

ON THE EFFECT OF PRESSURE ON THE SOLUBILITY OF SOLIDS IN LIQUIDS.

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ABSTRACT.

From an empirical analysis of the data concerning the effect of pressure on the solubility of solids in liquids, the volume changes and compressibilities of solutions, it is concluded that only in somewhat exceptional cases is the solubility of a solid in a liquid raised by pressure, a conclusion which is not novel. However, solutions of the carbonates, sulphates, sulphides, fluorides, and hydroxides of some alkalis, the alkaline earths, and the heavy metals in water, especially where the saturated solutions are very dilute, are definitely to be classed among these exceptional cases, and it is pointed out that the solubilities of these substances may be very significantly increased by pressures below 1000 atmospheres. It seems unlikely that the solubility of silicate minerals in molten silicates will be increased by pressure, and, indeed, the opposite effect is more to be expected, although the complications introduced by structural effects in these liquids render general statements quite risky.

The empirical arguments leading to these conclusions are given in some detail and especial emphasis is laid on the volume change which takes place when the liquid components are mixed, a quantity which at low pressures plays an important rôle in determining the piezochemical behavior of poly-component systems and sometimes renders deductions based solely on the thermodynamic behavior of the pure components inapplicable to solutions. The effect of pressure on the solubility of solids is correlated qualitatively with the types of cohesive forces in the pure components and the solutions involved.

New data on the solubility of cesium bromide in water at pressures up to 1500 atmospheres and the partial volumes of sodium chloride at 1 and 1000 bars pressure and at temperatures between 25 and 95° C. are also included.

INTRODUCTION.

The influence of pressure on the solubility of solids in liquids is of special interest in any study of naturally occurring solutions such as molten silicates or aqueous solutions of sparingly soluble substances, where one part of the problem requires a knowledge of the conditions under which a solution and a number of solids exist at equilibrium under the high pressures prevailing at moderate depths below the surface of the Earth.

In the last two decades it has been found experimentally that the solubilities of solids in water and other solvents may be altered very significantly by pressure changes of a few thousand atmospheres. The pressure-solubility curves that are available for binary systems, however, are of all possible types, and superficially, at least, show few regularities in behavior.

For example, the solubility of sodium chloride in water¹ rises slightly with pressure, passes through a maximum, and then slowly decreases at the highest pressures; the solubility curve for potassium sulphate² in water is similar in shape but the changes in solubility are very much larger. The solubility of ammonium nitrate³ in water falls as the pressure is raised, decreasing steadily from 67.6 per cent at 1 bar (approximately an atmosphere) and 25° C. to 29.7 per cent at 10,000 bars. In Table I we give new data for the solubility of cesium bromide

TABLE I.

The solubility of cesium bromide in water at 25° and different pressures.

Pressure (bars)	Grams of CsBr per 100 grams of water
1	123.7
505	117.9
1010	111.9
1510	106.8

in water at different pressures. These solubilities were measured directly by the method of Adams and Gibson,³ and the results are similar to those for the ammonium nitrate-water system. On the other hand, the solubility of potassium iodide⁴ in water increases with pressure up to 10,000 bars, the solubility of zinc sulphate heptahydrate in water is lowered, while that of cadmium sulphate octotritrahydrate⁵ is raised by pressure. The solubility of barium hydroxide⁶ increases rapidly with pressure in the short range that has been studied.

Analysis of these results, and of a large number of results of determinations of the compressibilities and volume changes on mixing of solutions of salts in water and other solvents does, however, reveal certain regularities which render possible predictions as to the sign and approximate magnitude of

¹ Adams, L. H.: *J. Am. Chem. Soc.*, 53, 3769, 1931.

² Adams, L. H.: *J. Am. Chem. Soc.*, 54, 2229, 1932.

³ Adams, L. H., and Gibson, R. E.: *J. Am. Chem. Soc.*, 54, 4520, 1932.

⁴ Gibson, R. E.: *J. Am. Chem. Soc.*, 56, 865, 1934.

⁵ Cohen, E., and Sinnige, L. R.: *Z. phys. Chem.*, 69, 102, 1909.

⁶ Sill, H. F.: *J. Am. Chem. Soc.*, 38, 2632, 1916.

the change of solubility with pressure in certain types of solutions. The object of this paper is to give some recent results of such an analysis, to relate the effect of pressure on the solubility of solids in liquids to measurable properties of the pure components and of the solutions involved, to give some new examples particularly of the effect of temperature changes, and to present some conclusions of general interest.

THERMODYNAMIC CONSIDERATIONS.

We may begin this discussion with the thermodynamic formula which gives exactly the variation of composition with pressure which must be obeyed if a solid and a solution are to coexist in equilibrium. This may be written as follows:⁷

$$\frac{dx_2}{dP} = - \frac{v_2 - v_2^s}{(\partial\mu_2/\partial x_2)_{P,T}} \quad (1)$$

where x_2 is the composition of the saturated solution, P is the pressure, v_2 is the partial volume of the solute in the solution, v_2^s its specific volume in the solid phase, and $(\partial\mu_2/\partial x_2)_{P,T}$ is the rate of change of the chemical potential of the solute in the solution with change of concentration at the temperature and pressure of the experiment. It follows directly from the two laws of thermodynamics that $(\partial\mu_2/\partial x_2)_{P,T}$ must always be positive, and hence dx_2/dP is positive if $(v_2 - v_2^s)$ for the saturated solution is negative and negative if $(v_2 - v_2^s)$ is positive,⁸ that is to say, pressure will increase or decrease the solubility of a solid according to whether $(v_2 - v_2^s)$ is negative or positive and it becomes of interest to see how the various chemical and physical properties of the pure components and of the solution influence the sign of $(v_2 - v_2^s)$.

In Fig. 1 we have plotted $(v_2 - v_2^s)$ as a function of the concentration for a number of different solutions at room temperature. These values were calculated from direct

⁷ This expression holds for a pure solid, i.e., one of invariant composition in equilibrium with a binary solution. The complete expression, taking into account the possibility of solid solution, is given by Adams: Ref. 1, p. 3803.

⁸ As $(v_2 - v_2^s)$ is exactly the volume increase when 1 gram of the solid dissolves in an infinitely large amount of the saturated solution, we see that equation (1) is a quantitative statement of the Le Chatelier-Braun theorem. Equation (1), however, was given in substance by Gibbs many years before the qualitative theorem was rediscovered.

measurements of the specific volumes of solutions and illustrate how $(v_2 - v_2^s)$ depends on the concentration of the solute in the solution, the compressibility of the solvent, and the

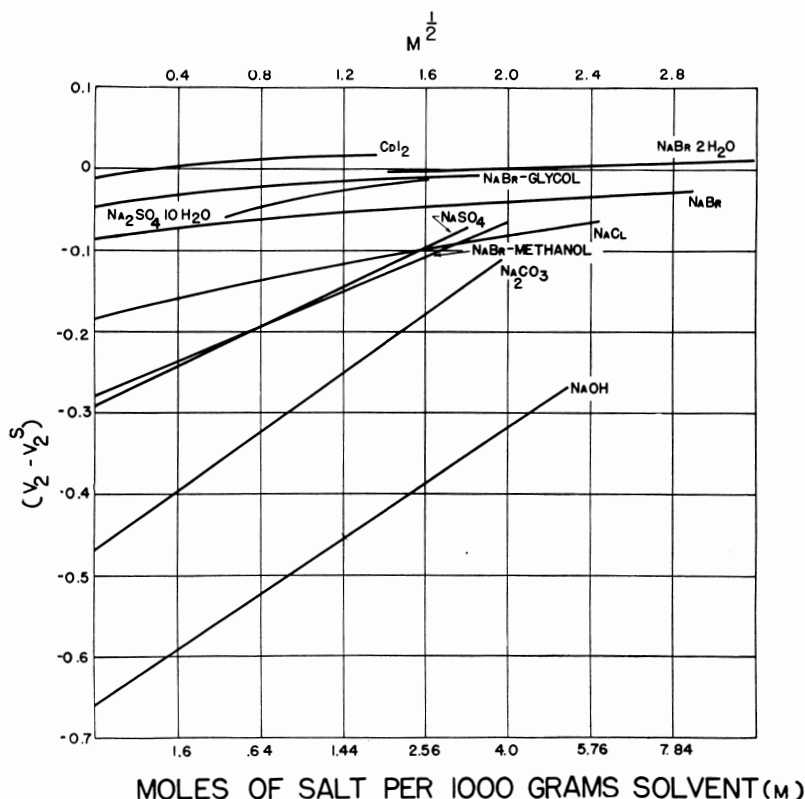


Fig. 1. The expansion in milliliters per gram of different solids when they dissolve in solutions of different concentrations. Unless otherwise stated the solvent is water. Comparison of the curves for sodium bromide in methanol, water, and glycol illustrates the effect of the compressibility of the solvent. Note that in all the dilute solutions the expansion is negative.

chemical nature of the solute.⁹ A general discussion of the factors influencing $(v_2 - v_2^s)$ is complicated by the fact that when a solid dissolves in a liquid, two distinct processes occur—the solid melts with a given volume change and the liquefied

⁹ At 25° the compressibilities of glycol, water, and methanol are respectively 36.6, 44.5, and 125 $\times 10^{-6}$ reciprocal bars.

solute mixes with the solvent with another volume change. We should, therefore, write $(v_2 - v_2^s) \equiv (v_2 - v_2^1) + (v_2^1 - v_2^s)$ where v_2^1 is the hypothetical volume of the pure liquefied solute at the temperature and pressure of the experiment, and then discuss separately the volume change on melting $(v_2^1 - v_2^s)$ and the volume change on mixing $(v_2 - v_2^1)$. It will be shown that this latter term plays an important part in determining the effect of pressure on equilibria in many binary systems. Indeed, the volume change on mixing term is so significant that its consideration may require a complete revision of conclusions about the behavior of polycomponent systems under pressure that have been based on careful considerations of the thermodynamics of pure substances.¹⁰

THE VOLUME CHANGE ON MELTING OF SOLIDS.

Most substances expand on melting, $(v_2^1 - v_2^s)$ being, therefore, positive. Exceptions are known at low pressures, notably water, bismuth, and perhaps potassium nitrate and potassium and rubidium iodides,¹¹ but Bridgman¹² has found that at higher pressures such substances frequently undergo polymorphic transitions and thereafter melt with increase in volume. At high pressures, therefore, it is very exceptional to find $(v_2^1 - v_2^s)$ negative. Although liquids are more compressible than the corresponding solids the difference in compressibility does not produce a change of sign in the volume change on melting even at very high pressures. Simon,¹³ who proposed a semi-theoretical equation which represents the pressure-temperature relation along the melting curve of a pure solid sufficiently well in known cases to justify its use in extrapolation, concludes that even at very high pressures $(v_2^1 - v_2^s)$ never becomes zero and *a fortiori* never negative.

THE VOLUME CHANGES ON MIXING OF LIQUIDS

The quantity $(v_2 - v_2^1)$ represents the increase in volume which occurs when one gram of pure liquid solute mixes with a large amount of the saturated solution. In an ideal solu-

¹⁰ See J. Johnston: J. Geol., 23, 740, 1915.

¹¹ Cohen, E., and Moesveld, A. L. Th.: Z. phys. Chem., 93, 385, 1919.

¹² See Bridgman, P. W.: Proc. Nat. Acad. Sci., 23, 204, 1937.

¹³ Simon, F.: Trans. Faraday Soc., 33, 65, 1937.

tion as usually defined,¹⁴ $(v_2 - v_2^1)$ is zero. In such a solution the potential energy of a molecule due to its neighbors is approximately the same in the solution as in its own pure liquid. In such a case $(v_2^1 - v_2^s)$ is the predominating term and dx_2/dP is negative.¹⁵ Examples are known especially in mixtures of organic liquids where $(v_2 - v_2^1)$ is positive and hence dx_2/dP is decidedly negative. It is of interest to note that in these liquid mixtures considerable progress has been made in calculating the volume change on mixing from the free energy changes and hence approximately from the heats of evaporation of the pure liquids,¹⁶ showing a quantitative relationship between the cohesive forces in the pure components and the volume change on mixing.

In the majority of cases, however, especially where the solutes are solid at the temperature of the solution, a contraction occurs when the liquefied solute and the solvent mix, and if $(v_2 - v_2^1)$ is negative and larger than $(v_2^1 - v_2^s)$ the solubility of the solid will be raised by pressure, as in the cases of potassium sulphate or sodium chloride in water. It will be seen, therefore, that in general a solid is less soluble in a given liquid solution under high pressures than under low pressure, the only exceptional cases being those where the pure solid contracts on melting or where the volume change on mixing is negative and abnormally large.

TYPES OF COHESIVE FORCES AND THEIR INFLUENCE ON COMPRESSIBILITY AND VOLUME CHANGES.

When a given amount of one liquid dissolves in a solution the contraction in volume is proportional to the compressibility of the solution and to the magnitude of the intermolecular attractive forces between the solvent and the solute, modified by possible changes in the structure of the solution. It is

¹⁴ Hildebrand, J. H.: *Solubility of Non Electrolytes*, Reinhold Publishing Corporation, New York, p. 59, 1936.

¹⁵ For an ideal solution the change in solubility with pressure is given by the well-known formula

$$\frac{d \ln X_2}{dP} = - \frac{\Delta V}{RT}$$

where X_2 is the mol fraction of solute in the saturated solution, ΔV is the volume change per mole when the solute melts, and R is the ordinary gas constant.

¹⁶ Scatchard, G.: *Trans. Faraday Soc.*, 33, 160, 1937.

generally assumed that the intermolecular forces which hold the various units (molecules or ions) together in solids also account for the cohesion of liquids whether pure or mixed. The nature of these cohesive forces is now understood,¹⁷ and for convenience we may classify them as follows.

A. Non-directed Forces. (1) (a) Coulomb forces between charged ions. e.g. Forces in ionic crystals or liquids like NaCl. (b) Ion dipole forces. e.g. NaCl-H₂O solutions or electrolytes in general. The forces in group A (1) are strong and act over relatively long ranges. (2) Van der Waals' forces—under which heading come (a) The forces between permanent dipoles and between permanent and induced dipoles. (b) Dispersions forces; these are always present and predominate in organic liquids and solids. Dispersion forces account for the liquid and solid rare gases. (3) Repulsive forces.

B. Directed Forces. (1) Partially directed forces of the hydrogen or hydroxyl bond type¹⁸ as in water, ammonia, organic compounds containing oxygen and nitrogen, alcohols, amines, sugars. (2) *Covalent or homopolar* bond type of forces as in SiO₂, B₂O₃, silicates, phosphates, plastics, diamond. These forces are very strong and may range from a highly polarized electrostatic bond (A1) to the type of forces which hold the oxygen atoms together in a molecule. In addition to these, we have the cohesive forces in metals which fall in a different category.¹⁹

A knowledge of the chemical nature of a liquid or solid and structural information as given by X-ray diffraction patterns enables one to say what types of cohesive forces act in the liquid, but quantitative information about their macro-

¹⁷ Lennard-Jones, J. E.: Proc. Phys. Soc. London, 43, 461, 1931; Seitz, F., and Johnston, R. P.: J. Applied Phys., 8, 84, 186, 246, 1937; Herzfeld, K. F.: *ibid.*, 8, 319, 1937. London, F. (Trans. Faraday Soc., 33, 65, 1937) gives a clear account of van der Waals' forces. Hildebrand, J. H. (*ibid.*, p. 145), summarizes the types of forces encountered in solutions. Ewell, R. H. (J. Applied Phys., 9, 252, 1938), classifies the various types of forces in liquids in their relation to viscosity.

¹⁸ See Bernal, J. D., and Megaw, H. D.: Proc. Roy. Soc. A151, 384, 1935. For summary of recent literature see Ann. Reports Chem. Soc. Lond., 34, 89, 1937.

The term hydrogen bond is still vaguely used and in this paper it may be interpreted as meaning an electrostatic directed bond between residual charges associated with definite groups or atoms in different molecules.

¹⁹ See Mott, N. F., and Jones, H.: Theory of the Properties of Metals and Alloys, Clarendon Press, Oxford, 1936; also Mott, N. F.: Science Progress, 414, 1937.

scopic effects is obtainable only in simple cases. Much work has been done in relating heats of sublimation and evaporation, the melting points, the viscosity, the compressibility, etc. to the type and magnitude of the intermolecular forces.²⁰

Concerning the compressibility, we may make the following approximate statement about substances in the vicinity of their melting temperatures. In non-polar compounds (e.g. hydrocarbons, benzene, etc.) where only dispersion forces act, the compressibility is large; introduction of polar groups (e.g. chlorobenzene) to give permanent dipoles lowers the compressibility, hydrogen or hydroxyl bonds produce a still greater diminution, ionic forces still more, and the covalent bond type of cohesive forces produces the lowest compressibilities in liquids or solids. It should be mentioned that directed forces in a liquid may produce structural effects which complicate these simple conclusions. These will be dealt with later.

Empirically it has been found that the internal pressure set up by these cohesive forces is a useful quantity in a semi-quantitative treatment of liquids and solutions under pressure, and a consideration of this internal pressure leads to a formula which gives a clear picture of the factors determining $(v_2 - v_2^1)$ in certain types of solutions.

INTERNAL PRESSURE AND THE COMPRESSIBILITY OF LIQUIDS AND SOLIDS.

The compressions of a wide variety of liquids may be represented quite accurately by the Tait equation

$$-\Delta_P v = C \ln \frac{B + P}{B} \quad (2)$$

which in all cases holds best at the higher pressures. ($-\Delta_P v$ represents the change in specific volume when the pressure changes from zero to P , and C and B are positive constants.) By studying the compressions of benzene²¹ at different temperatures we have found that B may be taken as a measure of the difference between the expansive pressure due to the thermal energy of the molecules and the cohesive pressure due to the

²⁰ See, for example, the tables given by A. G. Ward, *Trans. Faraday Soc.*, 33, 91, 1937; also T. W. Richards, *Chem. Rev.*, 2, 331, 1925.

²¹ Gibson, R. E., and Kincaid, J. F.: *J. Am. Chem. Soc.*, 60, 511, 1938.

temperature-independent attractive forces between the molecules, and it seems safe to extend this conclusion qualitatively to other liquids.²² The quantity B , therefore, measures the net cohesive pressure, decreasing as the temperature is raised and increasing as the intermolecular attractive forces increase, and it may be determined directly from compressions at different pressures. In Table II we give values of the constants in the Tait equation for some substances at 25°.

TABLE II.

Values of the constants B and C' in the Tait equations for different substances.

$$-\frac{\Delta V}{V(P=0)} = C' \log \frac{B+P}{B}.$$

Substance and temperature	C'	B (in bars)
Benzene (25°)	0.2159	970
Benzene (65°)	0.2159	701
Aniline (25°)	0.2159	2009
Aniline (65°)	0.2159	1606
Methanol (25°)	0.2208	764
Glycol (25°)	0.2280	2706
Water (25°)	0.3150	2996
Water (65°)	0.3150	3053
Sodium chloride (25°)	0.5013	51970

INTERNAL PRESSURES OF SOLUTIONS.

The internal pressures in pure liquids are set up by cohesive forces between like molecules, and these generally involve only one or two of the types of cohesive forces mentioned above. In solutions, however, the picture is complicated. The potential fields around the solvent and solute molecules are in general different not only in magnitude, but also they may arise from different types of forces.²³ Thus, as we vary the proportions of the components, we may expect significant changes in the

²² For theoretical discussions of equations of state similar in form to the Tait equation see Kincaid, J. F., and Eyring, H.: *J. Chem. Phys.* 5, 587, 1937; and Hudleston, L. J.: *Trans. Faraday Soc.*, 33, 98, 1937.

²³ It should be noted that we do not mean fundamentally different types of forces as all arise from electronic distributions, but only different types in the classification given above, a classification which is now widely used for the sake of convenience.

internal pressures of solutions, and it is found that this change of internal pressure with concentration is a useful quantity to consider and may be related to the compressibilities of the pure components.

If we have two molecular species, X representing the solvent and Y the solute, mixing to form a solution, it is clear that the mutual potential energy of molecules X and Y must be approximately the same or greater than the mutual potential energies of the molecules X and X or Y and Y . Thus with solutes possessing high internal pressures (large Y — Y forces) and hence low compressibilities in the pure solid or liquid state, we should expect large X — Y forces and hence a large volume change on mixing, especially if the X — X forces are small. It is convenient, therefore, to divide solutions into two classes: (a) those in which the compressibilities of the pure components are close together, and (b) those in which the compressibilities of the pure components are widely different.

In solutions of type (a) the solubility of the solid solute will decrease with pressure (provided the solid expands on melting) even at low pressures and we need discuss this no further at present. On the other hand, in solutions of type (b) increase in solubility with pressure will occur under certain conditions, and, as this represents an important class of solutions, we shall discuss it further, particularly as solutions of this class are well adapted to a quantitative treatment.

Application of the hypothesis of Tammann²⁴ that the solvent in a solution behaves as the pure solvent under a given external pressure P_e leads to an equation for the compressions of solutions which we have found empirically to be valid over wide pressure ranges,²⁵ the quantity P_e being computed from the compression at one pressure. According to this hypothesis the apparent volume of the solvent in the solution, ϕ_1 , computed on the assumption²⁶ that the specific volume of the solute in the solution is v_2^1 is given by

$$\phi_1 = v_w - C \ln \frac{B + P_e + P}{B + P} \quad (3)$$

²⁴ Tammann, G.: *Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen*, Leipzig, p. 36, 1907.

²⁵ Gibson, R. E.: *J. Am. Chem. Soc.*, 56, 865, 1934.

²⁶ A justifiable assumption if the compressibility of the solute is much less than that of the solvent.

Now it may readily be shown²⁷ that

$$(v_2 - v_2^1) = -x_1^2 \frac{d\phi_1}{dx_1} \quad (4)$$

On combining equations (3) and (4) we obtain

$$(v_2 - v_2^1) = x_1^2 \frac{C}{B + P_e + P} \frac{d(B + P_e)}{dx_1} \quad (5)$$

or, as it is very convenient in comparing solutions with the same solvent but different solutes to use as the concentration unit the number of gram molecules of solute per 1000 grams of solvent and to use the molal volumes V_2 and V_2^1 of the solute, we may make the transformation and obtain the desired equation (6):

$$(V_2 - V_2^1) = -\frac{1000 C}{B + P_e + P} \frac{d(B + P_e)}{dm} \quad (6)$$

This equation, which is empirical, seems to be valid at any pressure and it should be noted that B , C , and P_e are all independent of pressure. It must be admitted, however, that the equation is approximate. In the calculation of P_e from compressibility data some assumption must be made about the contribution of the solute to the compressibility of the solution and this assumption is rather important in determining the slope of the $(B + P_e)$ -concentration curves at high concentrations. Little is known about the difference between the compressibilities of solids and liquids²⁸ and we have generally assumed that the compressibility of the solute in the solution is the same as that of the solid solute. Comparison of $(V_2 - V_2^1)$ as

²⁷ If x_1 and x_2 are the weight fractions of solvent and solute respectively, if v is the specific volume of the solution and v_1 and v_2 are the partial volumes of the solvent and solute, then by definition

$$\begin{aligned} v &= x_1 v_1 + x_2 v_2 \\ v &= x_1 \phi_1 + x_2 v_2^1 \end{aligned}$$

whence $(v_2 - v_2^1) = \frac{x_1}{x_2} (\phi_1 - v_1)$.

But $v_1 = x_1 x_2 \frac{d\phi_1}{dx_1} + \phi_1$, whence equation (4) follows.

²⁸ Richards, T. W., and Speyers, C. (J. Am. Chem. Soc., 36, 494, 1914) found that liquid water was about four times as compressible as ice at approximately the same temperature, and Richards, Bartlett, and Hodges (J. Am. Chem. Soc., 43, 1538, 1921) found that melting doubled the compressibility of benzene.

computed from equation (6) with directly observed values of V_2 shows that V_2^1 diminishes slightly with concentration, whereas it should be constant. If one assumes that the compressibility of the solute is three times as great in the solution

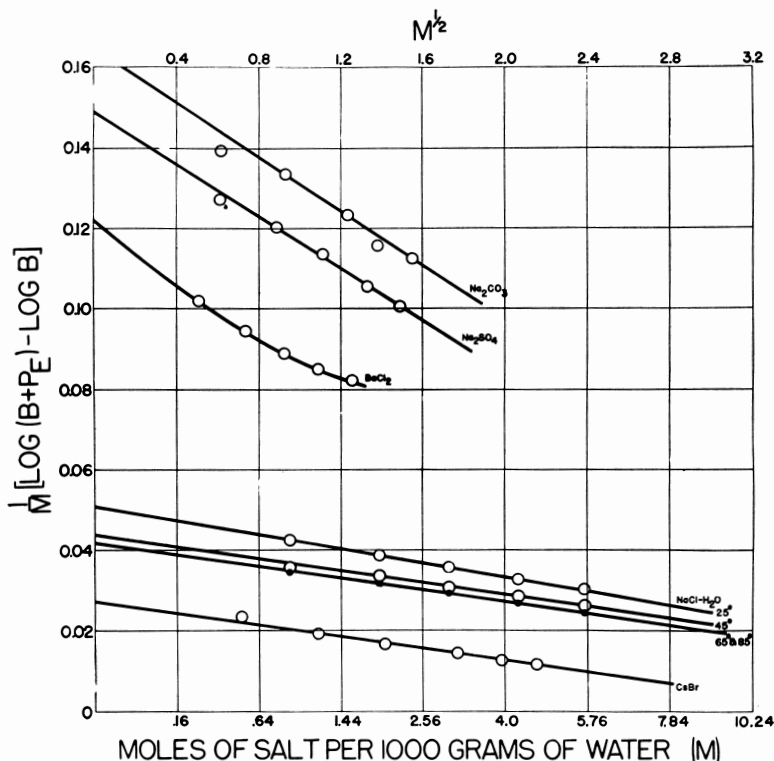


Fig. 2. Curves showing the relationship between $(\log(B + P_e) - \log B)/m$ and the square root of the molal concentration for different salts. The ordinate is determined from compressibility measurements and is directly related to the volume change on mixing of the liquid solvent and solute. In cases where V_2 varies approximately linearly with $m^{1/2}$ the same relation holds for $(\log(B + P_e) - \log B)/m$ vs. $m^{1/2}$. Neither curve is linear in the case of $\text{BaCl}_2\text{-H}_2\text{O}$ solutions.

as in the solid state, the values of V_2^1 obtained are quite independent of concentration. On the other hand, it has been shown by a number of investigators²⁰ that V_2 is a linear func-

²⁰ The literature is extensive. A good résumé is given by F. T. Gucker, J. Phys. Chem., 38, 307, 1934.

tion of the square root of the concentration for electrolytic solutions, and hence if equation (6) is valid, the expression $(\log (B + P_e) - \log B)/m$ should also be a linear function of the square root of the concentration. The curves in Fig. 2 show that this is the case. If the lines in this figure are expressed by the equation

$$(\log (B + P_e) - \log B)/m = a + \beta m^{1/2}$$

it follows from equation (6) that $(V_2 - V_2^1) = -2303 C (a + \frac{3}{2} \beta m^{1/2})$. Equation (6) is interesting from two points of view; in the first place it enables one to calculate approximate values of the volume change on mixing from compressibilities alone, and in the second place it summarizes concisely the factors which determine the sign and magnitude of $(V_2 - V_2^1)$.

The term $\frac{1000 C}{B + P_e + P}$ represents the compressibility per

1000 grams of the solvent³⁰ at an external pressure $(P_e + P)$. By Tammann's hypothesis it is the compressibility of the solvent in the solution at pressure P . We thus see the rôle played by the compressibility of the solvent in determining the volume change on mixing, a feature which has not been sufficiently emphasized in the past.

The second half of the right-hand side of equation (6) represents the change in the net internal pressure of the solution per gram molecule of solute added, and is related to the compressibility of the pure solute. In solutes with high internal pressures, and hence low compressibilities in the pure solid or liquid state, we have seen that large $X-Y$ forces and hence large values of $d(B + P_e)/dm$ when they dissolve in a solvent are to be expected. Equation (6) shows, therefore, that $(V_2 - V_2^1)$ will be large if the pure components differ widely in compressibility and that a knowledge of the compressibilities of the components gives some clue as to the effect of pressure on solubility. Furthermore, as P_e increases with the concentration of the solute, and as equation (6) indicates that $(V_2 - V_2^1)$ varies inversely as P_e , it follows that the more soluble a solid is at atmospheric pressure, the less chance there

³⁰ This follows if equation (2) be differentiated with respect to pressure and it is noted that $\frac{dv_w}{dP} = -\frac{C}{B + P}$, where τ_w is the specific volume of the pure solvent.

is that its solubility will increase with pressure. The inverse proportionality between $(V_2 - V_2')$ and the external pressure P also indicates that at sufficiently high pressures $(V_2 - V_2')$ will become so close to zero that the pressure coefficient of the solubility will be negative for all normally melting solids. Likewise if the pure solvent has a low compressibility, B itself will be large and $(V_2 - V_2')$ be correspondingly reduced in magnitude. To sum up, we may say equation (6) shows that a high concentration of solute, high external pressure, low compressibility of the solvent, and low change of internal pressure with concentration all tend to prevent the solubility of a solid from increasing with pressure.

AQUEOUS SOLUTIONS.

Compared with other substances which are liquid at the same temperature, water has a low compressibility and the cohesive forces are large, being of the types A2 and B1.³¹ Water is, however, between five and ten times as compressible as many of the solids which dissolve freely in it. These solids are of two main classes: (1) organic compounds containing oxygen, especially OH groups or nitrogen such as alcohols, sugars, amides, etc., in which forces of type B1 prevail; and (2) inorganic compounds in which the main cohesive forces are of type A1 together with van der Waals' forces. In the soluble inorganic substances the ionic forces account for most of the cohesive energy of the solids as in the alkali halides, whereas in the insoluble salts the van der Waals' forces contribute significantly to the cohesive energy as in silver or cuprous chlorides.³² In organic compounds containing many hydroxyl groups, the internal pressures may become very large as in the sugars, and when these dissolve in water a very significant contraction occurs, or, in other words, $d(B + P_e)/dm$ is large. For example, the solubility of mannitol increases initially with pressure.³³ In solutions of inorganic substances in water very large cohesive forces prevail owing to the interaction of their ions on the water dipoles, and these forces increase with the charge on the ions and diminish as their radii

³¹ Bernal, J. D., and Fowler, R. H.: *J. Chem. Phys.*, 1, 540, 1933.

³² Mayer, J. E.: *J. Chem. Phys.*, 1, 327, 1933.

³³ Cohen, E., Inouye, K., and Euwen, C.: *Z. phys. Chem.*, 75, 257, 1911.

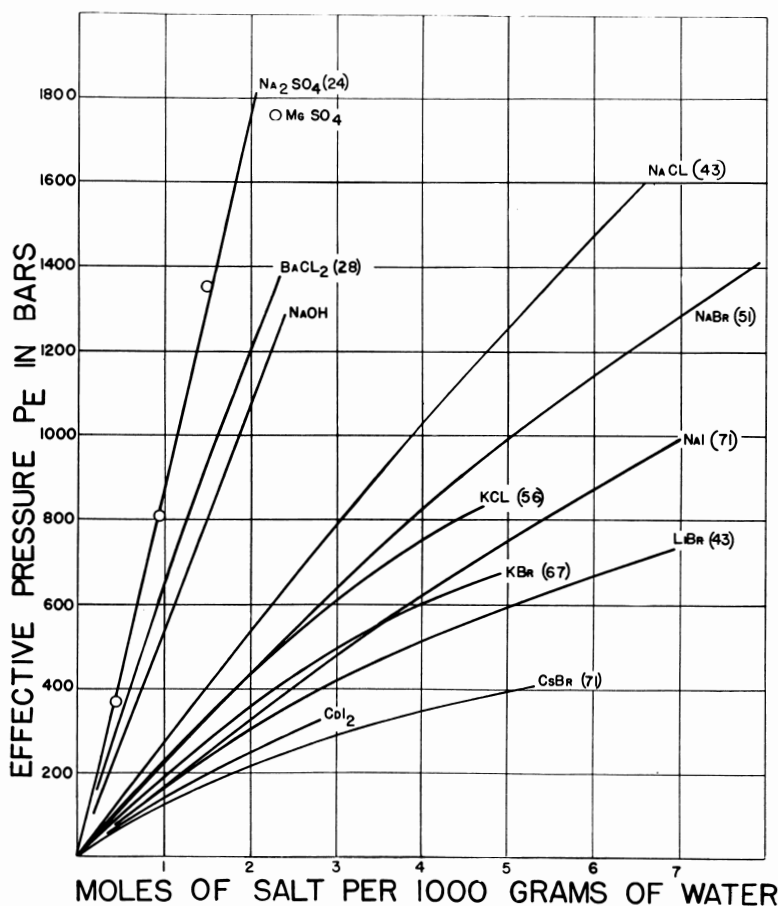


Fig. 3. Illustration of the dependence of the slope, $\frac{d(B + P_e)}{dm}$, on the nature of the solute for aqueous solutions. The figures in parenthesis give the compressibilities of the solid solutes at atmospheric pressure in reciprocal bars $\times 10^{-7}$. The parallelism between the slopes of the curves and the compressibility of the solute will be noted. Exceptions are illustrated by LiBr and CsBr solutions. In the latter case a change in solid structure gives rise to a lower compressibility of the solid than would be expected from a consideration of other alkali bromides.

increase. A glance at Fig. 3 will show the effects of these two factors, which have been discussed more fully elsewhere.³⁴

³⁴ Gibson, R. E.: Sci. Monthly, 46, 103, 1938.

P_e rises most sharply with concentration in solutions containing the most highly charged ions, and especially in solutions of sulphates and carbonates (bivalent anions). In solutions of hydroxyl ions the greatest values of $d(B + P_e)/dm$ for monovalent ions are found. It will be noticed that $d(B + P_e)/dm$ increases as the compressibility of the solute decreases, and in this connection it is of interest to note an empirical relation between the compressibility β , the molal volume V , and the valency Z in ionic crystals, viz. $\beta = V/Z \times 5.6 \times 10^{12}$ given by Balce.³⁵

These considerations lead to one definite conclusion of direct geochemical interest. Saturated solutions of sparingly soluble salts such as the sulphates, fluorides, carbonates, or the sulphides of the alkaline earths, the rare earths and the heavy metals, the metallic oxides or hydroxides, are examples of the one case where we may definitely say that pressure will increase their solubility. Chemically and physically they give solutions of the potassium sulphate—water type. Referring to equation (6) we may say that $d(B + P_e)/dm$ is large, $(B + P)$ is small, and as the solutions are very dilute, P_e is also small—the conditions are right for $(V_2 - V_2^1)$ being large and negative.

In order to estimate roughly the magnitude of the increase with pressure of the solubility of sparingly soluble substances, we may throw equation (1) into the following form.³⁶

$$\frac{dm}{dP} = - \frac{(V_2 - V_2^s)m}{v RT \left(1 + m \frac{\partial \ln \gamma}{\partial m} \right)} \quad (7)$$

The quantity $\partial \ln \gamma / \partial m$ is always negative in dilute solutions of electrolytes,³⁷ and if m is small we may take RT as the upper limit of the denominator and notice that neglect of $m \partial \ln \gamma / \partial m$ gives us the lower limit of dm/dP .

Data from which we might calculate V_2 in saturated solutions of sparingly soluble substances are practically nonexistent, but it is possible to arrive at fair estimates from values of v_2 for the corresponding types of salts at low concentrations obtainable from curves such as are given in Fig. 1. The results of a

³⁵ Balce, S.: *Philippine J. Sci.*, 60, 251, 1936.

³⁶ In this equation γ is the activity coefficient of the solute as usually defined (see Adams, L. H.: *Chem. Rev.*, 19, 1, 1936). v is the number of ions into which the electrolyte dissociates.

³⁷ See Harned, H. S.: *Taylor's Treatise on Physical Chemistry*, 2d ed. p. 773. Van Nostrand Co., New York, 1930.

few approximate calculations of dm/dP for different insoluble substances are given in Table III. They show quite clearly

TABLE III.

Rough estimates of the percentage change in the solubility of sparingly soluble substances in water produced by an increase of pressure from 1 to 1,000 bars.

Substance	Solubility moles per 1000 grams water	V_2^s (ml/mole)	V_2 (ml/mole)	v_2RT ml × kilobars	Percentage increase in solubility per 1000 bars increase in pressure
CaCO ₃	0.00057	36.9	<0	49.5	75
Ca(OH) ₂	.022	33.1	<0	74.3	44
CaSO ₄ (anhydrite)	.0046	47.8	10	49.5	77
CaSO ₄ ·2H ₂ O	.0153	74.0	46	49.5	57
CaF ₂	.00021	24.5	0	74.3	33
CaS	.028	28.2	0	49.5	57

that even a pressure increase of 1000 bars (corresponding to the pressure in the depths of the ocean) will increase the solubility of sparingly soluble electrolytes in water between 10 and 50 per cent of its value at atmospheric pressure. Movement of water from deeper to shallower parts of the ocean may account, therefore, for considerable transport and reprecipitation of solids if saturation conditions are approached. Experimental work to determine the effect of pressure on the solubility of interesting sparingly soluble substances in water is being started, and further discussion of its implications must await quantitative results.

THE EFFECT OF TEMPERATURE.

Normally, rise of temperature increases the compressibility of solids and liquids and thus we should expect $(v_2 - v_2^s)$ to become more negative as the temperature is raised; in other words the partial thermal expansion of the solute should be negative. This is the case in many solutions where contraction occurs on mixing, e.g. sodium iodide in glycol, sodium iodide in methanol.³⁸ Water, however, is exceptional in that its compressibility falls off as the temperature rises, passing through a minimum near 50°. In aqueous solutions below about 65° v_2 increases rapidly with temperature and $(v_2 - v_2^s)$ gets closer to zero. Thus in aqueous solutions where the solubility

³⁸ Gibson, R. E., and Kincaid, J. F.: J. Am. Chem. Soc., 59, 579, 1937.

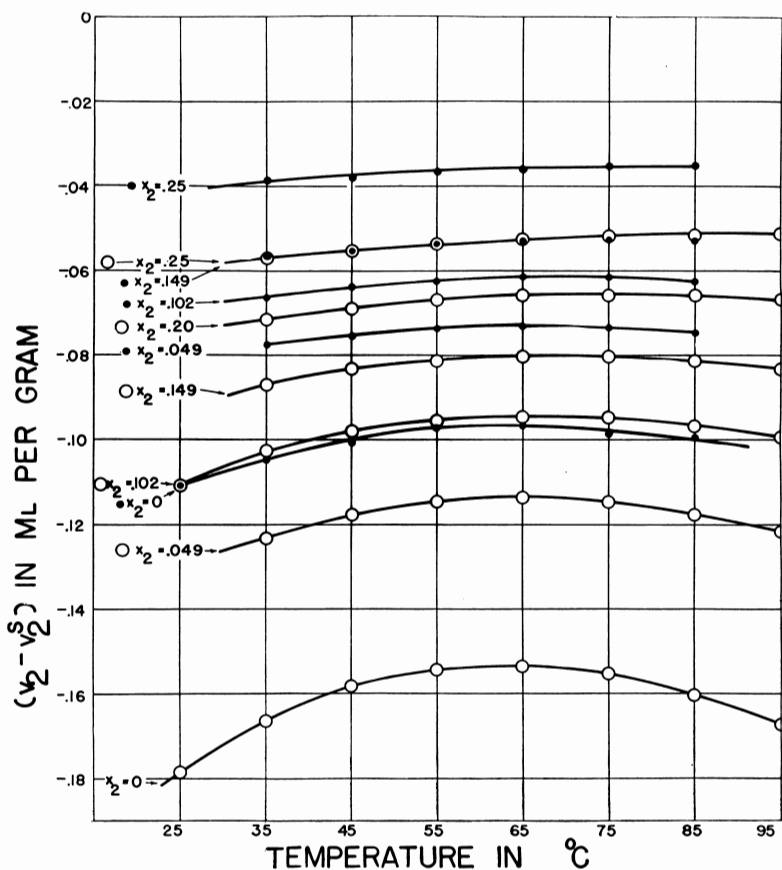


Fig. 4. The expansions per gram when sodium chloride dissolves in solutions of different concentration at different temperatures and pressures. The open circles $\circ$ refer to atmospheric pressure and the dots $\bullet$ refer to measurements at 1000 bars.

It will be noted that the expansions pass through maxima as the temperature is raised and that increase of pressure and of concentration flattens the curves and makes the values of $(v_2 - v_2^s)$ less negative.

increases with pressure, increase of temperature will lower $\frac{dm}{dP}$. However, above 65° the partial volumes of electrolytes dissolved in water go through a maximum and begin to diminish as temperature continues to rise.³⁹ With Mr. O. H.

³⁹ Bousfield, W. R., and Lowry, T. M.: *Trans. Faraday Soc.*, 6, 15, 1910; Pesce, B.: *Gazz. chim. ital.*, 66, 99, 1936; Akerlof, G., and Teare, J.: *J. Am. Chem. Soc.*, 60, 1226, 1938.

Loeffler⁴⁰ we have recently obtained data for sodium chloride, sodium bromide, and lithium bromide solutions up to 95° and a sample of the results is shown in Fig. 4. It will be seen that the maximum occurs at lower temperatures in the dilute than in the concentrated solutions. In 5.5 and 45.1 per cent lithium bromide solutions the maxima are at 45 and 55° respectively.

Bousfield and Lowry showed that the apparent volumes of lithium and calcium chlorides and alkali hydroxides in water passed through maxima at still lower temperatures and thereafter decreased very rapidly. The curves given in Fig. 4 are, therefore, typical and we may conclude that at temperatures above 60° the effect of pressure in increasing the solubility of the sparingly soluble salts we have discussed will be enhanced by rise of temperature, and there is no reason to suppose that this conclusion needs to be modified at the critical temperature.

We have mentioned that in liquid water partially directed forces of the hydrogen or hydroxyl bond type exist among the molecules and this produces a type of structure in the liquid.³¹ In the effect of temperature and addition of solutes on this liquid structure lies the explanation of the curious partial volume-temperature curves we have discussed—this will be set forward elsewhere. It is to be emphasized, however, that the liquid structures set up by the directed forces among the molecules do cause considerable modification of the conclusions we have just given. For example, although the forces between lithium ions and water molecules are very large, $(V_2 - V_2^s)$ is actually positive in concentrated solutions of several lithium salts, whereas the comparative compressibilities of these salts and water would lead one to expect it to be large and negative. Furthermore, in glycol, which is only three quarters as compressible as water, $(V_2 - V_2^s)$ for lithium bromide is much less than in water solutions. These apparent anomalies have been explained elsewhere on the basis of the arrangement of the molecules in water.⁴¹

COMPOUNDS AS SOLID PHASES.

Frequently the solid phase in equilibrium with a solution is a compound of both end members of the system, hydrates such as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ being typical examples. Such solids are always more compressible than the solute end-member and the

⁴⁰ Gibson, R. E., and Loeffler, O. H.: Unpublished results of work at the Geophysical Laboratory.

⁴¹ Gibson, R. E., and Kincaid, J. F.: *J. Am. Chem. Soc.*, 59, 579, 1937.

foregoing discussion leads to the conclusion that their solubilities will be raised by pressure much less than those of the end members. The partial molal volume V_{XY} of a compound whose formula is $mXnY$ is given by $V_{XY} = mV_X + nV_Y$ where V_X and V_Y are the partial molal volumes of the solvent X and the end member Y in the solution. Using this formula, together with the densities of the solid hydrates given in the literature, we obtained $(v_2 - v_2^s)$ for the hydrates $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{NaBr} \cdot 2\text{H}_2\text{O}$. These are plotted against the concentration in Fig. 1. In both cases $(v_2 - v_2^s)$ is less negative than for the corresponding pure salt and, indeed, it will be seen that for $\text{NaBr} \cdot 2\text{H}_2\text{O}$ it is actually positive in the concentrated solutions. Thus while the solubility of NaBr in water, like that of NaCl , is initially raised by pressure, the solubility of $\text{NaBr} \cdot 2\text{H}_2\text{O}$ is always diminished by pressure, and direct experiments made in this Laboratory have shown that this diminution is considerable.

THE EFFECT OF PRESSURE ON THE SOLUBILITY OF MINERALS IN SILICATE MELTS.

In applying the foregoing discussion to a consideration of the effect of pressure on the solubility of solid silicate minerals in silicate melts we may note at once that the intermolecular forces are large both in the solvent and the solute, that the compressibilities are very low, and that the solutions and the solid phases are chemically similar. These systems are of type (a) in which the compressibilities of both components are close together and also share the characteristics we have mentioned in the previous section on compound formation. We may therefore state with some confidence that these considerations all make it improbable that increase of pressure will increase the solubilities of these solids, and that they really favor the opposite conclusion.

The data given by Day and Allen⁴² on the densities of albite-anorthite glasses and solid solutions indicate no appreciable volume change on mixing and thus the volume changes on melting of the end members govern the effect of pressure on the solidus and liquidus curves in this system. Bowen,⁴³ indeed, has shown that the solutions in this system conform very closely

⁴² Day, A. L., and Allen, E. T.: *The Isomorphism and Thermal Properties of the Feldspars*, Carnegie Inst. Wash. Pub. No. 31, 74, 1905.

⁴³ Bowen, N. L.: *This Journal*, 35, 577, 1913.

to ideal behavior. From the data on the densities of soda-silica glasses⁴⁴ one may compute the partial volumes of SiO_2 dissolved in Na_2SiO_3 , at room temperature. The partial volumes of SiO_2 in solutions from 60 to 100 per cent SiO_2 are greater than the specific volume of tridymite at the same temperature. In view of the interval between room temperature and the temperature at which tridymite and soda-silica melts are in equilibrium, we cannot attach much weight to this observation. Qualitatively it is compatible with the foregoing discussion.

We have noted that the cohesive forces in silicate solids and liquids are of the covalent bond type, strong and directed forces which produce a quasi structure in the liquids, accounting among other phenomena for the high viscosity of melted silicates.⁴⁵ The structural or association effects in silicate liquids introduce complications which make further speculations very risky. Suffice it to say that influences of the structural effects in the liquids both on the volume change on melting and on the volume changes on mixing when components of different valencies and coordination numbers are introduced must be expected and investigated before further progress is made.

⁴⁴ Morey, G. W., and Merwin, H. E.: *J. Optical Soc. Am.*, 22, 632, 1932.

⁴⁵ Ewell, R. H.: *op. cit.*