

a progressively increasing compression as the dilution becomes greater; but an approximate constancy is reached at dilutions where the electrolytic dissociation is practically complete. Of the solutions studied, sodium carbonate alone presents an anomalous behavior in this particular, for in very dilute solution the contraction becomes less rather than greater; but it has been shown that this can be explained on the basis of the unusual contraction which is found to occur during the neutralization of carbonic acid.

THE PHENOMENA OF EQUILIBRIA BETWEEN SILICA AND THE ALKALI CARBONATES.

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In a previous publication¹ we have discussed a ternary system, made up of one volatil and two involatil components, in which no compounds occur. Such systems have been investigated chiefly by Smits, to whom we owe our present somewhat limited knowledge of their behavior; they are very important in view of the existence of similar complex systems in liquid magmas. The magma contains a number of substances which appear as gases or vapors in volcanic exhalations; of these the most important are H₂O, CO₂, S, and the mutual reaction products of these substances. Such vapors can unite with the involatil constituents of the magma to form compounds which are still liquid at temperatures lower than the general solidification temperature of the magma. That, under those conditions, compounds of this type actually exist has been established by petrographic investigation, which has shown that minerals containing water or fluorine, and in all probability minerals such as calcite and cancrinite, have in some cases crystallized directly out of the magma.² It is evident, therefore, that a more extended knowledge of the behavior of systems of volatil and involatil components, which can interact to form compounds, is very desirable.

Such a system is the system, *alkali oxide, silica, carbon dioxide*; it can be readily investigated, and at the same time it is of importance (at the least, indirectly) in connection with magmatic processes. The complete investigation of this ternary system would require a very long time; apart altogether from the technical difficulties associated with work at high pressures and high temperatures. Consequently, the work here recorded deals with only a limited portion of the whole field; it treats of the phenomena of equilibrium between R₂O, SiO₂ and CO₂ in melts at temperatures of 900–1000° under a pressure of 1 atm. CO₂. The relation of the

¹ P. Niggli, *Z. anorg. Chem.*, **75**, 161; **77**, 321 (1912).

² See e. g., F. D. Adams, *Am. J. Sci.*, [3] **48**, 14 (1894); O. Stutzer, *Centr. Min. Geol.*, **1910**, 433; R. Workman, *Geol. Mag.*, **1911**, 193, etc.

results obtained to the complete PTX diagram is briefly discussed at the close.

When silica is introduced into melts of the alkali carbonates, a reaction takes place and carbon dioxide escapes. This phenomenon has frequently been examined, although it has not been thoroughly studied; what we wish to know is the amount of carbon dioxide evolved in relation to the concentration (composition) of the melt, the temperature, and the pressure.

Previous Investigations.

The purpose of the first investigations was to obtain information as to the valence of silicon or the molecular weight of silica; on the basis of the (incorrect) assumption that the amount of carbon dioxide evolved is equivalent to the silica added. The experiments were carried out at rather indeterminate temperatures ("red heat" or "white heat"), and no attempt was made to regulate the partial pressure of carbon dioxide.

Yorke¹ showed that addition of a given amount of silica to the various alkali carbonates gives rise to different volumes of carbon dioxide; this result he attributed to a variation of the molecular weight of silica from one melt to another, assigning to it the value 30.7 in K_2CO_3 , 21.3 in Na_2CO_3 and 15.0 in Li_2CO_3 .

Scheerer² established the facts, that smaller volumes of carbon dioxide are evolved from either potassium or sodium carbonate at red heat than at white heat, and that, with increasing amounts of silica, each mol added decomposes progressively less carbonate.³ The silicate richest in soda is (in present-day notation) $2Na_2O \cdot SiO_2$, the lower limit is $Na_2O \cdot SiO_2$; and he believed in the existence of an intermediate compound $4Na_2O \cdot 3SiO_2$. In the case of potassium carbonate he considered the end members to be $4K_2O \cdot 3SiO_2$ and $2K_2O \cdot 3SiO_2$.

Mallard⁴ investigated the rate of decomposition, and found that at each temperature ("red heat," etc.), the volume of carbon dioxide evolved tends toward a definite limiting value.

All of these observations indicate that a state of equilibrium is attained in melts composed of alkali carbonate and silica. Wittorf⁵ made a series of experiments with the object of establishing this fact. He melted up mixtures⁶ of alkali carbonate and silica in platinum crucibles held in a definite position in the flame of a Bunsen burner, this position correspond-

¹ Yorke, *Phil. Mag.*, [4] 14, 476 (1857). See also H. Rose, *Gilberts Annalen*, 73, 84 (1823).

² Th. Scheerer, *Ann. Physik*, 116, 149 (1860).

³ This was also shown by Ebell, *Dingler's Polytech. J.*, 228, 160 (according to Gmelin-Kraut).

⁴ Mallard, *Ann. chim. phys.*, [4] 28, 105 (1873).

⁵ M. Wittorf, *Z. anorg. Chem.*, 39, 187 (1904).

⁶ Consisting of 1 equivalent SiO_2 with 1 K_2CO_3 , Rb_2CO_3 , Cs_2CO_3 , with 2 Na_2CO_3 , and 4 Li_2CO_3 .

ing—according to Wittorf—to a partial pressure of CO_2 of 0.07 atm.; this heating was continued until constant weight was attained.¹ Carbon dioxide was then led into the crucible; this resulted in an absorption of some CO_2 by the melt, but, at the same time, in a lowering of its temperature. On reverting again to the previous conditions, the corresponding weight was regained. No details of the temperature measurement are given; but, since the thermoelement junction was not in the melt and the source of heat was an unprotected Bunsen flame, no great reliance can be placed in the temperature (870° and 780°) as given by Wittorf. These experiments constitute no certain proof of the existence of a true equilibrium, for the limiting values were reached from one side only, namely, by escape of carbon dioxide; they show only that these limiting values are reproducible under constant external conditions, and hence do not exclude the possibility that the final state is only an apparent equilibrium. Moreover, Wittorf's deductions with regard to the influence of the partial pressure of CO_2 are to some extent misleading, because the change of partial pressure was accompanied by a change of temperature; the direction of these changes being such, that in Wittorf's experiments the two effects supplement one another.

There is thus no record of any investigation in which temperature and pressure were carefully controlled; from which alone reliable information as to the nature of the equilibrium can be obtained.

Experimental.

In these experiments uniform temperature was secured by the use of an electric resistance furnace; the whole arrangement is very simple, but the observance of certain precautions is essential. Wittorf noticed that the loss of alkali carbonate by vaporization, which may be considerable if a rapid current of CO_2 is led over the surface of the melt, is negligible in a closed platinum crucible. The following scheme was therefore adopted:

In the furnace was inserted a glazed porcelain tube, about 45 cm. long and 45 mm. external diameter, placed so that its ends were some distance outside the furnace and therefore cool. The upper end of this tube was closed by a graphite stopper, through which passed the protecting tube for the thermoelement; close to the lower end of the latter tube a hollow cylinder of magnesia, closed at the lower end and ground so as to fit into the large porcelain tube, (see Fig. 1) was fastened. The carbon dioxide was led in through a tube passing through the rubber stopper which served to close the lower end of the wide porcelain tube and at the same time to support three magnesia cylinders, hollow but closed at one end. In the uppermost of these the platinum crucible containing the melt was placed. The thermoelement junction was close to the surface of the

¹ In covered platinum crucibles the amount of alkali carbonate lost by vaporization is so small that the loss of weight is a satisfactory measure of the amount of CO_2 evolved.

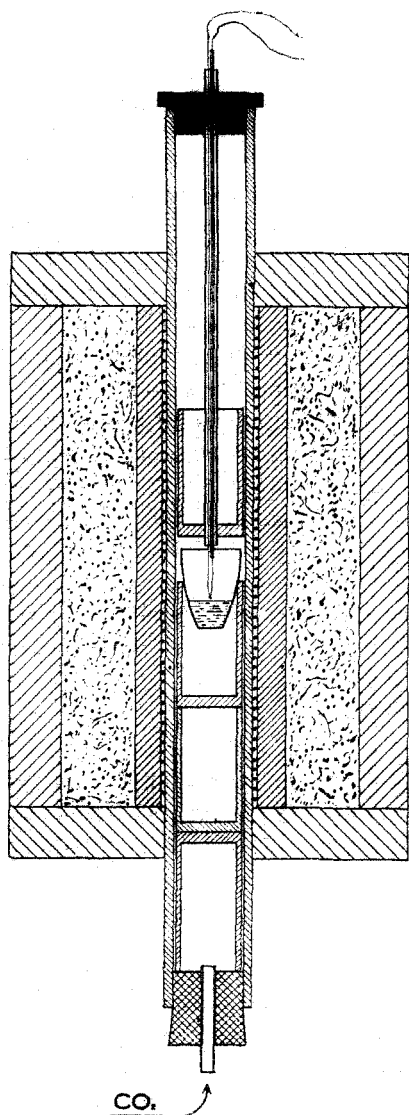


Fig. 1.—Diagram to illustrate furnace arrangement in section. This arrangement enables one to withdraw the charge rapidly and secures the maintenance of a definitely known atmosphere around the charge. The crucible is supported by cylinders of magnesia; the thermoelement junction is close to the surface of the charge.

melt, and the bottom of the upper magnesia cylinder was only about 1 mm. above the edge of the open platinum crucible. By means of this arrangement the melt was surrounded by carbon dioxide at a pressure of 1 atm., and yet without danger of serious loss by vaporization of carbonate; moreover, the crucible was in a region of uniform temperature, so that, after a certain interval of time, the difference between the temp. of the melt and that of the thermoelement junction (the position of which was inside the crucible, although above the melt) was less than 5° .¹

It is essential, since the weighings were made at ordinary temperature, that the charge be chilled as rapidly as possible; this was accomplished satisfactorily by means of the procedure adopted. That no carbon dioxide escapes during solidification of the melt, had been previously shown, and was confirmed by special observations which are detailed later. On the contrary, carbon dioxide (even at extremely small partial pressure) is absorbed by the melt as its temperature is lowered; this tendency is exhibited even by the solidified mixture. The state of the system could, therefore, be fixed by letting the crucible cool in a desiccator free from carbon dioxide. To transfer the crucible from the furnace the rubber stopper was taken out

¹ It is a matter of experience that a thermoelement, which is not actually in the melt, tends to give readings which under the most favorable conditions are often as much as 5° lower than the true temperature of the melt. This source of error is nearly constant, and so affects here only the absolute magnitude of the temperatures.

and the crucible placed in the desiccator; this could be accomplished in a very few seconds, and ensured the solidification of the system without appreciable change in its content of carbon dioxide.

The temperature, which was measured by the usual type of potentiometer arrangement, was by hand regulation kept constant to about $1-2^{\circ}$, even at 1000° . The carbon dioxide, either prepared from marble and hydrochloric acid (purified by means of copper sulfate) or obtained from a bomb, was dried by means of sulfuric acid and calcium chloride.

Equilibrium in the System $K_2CO_3 - SiO_2$.

Preliminary.—The materials used were pulverized pure quartz and potassium carbonate from J. T. Baker.¹ Powdered potassium carbonate absorbs moisture from the air, and hence cannot readily be accurately weighed; the fused salt changes in weight more slowly. For this reason the carbonates were always fused, the process being carried out rapidly in order to obviate dissociation.

The following experiment serves to show the small extent of vaporization at 900° with the arrangement described above:

Weight of dried K_2CO_3	4.905
“ “ crucible + K_2CO_3 initial.....	25.805
“ “ “ “ after $1/2$ hour at 900°	25.800
“ “ “ “ “ 1 hour at 900°	25.799
“ “ “ “ “ $1 1/2$ hour at 900°	25.799
“ “ “ “ “ 2 hours at 900°	25.799
“ “ “ “ “ $2 1/4$ hours at 900°	25.799

The loss of weight (5 mg.) in the first half hour, while in part possibly representing moisture, is in all probability to be attributed to a dissociation of the carbonate in the melt; this question is treated later. Apart from this, there is no appreciable loss of carbon dioxide from potassium carbonate held for three hours at 900° . In presence of silica this loss would tend to be smaller, since addition of silica lowers the vapor pressure of the carbonate in the melt.

In some of the experiments a slightly different position of the crucible was used; but the vaporization was no greater in this case, as is shown by the following: A mixture composed of 1.304 g. K_2CO_3 and 0.8035 g. SiO_2 was kept for 60 hours at $900-1000^{\circ}$, the temperature being close to 1000° for at least 16 hours continuously. Analysis of the melt when cold showed that the amount of silica was unchanged, while the amount of K_2O had decreased only from 0.889 g. to 0.874 g., corresponding to a mean loss by vaporization of 1 mg. in four hours.

That the system $K_2CO_3-SiO_2$ readily reaches a state of real equilibrium, is shown by the two series of weighings recorded in Table I. Thus, in

¹ The maker's analysis follows: K_2CO_3 , 99.9754%; Al_2O_3 , 0.0001; CaO, 0.001; Fe, 0.0005; SiO_2 , 0.001; Na, trace; Cl, 0.002; SO_2 , 0.020; KNO_3 , trace; KOH, trace.

experiment A for instance, the same weight (22.2485 ± 0.0005) was reached when equilibrium was approached either by evolution or by absorption of carbon dioxide. The attainment of the same end result from either direction shows that there is a state of real equilibrium, and that the loss by vaporization at these temperatures is inappreciable in the period required for the establishment of equilibrium. In melts containing very little silica, where it is necessary to weigh to 0.1 mg., a small correction is necessary.

TABLE I.—TO SHOW THE CONSTANCY OF WEIGHT OF K_2CO_3 - SiO_2 MIXTURES WHEN HEATED AT DEFINITE TEMPERATURES UNDER A PRESSURE OF CO_2 OF 1 ATM.

A. 1.559 grams K_2CO_3 + 0.211 gram SiO_2 . Total initial weight of crucible and contents 22.371 grams.

Temperature. ¹	Interval of constant temperature between two weighings.	Weight ² of crucible and contents.
898°	Initial	22.371
	$\frac{3}{4}$ hour	22.2515
	$\frac{1}{2}$ hour	22.2505
	$\frac{1}{2}$ hour	22.2495
	$\frac{1}{2}$ hour	22.2485
	$\frac{1}{2}$ hour	22.2490
	$\frac{1}{4}$ hour	22.2485
956°	Initial (from 898°)	22.2485
	$\frac{1}{2}$ hour	22.237
	$\frac{1}{2}$ hour	22.2375
898°	Initial (from 956°)	22.237
	$\frac{1}{2}$ hour	22.248
	$\frac{3}{4}$ hour	22.2485
	$\frac{1}{2}$ hour	22.248

B. Mixture of 90 mol % K_2CO_3 , 10 mol % SiO_2 .

898°	Initial	23.450
	$\frac{1}{2}$ hour	23.383
	$\frac{1}{2}$ hour	23.384
	1 $\frac{1}{2}$ hours	23.3835
898°-910°	1 $\frac{1}{2}$ hours	23.383
956°	Initial (from 910°)	23.382
	$\frac{3}{4}$ hour	23.377
	$\frac{1}{2}$ hour	23.376
	$\frac{1}{2}$ hour	23.377
898°	Initial (from 956°)	23.377
	$\frac{1}{2}$ - $\frac{3}{4}$ hour	23.3835
998°	Initial (from 898°)	23.3835
	$\frac{1}{2}$ hour	23.373
	$\frac{3}{4}$ hour	23.3725
956°	Initial (from 998°)	23.3725
	$\frac{3}{4}$ hour	23.3765

¹ The temperature was regulated by hand so that the deviation from the mean was less than $\pm 2^\circ$. Cf. also p. 7, footnote.

² The weighings were made to 0.5 mg.

With regard to the accuracy of the data the following points may be noted. It proved advantageous to work with quantities of material ranging from 1.4 to 3.1 g., the weighings being made to 0.5 or 1 mg.; this accuracy is sufficient, since fluctuations of this magnitude were observed in the weight at equilibrium. From this, it follows that the values of the number of equivalents of silica displacing one equivalent of carbon dioxide, or of the mol percentage loss of the original content of carbon dioxide, as deduced from the observed losses of weight, are accurate only to 1-2%. When much silica is present the absolute loss of weight is larger but the accuracy is limited then by another factor—the viscosity of the melts, which retards the attainment of equilibrium.

The Equilibrium Determinations.—The loss of weight—that is, the amount of carbon dioxide evolved—was determined for a series of mixtures of K_2CO_3 and SiO_2 at 898° , 956° and, wherever possible, at 998° (corrected temperatures¹). The heating was always performed in a current of carbon dioxide; that is, the partial pressure of this component was kept at 1 atm. From the loss of weight observed two quantities were calculated: (1) the loss of CO_2 as a percentage of the initial amount of CO_2 present, (2) the number of mols CO_2 displaced by 100 mols SiO_2 at the particular concentration. The resultant values are presented in Table II and in Figs. 2 and 3. The last column of the table gives, for comparison, the percentage loss of CO_2 which would have been observed if each mol of SiO_2 were to displace 1 mol CO_2 ;² if this were so, the CO_2 would, of course, be completely displaced from all mixtures containing initially 50 mol % or more of silica.

The table and the diagrams bring out the following points: The loss of CO_2 is always smaller than would correspond to the ratio 1 mol SiO_2 : 1 mol CO_2 . The smaller the concentration of SiO_2 (at constant temperature); the more CO_2 is displaced by 1 mol SiO_2 . The slight irregularity apparent in the melts containing the least SiO_2 , is attributable to the insufficient accuracy of the weighings; for in these cases, by reason of the small absolute amount of SiO_2 used, the loss of weight was also very small, so that a difference of even 0.1 mg. would appreciably affect the calculated quantities. On this account, and also because of the slight, and somewhat uncertain, loss by vaporization, the observed positions of equilibrium vary to some extent in the mixtures poor in SiO_2 ; in the more concentrated melts, both of the above disturbing factors cease to be appreciable. In general, it may be said that the results obtained at 956° deserve more confidence than those at 898° ; because, on the one hand, the amount of vaporization is small, except in melts containing very little

¹ The absolute value of these temperatures may, as previously noted, be 5° too low; the effect of this difference is, of course, inappreciable in the present case.

² The corresponding curve is the broken curve 11, Fig. 3.

TABLE II.—PRESENTING THE EQUILIBRIUM DETERMINATIONS.

No.	K ₂ CO ₃ cent.	Initial mixture.		Loss of weight at 898°.		Loss of weight at 956°.		Loss of weight at 998°.		Calculated loss of wt. if 1 mol SiO ₂ displaced 1 mol CO ₂ .				
		Wt. per cent.	Mol per cent.	in mol per cent. of the initial CO ₂ content.	in equivalent per cent. of the SiO ₂ .	(a) expressed in mol per cent. of the initial CO ₂ content.	(b) expressed in equivalent per cent. of the SiO ₂ .	(a) expressed in mol per cent. of the initial CO ₂ content.	(b) expressed in equivalent per cent. of the SiO ₂ .	(a) expressed in mol per cent. of the initial CO ₂ content.	(b) expressed in equivalent per cent. of the SiO ₂ .		(a) expressed in mol per cent. of the initial CO ₂ content.	(b) expressed in equivalent per cent. of the SiO ₂ .
I.....	96.9	3.1	6.9	6.6	89.6	7.4	100	Results corrected for loss by vaporization.		
II.....	96.2	3.8	8.2	8.3	92.9	8.9	100			
III.....	95.3	4.7	10.2	9.7	85.5	11.4	100			
IV.....	94.9	5.1	10.9	10.5	85.4	11.1	90.9	12.3	100			
V.....	92.5	7.5	15.7	15.4	82.4	16.6	88.9	18.6	100			
VI.....	90.3	9.7	19.8	20.5	83.1	24.7	100	Preliminary expt.; K ₂ CO ₃ not previously fused.		
VII.....	88.1	11.9	23.8	24.7	79.2	26.9	86.4	28.6	91.7	31.2	100			
VIII.....	83.1	16.9	31.9	36.2	77.3	38.9	83.4	46.7	100			
IX.....	80.4	19.6	36.1	42.6	75.5	46.3	82.1	48.6	86.2	56.3	100			
X.....	79.5	20.5	37.3	44.8	75.5	48.6	81.9	51.4	86.4	59.3	100			
XI.....	70.7	29.3	48.8	66.7	69.7	71.3	74.5	75.9	79.4	95.6	100			
XII.....	69.7	30.3	49.9	68.4	68.5	73.0	73.2	77.7	77.8	99.8	100			
XIII.....	67.5	32.5	52.6	74.8	67.4	79.3	71.4			
XIV.....	61.5	38.5	59.1	Liquid + solid	Liquid	91.9	63.7	143	100	Analyzed				
XV.....	61.0	39.0	59.6	Liquid + solid	Liquid + solid	91.4	61.9	..	147	100				
	56.8	43.2	63.6	Liquid + solid	Liquid + solid	Liquid + solid	Liquid + solid	Melt too viscous.		
	54.9	45.1	65.0	Consists almost entirely of crystals of a single kind.		
	53.4	46.6	66.7	Solid	Solid	100.0	50.0	200.0	100					

SiO_2 , and, on the other hand, the viscosity, which is considerable at 898° for melts containing more than about 50 mol % SiO_2 , does not interfere at 956° with the rapid attainment of equilibrium. All melts with much free K_2CO_3 are quite liquid at all the temperatures. The results obtained at 998° cannot be regarded as accurate; they suffice to show the course of the curve.

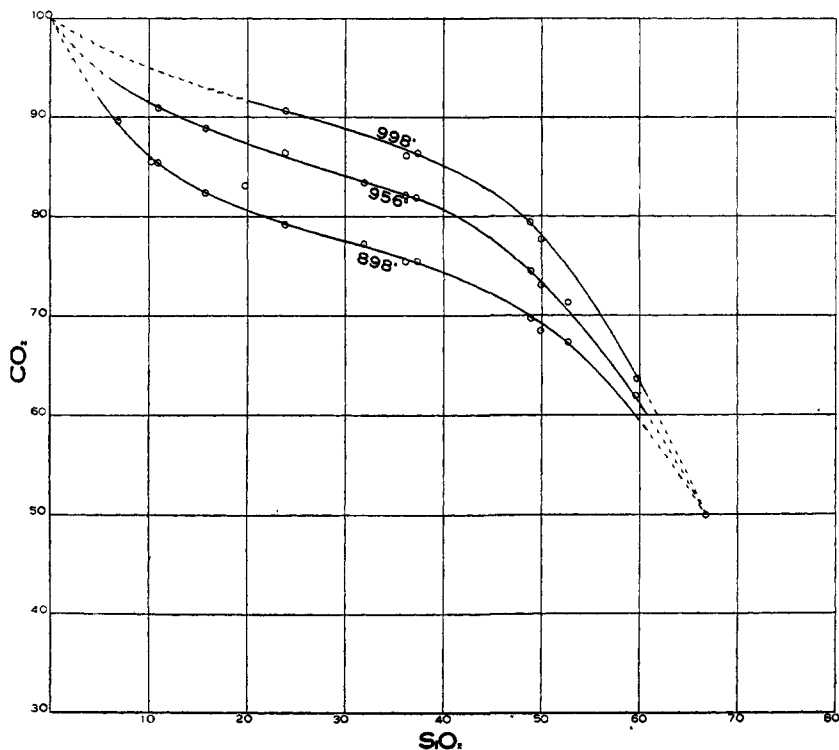


Fig. 2.—Graphs showing the relation between the number of mols CO_2 displaced by 100 mols SiO_2 (at 898° , 956° and 998° , respectively) and the mol percentage of SiO_2 in melts of $\text{K}_2\text{CO}_3 + \text{SiO}_2$ at equilibrium.

These experimental results are plotted in Fig. 2, the abscissas being the mol percentage of SiO_2 in the original mixture (thus, *e. g.*, the point 10 denotes 90 mols K_2O , 10 mols SiO_2), and the ordinates are the number of mols CO_2 displaced by 100 mols SiO_2 .¹ The several points lie very well on smooth curves, which are very similar for the three temperatures; they tend towards 100 when the initial content of SiO_2 is 0% and towards 50 when the melt contains 2 mols SiO_2 to 1 mol K_2O , while at intermediate concentrations the amount of CO_2 displaced is greater the higher

¹ This is, when 1 mol SiO_2 displaces 1 mol CO_2 , the point is 100; when it displaces one-half equivalent, 50; and so on.

the temperature. That the curves converge at both ends is shown by the subjoined table, which exhibits the differences, at a range of concentrations of SiO_2 and at constant temperature difference, in the percentage equivalent loss of CO_2 . From this, it is apparent that the temperature coefficient of the amount of CO_2 displaced by 1 mol SiO_2 shows a maximum about 25-30 mol % SiO_2 , and diminishes as we recede thence in either direction:

Mol % SiO_2 initial	10.9	15.7	23.8	31.9	37.0	49.4	52.6	59.5
Difference in the percentage equivalent loss between 898° and 956°	5.5	6.5	7.2	6.1	6.5	4.8	4.0	...
Difference in the percentage equivalent loss between 956° and 998°	5.3	...	4.3	4.7	...	<1.8

From Fig. 2 it follows, therefore, that a small amount of SiO_2 displaces almost the equivalent amount of CO_2 from K_2CO_3 ; further, that each successive addition of SiO_2 displaces a progressively smaller quantity of CO_2 , until, when the initial proportions are 1 mol K_2O to 2 mols SiO_2 , the silica displaces only half the equivalent amount of CO_2 . These relations are exhibited in another way in Fig. 3.

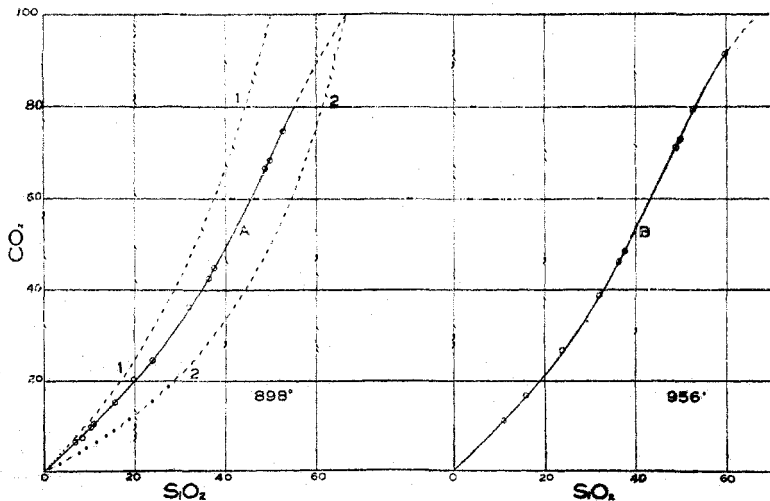


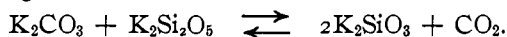
Fig. 3.—Graphs showing the relation between the amount of CO_2 displaced—expressed as a percentage of the initial amount—and the percentage of SiO_2 in melts of $\text{K}_2\text{CO}_3 + \text{SiO}_2$ at equilibrium; A for the temperature 898°; B for 956°. The dotted curve 11 is that which would have been obtained if K_2SiO_3 only were formed; 22 correspondingly if $\text{K}_2\text{Si}_2\text{O}_6$ were the sole product.

In Fig. 3 the amount of silica present, expressed again in molecular percentages (of $\text{K}_2\text{O} + \text{SiO}_2$), is plotted against the loss of carbon dioxide, expressed as a percentage of the total original content of CO_2 (*i. e.*, all the

K_2O as K_2CO_3). Curve *A* is for a temperature of 898° , curve *B* for 956° . The broken curve *11* represents what would be observed if SiO_2 always displaced the equivalent quantity of CO_2 , that is, if only the compound K_2SiO_3 were formed; curve *22* is that calculated for the case that only half of the equivalent is replaced, corresponding to the compound $\text{K}_2\text{Si}_2\text{O}_5$. The experimental curves lie between the two calculated curves, approaching the K_2SiO_3 curve when the silica content is low, and the $\text{K}_2\text{Si}_2\text{O}_5$ curve when more silica is present. They tend towards the point corresponding to a complete displacement of the CO_2 at 66.66 mol % SiO_2 ; this point itself is not attainable at the experimental temperatures, because of the previous appearance of a solid compound, of $\text{K}_2\text{Si}_2\text{O}_5$, as we shall see later. This method of representation is in complete agreement with that of Fig. 2; for, while the latter shows that at 66.6 mol % SiO_2 the silica displaces half of the equivalent amount of CO_2 , this is really all of it, since originally there was just 33.33 mol % K_2CO_3 .

The Equilibrium.

From these curves one concludes that in the melts there is equilibrium between the substances K_2CO_3 , K_2SiO_3 and $\text{K}_2\text{Si}_2\text{O}_5$; an equilibrium, the attainment of which must, apart from possible molecular associations, proceed according to the scheme



Application of the law of mass action yields deductions in complete harmony with observation. Thus, in the presence of much K_2CO_3 (corresponding to a small initial concentration of SiO_2), the amount of $\text{K}_2\text{Si}_2\text{O}_5$ must be small relatively to the amount of K_2SiO_3 in the melt; accordingly, when little SiO_2 is present, practically nothing but K_2SiO_3 is formed, corresponding to a displacement of CO_2 in nearly equivalent quantity. With progressively smaller amounts of K_2CO_3 , $\text{K}_2\text{Si}_2\text{O}_5$ is formed at the expense of the K_2SiO_3 , until it alone is present when the initial mixture contains 2 mols SiO_2 to 1 mol K_2O (as K_2CO_3). Hence the silica, introduced originally in the form of quartz, disappears completely as such, and goes to form K_2SiO_3 and $\text{K}_2\text{Si}_2\text{O}_5$ in proportions which depend upon the original relative concentrations; nor does the solid phase which separated out on heating the mixtures richest in SiO_2 consist of silica, but of a potassium silicate, presumably $\text{K}_2\text{Si}_2\text{O}_5$.

If the above equation really represents the equilibrium in this system, then there must be at least a double reaction when silica is melted up with potassium carbonate. As a matter of fact, the weight of such a system decreases to a minimum, and then, by absorption of carbon dioxide, increases again to its value when the equilibrium has been finally established—an overshooting of the mark which could hardly occur if a single reaction only were concerned. In order to show this concretely, an endeavor was

made to determine roughly the rate of loss of carbon dioxide at constant temperature. For this purpose a melt, consisting of 2.9023 g. K_2CO_3 and 0.0939 g. SiO_2 , was kept at 900° for 15 minutes, then rapidly cooled and weighed; then rapidly reheated—a process which required from 5 to 7 minutes—kept at 900° for another period, cooled and weighed again; and so on. The weights observed, which have been corrected for a small loss¹ by vaporization, are given in the subjoined table. The last two differences are no greater than the error inherent in the mode of experiment (due largely to differences in rapidity of chilling, and to slight temperature variations); this constancy of weight is evidence of the attainment of equilibrium:

TABLE III.—TO ILLUSTRATE THE PROCESS OF ATTAINMENT OF EQUILIBRIUM WHEN K_2CO_3 IS HEATED WITH SiO_2 .

Weight initial ²	Successive differences.	
	Grams.	Milligrams.
.....	23.5915
“ after a period of 15 minutes at 900°	23.5310	--60.5
“ “ further period of 15 minutes at 900°	23.5294	— 1.6
“ “ “ “ 15 “ “	23.5285	— 0.9
“ “ “ “ 20 “ “	23.5275	— 1.0
“ “ “ “ 20 “ “	23.5287	+ 1.2
“ “ “ “ 15 “ “	23.5304	+ 1.7
“ “ “ “ 15 “ “	23.5297	— 0.7
“ “ “ “ 15 “ “	23.5300	+ 0.3

This behavior is exhibited more clearly by Fig. 4, in which the above

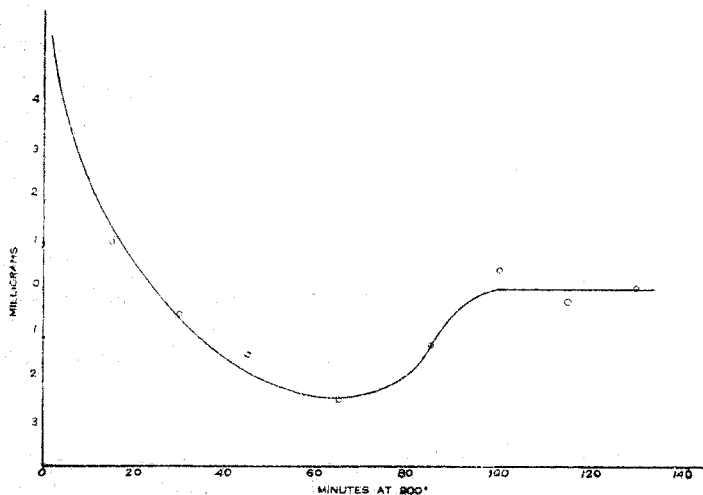
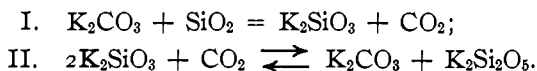


Fig. 4.—Graph showing the variation of weight of the charge ($K_2CO_3 + SiO_2$) with the time. The amount of CO_2 evolved reaches a maximum, after which equilibrium is attained by absorption of CO_2 .

¹ Previously determined under identical conditions.

² Platinum crucible and contents.

weighings have been plotted against the time. A curve of this form is most readily interpreted as a superposition of two reactions; in the present case, for instance,



The first reaction, the formation of metasilicate, predominates at first; the second reaction increases in importance as the concentration of this metasilicate increases. From the above, moreover, it is obvious that any systematic error, which might be present if equilibrium had not been completely attained in the experiments recorded, would be in the direction of a too great loss of weight; for the reaction (II) which determines the equilibrium, is accompanied by absorption of carbon dioxide.

It formed part of the original plan to investigate the solidification diagram of the system, and thereby to ascertain what compounds exist in the melts; but this could be carried out only in part, because most of the melts solidified to glasses. Before these experiments are described, we shall discuss the possibility of expressing the composition of the melts at equilibrium in terms of K_2CO_3 , K_2SiO_3 and $\text{K}_2\text{Si}_2\text{O}_5$; in other words, we shall proceed to consider whether there are in the melts, besides these three substances, appreciable quantities of free carbon dioxide or of any dissociation products.

Substances Present in the Melts.—Molten potassium carbonate undergoes, even in a current of CO_2 , a loss of weight, which proceeds to a definite limiting value and, hence, cannot be due to vaporization. That this loss of weight is due to the escape of CO_2 may be shown in several ways. Wittorf¹ found that fused carbonate contained 0.02% free alkali, whereas potassium carbonate, dried at 350° , precipitated with barium chloride and tested with phenolphthalein gave no indication of the presence of free alkali. Furthermore, the fused carbonate gives, on treatment with a solution of silver nitrate, a precipitate which is not a pure white. Another line of evidence is, that potassium carbonate kept fused for some time in a platinum crucible exhibits a reddish color when cold. This coloration diminishes when the material is heated at about 600° in a current of carbon dioxide, and at the same time the weight increases again. The color, therefore, depends upon the presence of free alkali; its appearance is evidence that platinum is attacked to some extent at high temperature by potassium oxide or peroxide.

Thus, in melted potassium carbonate at temperatures of 900° or 1000° , there is an appreciable amount of dissociation accompanied by the escape of some carbon dioxide, which tends to increase with the temperature. Its extent, as calculated from the loss of weight when the carbonate

¹ N. M. Wittorf, *Z. anorg. Chem.*, **39**, 194 (1905).

was heated between 900° and 960° in a current of carbon dioxide, ranged from 0.15 to 0.45%. The equilibrium pressure corresponding to the purely thermal dissociation of potassium carbonate is, of course, very much less than 1 atm.;¹ that the phenomenon is not a thermal dissociation is indicated by the relative smallness of its temperature coefficient. Apparently this phenomenon is peculiar to the liquid phase; it is presumably the consequence of a slight electrolytic dissociation which results finally in the evolution of some free carbon dioxide.

Thus, in melts of pure potassium carbonate there is apparently equilibrium between K_2CO_3 , K_2O and CO_2 , although at 900° the amount of free alkali is very small. It may be pointed out that the loss by vaporization may be attributed to a vaporization of K_2O ,² the concentration of which in the melt is kept constant by the dissociation process. However this may be, the fact remains that the loss by vaporization from melts containing alkali carbonate is greater, the greater the amount of dissociation. The addition of silica to a melt of potassium carbonate at 900° causes the complete disappearance of the reddish color, a fact which indicates that the silica represses—as is to be expected—the dissociation of the carbonate. From this we may conclude that but very small amounts of free alkali are present in silicate-carbonate melts at 900° ; although between 960° and 1000° , especially in the mixtures containing much carbonate, there is again a slight coloration, pointing to a slight dissociation under those conditions.

With regard to the presence in the melt of free carbon dioxide, the following points may be noted: No escape of carbon dioxide is ever observed when the melt solidifies, either by crystallizing or by its viscosity increasing. The curves of Figs. 2 and 3 tend so markedly towards the points 100 and 50, respectively, that the presence of appreciable amounts of free carbon dioxide is for this reason excluded. Moreover, it is not to be expected that carbon dioxide at low pressures should be soluble as such (*i. e.*, in uncombined state) in an involatil melt at high temperature; though at considerable gas pressures the situation might well be very much different.

The above discussion, while it does not, of course, exclude the possibility of the presence of associations (double molecules, etc.), renders very probable the view that silicate-carbonate melts, under a pressure of 1 atm. CO_2 , contain at most very small amounts of free carbon dioxide, and are dissociated to but a slight extent. We are therefore justified in calculating for each mixture the quantitative equilibrium between K_2CO_3 ,

¹ Thus P. Lebeau (*Compt. rend.*, 137, 1756 (1903)), gives the following figures:
 t° , 790, 810, 890, 960, 970, 1000.

Equil. pressure in mm., 0.5, 1.3, 5, 9, 12.

² Which would immediately as vapor react with CO_2 , thus giving rise to an apparent sublimation of carbonate.

$K_2Si_2O_5$ and K_2SiO_3 , by considering the carbon dioxide remaining in the melt to be present altogether as carbonate, and the K_2O , not thus accounted for as K_2CO_3 , to be in combination with the whole of the silica added; this potash then is present partly as K_2SiO_3 and partly as $K_2Si_2O_5$, the relative amounts of these two compounds being perfectly determinate, since we are dealing with definite total amounts of K_2O and SiO_2 . The distribution ratios of the various substances, as calculated in this way, are given in Table IV and in Fig. 5:

TABLE IV.—COMPOSITION OF THE MELTS IN EQUILIBRIUM, EXPRESSED IN MOL PERCENTAGES.

Number of expt.	898°.			956°.			998°.		
	K_2CO_3 .	K_2SiO_3 .	$K_2Si_2O_5$.	K_2CO_3 .	K_2SiO_3 .	$K_2Si_2O_5$.	K_2CO_3 .	K_2SiO_3 .	$K_2Si_2O_5$.
III.....	90.3	8.1	1.6
IV.....	89.6	8.6	1.8
V.....	84.6	12.1	3.3	83.4	14.5	2.1
VI.....	79.4	16.4	4.2
VII.....	75.4	18.0	6.6	73.1	22.7	4.2	71.5	25.9	2.6
VIII.....	63.7	25.6	10.7	61.0	31.2	7.8
IX.....	57.3	28.9	13.8	53.7	36.2	10.1	51.3	40.8	7.9
X.....	55.1	30.4	14.5	51.4	37.9	10.7	48.7	43.3	8.0
XI.....	33.3	37.7	29.0	28.7	47.0	24.3	23.9	56.4	19.7
XII.....	31.9	36.4	31.7	27.0	46.2	26.8	22.5	55.5	22.0
XIII.....	25.1	38.7	36.2	20.7	47.5	31.8
XIV.....	7.9	39.4	52.7
XV.....	8.6	35.2	56.2

Discussion of the Diagram.—In the ternary system K_2CO_3 – K_2SiO_3 – $K_2Si_2O_5$ at constant pressure, the points representing the compositions of all the melts realizable, at any given temperature, lie on a curve which extends from pure K_2CO_3 to pure $K_2Si_2O_5$. Any melt, whose composition does not lie on this curve, will change, either by absorption or by evolution of CO_2 , until the appropriate equilibrium state has been attained. For instance, melts consisting solely of K_2CO_3 and $K_2Si_2O_5$ cannot be obtained within the temperature range 900° – 1000° , and K_2SiO_3 decomposes always into K_2CO_3 and $K_2Si_2O_5$, at least so long as CO_2 is available.

With rise of temperature, the equilibrium is displaced in favor of the right hand side of the equation $K_2CO_3 + K_2Si_2O_5 \rightleftharpoons 2K_2SiO_3 + CO_2$; in other words, with increasing temperature the equilibrium curve is displaced more and more towards the left hand side of the diagram. Consequently at some definite temperature¹ the equilibrium curve must coincide with the two sides K_2CO_3 – K_2SiO_3 , K_2SiO_3 – $K_2Si_2O_5$ of the triangular diagram; at that temperature K_2SiO_3 is stable even in presence of CO_2 . With regard to how high this temperature is, nothing can be said; except that, if the temperature coefficient of loss of CO_2 remain constant (a sup-

¹ Provided at least that the dissociation of the carbonate has not then progressed so far as to result in radically different equilibrium relations.

position which is hardly likely) it would lie in the region 1200–1300°. When K_2CO_3 is heated up in a gas furnace with one equivalent (or more) of SiO_2 , small amounts of CO_2 remain in the melt, even after half an hour

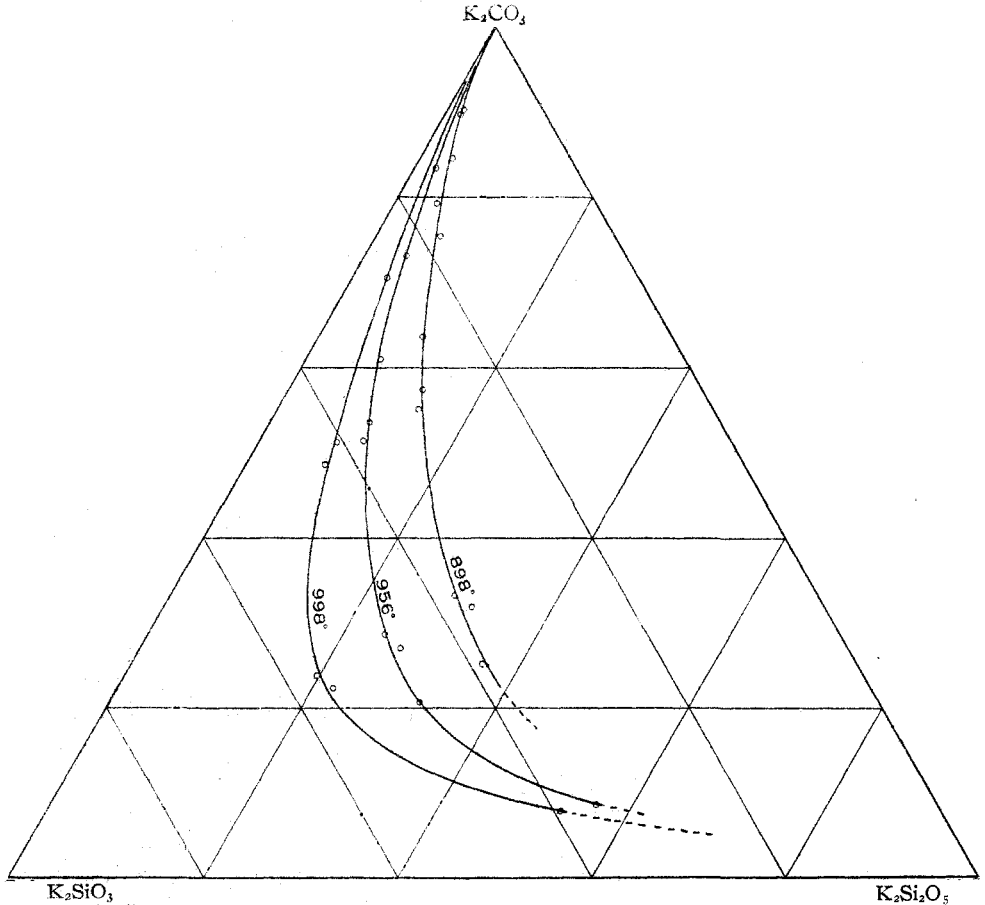


Fig. 5.—Triangular diagram showing the relative concentrations of K_2CO_3 , K_2SiO_3 , and $K_2Si_2O_5$ in equilibrium in melts at 898°, 956° and 998°, respectively.

at 1400–1500°; but this fact is not an absolute contradiction of the above estimate, since the evolution of CO_2 in a time phenomenon. Nevertheless, it may be remarked that a higher end temperature is entirely possible.

The equilibrium is displaced towards the side K_2CO_3 – $K_2Si_2O_5$, when the temperature is lowered; consequently, below a certain definite temperature—unless the solidification surface has previously been reached— $K_2Si_2O_5$, but no K_2SiO_3 , is formed when SiO_2 is added to K_2CO_3 . In this system, therefore, the silicate containing less silica is favored by high tem-

perature, while that with more silica appears more readily at lower temperatures. All of the experimental curves end before the corner $K_2Si_2O_5$ is reached, owing to the separation of a solid phase. In other words, each curve ends at the point at which the solidification surface is intersected; these points as given in the diagram—namely, the transition from full to dotted line—are of course only approximate.

Behavior of the Melts.—The melting point of potassium carbonate was determined as 891° ; in connection with which, it may be mentioned that the small extent of dissociation must be taken account of. For comparison the values obtained by different observers are brought together:

Quincke.....	1200°
V. Meyer.....	878.6°
Carnelley.....	834°
Le Chatelier.....	885°
Ramsay and Eumorfopoulos.....	88c°
Hüttner and Tammann.....	894°
Niggli.....	891°

The carbonate does not crystallize well. The cooled melt consists of a mass of very small plates showing very high birefringence; their optical character could not be determined with certainty. The general appearance of the mass resembles that of poorly crystallized lithium carbonate. Mixtures containing little silica exhibit a thermal effect about 880° on heating; but whether this corresponds approximately to the eutectic K_2CO_3 - $K_2Si_2O_5$ could not be ascertained, owing to the simultaneous occurrence of the reaction between the components.

All of the mixtures for which points are plotted on the equilibrium diagram, are fluid at 900° . If amorphous silica is used, melts containing more original silica can be obtained, but they are exceedingly viscous. When quartz is heated with potassium carbonate, reaction takes place to some extent before the melting point of the carbonate is reached; but in the main it occurs about that point. When an intimate mixture of $1K_2CO_3 + 2SiO_2$ is heated to 900 – 1000° , the mixture retains throughout the aspect of a solid; after a certain period the carbon dioxide is all displaced, and the contents of the crucible consists of a mass of crystals of a single kind interspersed with some glass, the amount of which (as also the amount of undecomposed carbonate and quartz) depends upon the intimacy of the original mixing of the components. This phenomenon can be interpreted thus: the carbonate begins to melt, dissolves silica, and reaction takes place with formation of $K_2Si_2O_5$, and of this alone, since the proportions are right; the $K_2Si_2O_5$ separates out immediately as a solid, since its melting point lies at a higher temperature. This is a case of a complete transformation, although not more than a very small fraction of the reacting mixture is liquid at any particular moment. It is analogous to many processes of rock metamorphism, especially of meta-

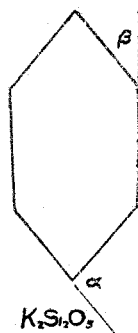
morphism under stress, in which the rock (mineral mixture) as a whole is always solid, while the reactions take place through the intervention of an altogether temporary liquid state, localized in numerous discrete points.

The same phenomena are observed with mixtures whose composition, at the particular temperatures, lies between the end point of the corresponding curve and the ratio $2 \text{ SiO}_2 : 1 \text{ K}_2\text{O}$; except that there is more or less liquid phase (the amount of which depends upon the original composition) in which a solid phase is immersed. This solid phase is thus in equilibrium with the melt, and consists of the compound whose saturation concentration is reached under the particular conditions; that it is the compound $\text{K}_2\text{Si}_2\text{O}_5$ is evident from what follows.

The Compound $\text{K}_2\text{Si}_2\text{O}_5$.—An intimate mixture composed of $1 \text{ K}_2\text{CO}_3 + 2 \text{ SiO}_2$ is, under the most favorable conditions, transformed almost completely into a crystallin silicate, and the accompanying loss of weight corresponds, within the limit of error, to the total loss of carbon dioxide. Moreover, the use of less silica results in the appearance of a liquid phase, while unattacked quartz is found if more than two equivalents are used. The composition of the silicate is therefore $\text{K}_2\text{Si}_2\text{O}_5$.

On heating the purest samples of crystallin $\text{K}_2\text{Si}_2\text{O}_5$ (which contained little glass) it was found that they were still completely solid at 1005° , but all melted at 1025° ; its melting point is therefore $1015 \pm 10^\circ$. The melts are very viscous, and on cooling solidify entirely to glass. We have, therefore, four points on the saturation surface of $\text{K}_2\text{Si}_2\text{O}_5$ in this system, namely: its melting point and the end points (900° , 956° and 1000°) on the three equilibrium curves. The shape of this surface, which is of the usual type, indicates that the binary melting curve between $\text{K}_2\text{Si}_2\text{O}_5$ and its eutectic with K_2SiO_3 is rather flat.

Optical Properties of $\text{K}_2\text{Si}_2\text{O}_5$.—The optical investigation of the crystals of $\text{K}_2\text{Si}_2\text{O}_5$, for which I am indebted to Mr. C. N. Fenner, was difficult because they deliquesce and enter into reaction with the immersion liquids. The results obtained follow: The crystals are optically biaxial, negative, with medium birefringence. The refractive indices are ≤ 1.500 . The angle of the optic axes is fairly large. The outline of the crystals is seldom good, though the same forms always appear; these are shown in the sketch.



The angles measured gave, $\alpha = 100-104^\circ$, $\beta = 36-40^\circ$. The elongation is \mathcal{C} , perpendicular to the face \mathcal{M} shown in the Figure. Some of the crystals showed forms in perspective having the habit of a more or less rectangular parallel-pipedon (3 pinacoids). Very frequently perfectly rectilinear or somewhat irregular polysynthetic twinning parallel to the elongation is observed, which resembles albite-twinning.

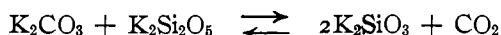
The direction of elongation forms with the twinning plane a very small angle. Single individuals often show, within the limits of error, parallel extinction, but perfectly sharp extinction was never observed.

It may be mentioned that G. W. Morey, working in this laboratory, has succeeded in preparing by a hydrothermal process this same silicate, the analogous compound $\text{Na}_2\text{Si}_2\text{O}_5$ ¹ and an acid silicate of the formula KHSi_2O_5 ; details of this work will be published shortly.

The work recorded in the preceding pages serves to orient us, both as to the main features of the solidification diagram of melts containing K_2CO_3 , K_2SiO_3 and $\text{K}_2\text{Si}_2\text{O}_5$, and to the quantitative equilibrium relations between these three substances. The reason that the melting point of K_2SiO_3 could not be realized is now evident; for, within the temperature region in question, this compound cannot be obtained from carbonate and silica, nor can it be maintained free from admixture of carbonate and $\text{K}_2\text{Si}_2\text{O}_5$. On the other hand, melts of K_2SiO_3 , prepared out of contact with CO_2 , always cool to glass. It is not yet certain whether a compound richer in silica than $\text{K}_2\text{Si}_2\text{O}_5$ can be realized; but this much can be affirmed, that the products obtained by heating up $x\text{K}_2\text{CO}_3 + (2 + x)\text{SiO}_2$ were always $\text{K}_2\text{Si}_2\text{O}_5$ and free quartz.

General Discussion of the Equilibrium.

The equilibrium,



is one of the first of its type to be studied experimentally. This type is important, because essentially similar equilibrium relations subsist between some of the components of liquid magmas; hence it merits some discussion. It may be defined as an equilibrium in a variable liquid phase in presence of a variable gas phase. That the gas phase must be regarded as variable, in spite of the fact that it consists practically of carbon dioxide, follows from the theory of distribution of a substance between a gas and a liquid phase. The equilibrium in the gas phase determines that in the liquid phase, and *vice versa*.

According to the law of mass action, the equation

$$\frac{[\text{K}_2\text{SiO}_3]^2[\text{CO}_2]}{[\text{K}_2\text{CO}_3][\text{K}_2\text{Si}_2\text{O}_5]} = \text{const.} = K'$$

should hold at constant temperature; the quantities in brackets denote the "active masses" of the various components when equilibrium has been attained. The concentration of CO_2 in the melts is, at the low pressure of 1 atm., so small that it could be neglected in calculating the concentrations of the other components; but, although very small, it is not

¹ According to F. Zambonini (*Appendice Min. Vesuv. Atti. Accad. Napoli*, 15, 12 (1912), the natural mineral rivaite has the related formula $(\text{CaNa}_2)\text{Si}_2\text{O}_5$, with some Na occasionally replaced by K.

necessarily constant. In general the concentration of CO_2 will be a function of the composition and temperature of the melt.

If we assume that the active mass of each factor is proportional to its total concentration, we can calculate values of the expression

$$\frac{[\text{K}_2\text{SiO}_3]^2}{[\text{K}_2\text{CO}_3][\text{K}_2\text{Si}_2\text{O}_5]} = \frac{K'}{[\text{CO}_2]} = K$$

K will be constant only if the above assumption should hold and if, at the same time, the factor $[\text{CO}_2]$ happen to be independent (within the error of experiment) of the composition of the melt; if either of these conditions does not obtain, K will be variable, but yet should be, at constant temperature, a function of the composition of the melt. Values of K have been derived, using the concentrations of the three components presented in Table IV; they are brought together in the subjoined table.

TABLE V.—THE CALCULATED EQUILIBRIUM "CONSTANT."

Number of experiment:	III.	IV.	V.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XV.
Initial conc. (mol %) of											
SiO ₂	10.2	10.9	15.7	23.8	31.9	36.1	37.3	48.8	49.9	52.6	59.6
K ₁ at 898°.....	0.44	0.45	0.52	0.66	0.96	1.05	1.26	1.47	1.31	1.65	..
K ₂ at 956°.....	1.21	1.66	2.02	2.42	2.63	3.13	2.91	2.46	2.52
K ₁ /K ₂	2.3	2.5	2.1	2.3	2.1	2.1	2.2	2.1	..

From Table V we see that neither K_1 nor K_2 can be considered constant. On the other hand, they are simple and very similar functions of the composition of the melt; this is evident from Fig. 6, in which the values of

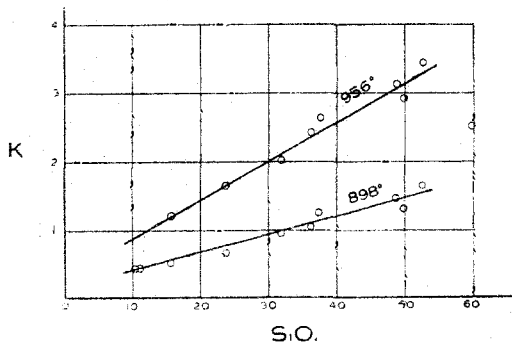


Fig. 6.—Graphs to show the relation between K (at 898° and 956°) and the mol percentage of SiO_2 in the melt.

K have been plotted against the original content of silica in the melts.

If K_1 and K_2 were the true equilibrium constants of two temperatures, T_1 and T_2 , not too far apart, then

$$\frac{K_1}{K_2} = \frac{Q(T_2 - T_1)}{RT_1T_2}$$

or in other words, the ratio K_1/K_2 would be constant. As a matter of fact, as is evident from the last row of Table V, this ratio is sensibly constant within the error of experiment. This interesting fact is only noted here; a discussion of it would require special assumptions as to the solubility of the gas, or the association of the components, in the melt, and it seems premature to attempt this until more of the requisite experimental facts have been ascertained.

Influence of Pressure on the Equilibrium, $K_2CO_3 + K_2Si_2O_6 \rightleftharpoons 2K_2SiO_3 + CO_2$.—The influence of pressure upon this equilibrium is complex. On the one hand, the equilibrium is displaced to some extent by changed total pressure, because the reaction is accompanied by a volume change. On the other hand, the partial pressure of carbon dioxide in the gas phase regulates, in accordance with Henry's law, the (very small) concentration of free carbon dioxide in the melt, hence the concentration of the other components also.

Wittorf¹ concluded that diminution of the partial pressure of carbon dioxide causes considerable displacement of the equilibrium towards the right hand side of our equation; that, as he says, the melts take up considerable carbon dioxide when the partial pressure is increased from 0.07 atm. up to 1 atm. But in his experiments the change of partial pressure was accompanied by a simultaneous change of temperature, the total pressure on the melt remaining constant (1 atm.). Indeed, the change in composition which his mixtures underwent can be accounted for by the difference between the temperatures at which the two experiments were made, presuming that the temperature difference as given by him is approximately correct. In consequence of his method of experiment (a platinum crucible over a bunsen flame) the temperature could be measured only very roughly; indeed, it appears from my work (with Na_2CO_3 as well as with K_2CO_3) that the temperatures were actually from 50 to 100° higher than the values which Wittorf assigned to them.

Consider the following comparison of data for a mixture which contained originally 50 mol % SiO_2 :

	Wittorf.		Niggli.	
Temperature (as given).....	870°	780°	1000°	910°
Partial pressure of CO_2 in atm.....	0.07	1	1	1
Equivalent loss of CO_2	80.7	74.5	77	70
Difference in loss of CO_2 for 90°.....	6.2		7	

According to Wittorf's experiment at 0.07 atm. CO_2 , 100 mols SiO_2 displace 80.7 mols CO_2 ; such a loss corresponds to a temperature in excess of 1000°, since the actual loss at 1000° is only 77 equivalents. Wittorf's temperature difference was 90°, a difference which, according to our work, corresponds to a change of 7 equivalents CO_2 , when the partial pressure remains unchanged; while Wittorf found a difference of 6.2, which he ascribed to change of partial pressure. These figures would tend to show, if we suppose that his temperature measurements are right (which they certainly are not), that change of partial pressure has the opposit influence to that asserted by Wittorf. Moreover, comparison of the dependence of loss of weight on the composition shows no essential difference between its trend at 0.07 atm. and at 1 atm., a result

¹ Wittorf, *Z. anorg. Chem.*, 39, 187 (1904).

which indicates that the influence of the partial pressure of carbon dioxide is inconsiderable. That this should be so is obvious on theoretical grounds; for in Wittorf's experiments the total pressure was constant, so that the change of pressure could affect only the concentration of free carbon dioxide in the melt. This influence must be very small at low pressures, by reason of the very small absolute value of this concentration.

If the total pressure acting on the melt is equal to the partial pressure of carbon dioxide, the magnitude of the effect produced by change of pressure will be somewhat different. Consider a very high pressure of carbon dioxide. The progress of the reaction is accompanied by a considerable increase of volume so long as the carbon dioxide is set free as a gas; consequently, if this condition obtains, increase of pressure displaces the equilibrium towards the left, *i. e.*, favors the substances K_2CO_3 and $K_2Si_2O_5$. But if the carbon dioxide produced should be completely absorbed by the melt, the volume change would be slight, and its direction could not be predicted. But there is a second effect produced in this case; for change of pressure of carbon dioxide in the gas phase brings about, in accordance with Henry's law, a change of concentration of free carbon

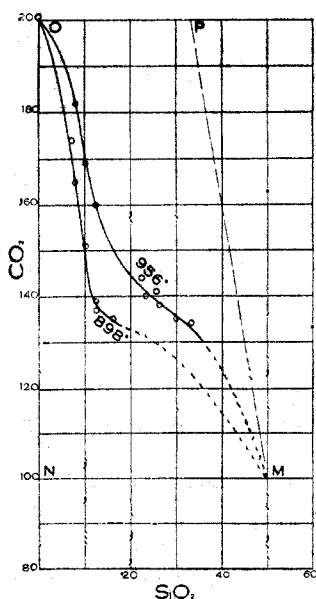


Fig. 7.—Graphs showing the relation between the number of moles CO_2 displaced by 100 moles SiO_2 (at 898° and 956° , respectively) and the mol percentage of SiO_2 in melts of $Na_2CO_3 + SiO_2$ at equilibrium.

dioxide in the melt, and in this way displaces the equilibrium. Indeed, it is largely upon the increase, with increasing pressure, of the solubility of the gas in the melt that the resultant effect will depend.

This point has been brought up, because of the complete analogy with the relations existing between the volatil and non-volatil components of magmatic liquids; in the discussion of these, as in the present case, the solubility of the gas (or gases) in the particular liquid phase must always be taken into consideration.

Equilibrium in the System $Na_2CO_3 - SiO_3$.

The equilibrium between Na_2O , SiO_2 and CO_2 in melts at 900° and 956° and under a pressure of one atmosphere of carbon dioxide was investigated in the same way. We shall therefore present only the final data; which, again, computed in the same way, are given in Table VI and in Figs. 7, 8 and 9.

The numbers in the first column pertaining to each temperature represent the number of moles CO_2 displaced in each case by 100 moles SiO_2 . As before, these numbers diminish with increase in the relative amount of silica; this

TABLE VI.—PRESENTING THE EQUILIBRIUM DETERMINATIONS FOR THE SODA SYSTEM.

No.	SiO ₂ in original mixture mol per cent.	898°.					956°.				
		No. of mols CO ₂ displaced by 100 mols SiO ₂ .	Mol percentages at equilibrium.			No. of mols CO ₂ displaced by 100 mols SiO ₂ .	Mol percent- age loss of CO ₂ .	Mol percentages at equilibrium.			
			Na ₂ CO ₃ .	Na ₂ SiO ₄ .	Na ₂ SiO ₃ .			Na ₂ CO ₃ .	Na ₂ SiO ₄ .	Na ₂ SiO ₃ .	
I.....	7.1	174	91.8	6.0	2.2
II.....	8.0	165	90.9	5.9	3.2	182	15.8	90.8	7.6	1.6	
III.....	10.1	151	88.1	6.1	5.8	169	19.1	87.8	8.4	3.4	
IV.....	12.3	139	85.1	5.9	9.0	
V.....	12.5	137	84.9	5.5	9.6	160	22.8	84.3	9.4	6.3	
VI.....	16.1	135	79.5	7.1	13.4	
VII.....	22.3	...	Liquid + solid			144	41.7	66.3	14.7	19.0	
VIII.....	23.2	...	Liquid + solid			140	42.6	65.5	13.9	20.6	
IX.....	25.6	...	Liquid + solid			141	48.6	59.6	16.3	24.1	
X.....	26.1	...	Liquid + solid			138	50.0	58.1	16.3	25.6	
XI.....	30.0 ¹	...	Liquid + solid			135	..	47.8	18.9	33.3	
XII.....	33.1	...	Liquid + solid			134	66.4	40.3	20.3	39.4	
XIII.....	37.1	...	Liquid + solid			Liquid + solid			
XIV.....	50.0	...	Solid			100	100	Solid	0	100	

time, however, they all lie between 200 and 100, or, in words, the amount displaced is between two equivalents and one equivalent. This is best seen from the curves of Fig. 7, which were obtained by plotting the original mol percentage of SiO₂ (*i. e.*, the number of mols SiO₂ to 100 mols SiO₂ + Na₂O in the melt) against the equivalent percentage losses of CO₂. The points lie consistently on rather steep curves; the end points for equilibrium in a homogeneous liquid system are about the end of the full line. When the silica content is greater than these limits, Na₂SiO₃ separates as solid phase. At 50 mol % SiO₂, the CO₂ is completely displaced, with formation of metasilicate; consequently when the curves are produced they must pass through the point *M*.²

The amounts of carbon dioxide lost at 956° by the several mixtures have also been expressed as a percentage of the original total content of CO₂ (*i. e.*, all Na₂O as Na₂CO₃), and

¹ Mean of 2 experiments.

² At 50 mol % SiO₂ the displacement of 1 equivalent CO₂ means that all of the original 50 mols are lost. Broken lines are used to represent the curves from the experimental end point to this point.

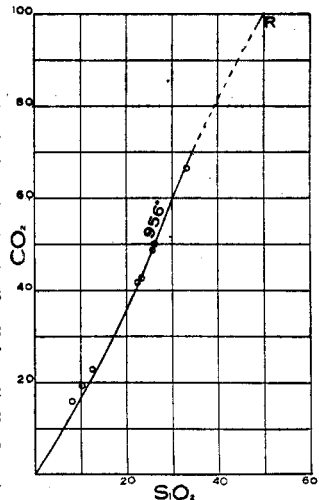


Fig. 8.—Graph showing the relation between the amount of CO₂ displaced—expressed as a percentage of the initial amount—and the mol percentage of SiO₂ in melts of Na₂CO₃ + SiO₂ at equilibrium at 956°.

plotted in Fig. 8. This curve evidently tends towards the point *R*; this point can be realized, but the compound Na_2SiO_3 is solid at this temperature (956°). Further, in the melts containing less than 1 mol SiO_2 to 1 mol Na_2CO_3 there is, besides the remaining Na_2CO_3 and the metasilicate, a second silicate containing more Na_2O , namely the orthosilicate Na_2SiO_4 . That it is the orthosilicate follows from the fact that the curves of Fig. 7 tend towards 200; for its formation requires the displacement of double the equivalent amount of CO_2 .

The Equilibrium.—The equilibrium in this case is consequently $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SiO}_3 \rightleftharpoons \text{Na}_4\text{SiO}_4 + \text{CO}_2$. Considerations based on the law of mass action, similar to those adduced in the previous case, show that the curves are in complete accord with the requirements of this equilibrium. Incidentally it may be remarked, that Mallard¹ from his experiments deduced the existence of this equilibrium.

Before proceeding to the calculation of the concentrations of the several components in the melt, we shall discuss briefly the accuracy of the data. In general this system is less favorable than the corresponding potash system, because the losses by vaporization are greater; this is, however, partially compensated by the more rapid attainment of equilibrium in this case. A second adverse influence is that in the Na_2O -system more rapid fixation is requisite, because the melts are less viscous and hence, absorb or evolve carbon dioxide more readily when the equilibrium is displaced by changing conditions. On this account it may be that the data presented do not correspond exactly to the temperature as given; this limitation does not, however, affect the continuity or form of the curves, nor the conclusions as to the type of equilibrium or its displacement with temperature.

Sodium carbonate, when melted alone, undergoes a slight dissociation, apparently somewhat greater than that observed with potassium carbonate, but yet amounting to less than 1%. Wittorf found that his dried Na_2CO_3 contained no free alkali; after being fused, about 0.4% free alkali was present. The precipitate formed when silver nitrate is added to an aqueous solution of fused sodium carbonate is a darker brown than that obtained from fused potassium carbonate. It proved difficult to determine accurately the extent of this dissociation from the loss of weight; but everything indicates that it is less than 1% at temperatures of 900 – 960° . The melts do not become colored when heated in platinum. As regards the solubility of free carbon dioxide in the melts, the same remarks apply as in the previous system.

Discussion of the Diagrams.—One can therefore calculate, just as for the K_2O -system, the relative concentrations of the substances in equilibrium; the data have been collected in Table VI, and presented in graphic

¹ Mallard, *Ann. chim. phys.*, [4] 28, 125 (1873).

form in Fig. 9. The curves, for 898° and 956° respectively, are very short, because they soon intersect the saturation surface of Na_2SiO_3 . Their form is what would be expected at lower temperatures in the potash system (if solidification did not occur there); the greater degree of curvature in the neighborhood of the point Na_2CO_3 is a necessary consequence of the equilibrium relations, which require that the curves should be more or less asymptotic to the side $\text{Na}_2\text{CO}_3\text{-Na}_4\text{SiO}_4$.

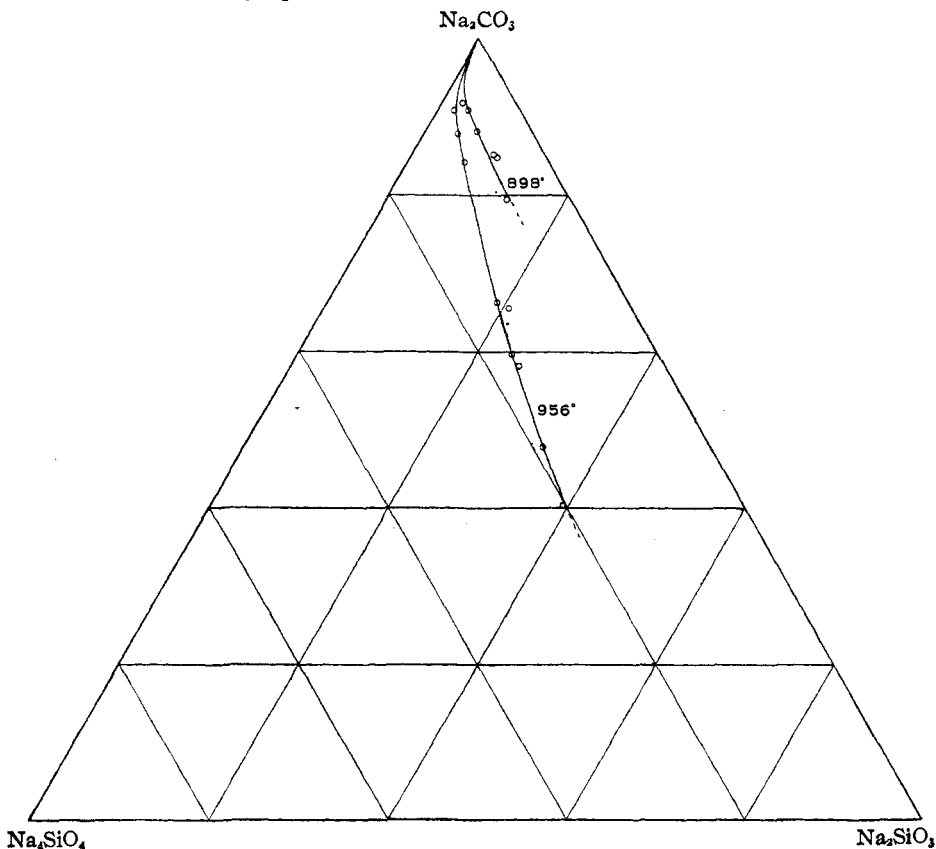
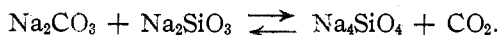


Fig. 9.—Triangular diagram showing the relative concentrations of Na_2CO_3 , Na_4SiO_4 and Na_2SiO_3 in equilibrium in melts at 898° and 956° , respectively.

Here again rise of temperature displaces the equilibrium towards the silicate containing less silica. At a high temperature therefore the equilibrium curve will coincide with the sides $\text{Na}_2\text{CO}_3\text{-Na}_4\text{SiO}_4$, $\text{Na}_4\text{SiO}_4\text{-Na}_2\text{SiO}_3$ of the triangle (Fig. 9); at some low temperature with the side $\text{Na}_2\text{CO}_3\text{-Na}_2\text{SiO}_3$. In the latter case only Na_2SiO_3 would be formed and the isotherm in Fig. 7 would become the line NM . In the former case, orthosilicate would be formed up to 33.3 mol % SiO_2 , and a mixture of

orthosilicate and metasilicate thereafter; the corresponding isotherm in Fig. 7 would then be the lines OP , PM . Between these two limits lie the actual isotherms of the equilibrium

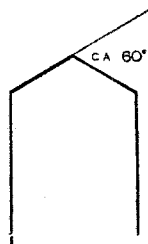


Now imagine the whole area $OPMN$ filled up with a series of isotherms: it is obvious that the form of the curves will be, at higher temperatures, markedly convex (in the neighborhood of P); at lower temperatures, markedly concave (in the neighborhood of N). From this we should expect that intermediate isotherms should exhibit double curvature, as those actually realized do. Analogous considerations apply to the potash system, the corresponding isotherms of which (Fig. 2) are similar.

Properties of Sodium Metasilicate.—From the shortness of the curves in Fig. 9, the end points of which correspond closely to the point of intersection with the saturation surface of Na_2SiO_3 , it is evident that this saturation surface extends over a very large portion of the field. The melting point of Na_2SiO_3 is, according to Wallace,¹ 1018° ; that of Na_2CO_3 , according to Hüttner and Tammann,² 853° . The eutectic between these two substances must lie very close to pure Na_2CO_3 .

Crystallin sodium metasilicate can be prepared by heating an intimate mixture of equivalent quantities (1 : 1) of quartz and carbonate to a temperature of $900\text{--}1000^\circ$ for some time. With somewhat less quartz, the system is heterogeneous. This heterogeneous equilibrium could of course also be quantitatively investigated; but preliminary experiments in this direction showed that without some sort of mixing device concordant results were not attainable.

According to determinations carried out by C. N. Fenner, the crystals of Na_2SiO_3 show the following properties: The form of the crystals is more or less prismatic. End faces are here and there developed and then the angle between terminal faces is not far from 60° .



Fibrous and spherulitic development is frequent. Refractive indices, $\gamma = 1.520$, α plainly lower. Elongation is always γ . The flat faces always give parallel extinction; whether the fibrous forms show a small oblique extinction cannot be decided because of their small thickness. In spite of the fairly good development of the crystals the interference figure could not be satisfactorily determined, as sections perpendicular to the axes could not be found. There are indications that the optical character is negative, axial angle large, and α perpendicular to the elongation.

Cleavage is well developed parallel to c (001); it can be used as a means

¹ R. Wallace, *Z. anorg. Chem.*, **63**, 1 (1909).

² Hüttner and Tammann, *Ibid.*, **43**, 215 (1905).

of identification. This cleavage is visible both on faces with high interference (the more fibrous forms) as well as upon faces with low interference (flat faces); so that a cleavage parallel to two pinacoids (100) (010) may be conjectured. The value of the interference was determined in four measurements, which gave 0.017, 0.012, 0.014 and 0.014.

Wallace also has described¹ the crystal form of sodium metasilicate; his crystals were not so well formed, but the few data which he gives agree in general with our observations.

When sodium carbonate was heated with more than one equivalent of quartz, the product was, in my experiments, always sodium metasilicate mixed with quartz. Wallace considers that in melts composed of $\text{Na}_2\text{SiO}_3 + \text{SiO}_2$, no silicate richer in silica than the metasilicate separates, and that the latter may take up some silica in solid solution. This apparent agreement is, of course, no evidence against the formation under other conditions of an anhydrous sodium silicate containing more than one equivalent of silica. Indeed, Morey has succeeded in preparing in the hydrothermal way the compound $\text{Na}_2\text{Si}_2\text{O}_5$, which is analogous to $\text{K}_2\text{Si}_2\text{O}_5$.²

Equilibrium in the System $\text{Li}_2\text{CO}_3 - \text{SiO}_2$.

A very large number of analogous experiments were made on the system $\text{Li}_2\text{CO}_3 - \text{SiO}_2$ at 900° ; but the results obtained hitherto are not deemed worthy of publication, by reason of the serious sources of error in this case. The vaporization loss of Li_2CO_3 is much greater, and the platinum vessel is much attacked even in a current of carbon dioxide; the latter effect is due presumably to the formation of some peroxide by union of the oxide with traces of oxygen in the carbon dioxide. On account of the change of weight of the platinum vessel and by reason of the lightness of lithium compounds, the errors invalidate the results, especially at low concentrations of silica.

Nevertheless the results obtained afford some qualitative information concerning the equilibrium in question. From mixtures containing one mol SiO_2 to two mols Li_2CO_3 , all the carbon dioxide is driven off on heating, leaving the beautifully crystalline orthosilicate, Li_4SiO_4 . When less silica is present, it displaces relatively more carbon dioxide; the equivalent percentage loss ranges according to our experiments from 200 to 400, the former number corresponding to the formation of orthosilicate. Hence there must be in the melts a subsilicate, the formula of which is probably $\text{Li}_3\text{SiO}_6 (= 4\text{Li}_2\text{O} \cdot \text{SiO}_2)$, since the percentage loss tends towards 400 when the original silica content is very small. Between 5 and 10 mol % SiO_2 there is an irregularity, which might indicate the appearance of a double salt, except that the optical investigations showed no evidence of such a

¹ Wallace, *Z. anorg. Chem.*, 63, 1 (1909).

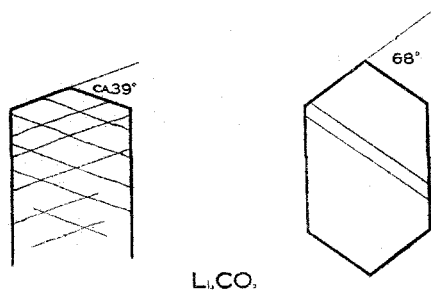
² This work will be published very shortly.

thing; presumably, therefore, it was due to the sources of error mentioned above.

The following points have been definitely ascertained: That there is an equilibrium; that Li_4SiO_4 is the silicate richest in silica to separate from the melts; that there is also present in the melts a silicate containing less silica.¹ It is very probable that the equilibrium proceeds according to the scheme $2\text{Li}_2\text{CO}_3 + \text{Li}_4\text{SiO}_4 \rightleftharpoons \text{Li}_3\text{SiO}_6 + 2\text{CO}_2$. From this it is evident that the curves exhibiting the equivalent loss of carbon dioxide are very steep, arising from 200 to 400, while the silica content diminishes from 33.3% to zero; a circumstance which of itself renders the quantitative investigation of this equilibrium much more difficult. The approximate position of the equilibrium curve is given as a broken line in Fig. 10; this could be done because at small contents of silica the irregularities are here of less consequence.²

Melts made by heating lithium carbonate with silica crystallize easily; but the subsilicate, of which small amounts were to be expected, could not be satisfactorily identified.

The optical data for the Li_2CO_3 crystallizing out of the melt, which were determined by C. N. Fenner, agree with those given by Mallard.³ Many



cleavage flakes are visible, which show the following forms: Forms twinned in a manner resembling that of calcite are numerous. The acute bisectrix is α , optical character negative. The axial angle measured in air gave about 23° (according to Mallard $2E = \text{about } 24^\circ$); γ and β about 1.57 (Mallard, $\beta = 1.567$, $\gamma = 1.572$); α notably less

than 1.455 (as determined by comparison with the index of the lowest available index liquid) (Mallard, $\alpha = 1.428$); interference $\gamma - \alpha$ therefore very large.

Although the potassium and sodium carbonates could not be obtained in good crystals, there appears to be a close analogy between their mode of crystallization and that of lithium carbonate. There is agreement at least in the high birefringence as well as in the frequent appearance of cleavage and twinning.

Hautefeuille and Margottet⁴ obtained Li_4SiO_4 out of a lithium chloride

¹ Or some association (or dissociation) product thereof. The presence of such a silicate is indicated by Wittorf's experiments.

² The point *P* is the end point obtained experimentally; from mixtures containing more silica, solid Li_4SiO_4 separates out, leaving a melt of this composition.

³ Mallard, *Bull. soc. min.*, 15, 21 (1899).

⁴ Hautefeuille and Margottet, *Bull. soc. min. franc.*, 4, 242 (1881).

melt in pseudohexagonal combinations of a rhombic prism of about 61° . Balló and Dittler¹ obtained cellularly arranged crystals with refractive index 1.616–1.624. The crystals appeared to be optically biaxial, with very small axial angle, or optically uniaxial, and always positive.

The observations of C. N. Fenner on our preparations were as follows: Irregular, equidimensional grains without crystal outline; characterized by an albite-like twinning with large extinction angle; a second set of twinning striations inclined to the first is less well developed; optically biaxial with very small axial angle; positive; mean index of refraction in the neighborhood of 1.600; birefringence fairly strong.

SUMMARY AND CONCLUSION.

General Discussion of the Systems Alkali Oxide–Silica–Carbon Dioxide.

In melts at temperatures of 900–1000° and under a pressure of carbon dioxide of 1 atm., the systems $R_2O : SiO_2 : CO_2$ ($R = K, Na, \text{ or } Li$) behave similarly on the whole, and differ only in details. Silica added to alkali carbonate is transformed to silicate so long as any carbonate remains; in the melts there is equilibrium between carbonate and silicate containing different molecular proportions of silica. The solid phases which separate from them consist of silicate or carbonate, but contain no free silica until the proportion of silica corresponding to the higher silicate is exceeded.

Within the temperature range investigated, there may be in the melts a large proportion of carbonate in equilibrium with the other components. This amount is dependent only on the ratio R_2O/SiO_2 , when external conditions are constant; when this ratio becomes identical with that of the silicate richer in silica, the melt is free from carbon dioxide.

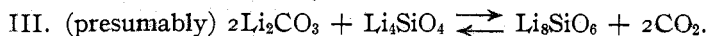
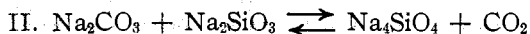
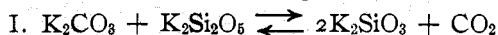
Consider now Figs. 10 and 11, in which the curves for the homogeneous ternary equilibrium $R_2O-SiO_2-CO_2$ have been drawn; they are based on the values in Table VII, which in turn were derived from the data in Tables IV and VI. It will be seen that at the pressure of 1 atm. CO_2 for each temperature in each system, homogeneous ternary equilibrium in the liquid phase occurs only with a single series of compositions, which lie on a simple curve. Any melt within the triangle, whose composition does not lie on the respective curve, is at that temperature unstable; the composition of such a melt will change, either by evolution or absorption of carbon dioxide, until it reaches a point on the curve or on its heterogeneous prolongation (liquid + solid). The equilibrium curves have the form of solubility curves with carbon dioxide as pole; indeed, they give the amount of carbon dioxide in the melt, although a complication is introduced by the fact that in the melt it exists combined as carbonate.

¹ Balló and Dittler, *Z. anorg. Chem.*, 76, 58 (1912).

TABLE VII.—SHOWING THE COMPOSITION OF THE MELTS AT EQUILIBRIUM IN TERMS OF R₂O, SiO₂ AND CO₂.

No. of mols SiO ₂ per mol R ₂ O.	898°.			956°.		
	Mol percentages in the melt.			Mol percentages in the melt.		
	R ₂ O.	SiO ₂ .	CO ₂ .	R ₂ O.	SiO ₂ .	CO ₂ .
System K ₂ O-SiO ₂ -CO ₂ .						
0.113	49.6	5.6	44.8
0.122	49.6	6.1	44.3
0.187	49.2	9.2	41.6	49.5	9.3	41.2
0.248	49.0	12.1	38.9
0.312	48.4	15.1	36.5	49.0	15.2	35.8
0.470	47.5	22.3	30.2	48.2	21.5	29.3
0.565	46.8	26.4	26.8	47.6	26.9	25.5
0.594	46.6	27.7	25.7	47.5	28.1	24.4
0.957	43.7	41.7	14.6	44.6	42.6	12.8
0.998	43.2	43.0	13.8	44.1	44.0	11.9
1.111	42.3	47.0	10.7	43.3	48.0	8.7
1.476	39.0	57.6	3.4
2.0	33.3	66.7	0	33.3	66.7	0
System Na ₂ O-SiO ₂ -CO ₂ .						
0.085	51.7	3.9	44.4
0.098	51.4	4.4	44.2	51.9	4.4	43.7
0.112	51.4	5.8	42.8	51.9	5.9	42.2
0.140	51.4	7.2	41.4
0.143	51.3	7.4	41.3	52.1	7.6	40.3
0.191	51.7	9.9	38.4
0.287	53.3	15.7	31.0
0.302	53.2	16.1	30.7
0.344	53.6	18.6	27.8
0.353	53.7	19.3	27.0
0.428	54.2	23.9	21.9
0.495	54.5	27.2	18.3
1.0 (solid)	50.0	50.0	0.0	50.0	50.0	0.0

The foregoing are the similarities; let us now turn to the differences exhibited by the three systems. Quantitatively the differences are due to the fact that the compounds in equilibrium in the melt are not the same in the three cases. Thus the equilibria are:



In each system, the compound containing more silica is the poorest in silica which can be prepared pure, at the particular temperature, merely by melting together carbonate and silica. Thus K₂SiO₃ or Na₄SiO₄ or Li₈SiO₆ (?) cannot be prepared in the pure state from carbonate and silica at temperatures about 1000°; the compounds K₂Si₂O₆, Na₂SiO₃ and Li₄SiO₄, which have relatively more silica, can readily be obtained. Correspond-

ingly, in Figs. 10 and 11, the equilibrium curves or their prolongations pass through these particular points on the side R_2O-SiO_2 .

When alkali carbonate is melted up with silica, the amount of carbon dioxide displaced in the (temperature) region of the ternary equilibrium ranges from 0.5 to 1.0 equivalent in the potash system, from 1 to 2 equivalents in the soda system, and from 2 to 4 equivalents in the lithia system.

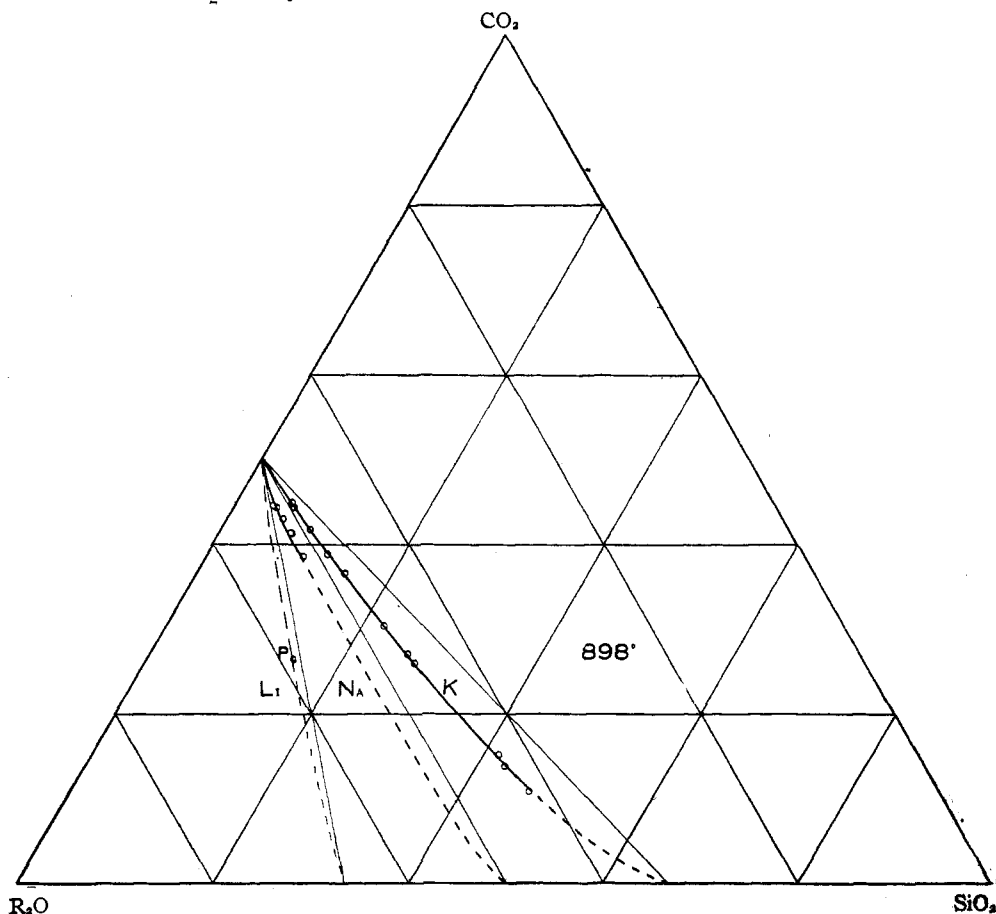


Fig. 10.—Triangular diagram showing the relative concentrations of R_2O , SiO_2 , and CO_2 ($R = K, Na, Li$) in equilibrium in melts at 898° .

The extent of the displacement of carbon dioxide from the carbonate by silica is parallel with the amount of carbon dioxide which the pure carbonate when melted alone loses by dissociation. Incidentally a point may be mentioned with regard to the relative compositions of the pairs of silicates in equilibrium in each system: namely, when the systems are taken in order as above, the ratio of base to silica for the right hand mem-

ber of one system is the same as for the left hand member of the following system. Rise of temperature, the pressure remaining constant, favors in each case the silicate poorer in silica; or, in other words, it increases the amount of carbon dioxide displaced.

It may be of interest to compare the older data with the results obtained in the present investigations. Scheerer¹ heated up carbonate with silica

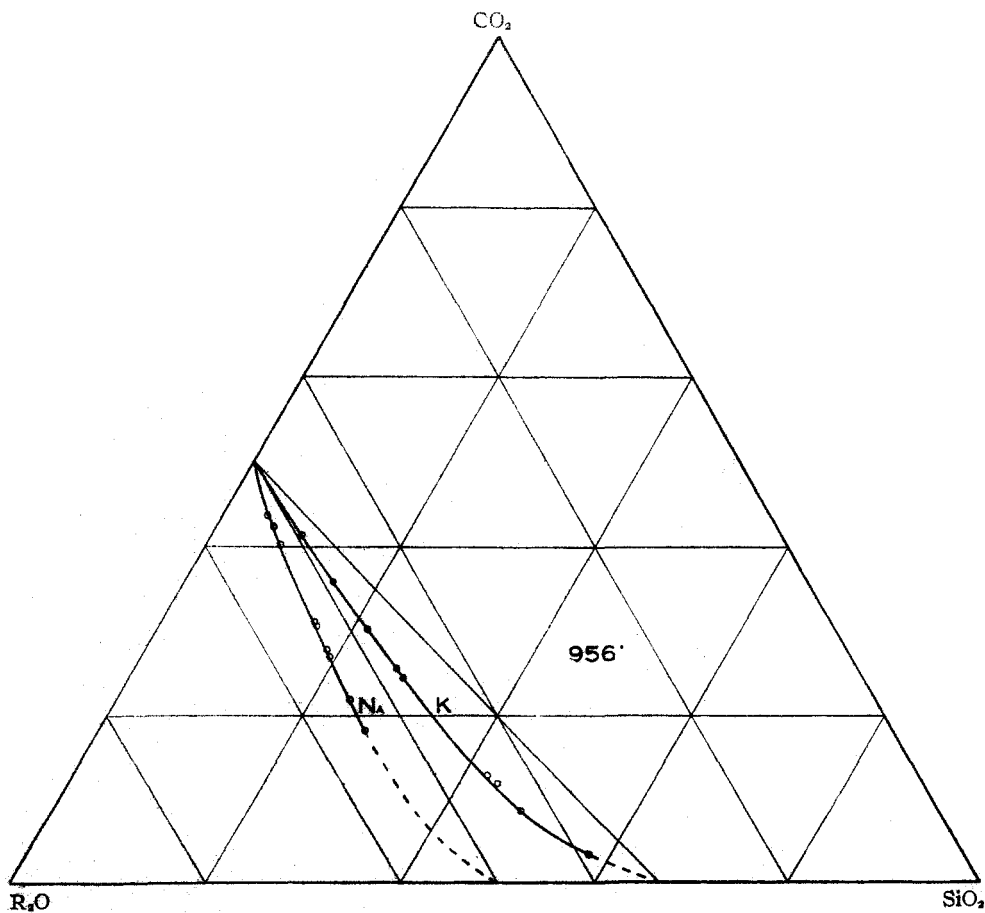


Fig. 11.—Triangular diagram showing the relative concentrations of R_2O , SiO_2 and CO_2 ($R = K, Na$) in equilibrium in melts at 956° .

(usually in amorphous form) in a platinum crucible over an open flame; the partial pressure of carbon dioxide is therefore unknown, but this is, as we have noted before, of little consequence. His results (in part recalculated) for "rotglut" and "gelblut" are brought together in the following table, along with ours obtained at 956° , which proves to be an in-

¹ Scheerer, *Ann. Chem. Pharmacie*, **116**, 129 (1860).

intermediate temperature. The trend of the results is in both cases similar; but one sees the magnitude of the vaporization loss in some of Scheerer's experiments, for only in this way can we account for equivalent losses in excess of 100 in the potash system.

TABLE VIII.—COMPARISON WITH SCHEERER'S RESULTS.
No. of mols CO₂ displaced by 100 mols SiO₂.

Original silica content mol per cent.	No. of mols CO ₂ displaced by 100 mols SiO ₂ .		
	"Rotglut" Scheerer.	956° Niggli.	"Gelbglut" Scheerer.
System K ₂ CO ₃ + SiO ₂ .			
3.0	114	96	129
14.3	94	89	107
20.0	89	87	104
33.3	81	83	99
50.0	76	73	83
60.0	61	61.5	..
System Na ₂ CO ₃ + SiO ₂ .			
3.0	...	193	197
9.9	...	171	186
14.3	150	156	178
20.0	135	145	168
33.3	110	134	138
50	99	100	100
60	All displaced	All displaced	All displaced

Mallard¹ investigated the system Na₂CO₃ + SiO₂ at three temperatures with the following results:

Amount of SiO ₂ mol per cent.	No. of mols CO ₂ displaced by 100 mols SiO ₂ .		
	At dark red heat.	At red heat.	At a higher temp.
20.0	107	129	148
8.7	116	143	...

His mean temperature was therefore somewhat lower than 900°, his highest temperature about 950°. Wittorf's results² have already been considered; they are subject to an error of from 50 to 100° in the temperatures given. The divergences in the older investigations are therefore all readily accounted for by sources of error such as were inevitable from the mode of experiment.

It would be a matter of great interest, from the petrologic as well as from the chemical standpoint, to carry out experiments at greatly increased concentrations of carbon dioxide in the gas phase (*i. e.*, higher pressures), and in this way increase our knowledge of the complete *PTX* figure of the system R₂O-SiO₂-CO₂. But in view of the technical difficulties associated with the work, it seemed preferable to study in the first place the analogous systems R₂O-TiO₂-CO₂ and R₂CO₃-SiO₂-Al₂O₃; with regard to the latter interesting results have already been obtained.

¹ Mallard, *Ann. chim. phys.*, [4] 28, 250 (1873).

² Wittorf, *Z. anorg. Chem.*, 39, 187 (1904).

Systems made up of Volatil and Non-volatil Components as Prototypes of the Magma.

The magma is, as I have pointed out in previous papers, a complicated system containing both volatil and non-volatil components; systems such as we have been considering serve therefore as simple prototypes of the complex system in the magma. An analogous system: $\text{HgBr}_2\text{-HgI}_2\text{-SO}_2$ has also been partially investigated; its main features may be compared with those of the systems $\text{R}_2\text{O-SiO}_2\text{-CO}_2$.

In the system $\text{HgBr}_2\text{-HgI}_2\text{-SO}_2$, which was investigated at relatively high pressures (70-100 atm.) of sulfur dioxide, the gaseous component is dissolved to a considerable extent in the melts of the non-volatil components (and hence lowers their melting points) but does not appear as a compound when crystallization takes place. Moreover, the gaseous phase in equilibrium with the melts (or at lower temperatures, with a solid phase) contains appreciable amounts of the two non-volatil components, HgBr_2 and HgI_2 . The system $\text{R}_2\text{O-SiO}_2\text{-CO}_2$ was investigated at a pressure of 1 atm. carbon dioxide; the latter is present (in much greater amount) in the melts, but in this case in the form of a compound. The likelihood of the existence in the melts of carbon dioxide in the free state increases with increasing pressure, so that in this regard there is not necessarily any essential difference between the two systems. In both cases the temperature range is far above the unary critical point of the volatil component; each of which is, as it happens, one of the so-called "gas-mineralizers" of the magma.

Thus two of the factors which determine the presence of the volatil component in the melts of the non-volatil components are increased pressure (*i. e.*, increased concentration of the gas phase) and the formation of relatively non-volatil compounds. Both factors are effective in the magma, especially in intrusive magmas; to them is due a large part of the effects hitherto quite generally attributed to "gas mineralizers," the mode of action of which was mysterious.

The behavior of the volatil components, when they are present in the melts, differs only in degree from that of the other components. The main difference is due to the vastly greater effect of changes of pressure and of temperature on the concentration (in the melt) of the volatil component, by reason of the close relation of this concentration to that of the gas phase itself. In consequence of this there is a "mobility" of equilibrium, which is characteristic of the magma and without doubt very closely associated with many aspects of its behavior, *e. g.*, with the possibility of eruption, differentiation, etc.

In conclusion, I wish to express my thanks to Dr. A. L. Day, Director of the Geophysical Laboratory, for his courtesy to me during my stay in Washington. To Dr. J. Johnston, with whom I had many fruitful dis-

cussions, I am especially indebted for assistance and advice. I also wish to thank Mr. C. N. Fenner, who kindly undertook the optical examination of the products.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C., JUNE, 1913.

THE PHYSICAL CHEMISTRY OF PHOTOGRAPHIC DEVELOPMENT.¹

By C. E. KENNETH MEES.

Received September 9, 1913.

If a precipitate of silver bromide be formed in a gelatin solution in a room lighted only by red light, and a solution of a moderately strong reducing agent be added to it, no reaction will occur for some time, whereas, if the precipitate is exposed for a very brief time to ordinary light, the reducing agent will reduce it rapidly to metallic silver. This reaction is the basis of the process which has made the whole of modern photography possible, namely, the selective action of some reducing agents upon a silver halide which has been exposed to light. The explanation of the reducibility of exposed silver bromide, while unexposed silver bromide is either reduced not at all or with much greater difficulty, has always had a great fascination for the chemist.

There are 3 factors in development:

- (1) The constitution of the emulsion.
- (2) The effect of light upon that emulsion.
- (3) The chemical nature of the reducing agent employed.

(1) *The Emulsion.*—A photographic emulsion is not an emulsion at all in the sense in which that word is used in colloid chemistry. It is a solution of gelatin, containing suspended in it a large number of extremely small crystallin grains of silver bromide which usually hold in solution a small quantity of silver iodide. What may be the exact nature of the relation between the bromide and iodide in ordinary photographic emulsions is not known, but in all probability the iodide is in solution in the bromide, in just the same way as the separate metals are in solution in each other in some alloys, and there would seem to be a possibility of the existence of one or more, probably two, bromo-iodides. The grains in a high-speed emulsion are from 1 to 2 μ in diameter, but there seems reason to believe that the grains themselves are agglomerates of small crystals forming a spongy network. Emulsions are made by the addition of silver nitrate, usually as a concentrated solution, to a gelatin solution containing potassium bromide and iodide. Under certain conditions the crystals, when precipitated, may be ultra microscopic, but

¹ Read at the Rochester meeting of the American Chemical Society, September 9, 1913.