

SILICATE-WATER SYSTEMS: THE "OSMOTIC PRESSURE" OF SILICATE MELTS

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The problem of determining the solubility of water in silicate melts when the two phases are subjected to the same confining pressure has occupied the attention of the writer for some time; and results of his work have been published in two previous papers (1931, 1936). There is, however, another important aspect of this work that merits attention, namely the evaluation of the solubility when the hydrostatic pressure is not the same on the two phases, water and silicate solution. The second case, with which this paper is concerned, is important in problems associated with volcanism and certain other phases of igneous activity.

Differential hydrostatic pressure on silicate and water would occur if the country rock surrounding a magma were pervious to water and impervious to the silicate melt; for such a case the magma would be under a pressure equivalent to the overlying rock whereas the water would be at a pressure equivalent to its own head. Solution of this problem is then related to that of the phenomenon described as "osmotic pressure."

As ordinarily stated, however, osmotic pressure refers to a condition wherein the membrane separating the solvent and solution is permeable only to the solvent whereas for the problem here considered the membrane is assumed to be permeable only to the solute which in this problem is water. Solute is a term used to designate the more dilute component and solvent the more concentrated component of a solution. Ordinarily water is the solvent but here it is the more dilute phase, therefore the solute, and the silicate melt has the role of solvent.

The direct determination of the solubility relations under these conditions would be extremely difficult to carry out experimentally and has therefore been obtained from other thermodynamic properties of the system. As it does not seem to be generally understood that two equally valid expressions may be written for the osmotic pressure, with usage and "rigor" somewhat divided between the two expressions, the thermodynamic relations will be formulated *first* for the case where the membrane is permeable only to the solvent and *secondly* where it is permeable only to the solute.

The following statement of the phenomenon seems to be generally accepted as the definition of osmotic pressure and is applicable to our first case. If a vessel contains a solution, consisting of solvent (component 1) and solute (component 2), which is separated from the pure substance "1" by a membrane permeable only to substance "1," and both phases

are at the same temperature and pressure, then the solution will tend to become more dilute by transference of solvent from the pure solvent phase. The increase in pressure that must be exerted on the solution in order to maintain equilibrium is called the osmotic pressure.

To conform with this statement let there be two phases, one of pure substance "1" and the other a solution of component "2" in "1," both at the same temperature but at different pressures such that they are in equilibrium with respect to component "1." Then the molar chemical potentials of "1" are the same in each phase or

$$\bar{F}_1(T, p, N_1) = F_1(T, p_0) \quad (1)$$

where $\bar{F}_1(T, p, N_1)$ denotes the molar chemical potential ($M_1\mu_1$) of "1" in the solution at temperature T , pressure p , and mol fraction N_1 of "1"; $F_1(T, p_0)$ denotes the free energy per mole (ξ/M_1) of the pure substance "1" at T and p_0 .

If $F_1(T, p)$ be subtracted from both sides of equation (1) then

$$\begin{aligned} \bar{F}_1(T, p, N_1) - F_1(T, p) &= - \int_{p_0}^p v \, dp \\ &\doteq -[v](p - p_0) = -[v]\pi \end{aligned} \quad (2a)$$

where v denotes the molar volume of pure substance "1", the square brackets indicating a mean value of v has been chosen for the pressure interval p_0 to p . (T, p, N_1) denotes the state in which the solution exists when in equilibrium with pure substance "1" at (T, p_0) . The left hand side of the equation is equivalent to $RT \ln a_1(T, p, N_1)$ where a_1 is the activity of the solvent.

If $\bar{F}_1(T, p_0, N_1)$ be subtracted from each side of equation (1) then

$$\begin{aligned} \bar{F}_1(T, p_0, N_1) - F_1(T, p_0) &= - \int_{p_0}^p \bar{v}_1 \, dp \\ &\doteq -[\bar{v}_1](p - p_0) = -[\bar{v}_1]\pi \end{aligned} \quad (2b)$$

where \bar{v}_1 denotes the partial molar (fictive) volume of solvent in the solution; (T, p_0, N_1) denotes the state in which the solution would exist if the pressure p were reduced to p_0 , temperature and concentration remaining constant. The left hand side of (2b) is equivalent to $RT \ln a_1(T, p_0, N_1)$.

Here are then two different expressions for osmotic pressure which become identical only if the solution can be considered as ideal, for then (2a) becomes

$$RT \ln N_1 = -[v]\pi$$

and (2b) becomes

$$RT \ln N_1 = -[\bar{v}_1]\pi = -[v]\pi$$

because $v = \bar{v}_1$ for an ideal solution.

A very useful function introduced by Bjerrum is the osmotic coefficient $g = (\pi/\pi_{\text{ideal}})$, here

$$g = \frac{\bar{F}_1(T, p, N_1) - F_1(T, p)}{RT \ln N_1} = \frac{\ln a_1(T, p, N_1)}{\ln N_1},$$

or

$$g_0 = \frac{\bar{F}_1(T, p_0, N_1) - F_1(T, p_0)}{RT \ln N_1} = \frac{\ln a_1(T, p_0, N_1)}{\ln N_1},$$

and the two expressions for g lose their identity unless it be specified to which of the two previous states p or p_0 the solution is referred.

Lewis and Randall's (1923, p. 214) expression is equivalent to (2b); Donnan and Guggenheim (1932, p. 357) write the osmotic pressure as (2a). Guggenheim (1933, pp. 85, 109) writes two expressions which would apply for (2b) but as they are given under a heading of ideal solutions it would be immaterial which (2) he took as the expression; however, for a non-ideal solution he writes (1933, p. 120) $\pi = g(\pi_{\text{ideal}})$ in which π seems to be a mixture of (2a) and (2b) because he writes \bar{v}_1 instead of v and yet states that g applies to the higher pressure p , which would not be correct. It is immaterial which expression be used provided the distinction in states be made because (2a) and (2b) are not in general equal.

The *second case* wherein the solute "2" is the permeable phase has, apparently, heretofore not received any attention; a similar treatment is also applicable here. For this second case we have, for equilibrium,

$$\bar{F}_2(T, p, N_2) = F_2(T, p_0) \tag{3}$$

where $p > p_0$, and N_2 denotes the mole fraction of solute (in this problem it is water). Then

$$\bar{F}_2(T, p, N_2) - \bar{F}_2(T, p, N_{2s}) = - \int_{p_0}^p v dp = -[v]\pi \tag{4a}$$

or

$$a_2(T, p, N_2)/a_2(T, p, N_{2s}) = \exp - \int_{p_0}^p \frac{v}{RT} dp \tag{4b}$$

where a_2 denotes the activity of the water in the solution, v the molar volume of the water phase, and (T, p, N_{2s}) the state in which the solution would exist if in equilibrium with the water phase at (T, p) , i.e. $p_0 = p$. If the solution be ideal this expression reduces to

$$N_2/N_{2s} = \exp - \int_{p_0}^p \frac{v}{RT} dp \quad (4c)$$

The expression corresponding to (2b) is of no interest to us here and is consequently omitted; to obtain it one need only substitute subscript 2 for 1, but there will be no corresponding activity function for this case. The treatment of these two cases is therefore very similar. In the first case, however, if $p \equiv p_0$ then the solution becomes more and more dilute by continual transference of phase 1 into the solution, whereas in the second case if $p \equiv p_0$ the transference of phase 2 into the solution continues only until the solution becomes saturated with respect to 2. Thus, in order to express the left hand sides of the equations for these two cases in terms of activities, their respective treatments must vary slightly to conform with the definitions of activity (Goranson, 1937).¹

In order to evaluate expression (4) for a silicate melt and water it is necessary to know the p - v isotherm for water at the temperature T considered; furthermore, in order to express activity in terms of concentration, one must know the chemical potential of the water in the silicate solution as a function of the concentration.

The 1000°-isotherm of v was plotted as a function of p using the following data as a starting point: The data of Keenan and Keyes (1936) were used to obtain the T - p - v relations of water at low pressures. The writer has made, at high pressures, a few rough measurements at 1000° C incidental to determining the feasibility of a method for obtaining T - p - v data at high temperatures and pressures. From this plot $v dp$ was then integrated, analytically over some portions of the curve and graphically over other portions. These data were then expressed in terms of fugacity ratios and correlated with the activity ratios of the water in solution expressed in equation (4b). The relation of activity coefficient, and thus of activity, to concentration was obtained from experimentally determined solubility and freezing point data for the system albite-water. The data presented herein are therefore calculated for the system albite melt and water on the 1000° isotherm. The similarity in solubility relations of albite-water and granite-water systems would indicate an equivalent similarity here.

The data, presented in the following table and figure, have been calculated for confining pressures, p , on the silicate melt of 4000, 3000, and 2000 bars. The first column in the table expresses the pressure of the water phase and the second column expresses the hydrostatic pressure on the silicate solution minus that of the water phase, or osmotic pressure of the silicate solution for the corresponding concentration given in the third column as weight per cent of water in solution in the silicate melt.

¹ The definition of activity is as adopted by the writer; for other definitions of activity these relations will be correspondingly altered.

TABLE 1. THE OSMOTIC PRESSURE (COLUMN 2) OF ALBITE-WATER SOLUTION IS GIVEN AS A FUNCTION OF WEIGHT PER CENT OF WATER IN SOLUTION (COLUMN 3) FOR DIFFERENT SILICATE SOLUTION PRESSURES, p AT 1000°C.

p_0 bars	$\pi = p - p_0$	Wt. per cent of water in solution	Weight per cent of water in solution for $p = p_0$
$p = 4000$ bars. $T = 1000^\circ$			
4000	0	9.0	9.0
3500	500	5.6	8.7
3000	1000	3.8	8.3
2500	1500	2.8	8.0
2000	2000	2.0	7.4
1500	2500	1.4	6.6
1000	3000	0.84	5.5
500	3500	0.48	3.6
$p = 3000$ bars. $T = 1000^\circ$			
3000	0	8.3	8.3
2500	500	5.3	8.0
2000	1000	3.45	7.4
1500	1500	2.3	6.6
1000	2000	1.35	5.5
500	2500	0.64	3.6
$p = 2000$ bars. $T = 1000^\circ$			
2000	0	7.4	7.4
1500	500	4.4	6.6
1000	1000	2.5	5.5
500	1500	1.1	3.6

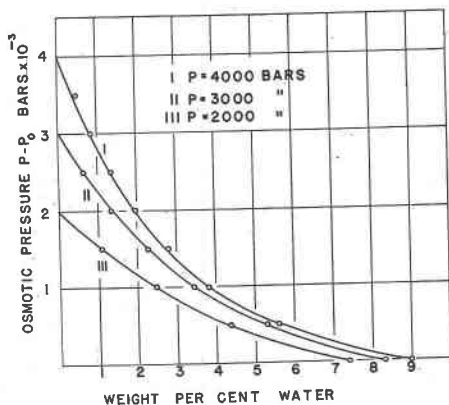


FIG. 1

Osmotic pressure, expressed as kilobars (bars $\times 10^{-3}$), is plotted as a function of the water concentration in the silicate (albite) melt, expressed as weight per cent, for three silicate melt pressures, namely 4, 3, and 2 kilobars (the corresponding curves being marked as I, II, and III respectively).

Columns 2 and 3 thus express the osmotic pressure of the silicate solution as a function of the water concentration. In the fourth column is given, for comparison, the weight per cent of water in solution in the silicate for the condition $p = p_0$, i.e. where the two phases are both at the same pressure p_0 .

The concentrations given in column 3 are considerably less than the corresponding concentrations of column 4, and this fact may explain the rarity of rock glasses of high water content, and why rock glasses with a high water content behave differently on heating from those with a low water content. Dr. E. S. Shepherd has found that when rock glasses of high water content are heated the water begins to come off immediately and continues to come off as heating is continued; furthermore, for slow heating, the glass does not puff up appreciably. When glasses of low water content (1% or less) are heated no appreciable amount of water comes off until somewhere about 850° when the glass puffs up to many times its original size. Again, glasses of high water content are "perlitic" and not clear or clean-looking in texture as are those of low water content. The inference is that in these glasses of high water content the water is not in solution but exists as a separate phase which did not have time to diffuse out of the block and that the consequent unequal contraction of these two phases and resulting strains set up on cooling have caused the perlitic structure which is thus a fracture structure. Deposition of material from the water phase in these minute cracks and pores would give the glass its cloudy appearance.

It will also be evident from these figures that, if an impermeable rock mantle enclosing a silicate-water solution were to become permeable to water, for example by fissuring, permitting the water to escape, the energy available for explosive phenomena is considerably in excess of that previously indicated by the writer from a consideration only of the experimental solubility relations; here is also a possible mechanism for intermittent volcanic activity.

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