses were annealed, and the lower curves being those determined from glass taken from slabs. and rod in a strained condition.

FIG. 10.

Effect of strain on density of glasses of general formula $6SiO_2(2-x)Na_2OxMgO$.



The thermal expansion of glass may be from 3 to 6 or 7% higher if it is strained. The electrical properties are affected still more noticeably. Gray and Dobbie[3] found a potash–lead oxide–silica glass to be a much better insulator when annealed than when under strain and observed the following striking figures for the specific resistance :

Glass composition.				Specific resistance
SiO_2.	PbO.	K_2O.	Temperature.	(ohms).
48·2	40·8	10·6 (annealed)	140°	29,000
50·1	39·7	10·0 (unannealed)	142	1,329

Ferguson and Mulligan have found differences of as much as 100% in the specific electrical resistance of soda–lime–silica glass according as it was annealed or not. Berndt[29b] also found a difference in the compression strength according to the state of annealing as illustrated by the following data :

Glass : Borosilicate Crown.

	Load.	Kg./cm.² Mean.	Kg./cm.² Maximum.
Strain severe.	Continually increasing	15,000	18,400
	Increasing in steps	15,200	17,500
Well annealed.	Continually increasing	14,200	16,900
	Increasing in steps	12,500	15,100

A series of investigations carried out at the Bureau of Standards by Tool and collaborators[30] have shown that the density of glass can be made to vary according to the heat treatment it receives, the maximum variation so far obtained being between 1 and 2%. Simeon and Twyman[31] have shown that the refractive index can also be made to vary as much as 5 units in the third place of decimals by heat treatment, and the recovery of the original refractive index depends on both the temperature and the length of time at which the glass is reheated.

In Russia, Lebedev[31a] published in 1921 the results of investigations on several properties, including the refractive index, on very similar lines to those made by the workers at the Bureau of Standards, although entirely without knowledge of their work. Lebedev found a series of transition points in physical properties which occurred in the neighbourhood of 570°.

Although glass is regarded merely as a supercooled liquid, the physical changes in which are continuous, nevertheless Tool and Valasek[32] showed that a definite heat evolution or absorption occurs over a certain range when the glass is cooled or heated respectively. This is shown by the curve in Fig. 11 and it is similar in character to that of any transition from one solid phase to another. Over this same range, the coefficient of thermal expansion of glass undergoes a sudden increase, between 3 and 7 times that immediately preceding the change point, dependent on the composition of the glass. Fig. 12 shows this change in one of a series of soda–lime–silica glasses (74·52% SiO_2, 8·14 CaO, 16·86 Na_2O, 0·40 Al_2O_3) recently

Fig. 11.

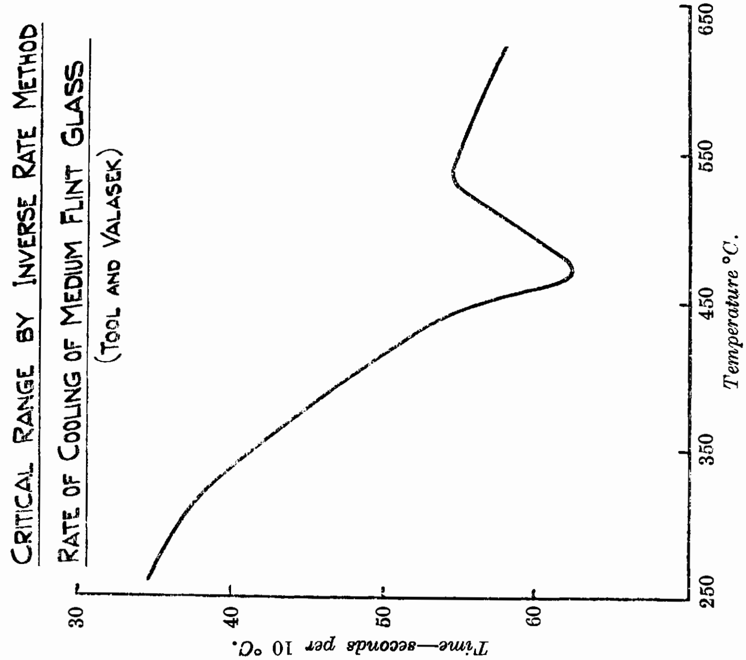
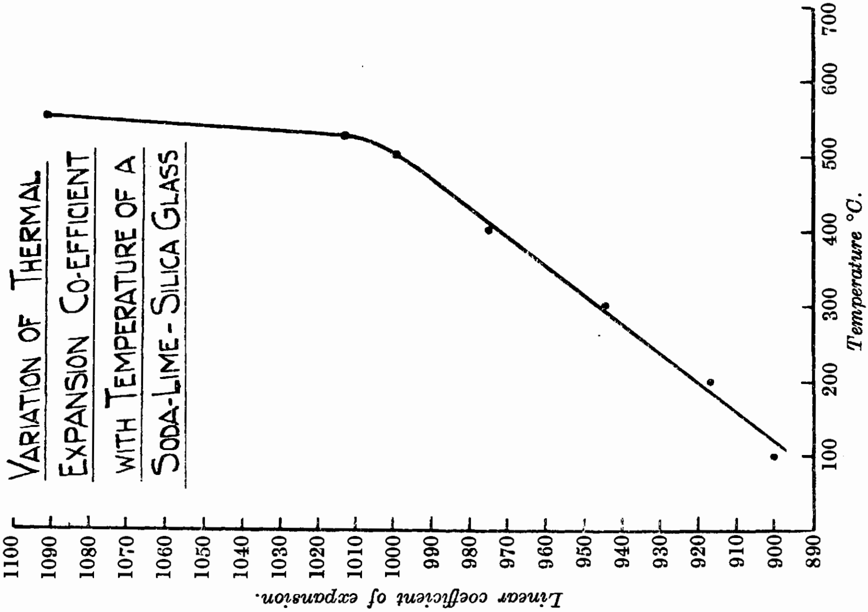

CRITICAL RANGE BY INVERSE RATE METHOD
RATE OF COOLING OF MEDIUM FLINT GLASS
(TOOL AND VALASEK)
Time—seconds per 10 °C.
30
40
50
60
Temperature °C.
250
350
450
550
650

Fig. 12.


VARIATION OF THERMAL
EXPANSION CO-EFFICIENT
WITH TEMPERATURE OF A
SODA-LIME-SILICA GLASS
Linear coefficient of expansion.
1100
1090
1080
1070
1060
1050
1040
1030
1020
1010
1000
990
980
970
960
950
940
930
920
910
900
890
Temperature °C.
100
200
300
400
500
600
700

investigated by us. Samsoen[33] has found, in the case of boric oxide glass, a still bigger change, the mean linear coefficient up to 240° being less than 15×10^{-6}, whereas at 240—250° it exceeded 200×10^{-6}.

Lebedev put forward the theory that the heat effect was related to the inversion of the silica in the glass corresponding to the inversion temperature at 575° between α- and β-quartz. Tool and Valasek had found, however, that the borates and boric oxide showed a similar phenomenon, and recently Lebedev has withdrawn his hypothesis as obviously untenable. Tool was inclined to relate the magnitude of the heat effects to the tendency of the glasses to crystallisation. It seemed to me, however, that the phenomenon might be a general property of all amorphous forms of matter, and, to test this view, in 1923 some work was carried out by a student working under my direction to ascertain if common resin showed exothermic or endothermic effects. As a matter of fact no such effects were noted, and I understand that Dr. F. W. Preston, studying the properties of pitch over a wide range of temperature, also found no such thermal effects. Recently, however, Prof. le Chatelier has informed me, when contributing to the discussion of one of my papers, that he believes he has proved that these heat effects are actually associated with a definite change in all amorphous bodies. He states that changes similar to those which are observed in glasses at temperatures between 250° and 550° occur in other amorphous substances at a temperature which is dependent on the viscosity. The change point takes place between 0° and 100° for resins, pitch, and concentrated acrolein, and below 0° for viscous liquids, like glycerol, which have been solidified by cooling. Le Chatelier pictures the change as one dependent on the viscosity. As the temperature rises, he supposes, the molecules themselves swell but do not separate from one another. When once the internal friction has become sufficiently weak, the molecules begin to be spaced out and accordingly the coefficient of expansion greatly increases.

The study of glasses, therefore, promises to throw light on the nature and characteristics of the amorphous state. Instead of the old view of glasses and amorphous substances undergoing perfectly continuous changes in their properties from temperatures at which they are very fluid to those at which they are rigid, we have to recognise a discontinuity not essentially different from a change of state. It may be of some significance in this study that the biggest change recorded as occurring in the thermal expansion of a glass at the change point is that in boric oxide glass, a simple substance which has never yet been obtained in the crystalline form.

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