HYDRATION IN SOLUTION AS THE CAUSE OF CERTAIN SOLUBILITY INFLUENCES.

By C. S. Hudson.

Received October 28, 1908.

The recent address by Prof. Victor Rothmund[1] on reciprocal solubility influences and the published discussion by Professor Abegg which follows it lead the writer to present the following criticism:

Löwenherz[2] has found that the solubility of anhydrous sodium sulphate at 32° is decreased considerably by the presence of urea in the solutions, but the solubility of sodium sulphate decahydrate at the same temperature is slightly increased by the urea. From these facts, according to Rothmund's[3] formula for the reciprocation of solubility influences, it is to be concluded that the solubility of urea will be increased in solutions of sodium sulphate decahydrate and decreased in those of the anhydride, but as the solutions of these two crystalline forms of the sulphate are identical in their physical and chemical properties their actions on the solubility of urea cannot be different as demanded above. There is here a direct contradiction between the formula of Rothmund and the experiments. This example is not an exceptional or isolated one, for it can be shown, when these solubility influences are considered from the point of view of the hydration in solution of the dissolved substances, that the influence of foreign substances in the neighborhood of the transition temperatures of all hydrates is necessarily such as to lead in all cases to similar contradictions of Rothmund's formula.

In a discussion of this question in 1901, Professor Abegg[4] gave a suggestion of the cause of these solubility influences which explains them in a very simple manner as due to the existence of hydrates in the solutions, and does not lead to such contradictions as have been mentioned above in the case of hydrated substances. In 1906 I published an article on hydration in solution[5] in which this simpler view was again suggested and developed mathematically; as this work gives a detailed explanation upon thermodynamic grounds of the solubility influences which Prof. Rothmund has discussed in his address, I take this occasion to repeat its main argument, in the hope that light may be thrown on the cause of the solubility changes. At the time that the article was published I was not acquainted with the fact that Professor Abegg had sug-

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[1] *Z. Elektrochem.*, **14**, 532–4 (1908).

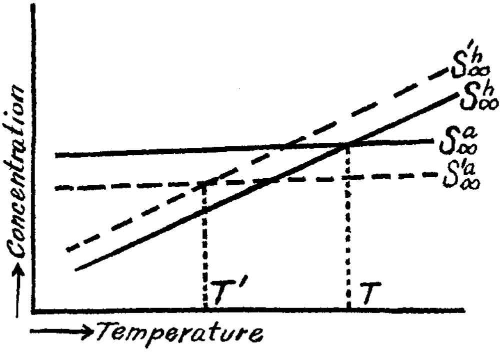
[2] *Z. physik. Chem.*, **18**, 85 (1895).

[3] *Z. Elektrochem.*, **7**, 675–7 (1901). *Z. physik. Chem.*, **40**, 612 (1902). The general statement of the formula is, "If the solubility of a substance A is decreased (or increased) by the addition of B, then in turn the solubility of B must be decreased (or increased) by the addition of A."

[4] *Z. Elektrochem.*, **7**, 677–8 (1901).

[5] *Physic. Rev.*, **23**, 370–81 (1906).

gested before me in a general way this cause of these solubility influences and it accordingly gives me pleasure now to recognize his prior work.



By aid of the accompanying diagram consider the solubility curves of a hydrate and its anhydride, differing in composition by n molecules of water, and having at T a transition temperature. At T the aqueous vapor pressure of a mixture of the two solids is equal by theory to the vapor pressure of their common saturated solution. If now a foreign substance be dissolved in this saturated solution, its vapor pressure becomes less[1] and consequently the transition temperature in the presence of the new solution becomes reduced to T'. The solubility curves of the hydrate and anhydride in the solution of the foreign substance must by theory cross at T', just as they cross similarly at T in the pure solvent. In order, however, that they may cross at T' it is necessary that the solubility of at least one of the two solids be changed by the presence of the foreign substance. Up to this point the considerations are the same as have been advanced by H. Goldschmidt,[2] who takes the further view that the solubility of the anhydride is unaffected, from which it follows necessarily that that of the hydrate must be increased by the foreign substance. It seems to the writer preferable, however, to follow the more general view that the solubilities of both hydrate and anhydride are affected and in the article mentioned this view is developed. If the true solubility of the anhydride be written S^a_0, and the concentration of the hydrate which is in equilibrium in the pure solution with this amount of the anhydride be C_h, the experimental solubility of the anhydride as shown by the curve S^a_∞ may be written $S^a_\infty = S^a_0 + C_h$. Now the ratio[3] $C_h/S^a_0 = \text{const.}\ (p)^n$, where p is the vapor pressure of the solution, and accordingly if p is decreased by the addition of a foreign substance to the solution the ratio C_h/S^a_0 must decrease. Since however S^a_0 is fixed by the presence of anhydride as solid phase C_h must decrease to C_h'. The experimental solubility of the anhydride in a solution of the foreign substance is thus $S'^a_\infty = S^a_0 + C'_h$, and $S'^a_\infty < S^a_\infty$

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[1] The classification of a given substance as "foreign" may accordingly be considered to indicate that its effects on the other dissolved substances are due chiefly to the lowering of the vapor pressure of the solution which follows its introduction.

[2] *Z. physik. Chem.*, **17**, 145 (1895).

[3] *Physic. Rev.*, **23**, 376 (1906); cf. also Nernst, *Z. physik. Chem.*, **11**, 345 (1893).

since $C_h' < C_h$. In other words, it is to be expected that *the solubility of those anhydrides which build hydrates in solution will be decreased* by the addition of foreign substances. By similar reasoning it may be shown that the solubility of the hydrate in the presence of the foreign substance becomes $S'^{h}_{\infty} = S^{h}_{0} + C'_a$ where $S'^{h}_{\infty} > S^{h}_{\infty}$. It thus results that *the same action which causes a decrease of the solubility of anhydrides produces an increase in the solubility of the corresponding hydrates*, a conclusion which agrees with the experiments of Löwenherz cited above, which are not in agreement with the formula of Rothmund. Lastly it may be shown that the solubility of an anhydride which forms in solution a series of hydrates will be decreased by the addition of a foreign substance, and that the solubility of the hydrate which has the highest water content will be increased, but that the solubility relations of the intermediate hydrates are more complicated; thus the experimental solubility of an intermediate hydrate in the pure solvent may be written $S^{h_1}_{\infty} = C_a + S^{h_2}_{0} + C_{h_2}$, and its solubility in the presence of a foreign substance, $S'^{h_2}_{\infty} = C'_a + S^{h_2}_{0} + C'_{h_2}$, where $C'_a > C_a$ and $C'_{h_2} < C_{h_2}$ by the preceding relation. The presence of the foreign substance thus causes an increase of the concentrations of those members of the hydrate series which are of lower water content than the hydrate which forms the solid phase and a decrease of the concentrations of those members of higher water content. Which of these opposing influences will then overbalance, is left undecided; but on the other hand, it is clear that if the changes of solubility of two members of the series are compared, the solubility of the member of higher water content will be increased more, or decreased less as the case may be, than that of the lower member. In experimental proof of this conclusion it may be mentioned that H. Goldschmidt[1] has found that the solubility of the tetrahydrate of sodium *p*-nitrophenol is increased to a greater extent by the addition of non-electrolytes than is that of the bihydrate of the substance.

In conclusion, this criticism may be summed up as follows: The thermodynamic theory of dilute solutions, in which is assumed the validity of the usual gas laws, including Dalton's, leads to the conclusion that the solubility of anhydrides which form hydrates in solution will be decreased by foreign substances, and that the solubility of hydrates will in general be increased, though exceptions to the latter rule are to be foreseen. As long as the investigations on solubility influences are restricted to anhydrous substances, as has been done in Rothmund's investigations, it is to be expected that decreases of solubility will predominate and that Rothmund's reciprocal solubility formula will hold qualitatively. This agreement does not, however, indicate the general correctness of Rothmund's formula and the theoretical views

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[1] *Loc. cit.*, p. 162.

which underlie it, because his theory assumes that Dalton's law is not valid for the solutions,[1] and as shown above, the hydration theory, which assumes Dalton's law valid and thus contradicts Rothmund's view, explains the observed solubility influences on anhydrides fully as well as does Rothmund's formula, and is further in agreement with the facts on the solubility of hydrates which contradict Rothmund's formula. It is not necessary to assume deviations from Dalton's law to explain these solubility influences, because the usual theory of dilute solutions predicts them mathematically as the result of the changes in the hydration of the dissolved substances which follow the addition of foreign substances to the solution. This hydration theory predicts no reciprocal solubility relation such as Rothmund's formula, and explains the solubility effects by an entirely different cause, the existence of hydrates in solution.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEP'T OF AGRICULTURE.]

THE SIGNIFICANCE OF CERTAIN NUMERICAL RELATIONS IN THE SUGAR GROUP.[2]

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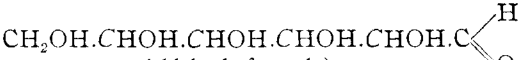
Received October 28, 1908.

Contents: (1) Introduction; (2) The Theoretical Basis of the Relations and Their Experimental Proof; (3) An Empirical Relation among the Equilibrium Constants of the Mutarotating Sugars; (4) A Systematic Nomenclature of the α- and β-Forms of the Sugars and Their Derivatives; (5) Calculations of the Rotatory Powers of Certain of the Sugars and Their Derivatives; (6) The Influence of Temperature on the Equilibrium in Solution between the α- and β-Forms of the Mutarotating Sugars; (7) The Rotatory Powers of the Glucosides; (8) Summary.

1. Introduction.

The selection of a structural formula for glucose which shall epitomize its reactions is one of the older problems of organic chemistry. Of the many formulas that have been proposed only two have withstood the criticisms that have arisen. The reasons that have caused chemists to prefer these formulas need not be repeated here as they have been presented in a very thorough and convincing summary by Lippmann[3] in his two-volume treatise on the chemistry of the sugars. The rival formulas are usually called the aldehyde and lactonic structures and are as follows:



$$\mathrm{CH_2OH.CHOH.CHOH.CHOH.CHOH.C}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{O}\end{smallmatrix}$$

(aldehyde formula)

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[1] See *Z. Elektrochem.*, **7**, 675, first paragraph; cf. Nernst, *Z. physik. Chem.*, **38**, 489.

[2] Published by permission of the Secretary of Agriculture.

[3] *Die Chemie der Zuckerarten*, 3rd edition (1904), Vol. 2, pp. 1675–1722.