

THE EFFECTS OF H₂O IN SILICATE SYSTEMS¹

G. J. WASSERBURG

Division of the Geological Sciences, California Institute of Technology

ABSTRACT

A theoretical discussion of the role of water in simple silicate melts is presented. It is shown that to a good approximation in the region $T \approx 1,000^\circ \text{C.}$, $P < 2.3 \times 10^3$ bars, both the solubility of water in an NaAlSi₃O₈ melt and the depression of the freezing point of albite from such a melt are grossly governed by a perfect-solution law. A more detailed theory is presented in which the entropy of mixing for an ideal mixture of the bridging oxygen atoms of the silicate with the oxygen atoms of the water is calculated. This model is shown to be in good agreement with the observed phase diagram of the NaAlSi₃O₈-H₂O system.

The depression of the melting point in silicate systems as affected by dissolved H₂O is a problem of considerable geological interest. The pioneer work done by Goranson has shown that relatively few weight per cent of dissolved water in silicate melts can depress the transition temperature by considerable amounts. Goranson has presented some theoretical discussion of his experimental observations. A more detailed explanation of the various effects has not, however, to the author's knowledge, been obtained. It is the purpose of this paper to present a more complete explanation for the phenomena of freezing-point depression and the solubility of water in simple silicate systems.

For simplicity, we shall discuss the case of equilibrium in a two-component system. The components are (1) water and (2) silicate. The possible phases assumed to exist are as follows: α , supercritical water (pure); β , silicate melt and dissolved water; and γ , a water-free crystalline silicate, identical in composition to the anhydrous melt. The pressure is assumed to be due to the water. Using the notation given by Guggenheim (1949), the following equations express the conditions of thermodynamic equilibrium for the system under consideration. In the liquidus field,

$$\mu_1^\alpha = \frac{1}{N_1^\alpha} G^\alpha = \mu_1^\beta. \quad (1)$$

For the equilibrium of crystal, melt, and H₂O vapor,

$$\mu_1^\alpha = \mu_1^\beta, \quad (2a)$$

$$\mu_2^\beta = \mu_2^\gamma = \frac{1}{N_2^\gamma} G^\gamma, \quad (2b)$$

where μ_i^k is the chemical potential of component i in phase k ; N_i^k and x_i^k are, respectively, the number of moles and the mole fraction of component i in phase k ; and G^k is the Gibbs free energy of phase k . The symbol λ_i^k will be used to represent the relative activity of component i in phase k , relative to a given standard state.

In terms of activities we may write

$$\mu_1^\alpha(T, P) = \mu_1^{\beta_0}(T, P) + RT \ln \lambda_1^\beta(T, P, x_1^\beta), \quad (1)$$

$$\mu_1^\alpha(T, P) = \mu_1^{\beta_0}(T, P) + RT \ln \lambda_1^\beta(T, P, x_1^\beta), \quad (2a)$$

$$\mu_2^\gamma(T, P) = \mu_2^{\beta_0}(T, P) + RT \ln \lambda_2^\beta(T, P, x_2^\beta). \quad (2b)$$

Here $\lambda_i^{\beta_0}(T, P)$ is the chemical potential of component i in phase β at some standard state, i.e., when $\lambda_i^{\beta_0}(T_0, P_0, x) = 1$. For convenience we will choose $\lambda_2^{\beta_0}(T_0, 0, 1) = 1$, where T_0 is the melting point of the silicate at $P = 0$ (in the absence of water). Assuming the λ 's to be independent of T and P , the differential form of equation (1) for a constant temperature reduces to

$$V_1^\alpha dP = V_1^\beta dP + \mathcal{R}T d \ln \lambda_1^\beta(x_1^\beta).$$

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Assuming λ_1^β to be a monotonic function of x_1^β , it follows that $(\partial x_1^\beta / \partial P)_T = 0$ when $V_1^\alpha = V_1^\beta$. From the solubility curves determined by Goranson, it is seen that saturation is approached at about 3 kilobars for the temperature ranges studied. The density of water is approximately 0.4 gm/cc (Kennedy, 1950) at 1,000° C. and 2,500 bars. We may estimate that $\rho = 0.5$ gm/cc at 3 kilobars in the 900° C. temperature range. This means that the molar volume of H₂O in silicate melts is approximately 36 cc/mol.

If, in the P, T region under consideration, $PV = RT$ for the pure water phase, and V_1^β remains relatively constant, we obtain

$$\ln \frac{P}{P_0} - \frac{V_1^\beta (P - P_0)}{RT} = \ln \left\{ \frac{\lambda_1^\beta (x_1^\beta)}{\lambda_1^\beta (x_0)} \right\}$$

or

$$\lambda_1^\beta (x_1^\beta) = \frac{P}{P_0} \lambda_1^\beta (x_0) e^{-V_1^\beta (P - P_0) / RT}, \quad (3)$$

where P_0 and x_0 are the end-points of integration.

An examination of experimental data (Kennedy, 1950) shows that equation (3) will hold rather well in the region $P \leq 2.3 \times 10^3$ bars and $T \approx 1,000^\circ$ C. Outside this region the approximation that water is a perfect gas breaks down badly. The right-hand side of equation (3) is seen to have a maximum at $P = RT/V_1^\beta$ and to diminish for $P > RT/V_1^\beta$. The existence of this maximum and its position depend explicitly on the use of the perfect-gas approximation and the assumption that V_1^β is independent of P . Both assumptions fail when the pressure is very great. A true extremum will occur for x_1^β when $\Delta V = V_1^\alpha - V_1^\beta = 0$, as discussed earlier.

If a confining pressure P^\dagger is applied to the melt in addition to the water pressure, the governing equation is

$$\begin{aligned} \frac{\partial \mu_1^\alpha}{\partial P^\dagger} dP^\dagger = 0 &= \frac{\partial \mu_1^\beta}{\partial P^\dagger} dP^\dagger + \frac{\partial \mu_1^\beta}{\partial x_1^\beta} dx_1^\beta \\ &= V_1^\beta dP^\dagger + RT d \{ \ln \lambda_1^\beta \} \end{aligned}$$

or

$$\lambda_1^\beta (x_1^\beta, P, P^\dagger) = \lambda_1^\beta (x_1^\beta, P, 0) e^{-V_1^\beta (P^\dagger - P) / RT}.$$

Therefore, when the system is in equilibrium at a fixed temperature T under a water pressure P and a confining pressure P^\dagger in excess of the water pressure, the activity is

$$\lambda_1^\beta (x_1^\beta) = \lambda_1^\beta (x_0) \frac{P}{P_0} e^{-(V_1^\beta (P - P_0) + V_1^\beta P^\dagger) / RT},$$

where x_0 is the mol fraction of water dissolved in the melt at temperature T and water pressure P_0 at zero excess confining pressure.

The relationship between P^\dagger and P , such that a constant concentration x_1^β and temperature T is maintained, is

$$V_1^\alpha dP = V_1^\beta dP + V_1^\beta dP^\dagger$$

or

$$\left(\frac{\partial P}{\partial P^\dagger} \right)_{x_1^\beta, T} = \frac{1}{V_1^\alpha / V_1^\beta - 1}.$$

These results were derived previously by Goranson (1937).

If the solution were ideal, $[\lambda_1^\beta = x_1^\beta]$, we would have, using equation (3),

$$x_1^\beta = \frac{x_0}{P_0} P e^{-V_1^\beta (P - P_0) / RT}. \quad (4)$$

Under the assumed conditions, equation (4) represents the mol fraction of dissolved water in the melt as a function of pressure at a constant temperature. To a good first-order approximation, this may be written as

$$x_1^\beta = \frac{P}{\frac{0P}{x_0} \left\{ 1 - P_0 \frac{V_1^\beta}{RT} \right\} + \frac{P_0 V_1^\beta P}{x_0 RT}} = \frac{P}{A + BP}.$$

This relationship is of the same simple form as was obtained experimentally by Goranson. He has found that the weight per cent of water dissolved in some silicate melts can be represented by a formula of the form $P/(a + bP)$, which is equivalent to $x_1^\beta = P/A' + B'P$.

For the crystal-melt equilibrium we ob-

tain, by Taylor expansion of equation (2b), to the accuracy required,

$$-S_2^\gamma(T_0, 0)(T - T_0) - \frac{1}{2}C_2^\gamma \frac{(T - T_0)^2}{T_0} \\ + V_2^\gamma P = RT \ln \lambda_2^\beta - S_2^\beta(T_0, 0)(T - T_0) \\ - \frac{1}{2}C_2^\beta \frac{(T - T_0)^2}{T_0} + V_2^\beta P.$$

This neglects second-order terms in $\partial^2/\partial P^2$ and $\partial^2/\partial P\partial T$; therefore,

$$\ln \lambda_2^\beta = \\ -\frac{\Delta S_2^0(T_0 - T)}{RT} + \frac{\Delta C_P(T_0 - T)^2}{2RTT_0} \quad (5) \\ -\frac{P\Delta V_2}{RT}.$$

This assumes that V_2^γ and V_2^β are constant over the P, T, x range of interest.

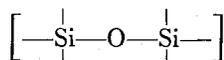
The change in the melting point can be computed if the activity is known. If the solution is again assumed to be ideal, [$\lambda_2^\beta = x_2^\beta$], it is clear that the resulting melting-point depression will be grossly the same as was observed experimentally. In the next section a more detailed theory will be presented. However, the gross effect is that of an ideal solution. It is important to observe (Buerger, 1948) that it is the mole fraction which occurs in the expressions and not the weight fraction. The mole fraction is not related linearly to the weight per cent, the non-linear character being strong in the case that the two components differ considerably in molecular or formula weight. For the system NaAlSi₃O₈-H₂O, 2 per cent by weight of dissolved water corresponds to 22.9 mol per cent. It is therefore not surprising to find large effects caused by a "small" weight per cent of water.

THEORY

The fact that a silicate melt resembles a three-dimensional high polymer suggests the application of a modified form of Flory's theory of linear high-polymer solutions (Meyer and Lohdemann, 1935; Flory, 1941).

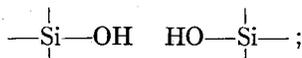
The silicate melt is considered here to be

an essentially rigid structure composed of a tetrahedral segment as the fundamental unit. These units are linked in three dimensions to one another through shared corners,



silicon-oxygen-silicon bridges, or they have oxygens which are unshared with other SiO₄ tetrahedra. We will assume that the partial molar volumes V_1^β and V_2^β for all structural positions are constants. Let N_1 and N_2 represent the number of "molecules" of H₂O and silicate, respectively; r is the number of shared oxygens per "molecule" of silicate; and N_0 is Avogadro's number. We may calculate the entropy of mixing S_m by using the Boltzmann expression $S_m = k \ln \Omega$, where Ω is the number of accessible states. It will be assumed that the energy differences between the states discussed are negligible.

Consider a volume $V = 1/N_0\{N_1V_1^\beta + N_2V_2^\beta\}$ occupied by the mixture of silicate melt and water molecules. The water may occur (a) as H₂O molecules segregated in small pockets or in positions hydrating cations (other than silicon) or (b) it may break the rN_2 oxygen bridges, forming

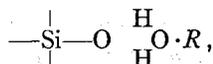


or (c) it may convert unshared oxygens in SiO₄ tetrahedra

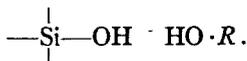


Here R represents a cation which is not in a silicon position. Because of the relatively large volume associated with cation holes (not Si), many H₂O molecules will tend to appear in these "spaces."

Positions a and c are considered equivalent, in that the water occurs in vacancies and can either bridge the unshared oxygen-cation positions as



or similarly as



As far as the oxygen positions are concerned, positions *a* and *c* are indistinguishable. Positions other than *b* will be considered to exist in rather regularly arranged fixed volumes throughout the structure of the silicate melt. Positions *b* are fixed in the quasi-crystalline liquid. From the original assumptions regarding the volume, we may use the following artifice to facilitate the enumeration of

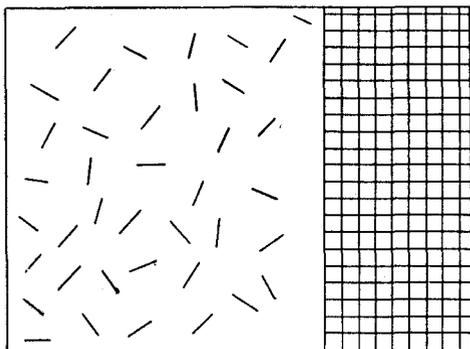


FIG. 1a

FIG. 1a.— rN_2 bridge positions (*dashes*) and N_1 "water positions" (*squares*). Water positions collected on right-hand side.

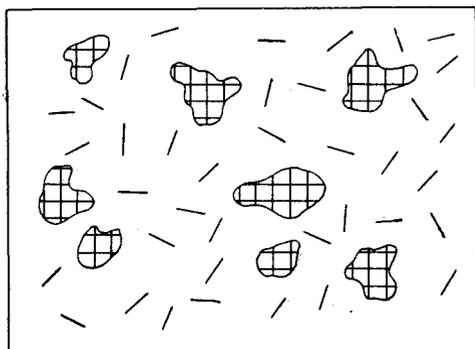


FIG. 1b

FIG. 1b.— rN_2 bridge positions (*dashes*) and N_1 "water positions" (*squares*) distributed in a fixed, random array with several water molecules in each group.

Ω . The total free volume (positions *a* and *c*) available to the water is $v_1 = N_1 V_1^\beta / N_0$, corresponding to N_1 positions. For simplicity, we will represent this as in figures 1a and 1b. Here the *a* and *c* positions, which we shall call "water positions," are collected into one unit. They should actually be distributed in some more random but fixed fashion throughout the silicate melt (see fig. 1b). The minimum volume of each water unit is assumed to be several water molecules in size. The assumed large volume of each of these water groups tends to minimize the contribution to S_m from their various arrangements.

In addition to these N_1 units, there are available rN_2 oxygen bridges. When the bridge is ruptured by the formation of two

OH bonds, an increase in volume of V_1^β / N_0 occurs. We shall first consider the counting of positions in this rigid structure of oxygen bridges (indicated as dashes in fig. 1) and water positions, ignoring the dilation.

In this array of positions there are $N_1 + rN_2$ ways of placing the first water molecule, $N_1 + rN_2 - 1$ ways for the second, and, in total,

$$\Omega = \frac{(N_1 + rN_2)(N_1 + rN_2 - 1) \dots (rN_2 + 1)}{N_1!}$$

$$\Omega = \frac{(N_1 + rN_2)!}{N_1!(rN_2)!}$$

distinguishable configurations. (If there exist, in addition to the rN_2 bridging positions, q vacancies per molecule of silicate, the number of accessible states will be simply that obtained by substituting $q + r$ for r . These vacancies would, however, contribute nothing to the partial molar volume V_1^β . This case will not be considered further.) Having assigned the N_1 H_2O molecules to any given set of positions (N_p , "water positions," and $[N_1 - N_p]$ bridge positions), we may permit the silicate structure to expand to accommodate the units which rupture the $(N_1 - N_p)$ bridges. The silicate will expand an amount $(N_1 - N_p)(V_1^\beta / N_0)$, filling the remaining volume left by the unfilled "water positions."

The value of Ω calculated is just that for

an ideal mixture of rN_2 bridging oxygen atoms of the silicate with N_1 oxygen atoms of the H₂O, the two kinds being distinguishable.

The average fraction of water molecules occupying positions a and c , compared to all possible positions a , b , and c , can be shown to be

$$\bar{N}_p/N_1 = \frac{N_1}{N_1 + rN_2} = \frac{x_1^\beta}{1 + (r-1)x_2^\beta}.$$

This should be compared with the fraction of water as H₂O to water as OH and H₂O in silicate glasses as a function of concentration and the index r .

(Note: For dilute solutions [$N_1 \ll rN_2$] or for solutions where only positions b exist, the positions occupied will be bridging positions and so Ω may be computed by ignoring the water associations. This gives

$$\Omega^* = \frac{[rN_2]!}{N_1! [rN_2 - N_1]!},$$

$$\frac{S_m^*}{R} = rN_2^\beta \ln rN_2^\beta - N_1^\beta \ln N_1^\beta - [rN_2^\beta - N_1^\beta] \ln [rN_2^\beta - N_1^\beta].$$

As N_1 approaches rN_2 , the deviation of Ω^* from Ω becomes apparent.)

Using Sterling's approximation, we obtain

$$S_m = -RN_1^\beta \ln \left\{ \frac{N_1^\beta}{N_1^\beta + rN_2^\beta} \right\} - RrN_2^\beta \ln \left\{ \frac{rN_2^\beta}{N_1^\beta + rN_2^\beta} \right\},$$

$$G^\beta = N_1^\beta \mu_1^{\beta_0} + N_2^\beta \mu_2^{\beta_0} - TS_m = N_1^\beta \mu_1^{\beta_0} + N_2^\beta \mu_2^{\beta_0}$$

$$+ RTN_1^\beta \ln \left\{ \frac{N_1^\beta}{N_1^\beta + rN_2^\beta} \right\} + RT rN_2^\beta \ln \left\{ \frac{rN_2^\beta}{N_1^\beta + rN_2^\beta} \right\}, \quad (6)$$

where $\mu_2^{\beta_0}$ is the chemical potential of the pure silicate melt at T and P and $\mu_1^{\beta_0}$ is the

chemical potential of water in the melt at great water concentration.

It follows from $\mu_i^k \equiv \partial G^k / \partial N_i^k$ that

$$\mu_1^\beta = \mu_1^{\beta_0}(T, P) + RT \ln \left\{ \frac{x_1^\beta}{x_1^\beta + rx_2^\beta} \right\}, \quad (7a)$$

$$\mu_2^\beta = \mu_2^{\beta_0}(T, P) + RT r \ln \left\{ \frac{rx_2^\beta}{x_1^\beta + rx_2^\beta} \right\}, \quad (7b)$$

$$\lambda_1^\beta = \frac{x_1^\beta}{r - (r-1)x_1^\beta}, \quad (8a)$$

$$\ln \lambda_2^\beta = r \ln \left\{ \frac{rx_2^\beta}{1 + (r-1)x_2^\beta} \right\}. \quad (8b)$$

Inspection of equation (6) shows that G^β is the Gibbs free energy of an "ideal" mixture of N_1 molecules and $\eta_2 \equiv rN_2$ "molecular segments." That is,

$$\frac{1}{N_0} \frac{\partial G^\beta}{\partial \eta_2} = \frac{1}{r} \frac{\partial G^\beta}{\partial N_2^\beta} = \frac{\mu_1^{\beta_0}}{r} + RT \ln \left\{ \frac{\eta_2}{N_1 + \eta_2} \right\}.$$

This can be interpreted as a perfect solution of the oxygen atoms of H₂O and of the bridging oxygens in the silicate. With equations (8a), (8b), (3), and (5) we obtain the equations which govern the freezing-point depression. A graph of the freezing point of albite as a function of the mol fraction of dissolved water, x_1^β , is given in figure 2. The circled points are the experimental data of Goranson, as given in *The handbook of physical constants*.

The thermodynamic data used were $\Delta S^0/R = 4.620$, $\Delta C_P/R = 1.89$, $\Delta V/RT_0 = 0.93 \times 10^{-4}$ bars⁻¹, and $T_0 = 1,388^\circ$ K. These values were taken from *The handbook of physical constants*.

Using equations (3) and (8a), the solubility of water in albite has been computed at a constant temperature. The integration constant is taken from one of Goranson's experimental points. As mentioned earlier, V_1^β is assumed to be 36 cc/mol. The calculated curve is shown in figure 3, along with Goranson's experimental data.

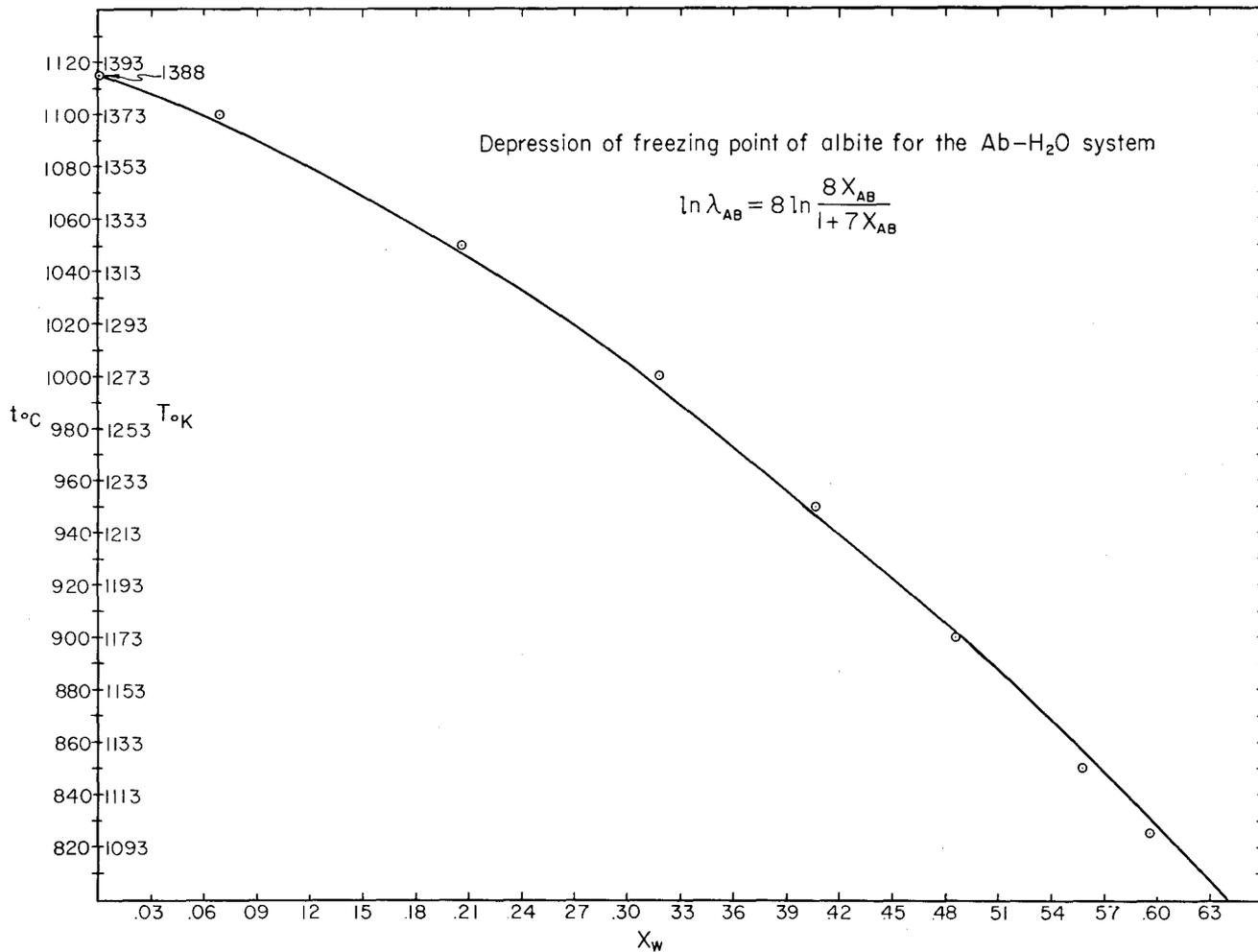


FIG. 2.—The depression of the freezing point of albite as a function of the mol fraction of dissolved water. Calculated for $\ln \lambda_2^g = 8 \ln \{8 x_2^g / (1 + 7 x_2^g)\} \cdot x_1^g \equiv x_w$.

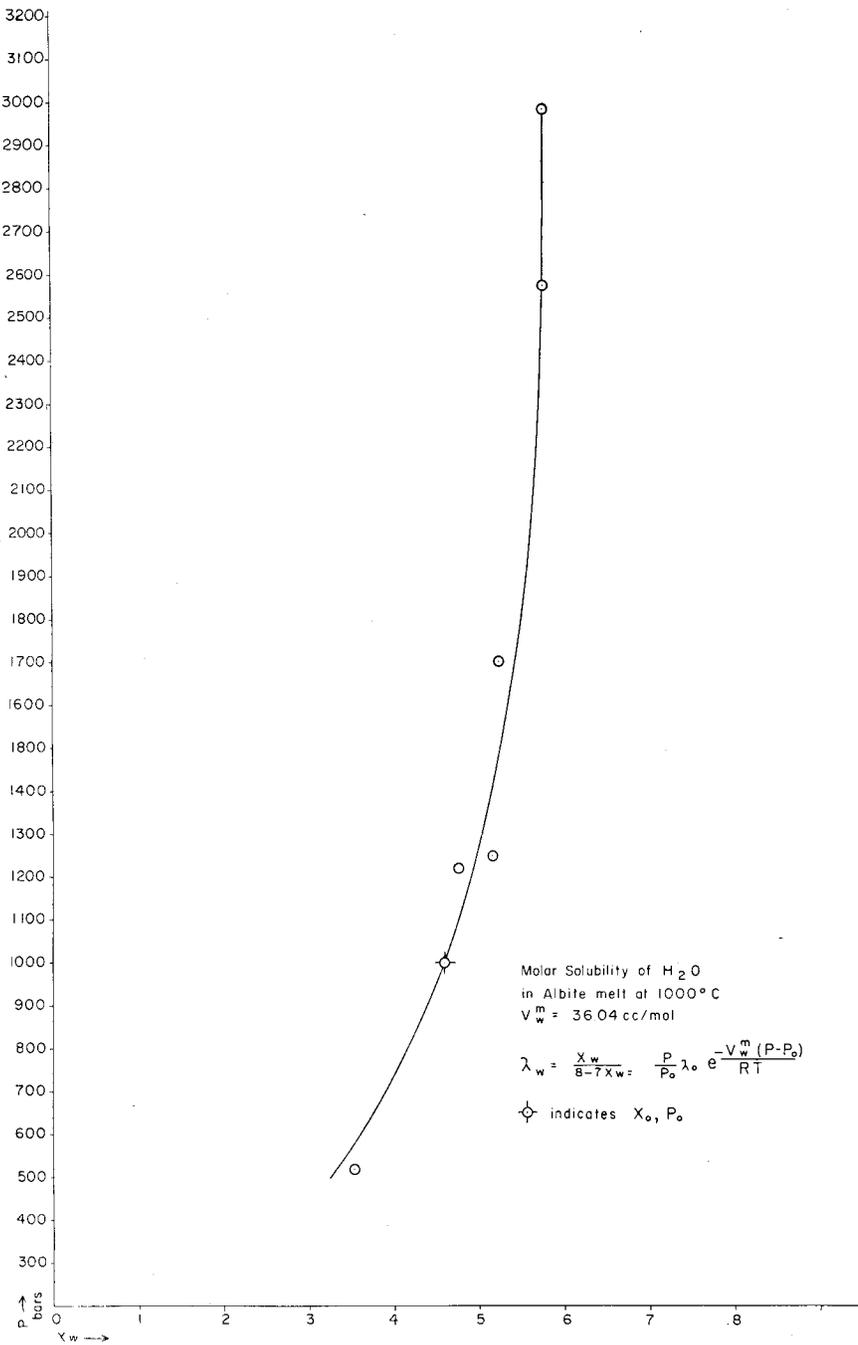


FIG. 3.—Mol fraction of H₂O dissolved in NaAlSi₃O₈ melt at 1,000° C. as a function of pressure. Circles indicate experimental points of Goranson. Curve drawn from $\lambda_1^\beta = x_1^\beta / (8 - 7x_1^\beta) \cdot x^\beta \equiv x_w$.

The agreement is extraordinary, considering the crudity of the model. Although the final calculation is not sensitive to changes in r and V_1^{β} , the agreement should not be taken as strong proof of the preceding theory, as the assumptions involved ignored bonding-energy differences and the use of an extremely simple-minded counting procedure. From considerations of the perfect-solution case, it is clear that any increase in the entropy of mixing would yield theoretical results in better accord with the experimental data. Inspection of the solubility data for granite-H₂O and KAlSi₃O₈-H₂O melts (Goranson, 1931) indicates that it is necessary to assume values for $\mu_1^{\beta_0}$ different from those obtained for the NaAlSi₃O₈-H₂O system. This clearly indicates that it is unsatisfactory to ignore energy effects.

A calculation of the depression of the minimum in the KAlSi₃O₈-NaAlSi₃O₈-H₂O system was made by neglecting the slight composition shift of the minimum. The entropy of fusion was assumed to be $\Delta S^0/R = 6.18$. This may be in error by as much as 15 per cent. The minimum is calculated to shift from 1,063° (dry) to 866° C. at 7.5 weight per cent water and 1 kilobar and to 843° C. at 9 weight per cent water and 2 kilobars. This can be compared with the data of 844° and 780° C. for the same compositions, as determined by Bowen and Tuttle (1950).

Using an extension of the calculation presented earlier to multicomponent systems, a calculation of the eutectic of the diopside-anorthite-water system at 5 kilobars was made. The non-ideality of the binary diop-

side-anorthite system was corrected for, using a regular solution term (Bowen, 1928). The results are $T = 1,120^\circ \text{C.}$ and $x_{\text{Di}}/x_{\text{An}} = 0.7577$ (assuming 8.8 per cent by weight dissolved water) compared with the experimental results of $T = 1,095^\circ \text{C.}$ and $x_{\text{Di}}/x_{\text{An}} = 0.475$ obtained by Yoder (1955). It is clear that the gross effect is obtained from the calculation. Nonetheless, the results are far from exact agreement. It is hoped that new experimental studies of water-silicate systems will permit a more thorough understanding of the role of water in melts.

Note added in proof.—R. H. Jahns has called the author's attention to a recent publication, "A Note on the System SiO₂-H₂O" by O. F. Tuttle and J. L. England (Bull. Geol. Soc. America, v. 66, p. 149, 1955). Tuttle and England report a lowering of the melting point of SiO₂ by 580° C. at 2 kilobars' water pressure. They report a solubility of 2.3 weight per cent water in the melt at 1.2 kilobars and 1,300° C. In order to explain these effects on the basis of the theory presented earlier, it would be necessary for the melt to contain 6 weight per cent water at 2 kilobars' pressure and 1,150° C. While the results which they report can be explained qualitatively on the basis of the preceding theory, they could not have been predicted quantitatively.

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