HYDRATION IN SOLUTION.

By C. S. Hudson.

IN the present article the formation of hydrates and their anhydrides in solution is considered and an explanation is attempted of some of the general phenomena of hydration, such, for example, as the occurrence of transition temperatures, the equality of solubilities at these temperatures, and the fact that the stable substance always has the smaller solubility. The explanation that I give of these general facts is based on the observations of the hydration of milk-sugar that I have published.[1]

1. The Related Solubilities of a Typical Hydrate, Milk-Sugar, and its Anhydride.

Suppose an anhydrous substance A, for example anhydrous milk-sugar, to form with water a single hydrate H, hydrated milk-sugar. The reaction which takes place in dilute solution between these two substances can be represented by the symbol of a balanced reaction.

$$A \rightleftharpoons H, \tag{1}$$

if the constant mass of the reacting water is omitted for brevity. If the initial solubility of A at a chosen temperature is s_a, and the concentration of H that is in equilibrium in solution with s_a of A is C_h, the final solubility of A is

$$S_a = s_a + C_h. \tag{2}$$

In like manner the final solubility of the hydrate is

$$S_h = s_h + C_a. \tag{3}$$

Since it has been shown by Nernst[2] that the proportion of hydrate

[1] Princeton Bulletin, April, 1902. Zeitschrift für physikalische Chemie, 44, 487–494 (1903); 50, 273–290 (1904). Journal of the American Chemical Society, 26, 1065–1082 (1904).

[2] Zeitschrift für physikalische Chemie, 11, 345 (1893).

that is in equilibrium with anhydride is nearly independent of con-
centration we may write as a close approximation
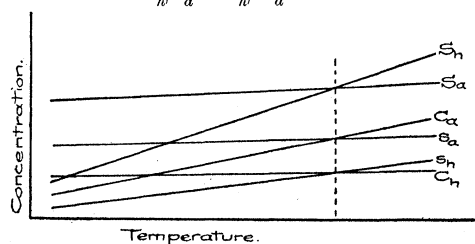
$$C_h/s_a = s_h/C_a = K. \tag{4}$$

Fig. 1.

In the accompanying figure the quantities that occur in the three
equations are represented over a range of temperature. Three of
these lines can be drawn at will for a typical substance, but the
others are then determined by the positions of these three. I have
drawn s_a, s_h and S_h from the solubility data of milk-sugar.

It follows from the equations (2), (3), and (4) that

$$S_a \gtreqqless S_h \text{ and } C_h \lesseqqgtr s_h \text{ when } s_a \gtreqqless C_a. \tag{5}$$

This relation, and also the figure, shows how it is that one of the
substances A and H is stable at a chosen temperature in the pres-
ence of water while the other is unstable, and also shows which of
the substances is the stable one. Thus, for example, if it is known
that $s_a > C_a$ it is to be concluded that the hydrate is the stabler
form, for since $C_h > s_h$, the finally saturated solution of anhydride
contains hydrate in greater concentration than that corresponding
to the initial solubility of the hydrate and is thus supersaturated
with respect to the hydrate; on the other hand, since $C_a < s_a$, a
finally saturated solution of the hydrate contains anhydride in less
concentration than its initial solubility, and such a solution is under-
saturated with respect to the anhydride and is stable. Or, briefly,
we may say that the stable substance is the one whose initial solu-
bility is greater than its concentration in the finally saturated solu-
tion of the other substance. This definition of the stabler substance
leads from (5) to the conclusion that the unstable substance in th
case of hydrates and anhydrides has the greater final solubility,

fact that is of the most common experience and which Van't Hoff[1] and Ostwald have proved holds for all substances. It is instructive to notice that though there is the necessity in the definition of the unstable substance that it have the greater final solubility, there is, on the contrary, no such relation between stability and initial solubility. This conclusion is evident when the equations (2), (3) and (4) are reduced to the form

$$s_a/s_h = S_a/S_h(1/K). \tag{6}$$

Since K, the equilibrium constant of the hydration reaction, is not known to depend on the relative stability of the two substances, it is not possible to decide from a knowledge of their relative stability anything regarding their initial solubilities.

2. The Transition Temperatures of Hydrates.

The relations shown by the equations (2), (3) and (4), and represented in the figure, also lead to a simple view of what takes place in a solution of a hydrated substance at its transition temperature. To show this we may first sum up the properties of such a solution that are peculiar to this temperature; they are, equality of the final solubilities of the hydrate and the anhydride, identity of the two resulting solutions, and equality of the vapor pressure of these solutions with that of a mixture of solid hydrate and anhydride. I know of no molecular-kinetic explanation of the last one of these general properties, but the first two receive a clear explanation from the equations and the figure, as follows : At whatever temperature $C_a = s_a$, $C_h = s_h$ and $S_a = S_h$, from (5). At this temperature, therefore, which may be defined the transition temperature,[2] the two substances have the same final solubility and also give solutions which contain the same substances in the same concentrations, and are therefore identical, which was to be shown.

If this is the correct explanation of the peculiar properties of solutions at the transition temperatures we should not expect at these temperatures any sudden or discontinuous change in any

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[1] Vorlesungen, 1903, II., p. 127.

[2] It has already been shown by Van't Hoff, Vorlesungen, 1898, I., 219, that at transition temperatures the concentrations of the substances in saturated solution are equal to their initial solubilities.

property of the solution, because the same substances exist in solution below, at and above the transition temperature, and the relative concentrations of these substances change gradually and continuously with the temperature. There is indeed no evidence at all that supports the alternative hypothesis, which is now generally abandoned, that below the transition temperature only the one form exists in solution, and above this temperature only the other form. It is certainly a more rational view to assume that both above and below this temperature both or indeed all forms of the substance exist together in solution, their concentrations and initial solubilities being related in the manner that has been indicated.

3. THERMODYNAMICS OF HYDRATION REACTIONS.

The solubility relations that are shown by the figure receive additional interpretation from the application to them of thermodynamic principles.

To begin with, let the free energy of the isothermal formation of solid hydrate from solid anhydride and water be calculated. This hydration can proceed reversibly in three ways, namely, by isothermal distillation of water, and by dissolution of anhydride and water in, and crystallization of hydrate from, saturated solutions of anhydride and hydrate respectively.

a. *Hydration by Distillation.*

If the vapor pressure of pure water at absolute temperature T is p_w and the pressure of the aqueous vapor that is in equilibrium with a mixture of solid hydrate and anhydride is P_h, then by isothermal evaporation of the water, expansion from p_w to P_h, and condensation on the solid anhydride, the hydrate can be produced isothermally and reversibly with the gain per mol of hydrate produced of the work,

$$W = nRT \log p_w/P_h, \tag{7}$$

where n is the number of molecules of water that occur in the hydrate.

b. *Hydration by dissolution in saturated anhydride solution.*

Imagine a reservoir composed of a finally saturated solution of the anhydride, containing anhydride and hydrate in the concentra-

tions s_a and C_h respectively. Draw out from this reservoir through a wall that is permeable for the solvent and the hydrate but impermeable for the anhydride one mol of hydrate at the constant concentration C_h, and at the same time allow one mol of anhydride to dissolve into the reservoir and n mols of water to evaporate at p_w, to expand to p_a, the vapor pressure of the saturated solution of the anhydride, and then to condense into the reservoir. The mol of withdrawn hydrate is then to be concentrated from C_h to s_h, the initial solubility of the hydrate, and crystallized from the solution. The final change that is produced by this process is the conversion of solid anhydride and water to solid hydrate because the reservoir remains unaltered, and the free energy of the hydration per mol of hydrate formed is

$$W = nRT \log (p_w/p_a) + RT \log (C_h/s_h). \tag{8}$$

c. Hydration by dissolution in a saturated hydrate solution.

By a process similar to the foregoing one dissolve one mol of anhydride at concentration s_a in water, concentrate it to C_a, and press it into a saturated solution of the hydrate; at the same time distil n mols of water into the saturated solution and crystallize from it one mol of hydrate. The free energy by this method of hydration is

$$W = nRT \log (p_w/p_h) + RT \log (s_a/C_a). \tag{9}$$

Since the three expressions (7), (8), and (9) for the free energy are equal it follows that

$$(p_w/P_h)^n = (p_w/p_a)^n (C_h/s_h) = (p_w/p_h)^n (s_a/C_a). \tag{10}$$

If we select as the distinguishing property of the transition temperature the fact that at it the finally saturated solutions of anhydride and hydrate respectively are identical, it follows that $p_a = p_h$ and therefore $C_h = s_h$ and $s_a = C_a$, which is the conclusion that has already been obtained in section (2). Also, since at this temperature $C_h/s_h = s_a/C_a = 1$, it follows that $P_h = p_a = p_h$, which expresses another general property of hydrates at their transition temperatures; as stated before, no molecular-kinetic explanation of this relation is known.

At temperatures other than that of transition the general fact that P_h is less than p_a or p_h below the transition temperature and greater above it can be used to determine which is the stable substance. For it follows from (10) that above the transition temperature, since P_h is greater than p_a or p_h, C_a is greater than s_a and s_h is greater than C_h, and therefore the anhydride is stable in the presence of its saturated solution. Similarly it can be shown that the hydrate is the stable substance below the transition temperature.

These conclusions from the thermodynamic relations agree completely with those already obtained from the solubility curves of the figure, which are based on the data for the solubility of milk-sugar. But the thermodynamic relations can give us further information which is not evident from the solubility curves. This is discussed in the two following sections.

4. A Method of Calculating the Solubility of Some Substances that Form Hydrates.

It is evident from (10) that

$$(p_a/P_h)^n = C_h/s_h, \tag{11}$$

and

$$(p_h/P_h)^n = s_a/C_a. \tag{12}$$

Since p_a, p_h, and P_h are usually measured with ease, these equations give a means of calculating the initial solubility of those substances for which C_h or C_a can be determined. For example, let the initial solubility of anhydrous milk-sugar at zero centigrade be calculated. Here $n = 1$, $C_a = 20$ millimols per 100 grams of water,[1] $P_h = 0.46$ cm. mercury nearly, since the saturated solution at zero is of 0.3 molal concentration and its vapor pressure is nearly the same as that of water, and I find P_h to have the values 43.3 at 90°, 7.2 at 60°, giving by extrapolation with the formula of Clausius, P_h at 0°, 0.062 cm. From these data s_a is calculated from (12) to be 148 millimols per 100 grams of water. By experiment I have found s_a to be 125. The agreement is as good as could be expected, considering the large possible error in the determination of P_h, which cannot be observed at 0° on account of the sluggishness of its establishment.

[1] Journal American Chemical Society, **26**, 1074 (1904).

It is noteworthy that in the experimental determination of the quantities from which s_a is calculated it is not necessary to isolate the anhydride. Only in the determination of P_h from a partially dehydrated sample of the hydrate is it needful to have the anhydride in the solid state and it is here mixed with hydrate in such an intimate manner that it cannot be described as isolated.

5. THE INFLUENCE OF FOREIGN SUBSTANCES ON THE SOLUBILITY OF HYDRATES AND THEIR ANHYDRIDES.

If the free energy of the hydration reaction that is described in section (3) be calculated by a method which is a combination of those under (b) and (c), employing a reservoir of an unsaturated solution containing hydrate in concentration c_h and anhydride in concentration c_a and having a vapor pressure p_s, it is found that per mol of hydrate formed the energy is

$$W = nRT \log p_w/p_s + RT \log s_a/c_a + RT \log c_h/s_h. \qquad (13)$$

If this value is put equal to (7),

$$\frac{c_h}{c_a(p_s)^n} = \frac{s_h}{s_a(P_h)^n}, \qquad (14)$$

which is independent of the concentration.

As Nernst[1] has pointed out, since the vapor pressure of a dilute solution changes only very slightly with the concentration, equation (14) shows that the ratio of hydrate to anhydride is nearly constant in dilute solution, particularly if n is small. It is, however, to be expected that when n is large there will be an appreciable decrease of the ratio of hydrate to anhydride if the vapor pressure lessens. For example, if a chosen dilute aqueous solution at 20° contains a dekahydrate and its anhydride in equilibrium in the ratio $c_h/c_a = 1.50$, the addition of a foreign substance in tenth molal concentration would be expected to change the vapor pressure of the solution, according to Raoult's law, from 1.750 cm. mercury to 1.747 cm., which by (14) would change c_h/c_a from 1.50 to 1.47, an alteration of 2 per cent. Although the magnitude of such changes of hydration

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[1] Loc. cit. Equation (14) differs from the similar one obtained by Nernst in the respect that the factors which compose Nernst's constant are here separated and identified with other physical quantities.

equilibrium is small, it is nevertheless sufficient, as I have shown at another place,[1] to account quantitatively for the lowered freezing temperatures of solutions, which are not inconsiderable depressions. I shall seek now to show that such changes of hydration equilibrium may also be the cause of well recognized regularities in the change of solubility of hydrates and anhydrides that occur when other, apparently indifferent, substances are present in the solution.

First, to determine the character of these regularities. I regard the best evidence on the change of solubility of hydrates to be that given by the experiments and the theory of Goldschmidt,[2] which he has summed up in the phrase " the molecular increase of solubility of hydrates."

These experiments give the solubility at room temperature of the bi- and tetra-hydrates of sodium paranitrophenolate in pure water and in molal solutions of urea, glycerine, acetone, propionitrile, acetonitrile, urethane and alcohol. It was found that all the solutions except the alcoholic dissolve more hydrate than does pure water, that the increase of solubility is nearly constant for the same hydrate in the different solutions, and that the ratio of increase of solubility of tetrahydrate to that of bihydrate is a constant 1.02.[3] The experiments of Löwenherz[4] also give evidence on the change of solubility of hydrates. He found that urea causes hardly a measurable change in the solubility of sodium sulphate dekahydrate, but a large decrease (13 per cent.) in the solubility of anhydrous sodium sulphate. To sum up then, it is found that the solubility of hydrates is frequently increased by foreign substances, never markedly decreased, and that the higher hydrate shows a greater increase of solubility than the lower.

The extensive evidence on the change of solubility of anhydrides has also been expressed in the form of a general regularity, namely, that the solubility of anhydrides is decreased by the presence of

[1] Physical Review, **21**, 16 (1905).

[2] Zeitschrift für physikalische Chemie, **17**, 145 (1895).

[3] Goldschmidt has given a theory of this change of solubility, and from it has calculated this ratio to be 1.02, in full agreement with observation. For the details of this instructive theory, which in many respects is similar to the one here given although their initial assumptions are different, I refer to Goldschmidt's article.

[4] Zeitschrift für physikalische Chemie, **18**, 70 (1895).

foreign substances,[1] which in most of the experiments, have been salts.

It can be shown that these changes of solubility are to be expected from theoretical considerations, as follows : If a typical anhydrous substance A forms a series of hydrates in solution, its final solubility can be expressed as

$$S_a = s_a + C_{h_1} + C_{h_2} + C_{h_3} + C_{h_4} + \cdots$$

where the numerical subscripts denote the number of molecules of water in the hydrate. A relation of the form of (14) connects s_a and each C_h, and it is evident from (14) that the dissolution of a foreign substance in the solution and the accompanying decrease of vapor pressure of the solution will change the final solubility of A to

$$S_a' = s_a + C_{h_1}' + C_{h_2}' + C_{h_3}' + C_{h_4}' + \cdots$$

where each C_h' is less than the corresponding C_h, and S_a' therefore less than S_a. Thus there is to be expected a decrease in the solubility of anhydrous substances which form hydrates in solution caused by the presence of foreign substances in solution, a conclusion that agrees with the previously mentioned observed regularity of anhydrides.

The final solubility of a hydrate, H_3 for instance, in water can be expressed as

$$S_{h_3} = C_a'' + C_{h_1}'' + C_{h_2}'' + s_{h_3} + C_{h_4}'' + \cdots$$

and its solubility in a solution of a foreign substance

$$S_{h_3}' = C_a''' + C_{h_1}''' + C_{h_2}''' + s_{h_3} + C_{h_4}''' + \cdots$$

It is evident from (14) that the concentration of the anhydride and those of the hydrates of lower water content than H_3 are increased by the presence of the foreign substance, but that the concentrations of the hydrates higher than H_3 are decreased. Two effects therefore oppose each other and it is not clear whether the final solubility of the hydrate will be lessened or raised by the foreign substance. On the other hand if the solubility equations of a

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[1] Rothmund, Zeitschrift für physikalische Chemie, **33**, 401 (1900). Rothmund has used the word "nonelectrolyte," but it is apparent that the substances whose solubility is decreased may be equally well classed as "anhydrides."

higher hydrate are expressed as has been done for H_3, it is evident. that the number of substances whose concentration is increased is greater and the number whose concentration is decreased is less for the higher hydrate, and it is to be concluded therefore that at temperatures where the two hydrates give saturated solutions of nearly the same concentration, the higher hydrate will show a greater tendency to increase in solubility in a solution of a foreign substance. This conclusion is strictly applicable only to hydrates at their transition temperatures, because it is only at these temperatures where the two solutions are identical that the relative change of solubility of the two hydrates can be determined by the relative number alone of dissolved substances whose concentrations are increased or decreased by the foreign substance. The conclusion agrees with the previously mentioned experiments of Goldschmidt which show that foreign substances increase the solubility of a tetra-hydrate to a greater extent than that of a bi-hydrate.

The theoretical conclusions regarding the influence of foreign substances on the solubility of hydrates and their anhydrides thus agree in a clear and natural manner with well-established and hitherto unexplained facts.

The solubility of many gases, oxygen, hydrogen, nitrogen, for example, is less in solutions than it is in pure water. As these gases are all anhydrous substances, it is possible that their decrease of solubility is due to their being markedly hydrated in solution. True, the solutions that have been examined are mostly electrically conducting salt solutions, in which complications are likely to occur, such as electrostriction,[1] which are here not considered at all. Nevertheless, most of the few experiments on solutions of non-electrolytes indicate in the same manner the formation of hydrates of these gases in solution.

6. Discontinuous Changes of Melting and Polymorphism.

The explanation of some of the peculiarities of the transition temperatures of hydrates that I have attempted assumes that the substance that is unstable in the solid state is nevertheless stable in

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[1] Drude and Nernst, Zeitschrift für physikalische Chemie, 15, 79 (1894). Nernst, Theoretische Chemie, 1900, 445.

solution, and that the formation of hydrate or anhydride which takes place discontinuously in the solid state at one temperature and pressure occurs in solution over a wide range of temperature and pressure. The discontinuity of such transition reactions as opposed to the continuous formation of most substances over a range of temperature, as, for example, the production of hydriodic acid from its elements, is so often emphasized that it seems to me important to understand that the discontinuity of the chemical change does not follow as a consequence of the discontinuity of the formation of the phases. The only reactions that take place at one temperature only are the transition reactions and the meltings. I have here endeavored to show that the transition of hydrates, and what is true of these transitions is quite applicable to all transitions, are not discontinuous in solution, and at another place [1] I have shown that the melting phenomena can also be clearly and quantitatively accounted for on the hypothesis that the solid exists dissolved in the liquid, like any ordinary solution, over a wide range of temperature, or, in other words, that the chemical reaction which gives rise under appropriate conditions of temperature and pressure to the phenomena of melting is quite similar to the ordinary balanced chemical reactions and are like these continuous, though some of its effects appear discontinuous. There is no example, as far as I know, of a chemical reaction which occurs at one temperature only.

8. SUMMARY.

The contents of this article may be summarized as follows:

The initial and final solubility curves for anhydrous and hydrated milk-sugar give an instructive view of the relations that cause the transition temperatures of hydrates. This theory, in which the two substances are regarded as present in equilibrium in solution over a wide range of temperature, shows how it is that the stable form has the smaller solubility and that there is no discontinuity in the properties of the solution at the transition temperature.

A thermodynamic theory of a typical hydration reaction is worked out, which expresses the relations of concentration and solubility that give rise to transition temperatures, leads to a method of cal-

[1] PHYSICAL REVIEW, l. c.

culating solubilities which is found to give an accurate value for milk-sugar, and forms the basis of an extension of Goldschmidt's theory of the influence of foreign substances on the solubility of hydrates.

Evidence is given that the discontinuous physical changes of state such as melting and transition, are the results of chemical changes (*i. e.*, the formation of new molecules) which are themselves continuous over a wide range of temperature.

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