

although the salt pair sodium chloride and sodium iodide is known to form solid solutions at the temperatures of the melting points, the system is

found to form neither double salts nor solid solutions at the temperatures here reported.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

## The Determination of Bound Water by Means of the Ultracentrifuge

BY JAMES W. MCBAIN

A considerable literature has accumulated around the problem, fundamental in physical chemistry and even more in biology, as to the amount of solvent which may be considered as existing as such in a solution, as distinguished from the solvent which is chemically or otherwise combined with the dissolved substance. Most methods are forced to rely either upon an interpretation of an observed deviation from ideal behavior or upon the assumption that a particular reference substance does not dissolve in, or in any way react with, the dissolved substance or its water of hydration. We have elsewhere<sup>1</sup> suggested, without elaboration, that the ultracentrifuge affords a new and sometimes more certain method of determining bound water. It is the purpose of this communication to discuss the theory of the new method.

That the subject has not been clearly understood is illustrated by the following quotation:<sup>2</sup> "Solvation is another factor affecting molecular weight determinations in various ways. In the case of osmotic pressure measurements in dilute solutions, solvation to the extent of 100 per cent. or so has a negligible effect on the calculated molecular weight. The same is true for ultracentrifuge determinations unless the partial specific volumes of the solvated and unsolvated molecules differ, whereupon there is a corresponding error in the calculated molecular weight. For cellulose esters and ethers in organic solvents, the effect is probably not marked." Evidently it has been overlooked that whenever sedimentation is observed the partial specific volumes of solvated and unsolvated molecules must differ significantly (see below and Fig. 1).

The best known discussion of the methods of deriving partial specific volumes is that of Lewis and Randall, who give four methods of calculating

(1) J. W. McBain, *Nature*, **135**, 831 (1935).

(2) E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 165 (1935).

them from the observed densities of a binary system.<sup>3</sup> We shall therefore first discuss partial specific volumes in a binary system as illustrated by their "Method IV (graphical, method of intercepts)" in Fig. 1.

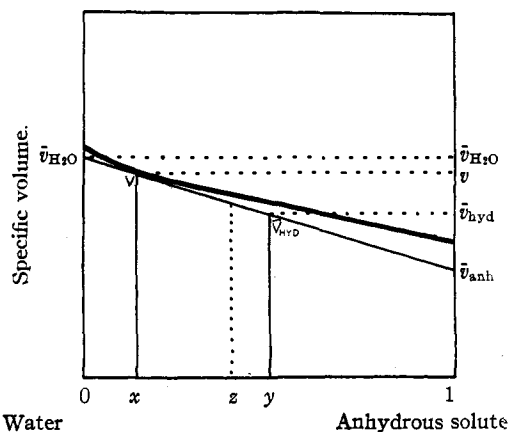


Fig. 1.—The relation between partial specific volumes of hydrated and anhydrous solute.

In Fig. 1, the reciprocal of the density, or the specific volume  $v$ , for a range of solutions is plotted against composition, from pure water on the left to anhydrous solute on the right. The particular solution under observation is taken as containing  $x$  grams of anhydrous solute and  $1 - x$  grams of water and having the specific volume  $v$ . The partial specific volumes of the pure constituents are designated as  $\bar{v}_{\text{H}_2\text{O}}$  and  $\bar{v}_{\text{anh}}$ , respectively, at the ends of the tangent.  $\bar{v}_{\text{hyd}}$  is therefore the partial specific volume of the hydrate referred to in the quotation above. It is at once evident from inspection that  $\bar{v}_{\text{hyd}}$  for the case quoted must lie closer to the value  $v$  than to the value  $\bar{v}_{\text{anh}}$ . In the extreme case where  $x = 0$  it will lie exactly half way between.

This is of essential importance because the very occurrence of any kind of sedimentation depends

(3) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 33-41.

upon the difference between  $v$  and  $\bar{v}$ . Observations in the ultracentrifuge necessarily depend upon the product  $M(1 - \bar{v}\rho)$  where  $\rho$ , the density of the actual solution equals  $1/v$ . Hence, for the quoted case, if sedimentation occurs,  $(1 - \bar{v}_{\text{hyd}}\rho)$  is less than half as great as  $(1 - \bar{v}_{\text{anh}}\rho)$ , and only for  $x = 0$  is  $(1 - \bar{v}_{\text{hyd}}\rho)$  just half as great as  $(1 - \bar{v}_{\text{anh}}\rho)$ . This is more obvious if these two quantities are expressed in the form  $(1 - \bar{v}_{\text{hyd}}/v)$  and  $(1 - \bar{v}_{\text{anh}}/v)$ , respectively, or  $(v - \bar{v}_{\text{hyd}})/v$  and  $(v - \bar{v}_{\text{anh}})/v$ .

Only for values of  $x$  so small as to be negligible is the actual sedimentation unaffected by solvation in a binary system with no additions. Very few such systems have ever been studied, as it is customary to add third substances or buffers and thus arbitrarily to increase  $\rho$ . However, for the pure binary systems it is readily shown that  $M_{\text{hyd}}(1 - \bar{v}_{\text{hyd}}\rho)$  is identical with  $M_{\text{anh}}(1 - \bar{v}_{\text{anh}}\rho)$  for all values of  $y$  but only for  $x = 0$ . In other words, strictly consistent calculation will in this case give the same weight of anhydrous solute in the heavier hydrated molecules as in the supposedly anhydrous molecule.

It is seen that in general

$$v = \bar{v}_{\text{H}_2\text{O}} - x(\bar{v}_{\text{H}_2\text{O}} - \bar{v}_{\text{anh}})$$

$$\bar{v}_{\text{hyd}} = \bar{v}_{\text{H}_2\text{O}} - y(\bar{v}_{\text{H}_2\text{O}} - \bar{v}_{\text{anh}})$$

and  $M_{\text{hyd}} = M_{\text{anh}}/y$ . For larger values of  $x$ , then, solvation will affect the actual sedimentation in the proportion  $[M_{\text{hyd}}(y - x)(\bar{v}_{\text{H}_2\text{O}} - \bar{v}_{\text{anh}})] / [M_{\text{anh}}(1 - x)(\bar{v}_{\text{H}_2\text{O}} - \bar{v}_{\text{anh}})]$  or  $(y - x)/(y - xy)$ . Hence the observed molecular weight will be in error by the same proportion if the solute is erroneously assumed anhydrous and the value  $\bar{v}_{\text{anh}}$  used instead of  $\bar{v}_{\text{hyd}}$ , for  $\bar{v}_{\text{anh}}$  and  $(1 - \bar{v}_{\text{anh}}\rho)$  are fixed quantities.

Now in the ultracentrifuge we have pointed out that the actual value of the partial specific volume of the solvated sedimenting material is exactly equal to the reciprocal of the density of the total solution if the density has been so adjusted by suitable additions that no sedimentation either upward or downward is observed. This is true no matter how complicated the system and no matter how much the solute has been contaminated or its solvation altered. Hence it is experimentally possible accurately to measure the partial specific volume of such a material as it actually exists in solution, even where only a minute quantity is available for measurement.

In general, the partial specific volume so determined may be compared with the values in

the binary system as illustrated in Fig. 1, and therefore  $M_{\text{hyd}}$  and the composition of the hydrate  $y$  be ascertained.

It is, of course, unnecessary to find the system in which sedimentation is completely inhibited. It is usually better to observe how sedimentation (velocity or equilibrium) depends upon alterations in the density brought about by progressive additions to the binary system. This shows whether or not the dissolved material is altered by such additions. Following the curve to zero addition will then give the unaltered solvation in the binary system. This procedure has exactly the same validity as the well-known Harned method of determining the activity of an organic acid using hydrogen and chloride electrodes and extrapolating, if desired, to zero additions of chloride.

The sedimentation in systems where the density  $S$  has been altered by additions such as buffers without altering  $M_{\text{hyd}}$  and  $\bar{v}_{\text{hyd}}$  will be affected in the following manner. If  $v$  has been made equal to  $\bar{v}_{\text{H}_2\text{O}} - z(\bar{v}_{\text{H}_2\text{O}} - \bar{v}_{\text{anh}})$  where  $z$  is merely chosen so as to express the alteration in the same units as are employed above,  $z$  being that composition in Fig. 1 where the point on the tangent equals the reciprocal of the density of the actual total system,  $\bar{v}_{\text{hyd}}$  is still equal to  $\bar{v}_{\text{H}_2\text{O}} - y(\bar{v}_{\text{H}_2\text{O}} - \bar{v}_{\text{anh}})$  and  $M_{\text{hyd}} = M_{\text{anh}}/y$ . Then the proportion in which the actual sedimentation is altered by the addition is

$$M_{\text{hyd}}(y - z)(\bar{v}_{\text{H}_2\text{O}} - \bar{v}_{\text{anh}}) / M_{\text{anh}}(1 - z)(\bar{v}_{\text{H}_2\text{O}} - \bar{v}_{\text{anh}})$$

or  $(y - z)/(y - yz)$ . It is readily seen that the so calculated molecular weight for the supposedly anhydrous solute is in error in this same proportion.

These considerations apply to all observations in any form of ultracentrifuge, whether one of the transparent forms or the opaque spinning top, and whether dealing with solutions, sols, jellies, curds or pastes.

It seems clear that precisely similar considerations must apply to sedimentation in a gravitational field as studied for example by des Coudres and others many years ago. Finally, it may be pointed out that the partial volumes commonly employed do not refer to the systems as they exist in the hydrostatic field of the ultracentrifuge but rather to those observed under ordinary laboratory conditions.

#### Summary

Simple formulas are derived to show the error caused in ultracentrifuge observations by neg-

lecting the solvation of the dissolved material. It is often insignificant, but may amount to hundreds of per cent.<sup>4</sup> 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 H<sub>2</sub>O-SO<sub>3</sub> (Lewis and Randall,<sup>3</sup> 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<sub>3</sub> (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<sub>3</sub> does not react with water to form the "hydrate" H<sub>2</sub>SO<sub>4</sub>, 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  $\infty$ . 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<sub>3</sub>.

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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<sub>2</sub>O and SO<sub>3</sub>, or alternatively as H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub>.

There arises the problem as to how the variables of composition (such as the gram fraction of the *i*<sup>th</sup> 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.<sup>1</sup> 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.

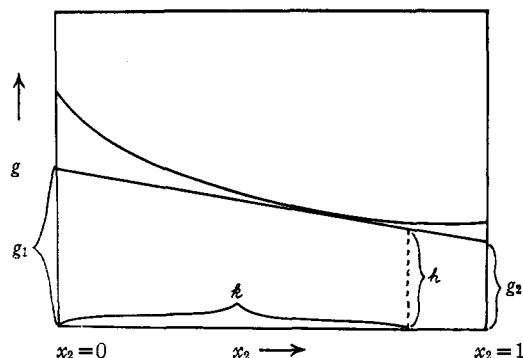


Fig. 1.—The relation of partial quantities to total values of a binary system.

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,<sup>2</sup> 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.