

lecting the solvation of the dissolved material. It is often insignificant, but may amount to hundreds of per cent.⁴ It is shown how the amounts of bound water may be measured by the ultracentrifuge.

(4) Both parts of this sentence may be illustrated by contemplation of the certainly non-ideal binary system $\text{H}_2\text{O}-\text{SO}_3$ (Lewis and Randall,³ Fig. 4, p. 39). For a dilute aqueous solution the error due to adhering consistently to use of the partial specific volume

of the anhydrous component SO_3 (in their figure, $\bar{v}_{\text{H}_2\text{O}} = 0.88$, $\bar{v}_{\text{hyd}} = \bar{v}_{\text{H}_2\text{SO}_4} = 0.44$, and therefore $\bar{v}_{\text{anh}} = \bar{v}_{\text{SO}_3} = 0.00$) is insignificant, even though it is being assumed that the anhydrous component SO_3 does not react with water to form the "hydrate" H_2SO_4 , sulfuric acid and its products. If, however, the density of the system in Fig. 4 has been suitably altered by additions of any indifferent substances, the error can be made as great as desired up to ∞ . Hence the behavior of this system as the density is altered would make it simpler to admit the existence of sulfuric acid rather than to record it as merely a deviation from ideal behavior of SO_3 .

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The Description of Binary Solutions

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In the description of a solution the chemical formulas assigned to the components are to some extent arbitrary; it is only the number of components that is fixed for given conditions. Thus, the two components of "sulfuric acid" may be taken as H_2O and SO_3 , or alternatively as H_2O and H_2SO_4 .

There arises the problem as to how the variables of composition (such as the gram fraction of the i^{th} component, x_i , or the mole fraction, N_i) and the partial quantities (such as the partial specific volume, v_i , or the partial molar volume, V_i) change when the *description* of a given solution, *i. e.*, the formula assigned to each component, is changed.¹ As a special case, of particular interest in the study of solvation, the following two descriptions of a binary solution are worthy of consideration.

Description 1.—The chemical formulas of the two components are symbolized by A and B. Furthermore, let x_1 and x_2 denote the gram fractions of A and B, respectively, g_1 and g_2 the values of any partial specific property, g the corresponding (total) specific property (capacity factor per unit volume).

Description 2.—The two components are taken as A and as a compound (real or fictitious) between A and B containing r grams of A to one gram of B. Let x_1' , x_2' , g_1' , g_2' , g' have the same meaning in Description 2 as the corresponding unprimed letters in Description 1.

Descriptions 1 and 2 are seen to be connected by the single parameter, r . In terms of this parameter the transformation equations relevant to the present discussion are readily shown to be

$$x_1' = x_1 - x_2r \quad (1)$$

$$x_2' = x_2 + x_2r \quad (2)$$

$$g_1' = g_1 \quad (3)$$

$$g_2' = (rg_1 + g_2)/(1 + r) \quad (4)$$

$$g' = g$$

(1) This problem is similar to the one discussed by P. J. Van Rysseberghe in *J. Phys. Chem.*, **39**, 403, 415 (1935).

From these equations the following useful property of the curve $g = g(x_2)$ is readily demonstrated. Let a tangent be drawn at any point of the curve $g = g(x_2)$, and let k , h denote the coordinates, in the $x_2 - g$ plane, of any point on this tangent. (See Fig. 1.) Then, for the solution corresponding to the point of tangency

$$g_2' = h, \text{ if } r = (1 - k)/k$$

The condition $r = (1 - k)/k$ evidently means that the composition of the second component in Description 2 is just that of the mixture corresponding to the abscissa k in Description 1.

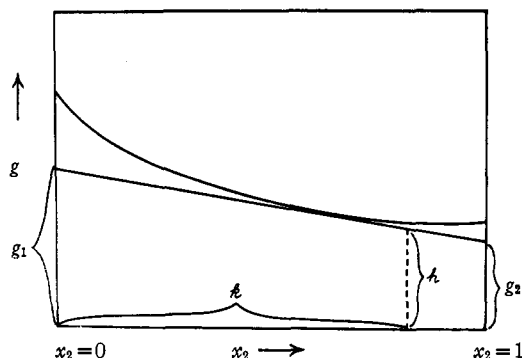


Fig. 1.—The relation of partial quantities to total values of a binary system.

This theorem, which was called to the author's attention by Professor J. W. McBain, and will here be referred to as the "tangent theorem," may be regarded as a generalization of the familiar fact,² indicated in Fig. 1, that the intercepts of the tangent upon the ordinates $x_2 = 0$ and $x_2 = 1$ are g_1 and g_2 , respectively. The usefulness of the theorem lies in showing how, when a value of g_2' for a given solution has been calculated from experimental data (say v_2' from a sedimentation experiment), the corresponding value of r (which measures the amount of solvation) can be found

(2) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, pp. 38-39.

graphically. It may be noted that the same thing is accomplished analytically by equation (4) above.

A proof of the tangent theorem is as follows. From the above mentioned familiar property of the intercepts at $x_2 = 0$ and $x_2 = 1$, it follows that the equation of the tangent in Fig. 1, *i. e.*, in Description 1, is

$$h = (g_2 - g_1)k + g_1$$

The elimination of k from this equation by means of the above condition

$$r = (1 - k)/k$$

gives

$$h = (rg_1 + g_2)/(1 + r) \quad (6)$$

But by equation (4) the right side of (6) equals g_2' . Q. E. D.

If, instead of the gram, the mole is used as the unit of mass, the above relations assume the following form:

Description 1.—Components A and B , mole

fractions N_1 and N_2 , partial molar quantities G_1 and G_2 , molar quantity G .

Description 2.—Components A and A_sB (*i. e.*, s moles of A to one mole of B), quantities N_1' , N_2' , G_1' , G_2' , G .

The transformation equations in terms of the parameter s become

$$N_1' = (N_1 - sN_2)/(1 - sN_2)$$

$$N_2' = N_2/(1 - sN_2)$$

$$G_1' = G_1$$

$$G_2' = sG_1 + G_2$$

$$G' = G/(1 - sN_2)$$

The tangent theorem becomes

$$G_2' = h/k \text{ if } s = (1 - k)/k$$

that is, G_2' is not given directly by the intercept of the tangent but by the quotient of the intercept by its abscissa.

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[CONTRIBUTION FROM THE CHEMICAL AND OCEANOGRAPHIC LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

Equilibria in the Saturated Solutions of Salts Occurring in Sea Water. I. The Ternary Systems $MgCl_2$ - KCl - H_2O , $MgCl_2$ - $CaCl_2$ - H_2O , $CaCl_2$ - KCl - H_2O and $CaCl_2$ - $NaCl$ - H_2O at 0°

BY IVER IGELSRUD WITH THOMAS G. THOMPSON

Sea water is a complex solution containing, in addition to small quantities of the ions of a large number of other substances, the four major cations Mg^{++} , Ca^{++} , Na^+ and K^+ and the two major anions Cl^- and SO_4^{--} . To these six ions may be added the ions of carbonic acid, for the carbonates are important constituents of many oceanic sediments. In the saturated solutions of the major salts derived from the sea, the carbonates are of minor importance. Because of their insolubility the influence they exert upon the solubilities of the other salts is small. In the natural evaporation of sea water, for example, they precipitate in the early stages of the concentration and are thus removed from the solution before it becomes saturated for any other salt, calcium sulfate excepted. As a first approximation then, sea water may be considered a six-component system composed of water and five independent salts.

A survey of the solubility data for the salts found in the sea, contained in the "International Critical Tables," together with data published since their appearance, shows the considerable gaps which exist. The solubilities of the individ-

ual salts are known except for calcium sulfate, down to their eutectic temperatures. Considerable is also known, but very incompletely, about the mutual solubilities of two or more salts. Sixteen ternary systems may be formed, each containing water and two different salts. Only five have been completely determined from above 100° down to the eutectic temperature. Of the remainder, six have been investigated with some degree of completeness above 0° , ten have not been investigated below 0° and one, the system $MgSO_4$ - $CaSO_4$ - H_2O , very incompletely at 25° only. Of the fourteen quaternary systems, consisting of three independent salts and water, only five have been worked out completely between 0 and about 100° . Fragmentary data at one or more temperatures exist for some of the others. Four have not been studied in any manner. Of the six quinary systems, one, the system consisting of water and the chlorides and sulfates of magnesium, sodium and potassium, has been determined in the temperature range of 0 to 83° . For two others, there are incomplete data and three have not been investigated at all. The six com-