SILICATE—WATER SYSTEMS: PHASE EQUILIBRIA IN THE $NaAlSi_3O_8$—H_2O AND $KAlSi_3O_8$—H_2O SYSTEMS AT HIGH TEMPERATURES AND PRESSURES.

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ABSTRACT.

The subject matter herein includes experimentally determined phase equilibria relations for the albite—water and orthoclase—water systems from 800 to 1200° C. and pressures to 4000 bars and is a part of the series constituting a program of research on silicate—water systems begun some years ago by the writer.

The freezing-point curves of these systems extend out into three-dimensional temperature-pressure-concentration space and have been completed for albite—water. The orthoclase—water system is somewhat more complex in that at low pressures, i.e. to about 2600 bars, orthoclase melts incongruently to leucite and liquid. The solubility of water in this liquid has not yet been completely determined as a function of temperature and pressure so that only the projection of the freezing-point curve on the temperature-pressure coordinate plane is given herein for the latter system.

In order to obtain other thermodynamic data such as apparent volumes and heats of evaporation it was necessary to obtain the temperature-pressure-volume relations of water in this region. These latter data are in large part extrapolated, consequently the derived thermodynamic quantities will have a lower degree of accuracy.

The data show that the pressures developed on crystallization may not only comply with but actually exceed the pressures necessary to explain certain volcanic phenomena.

INTRODUCTION.

In this paper are presented phase equilibria relations for the systems, $NaAlSi_3O_8$—H_2O and $KAlSi_3O_8$—H_2O, in the temperature range from 800° C. to 1200° C. and pressures to 4000 bars (metric atmospheres). In the course of these studies many improvements and plans for future improvement were evolved which will increase the accuracy of further studies on these systems. It is hoped, however, that the present report will be of interest not only because this combined temperature and pressure range is unique, but also because these systems represent the first laboratory investigation of truly rock-forming silicates which include water as a component.

In order to correlate the results of these studies and apply them to the understanding of other silicate-water systems it is necessary to know not only the heterogeneous equilibria relations but also the properties of each of the coexistent

homogeneous parts or phases. In these investigations the homogeneous parts are: (1) a vapor phase which is essentially water, (2) a liquid phase which is a saturated solution of water in silicate melt, and (3) solid phase or phases consisting of one or more silicates. As progress in this direction there is presented, in addition to the vapor-liquidus-solidus curves of these systems, (a) an equation of state for water in this temperature and pressure range, (b) experimentally determined solubility relations of water in silicate melts as functions of temperature and pressure, and (c) derivations of the necessary correlative thermodynamic equations together with such interpretations as could be made from these data.

APPARATUS AND TECHNIQUE.

The high pressure furnace or bomb in which the runs were made is a modification of the apparatus described elsewhere[1] and will be discussed in detail in a forthcoming paper.

The charges, consisting of very finely-ground powder of the silicate under investigation and water, are sealed gas-tight in platinum capsules. The water content is adjusted so that the minimum amount in excess of that necessary to saturate the silicate solution will be present. Fine grinding of the silicate is necessary to prevent puncture of the capsule and also to lessen the time necessary for attainment of equilibrium. The operation of sealing the capsules gas-tight is essential for several reasons, the most important one being to insure that a closed system is obtained.

If water could circulate freely in the bomb the vapor phase would be non-uniform as to temperature, and consequently leaching and deposition cycles would take place with a resulting change in composition of the silicate—presumably an eventual steady state might be attained for these particular conditions but it would not be the one desired.

For a particular run two or more of these capsules are inserted in the pressure furnace in close proximity to the two thermocouples, one of which is near the top end and the other near the bottom end of the capsules. The pressure medium is nitrogen and is compressed by a hydraulic piston which is operated from a hydraulic compressor. The compressed gas in the bomb acts only on the exterior of the platinum capsules.

[1] Goranson, R. W.: This Journal, *22*, 481-502, 1931.

The pressure is determined by measuring resistance changes under pressure of a 100 ohm. coil of manganin wire calibrated by comparison with a free-piston type gauge. The sensitivity of this pressure measuring device is about a tenth of a bar (a change of about 0.2 ohm. per kilobar) and is reproducible to within a bar. The temperature is then raised by applying electrical power to three electrodes which enter the bomb through gas-tight electrically-insulating packings and connect to a platinum-rhodium resistance furnace inside the bomb. The temperature is determined by measuring the electromotive force of two platinum—platinum rhodium thermocouples which enter the bomb through specially devised gas-tight electrically-insulating packings. They are calibrated by means of suitable fixed points such as the melting temperature of pure gold.

The silicate glasses were prepared synthetically to insure their purity and for them the writer is indebted to Dr. J. F. Schairer of this Laboratory.

For a particular run pressure and then temperature are raised to the desired amounts and held at these values for a length of time sufficient for attainment of equilibrium. Although these silicates are very sluggish in crystallizing from an anhydrous melt they crystallize very readily from hydrous solutions, in fact relatively large crystals have been grown in half an hour. At the end of the run the electric power supply is cut off, the temperature dropping rapidly enough to freeze the equilibrium, i.e. the charges are quenched. Finally the pressure is released. The capsules are then cut open and examined under the microscope for changes in state and if no crystallization has occurred the glasses are analyzed for water content. To do this the excess water in the capsule is evaporated off, the glass weighed on a micro balance, ignited, and then weighed again.

THERMODYNAMIC PROPERTIES OF WATER FOR TEMPERATURES BETWEEN 800 AND 1200° AND PRESSURES TO 4000 BARS.

Keenan and Keyes[2] have recently published superheated steam tables for temperatures to 875° C. and pressures to 380 bars. Van Nieuwenburg and Blumendal[3] have measured the

[2] Keenan, J. H., and Keyes, F. G.: Thermodynamic Properties of Steam, John Wiley and Sons, New York, 1936.

[3] Van Nieuwenburg, C. J., and Blumendal, H. B.: Recueil des travaux chimiques des Pays-Bas, 51, 707-714, 1932.

specific volumes between 350 and 480° C. at pressures from 160 to about 600 bars. Where overlapping occurs these two sets of data agree rather well. Tammann and Rühenbeck[4] determined the specific volume of water between 20° and 650° C. at pressures to about 2500 bars. This third set of high-temperature data does not, however, agree with the above two nor with the few measurements made by the writer. Tammann and Rühenbeck's method required the use of a mercury piston and consequently corrections of uncertain magnitude. Therefore, although their data were not used as such herein, it was assumed that their slopes would be considerably more accurate than their absolute values and thus some of the derivatives computed from their data were utilized.

The determinations which have been made by the writer are in the nature of trial runs carried out to test the feasibility of the method devised. Varying proportions of water are sealed up in platinum capsules and inserted in the bomb as described under "Apparatus." Pressure developed in the bomb acts only on the exterior of the capsules and when the amount desired is attained the temperature is then slowly raised as for a heating-curve run. When the internal pressure exerted by the water exceeds the nitrogen pressure applied externally on the walls of the platinum envelope the capsule punctures at a point of weakness and this is indicated by a sudden drop in the thermocouple reading. The shape and stretch of the capsule at the time of rupture are retained, the perforation preventing collapse, and therefore the volume capacity of the tube may be ascertained after removal from the bomb. The corrections to be made are for the volume change of the platinum itself between room temperature and atmospheric pressure and the temperature-pressure conditions at the time of rupture. Since the amount of water inserted is known, by previous weighing, the specific volume of the water at the temperature and pressure of rupture is determinable.

The many attempts to obtain equations of state and accurate interpolation formulae for gases have resulted in expressions of increased complexity and with increasing number of disposable constants. For example, Becker's expression, which will represent Bridgman's[5] data for nitrogen gas, has four disposable parameters and, since the data are for one tempera-

[4] Tammann, G., and Rühenbeck, Ad.: Ann. Physik, 13, 63-79, 1932.
[5] Bridgman, P. W.: Proc. Am. Acad. Arts Sci. 59, 209, 1924.

ture, these parameters may also be functions of temperature. However, owing to the inequalities and scattered nature of the data used here for water, the best expression for representation of this material is, paradoxical as it may first seem, one which contains few disposable parameters. Attempts were therefore made to fit two parameter equations such as the van der Waals and the Dieterici type.[6] On solving for the parameter

$$a = v^2 \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right]$$

in the van der Waals expression it was found that the parameter b must be treated as a function of temperature and perhaps of volume. On the other hand after solving for the parameter

$$a = \frac{2}{3} RT^{3/2} \frac{v}{p} \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right]$$

it was found that the other parameter b of the Dieterici type had no noticeable trend and deviated by only 3% from the mean over the twenty-one points fitted.

The equation finally adopted to express the p-v-T relations for water at high temperatures is

$$p = \frac{4.619\,T}{v - 1.9} \exp \frac{-1.08 \times 10^5}{vT^{3/2}} \qquad (1)$$

where p is expressed in bars, v in cm.^{3}/g. and T in degrees Abs. A plot of pv-4.619T against pressure is given in Fig. 1.

Although no particular attempt was made to fit the equation to low pressure data it was found that the values of p as calculated by this equation were less by about 0.4 bars than the values as given by Keenan and Keyes for the 871° C. isotherm but without any trend.

Moreover according to this equation the Boyle point is at about 1200° C., i.e. it reduces to $pv=RT$ for pressures less than 100 bars at 1200° C.

[6] Van der Waals' equation (1873): $\left(p + \frac{a}{v^2}\right)(v - b) = RT$

Dieterici's equation (1898): $p(v - b) = RTe^{-a/RTv}$

where a, b, and R are constants.

Now for an ideal gas we have

$$S(T, p) = S(T, 1) - \int_1^p R \, \mathrm{d} \ln p$$

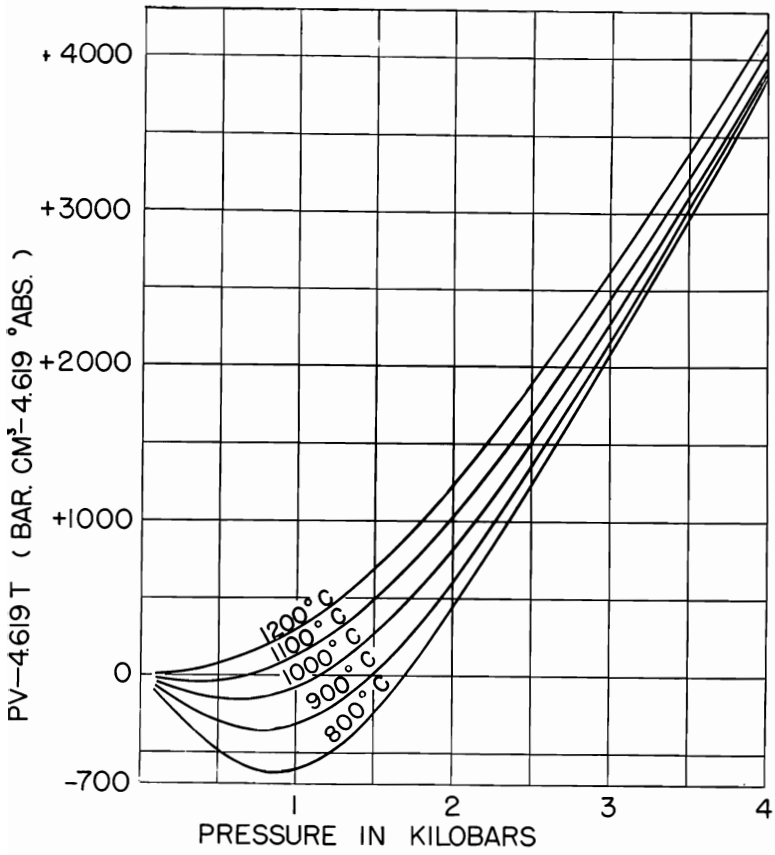

Fig. 1. p-v-T relations for water in the temperature range from 800 to 1200° C. Deviations from the perfect gas law, pv-4.619T, in terms of bar cm.³ are plotted as ordinates and pressures in kilobars as abscissae.

where $S\ (T,p)$ and $S\ (T,1)$ denotes the entropies at the states (T,p) and $(T,\ p=1$ bar) respectively; R denotes the gas constant. Thus $\partial^2 S/\partial T \partial p$ is zero, i.e. the change of entropy with temperature is the same for all pressures, and furthermore the change of enthalpy with pressure, $\partial H/\partial p$, is also zero. There-

fore, for pressures of 100 bars or less, the isopiestic enthalpy curves should all cross the 1200° C. isotherm at the same point and with the same slope, similarly the isopiestic entropy curves should all cross this isotherm with the same slope but separated by distances equal to $R\ ln\ (p_1/p_2)$ where p_1 and p_2 are the pressures of two neighboring curves. A plot of enthalpy and entropy data from Gordon's[7] spectroscopic measurements (1 atm. ideal gas) and from Keenan and Keyes' Tables[2] indicates that the isopiestic curves of

$$S\ (T, p) + \int_1^p R\ \mathrm{d}\ ln\ p$$

will extrapolate to meet at about 1200° and with the same slope, and that the enthalpy curves will do the same thing. The latter plot is not so diagnostic because of the greater curvature of the enthalpy diagrams.

SOLUBILITY RELATIONS OF WATER IN SILICATE MELTS.

The solubility relations of water in glasses of Stone Mountain granite and of albite compositions are very similar and have been described elsewhere.[8] Some additional data for albite are given in Table III. These data are expressible by hyperbolic equations of the form $x_2 = p/(a + bp)$ where x_2 denotes the concentration of water in weight per cent, p the pressure in bars, and a and b are constants for constant temperature and silicate composition. Values of a and b are given in Table I for albite melt at different temperatures and a plot of these curves in Fig. 2.

TABLE I.

Parameters in the equation $x = \mathrm{p}/(a + b\mathrm{p})$ which expresses the weight per cent of water, x, in solution in albite melt as a function of pressure in bars.

Temp. °*C.*	*a*	*b*
900	81.84	0.08458
1000	95.05	0.08715
1100	110.56	0.09008
1200	134.43	0.09100

[7] Gordon, A. R.: J. Chem. Phys., 2, 69, 1934.
[8] Goranson, R. W.: This Journal, 22, 481-502, 1931; Trans. Am. Geophys. Union, 17, 257-259, 1936.

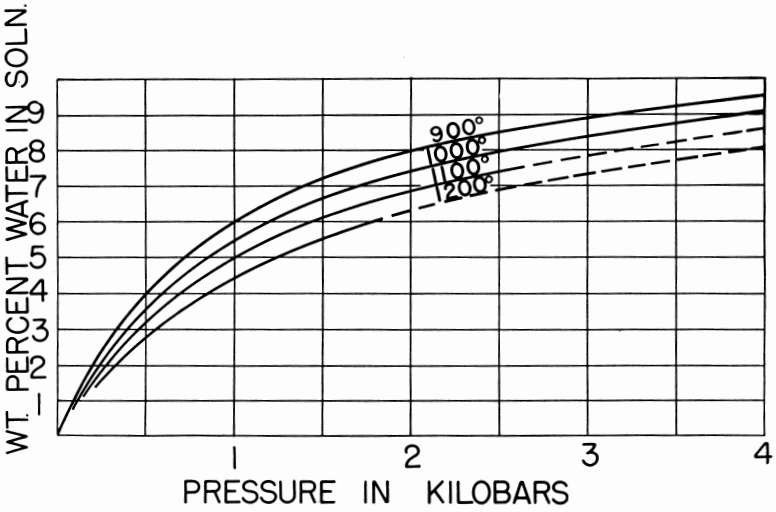

Fig. 2. Solubility relations of water in albite melt in the temperature range from 900 to 1200° C. Weight per cent of water in solution is given by the ordinate and pressure in kilobars by the abscissa.

We have for the concentration-pressure slope of the solubility curve the relation

$$\left(\frac{\partial N_2}{\partial p}\right)_T = \Delta v_2 \Big/ \left\{ RT \left[\frac{\partial \gamma}{\partial N_2}\right]_{T,\,p} + 1 \right\} \qquad (2)$$

where N_2 denotes the mole fraction of water in solution, Δv_2 the change in volume when one mole of water goes into solution without change of concentration, R the gas constant, T the absolute temperature, and γ the activity coefficient[9] of water in solution. For an ideal solution $(\partial N_2/\partial p)_T = \Delta V_2$.

Now if one assumes that the condensed water phase (the

[9] The expressions derived herein may be obtained by writing a fundamental equation in the desired variables (R. W. Goranson, Thermodynamic Relations in Multicomponent Systems, Carnegie Institution of Washington Pub. No. 408, 1929) for each of the homogeneous parts or phases and then solving the resulting set of equations simultaneously remembering only that for these conditions the temperature, pressure, and chemical potential of a component are the same in each of the phases. For the definition of activity coefficient as used herein see J. Chem. Phys., 5, 107-112, 1937.

analog of liquid water) would occupy the "apparent molal volume" on the hypothesis that it is an ideal solution or, in other words

$$v_{2\text{condensed}} = (\Delta v_2)_{\text{ideal}} - v_{\text{vapor}} = (\bar{v}_2)_{\text{ideal}}$$

$\bar{v}_2 = (\partial V/\partial n_2)$ denoting the "apparent molal volume" or volume which a mole of water would appear to occupy if added to the solution without changing its concentration, i.e. added to an infinite amount of solution, it is then possible to calculate the "condensed specific volume" of the water phase from the solubility slopes and Eqn. (1). The actual apparent molal volume, $\bar{v}_2$, may be calculated along the three-phase boundary curve from the expression given later (Eqn. 9) and the equation of state for water (Eqn. 1). The relation between these two calculated quantities namely

$$(\bar{v}_2)_{\text{id}} - \bar{v}_2 = RT\,(\partial N_2/\partial p)_T(\partial \gamma/\partial N_2)_{T,\,p}$$

appears to be approximately constant and given by the expression

$$\bar{v}_2 = (\partial V/\partial n_2) = (0.77_3 \pm 0.03_3)\ (\bar{v}_2)_{\text{ideal}} \qquad (2a)$$

The apparent volume occupied by a gram of water in solution is then 77 per cent of the volume assumed as that of the condensed water phase. A comparison of these quantities is given in Table II. It should be noted here that some of the quantities used in computing these values are not yet very well known as functions of concentration, e.g. Δv_1 and Δh_1 the volume and heat energy changes of the silicate on crystallizing, and that these calculations are to this extent only approximations.

It may be of interest to evaluate the relation $\bar{v}_2/(\bar{v}_2)_{\text{ideal}}$, found to be 0.77 for the conditions of this investigation, for water-bearing obsidians at room temperature. The Rocche Rosse ($H_2O = 0.31\%$; density = 2.370) and Forgia Vecchia ($H_2O = 1.01\%$; density = 2.363) rhyolite glasses of Monte Pelato are very similar and may be assumed to be the same except for water content. The ratio of the apparent specific

TABLE II.

Specific volumes and "apparent" specific volumes of water in the two phases vapor and solution. The second column lists the specific volume, $cm.^3/g.$, of water vapor as calculated from Eqn. (1) for the corresponding temperatures and pressures. The third column lists the "specific volume of the condensed water phase" which is herein defined as the apparent specific volume the water would have in solution were the solution an ideal one. These values are computed from Eqn. (2) for the solubility curves and Eqn. (1). The fourth column lists the true "apparent" specific volume of the water in solution. The relation between the values of columns 3 and 4 were obtained from the freezing-point curves by means of Eqn. (9).

Pressure in bars.	*Sp. vol. vapor, v.*	*Sp. vol. cond. water,* $(\bar{v}_2)_{ideal}$	*Apparent sp. vol. water,* $\bar{v}_2$
	Temp. 900° *C.*		
500	10.24	5.575	4.29
1000	5.09	3.62	2.785
1500	3.61	2.895	2.23
2000	3.01	2.59	1.99
2500	2.70	2.42	1.86
3000	2.52	2.32	1.79
3500	2.405	2.255	1.74
	Temp. 1000° *C.*		
500	11.45	6.02	4.63
1000	5.80	4.05	3.12
1500	4.09	3.21	2.38
2000	3.35	2.83	2.18
2500	2.95	2.61	2.01
3000	2.72	2.475	1.905
3500	2.56	2.38	1.83
	Temp. 1100° *C.*		
500	12.61	6.30	4.85
1000	6.47	4.40	3.385
1500	4.55	3.51	2.70
2000	3.68	3.06	2.36
2500	3.205	2.785	2.145
3000	2.92	2.625	2.02
3500	2.73	2.51	1.93
	Temp. 1200° *C.*		
500	13.75	6.44	4.96
1000	7.10	4.44	3.42
1500	4.99	3.69	2.84
2000	4.015	3.235	2.49
2500	3.47	2.95	2.27
3000	3.135	2.765	2.13
3500	2.91	2.63	2.025

volume to the specific volume of water (which is the equivalence of mixing with no change in volume, a criterion of an ideal solution) is

$$\bar{v}_2 = 0.72\ (\bar{v}_2)_{\text{ideal}}$$

and this value is in conformity with the result obtained above.

Attention has been called[10] to the fact that for obsidians of high water content the water appears to be present in two forms or phases, some of it in solution in the glass and some of it apparently present as adsorbed water.

The relation above or a similar one based on more comprehensive data could be used as a criterion of water of solution in obsidian glasses. For example, if the specific volume of a glass of high water content did not fall on the curve this fact would indicate that some of the water must be present in a different form. This relation might also permit of a quantitative estimate of the relative proportions of these two kinds of water.

Similarly the molal heat of evaporation, Δh_2, of the water from the silicate solution may be calculated from the relation

$$\Delta h_2 = -T\left(\frac{\partial N_2}{\partial T}\right)_p \left[RT\left(\frac{\partial \varrho}{\partial N_2}\right)_{T,\,p} + 1\right] = T\Delta v_2\left(\frac{\partial p}{\partial T}\right)_{N_2} \quad (3)$$

where $(\partial N_2/\partial T)_p$ denotes the slope of the solubility surface intercept on the concentration-temperature coördinate plane, N_2 being the mole fraction of water in solution. The other quantities are as given for Eqn. (2).

The heat of evaporation increases with increase in temperature and also varies considerably with pressure. A mean value over the temperature-pressure range of this investigation yields about 170 calories per gram but it may vary with temperature and pressure on either side of this mean by as much as 95 cal./g. In this connection an interesting comparison may be made with the heat of evaporation of water at 100° C. which is 539.36 cal./g.

The solubility relations of water in orthoclase melts are complicated by the fact that at pressures below about 2500 bars orthoclase melts incongruently to leucite plus liquid. The data so far obtained indicate that the solubility relations for ortho-

[10] Goranson, R. W.: Am. Mineral., *22*, 490, 1937; Trans. Am. Geophys. Union, 18, 247, 1937.

clase melt roughly parallel the curves for albite melt but are displaced toward the pressure axis by about 1.5 to 2 weight per cent of water; in other words water is less soluble in orthoclase melt by a mean value of about 1.8 weight per cent. These results are in approximate agreement with a previous determination on a 25 quartz—75 orthoclase-mixture.

FREEZING-POINT RELATIONS IN THE ALBITE-WATER SYSTEM.

Albite melts at 1115 ± 5° C.[11] at atmospheric pressure and with an estimated volume increase, Δv_1, of 0.039 cm.^{3} per gram. The heat of melting has not been experimentally determined but may be computed from the solidus-liquidus curves in the system albite-anorthite[12] as 203 joules per gram from the

$$\Delta h_1 = \frac{RT_0T}{M_1(T_0 - T)} ln \frac{N_1}{N_1'} + \Delta\bar{C}_{P1}\,(T_0 - T)\ \text{j/g}. \qquad (4)$$

ideal solution equation where Δh_1 denotes the heat of melting of albite, M_1 its effective molar weight, N_1 and N_1' the mole fractions of albite in the solidus and liquidus phases respectively, T the absolute temperature, T_0 the freezing point of the pure component "1," $\Delta\bar{C}_p = \bar{C}_p' - \bar{C}_p$ the mean heat capacity of the two phases between T_0 and T, and $R = 8.315$ the gas constant. Although the equation (4) is valid only for ideal solutions so that, in general, only initial slopes can be utilized, it has been our experience, from published data and theoretical considerations, that systems such as albite-anorthite which are miscible in all proportions in the solid as well as liquid state are the best examples we have of ideal solutions.

Increase in pressure will therefore raise the melting temperature of anhydrous albite and this initial rise may be computed from the Clapeyron equation, $(dT/dp) = T\Delta v_1/\Delta h_1$, to be 26° C. per kilobar. Δh_1 and Δv_1 are functions of pressure so that, in order to calculate the slope at higher pressures, they must be evaluated accordingly.

When water is a constituent of the system there are three phases present along the albite freezing-point curve, namely vapor essentially of water, a solution of water in silicate melt,

[11] Private communication from J. F. Schairer.

[12] Bowen, N. L.: This Journal, 35, 583, 1913. His calculated heat of melting agrees with the value adopted here.

and albite crystals. The experimental data are given in Table III and plotted in Figs 3 and 4.

TABLE III.

Experimental Data for the System $NaAlSi_3O_8$-H_2O.

The first two columns list the pressure in bars and temperature in deg. C. of the run. The third column lists the state of the silicate component after quenching. The fourth column lists the weight per cent of water in solution in the silicate melt.

Pressure in bars	*Temp. in °C.*	*State of silicate*	*Wt. % water in solution*
300	1040	glass	2.8 (high)
500	1030	glass	3.2, 3.2
509.5	960 ± 4	few xls. mostly glass	
	956 ± 5	xls.	
517	1000 ± 4	glass	3.65, 3.58
656	970 ± 5	glass*	4.45
(788)	1000 ± 7	glass**	3.54, 2.78, 2.6
790 ± 9	950	glass	5.8 (high)
887	905	xls.	
1000	1055 ± 10	glass	5.3
1000	1010	glass	5.45, 5.65
1000	950	glass	5.3, 5.5
1007 ± 9	910 ± 5	glass	5.8, 5.8
1146	910 ± 5	glass*	6.9 (high)
1220 ± 37	1010 ± 10	glass*	5.8, 5.9, 5.9
1245 ± 4	915	glass*	7.22, 7.22, 7.12 (high)
1250 ± 50	1000 ± 10	glass*	6.8, 6.8, 7.0, 6.8 (high)
1260	1200	glass*	4.8, 5.0, 5.0, 4.9
1262	1110	glass*	5.2, 5.2, 5.4
1315	905	glass*	7.5 (high)
(1413)	905	xls.**	4.13, 4.46
1450	910	glass	7.5, 7.3
1483 ± 60	810	xls.	
1535	845	xls.	
1567	849 ± 3	xls.	
1600	1050	glass	6.72
1694	1000	glass	7.15, 6.85
1700	847	xls.	
1700	860	glass	7.54
1770	910	glass	7.8, 7.8, 8.0, 8.2 (high)
2380	1110	glass	7.3, 7.6, 7.5
2414	830	glass*	8.8; 7.9, 7.8, 8.2 (low)
2414	830	xls.	
2575	1015	glass	8.0
2725	955	glass	8.48, 8.72, 8.49, 8.47
2772 ± 90	815 ± 5	xls.	
2813 ± 100	910 ± 10	glass	8.7, 9.0
2983	1020	glass	8.3, 8.45
3288	905 ± 5	glass	8.85, 8.85, 8.7, 8.87

* Indicates one set of charges consisted of ab. glass plus water and one set of ab. glass plus ab. xls. plus water.

** Indicates that the charges were unsaturated with respect to water.

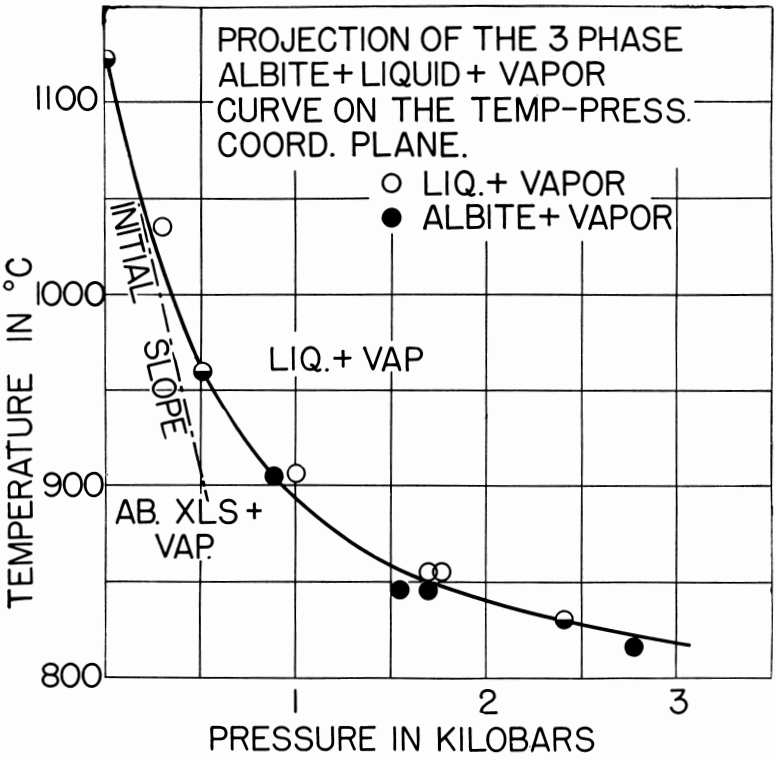

Fig. 3. The projection of the freezing-point curve of albite in the albite-water system on the temperature (ordinate)-pressure (abscissa) coördinate plane.

The equation expressing the slope, dT/dp, of the three-phase equilibrium curve projected on the temp.-press. coördinate plane is

$$\frac{dT}{dp} = \frac{T[\Delta v_1 - x_2(\Delta v_1 + \Delta v_2)]}{\Delta h_1 - x_2(\Delta h_1 + \Delta h_2)} \qquad (5)$$

where subscripts 1 and 2 refer to the components albite and water respectively, Δv_1 and Δh_1 denote the volume decrease and heat evolved respectively per gram of albite on crystallizing from solution, Δv_2 and Δh_2 denote the volume increase and heat absorbed respectively per gram of water on evaporating from solution, x_1 and x_2 denote the weight fractions of albite and water resp. in the solution, and T denotes the absolute tem-

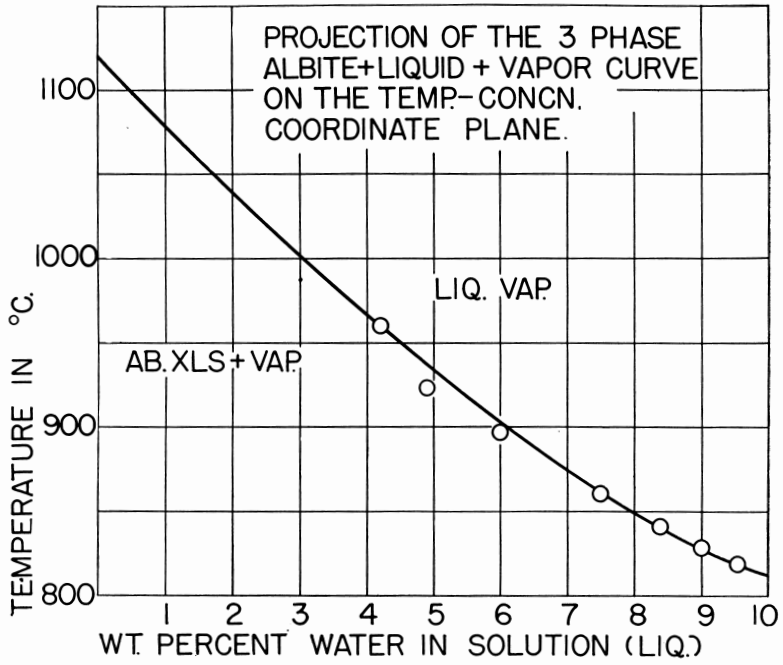

Fig. 4. The projection of the freezing-point curve of albite in the albite-water system on the temperature-concentration coördinate plane. Temperature is given along the ordinate and concentration of water in weight per cent along the abscissa.

perature. As may be observed this expression will reduce to the Clapsyron equation by making $x_2 = 0$.

The initial slope, dT/dp, of the freezing-point curve of anhydrous albite was calculated to be 2.6° per hundred bars. The initial freezing-point slope, dT/dp, of albite in the albite-water system is calculated from the equation

$$\lim_{x_2 \to 0} \frac{dT}{dp} = \frac{T}{\Delta h_1}\left[\Delta v_1 - \frac{RT}{M_2} \lim_{x_2 \to 0} \frac{x_2}{p}\right], \qquad (6)$$

where M_2 is the molar weight of water and the quantity

$$\lim_{x_2 \to 0} \frac{x_2}{p}$$

is evaluated from the solubility curves, to be —40.24° per hundred bars. The effect of increase in pressure for the latter

system is therefore to lower the freezing temperature of albite, and the difference between the two slopes, i.e. for the anhydrous and hydrous systems, is 43° per hundred bars.

The slope of the freezing-point curve projected on the temperature-concentration coördinate plane is given by the equation

$$\frac{dT}{dx_2} = -\frac{T[\Delta v_1 - (x_2/x_1)\Delta v_2]\ (\partial p/\partial x_2)T}{T\,\Delta v_1(\partial p/\partial T)_{x_2} - \Delta h_1} \qquad (7)$$

The initial slope is therefore

$$\lim_{x_2 \to 0} \frac{dT}{dx_2} = \frac{T}{\Delta h_1}\left[\Delta v_1 \left(\lim_{x_2 \to 0} \frac{p}{x_2}\right) - \frac{RT}{M_2}\right] \qquad (8)$$

and is evaluated as —41.4° per weight per cent of water. This slope is plotted as a dashed line in Fig. 4.

In order to realize a maximum pressure on the crystallization curve, i.e. to have the curve become tangent to the pressure axis, dT/dp must become infinite or

$$\Delta h_1 = (x_2/x_1)\ \Delta h_2 = (x_2/x_1)\ T\ (\partial p/\partial T)_{x_2}\ \Delta v_2$$

which occurs neither in the systems examined here nor in the "granite-water" system[13] and therefore, so far as is now known, does not occur for the rock-forming silicate systems.

In order to realize a minimum temperature on the crystallization curve, i.e. to have the curve become tangent to the temperature axis, dT/dp must become zero or

$$\Delta v_1 = (x_2/x_1)\Delta v_2.$$

Now there are two opposing effects, one tending to raise the freezing point—initially 26° per kilobar—and the other to lower the freezing point—initially 402° per kilobar. As is apparent from Figs. 3 and 5 the slope $-(dT/dp)$ decreases with increasing pressure. The reason for this is that the latter effect decreases with increasing pressure because, even though the concentration x_2 increases with pressure although at a diminishing rate, Δv_2 decreases and eventually the numerator of Eqn. (5) may become zero and the curve begin to rise with still further increase in pressure.

[13] Goranson, R. W.: This Journal, 23, 227-236, 1932.

The apparent specific volume $\bar{v}_2$ of the water in solution along the freezing-point curve may be computed from the equation

$$\bar{v}_2 = v - \left[\frac{\Delta v_1 - (\Delta h_1/T)(\mathrm{d}T/\mathrm{d}p)}{(x_2/x_1)\{1-(\mathrm{d}T/\mathrm{d}p)(\partial p/\partial T)_{x_2}\}}\right] \qquad (9)$$

where v denotes the specific volume of water in the vapor phase and is calculated from Eqn. (1), $\mathrm{d}T/\mathrm{d}p$ the temp.-press. slope of the freezing-point curve, $(\partial p/\partial T)_{x2}$ the press.-temp. slope of the solubility curve at constant concentration, and the other quantities are as previously defined.

The quantities Δv_1 and Δh_1, the volume decrease and heat evolved when a gram of albite crystallizes from the solution (at constant concentration), are functions of concentration but, since these relations are not known explicitly, Δv_1 is assumed as constant and Δh_1 is only partially corrected in the computations which establish the relationships of Eqn. (2a) and the tabulated values of column 4, Table II.

If we divide the heat of evaporation of water from the silicate solution into two parts, an internal and an external heat, such that

$$\Delta h_2 = (\Delta h_2)_{\text{int.}} + p\,\Delta v_2$$

it is found that the internal heat of evaporation, $(\Delta h_2)_{\text{int.}}$, along the f.p. curve varies about 10% from a mean value of 240 joules per gram of water whereas the external heat of evaporation, $(\Delta h_2)_{\text{ext.}} = p\,\Delta v_2$, decreases steadily with increasing pressure.

FREEZING-POINT RELATIONS IN THE SYSTEM, $KAlSi_3O_8$-H_2O.

This system is more complicated than the $NaAlSi_3O_8$-H_2O system in that at atmospheric pressure orthoclase ($KAlSi_3O_8$) melts incongruently to leucite ($KAlSi_2O_6$) and liquid at about 1120 ± 20,[11] the leucite in turn melting to form liquid of $KAlSi_3O_8$ composition at 1535° C.

The experimental results are given in Table IV and a projection plot of this data on the temp.-press. coordinate plane for the vapor-liquid-solid curves in Fig. 5.

The incongruent melting curve as plotted seems to be somewhat high and should perhaps extrapolate to about 1100° at atmospheric pressure. Some further data are being obtained

for this curve and for the solubility relations of the melt in equilibrium with leucite. Further calorimetric and volumetric data are also needed in order to evaluate the thermodynamic properties of this system. It is of interest to note, however, that the stability field of leucite becomes wiped out at about 2500 bars, the orthoclase melting congruently above this pressure.

TABLE IV.

Experimental Data for the System, $KAlSi_3O_8$-H_2O.

The first two columns list the pressure in bars and temperature in deg. C. of the run. The third column lists the state of the silicate after quenching. The fourth column lists the weight per cent of water in solution in the silicate melt.

Pressure in bars	*Temp. in °C.*	*State of silicate*	*Wt. % water in solution*
500	1030	leucite alt. to or.*	
1000	955	or. after lc.	
1000	1007 ± 7	leucite glass	
1000	1060	leucite glass	
1000	1085	leucite glass	
1007	1128 ± 5	leucite glass	
1007	1137 ± 10	glass	
1000	1140	glass	
1020	1145	glass	
1550	965	or. xls.	
1600	1035	leucite glass	
1600	1040	glass	
1900	995	leucite glass	
1900	1000 ± 5	glass	
2053	953 ± 5	intergrowth lc. + or.	(or. seems to be repl.g lc.)
2055	1015 ± 5	glass	⎫ 5.86 (mean of five
2060	1010	glass	⎭ determinations)
2185	975	glass	
2372	968	glass	
2486	960	glass	
2616	960	glass	5.97, 5.97
2622	950	all or. xls.	
2725	950	or. xls.	
2725	960	glass	
2813	897	or. xls.	
2983	1000	glass	6.2, 6.4
(3290)	905	or.**	0.4 **
3300	939	glass	
3360	960	glass	6.875
3400	948	glass	
3400	938	glass	
3582	940	glass	6.68
3636	934	or. xls.	
3640	937	glass	7.08

* or. xls. denotes orthoclase crystals; lc. indicates leucite.
** Indicates the system was unsaturated because of a leak.

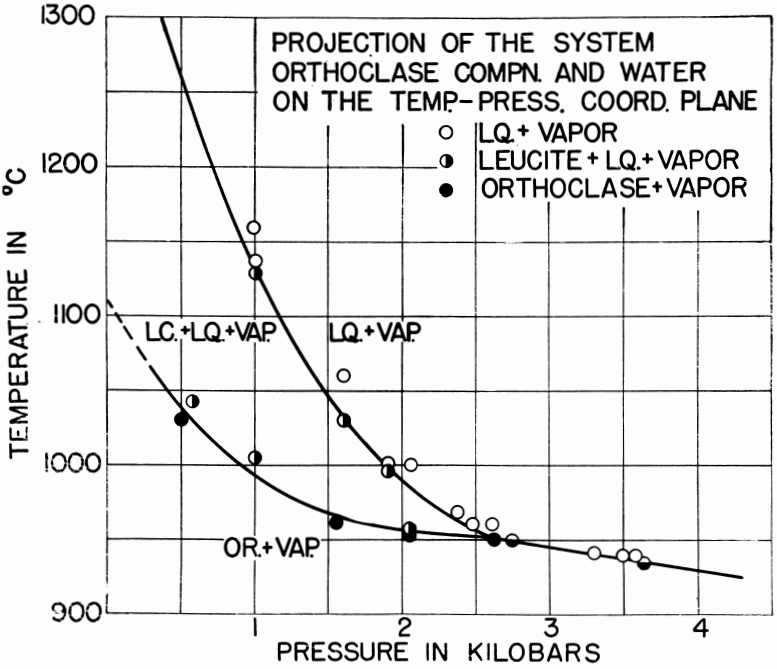

Fig. 5. Freezing-point curves in the system, orthoclase composition and water projected on the temperature-pressure coördinate plane. The lower curve from 0.001 to 2.6 kilobars pressure is the incongruent melting curve of orthoclase. Above 2.6 kilobars orthoclase melts congruently and the leucite field has disappeared.

GENERAL CONSIDERATIONS.

In order to demonstrate the tremendous pressures that may be built up in such systems as these on cooling and crystallizing let us assume we have an albite-water solution at a pressure of 606 bars (corresponding to a depth of about 2¼ km.) and temperature of 1100° C.; the water content of this solution at saturation is 4.2 weight per cent. Now let the solution cool—it will at first follow a line of slope $(\partial T/\partial p)_{x_2} = 1.32$ in Fig. 3 so that when it has reached the projected freezing-point curve, i.e. when the temperature has fallen to 960°, the pressure will have dropped to 500 bars. At this stage albite will begin to crystallize from solution and, if the enclosing chamber walls of the silicate-water melt are impervious and competent to retain the pressure developed, the system will move along

the freezing-point curve. When the temperature has fallen an additional 59°, i.e. to 819° C., the pressure will have increased sixfold to a value of 3000 bars. At this stage the system will consist of 56 per cent albite crystals and a melt containing 9.5 per cent water (see Fig. 4) if we neglect the amount of water that must be evaporated to build up this pressure.

Again if we have a melt saturated with water at 900° C. and 1000 bars pressure and let the temperature fall 81°, i.e. to 818°, under the same conditions as above the pressure will have risen threefold to 3000 bars. At this stage the system will consist of 37.2 per cent albite crystals and 62.8 per cent melt containing 9.5 per cent water.

If there is no minimum temperature on the freezing-point curve this development of pressure can continue until all the albite has crystallized. If a minimum freezing-point temperature exists then the pressure corresponding to this temperature will be the maximum that can be developed by cooling with crystallization. However, such a minimum must correspond to a pressure exceeding 4000 bars and perhaps 5000 bars as judged by the probable prolongation of the curve. Because of the limited miscibility relations no pressure maximum exists on the freezing-point curve.

In a previous paper[13] the liquidus curve for granite in the system "granite-water" was extrapolated to atmospheric pressure by an incorrect analogy. Extrapolation based on the systems studied herein would put the liquidus temperature of granite at atmospheric pressure as about 950° which is 100° lower than the previous estimate. This value seems not unreasonable and not inconsistent with the results of Greig, Shepherd, and Merwin[14] who found that in one week at 800° powdered granite became half liquid. The projected liquidus curve on the T-p coördinate plane for a granite-water system will be a discontinuous one but, as judged from the similarity to the albite-water system in solubility relations and from the few freezing-point measurements made, should roughly correspond to the crystallization curve of the latter with the exception that corresponding temperatures will be about 200° lower in the granite-water system. This development of pressure on crystallization should therefore be directly applicable to a

[14] Carnegie Inst. of Wash., Year Book No. 30, 77-78, 1931.

hydrous granite magma and thus indicates a very potent source of pressure development for explosive igneous activity.

This picture may be compared with that suggested by Morey[15] who used as analogy the system, H_2O—K_2SiO_3—SiO_2, studied by Morey and Fenner. They found that a maximum pressure of 340 bars existed on the freezing-point curve of the mixture $KHSi_2O_5$ and quartz, i.e. a point where $dp/dt = 0$, which does not exist in the systems studied by the writer. In the example used by Morey the maximum pressure that could be developed would then be of the order of 340 bars instead of the thousands of bars pressure realized herein.

In the orthoclase composition—water system, if we start with a melt at 1130° and 1000 bars and let the system cool in a competent chamber, leucite will crystallize and the system move along the liquidus curve, the solution increasing in water content and decreasing in silica content until it reaches a pressure of about 2600 bars and 955°. At this point leucite will redissolve and orthoclase crystallize from the solution. On further cooling orthoclase will continue to crystallize and at 930° the pressure will have increased fourfold to 4000 bars. If the chamber were not competent to withstand more than 1000 bars internal pressure, then the system instead of following the liquidus curve would follow the 1000 bar isopiestic line with leucite crystallizing out until a temperature of approximately 990° was reached, at which point orthoclase would separate out and leucite redissolve if cooling were slow enough; if the cooling rate were rapid at this point then one would obtain a glass studded with leucite crystals.

[15] Morey, G. W.: J. Wash. Acad. Sci. 12, 219-230, 1922.