

THE PHYSICAL REVIEW.

A STUDY OF APPARENT SPECIFIC VOLUME IN SOLUTION.

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I. INTRODUCTION.

THE research herein set forth had for its origin a desire to obtain further information as to the physical properties of dissolved substances when in very concentrated aqueous solution, that is, near the saturation point and even in the region of supersaturation. The percentage of ionization in such solutions being relatively low, it is reasonable to expect that the molecular properties of the solute will either resemble in large degree those of the pure substance in the liquid state, or else will be unique in some way and differ from those of the same solute in dilute solution.

The matter is here approached in one way only, perhaps the simplest. The immediate subject of the present paper relates to the volume of the solution as compared to the normal volume of the contained water, or what will be called the *apparent specific volume* of the dissolved solute; by which is meant, *the volume of the solution containing one gram of the solute, minus the natural volume of the pure water entering into it, at the same temperature*. The quantity just defined will be designated by Δ .

Δ will, of course, be generally less than the specific volume of the solid substance, sometimes very much less. In the case of potassium chlorate in saturated solution at ordinary temperatures, Δ is about 84 per cent. of the specific volume of the crystals, a ratio, it may be remarked, not differing very widely from that of the specific volume of liquid water and solid ice.

The values and variations of this quantity Δ under different circumstances and for different substances are here to receive attention. The first investigations relate to the variations of Δ with temperature at fixed concentration (what may be called the coefficient of expansion in solution), and the variations of Δ with concentration at fixed temperature.

II. EXPERIMENTAL ARRANGEMENTS FOR OBSERVING CONTINUOUS CHANGE IN DENSITY OF SOLUTION.

Determinations of Δ will of course depend upon measurements of the density of the solution. It so happens that the excellent standard tables of physico-chemical data which are so useful for general purposes, such, for example, as Landolt and Börnstein, Castell-Evans, etc., do not give values of sufficient minuteness and precision for this purpose. In most of the work herein described, the probable errors of the measured densities are in the fifth decimal place, while the solution densities published in standard tables are usually given to the third or fourth place only.

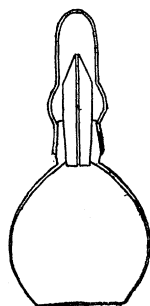


Fig. 1.

After considering and discarding in turn various forms of dilatometers and hydrometers, on account of the experimental difficulties involved in adapting them to highly precise absolute measurements with saturated solutions of accurately known concentration, the writer has adopted, as a standard, a specially designed pyknometer of the specific gravity bottle form and of about 25 c.c. capacity, shown in Fig. 1. The special features are (1) a tight-fitting glass cap, ground upon the neck of the bottle, which effectually prevents any measurable evaporation from neck and bore even after twenty-four hours in a desiccator; and (2) the conically pointed stopper, employed instead of the usual flat-topped stopper in order to prevent the formation of the overflow drop, which is so readily sucked in as the bottle cools after filling. The overflow immediately runs down the steep sides of the cone and cannot be sucked in.

In order to ensure still greater constancy of filling, the force with which the stopper is inserted is regulated and rendered uniform by means of a special instrument shown in Fig. 2. This is pressed down upon the conical stopper with the finger, against the spring, until the sharp point touches the finger, the overflow escaping through the slot in the side of the tube. The pressure on the stopper at this moment is about eight ounces.



Fig. 2.

In the process of filling, the liquid is placed in a closed jar or glass cell about 5 cm. in diameter, which is kept under precise thermostatic control. The open bottle is completely immersed in the liquid, where it remains for some time before being closed and removed. The stopper, held by a special clamp or handle, is also immersed in the liquid, so that all can come to the common temperature, indicated by a thermometer inserted

in the bottle, and reading to tenths of a degree. The conditions having become stable and uniform, the cell is uncovered and the bottle quickly stoppered. The stopper projects above the liquid surface, so that the pressure regulator can be applied. The bottle is now removed with another special forceps, quickly dried with desiccated gauze, and capped. When cool, it is ready for weighing.

The probable error of such a filling and weighing with this capped, cone-stoppered pyknometer has been found from a series of observations to be about 0.00025 g., or one-thousandth of one per cent., and is only half that with a flat-stoppered bottle similarly capped, the observations being therefore four times as reliable. The determination of Δ requires great absolute precision in the measurements of the density of the solution, and some of the earlier results, obtained with an ordinary specific gravity bottle loosely capped, were found later to be misleading.

Unusual care has to be exercised, also, in the weighing, since absolute results are required. To this end the balance resides permanently on a heavy pier in the center of a small room. The case is blanketed and otherwise shielded from temperature inequalities, as is very necessary,¹ and the pointer readings made at a moderate distance by means of a large collimating lens. Double weighings are always employed, the sensibility constants of the balance being determined with great care from time to time with standardized weights. The probable error of a single weighing has been found from several series of observations to be less than one millionth of the load. The vacuum correction is applied in the usual manner.

The dilatation constants of the pyknometer are also periodically determined by filling with water at different temperatures and weighing, as described above. Thus any gradual "creeping" of the glass with continued use is detected and eliminated from the results. Newly blown bottles are especially likely to exhibit such variations.

The stock solutions are carefully synthesized, of such strength as to become saturated at a predetermined temperature. They are made up one or two liters at a time and kept in tightly corked flasks. When desired for use, the flask is heated while still tightly closed until the crystals dissolve, and then cooled to about the required temperature, the specimen being then quickly removed to the closed thermostatic cell. The stock solutions are not exposed to evaporation for more than a few seconds during their entire history, and therefore remain very nearly constant.

All the earlier work was done directly by the pyknometer method

¹ Weld, Iowa Academy of Science, Proc., 1909, Vol. 16, p. 181.

above described, and it is hardly necessary to say that it was very tedious. Every point on the Δ curve represented a separate specimen from the stock solution and a filling and weighing of the pyknometer (an operation requiring from half to three-quarters of an hour), so that only a few points could be obtained in an afternoon's work.

In order to replace this slow process by a sufficiently reliable one that would be quicker and at the same time more nearly continuous in its indications of Δ , the writer has resorted to an Archimedes principle method, which may be called the *secondary* method, dependent upon the absolute pyknometer method as a *primary* standard of accuracy. The sinker consists of a loaded glass bulb of about 34 c.c. volume and weighing about 50 g. suspended from the balance beam by a very fine platinum wire. When immersed in the solution, and counterpoised with weights, this arrangement acts as a very sensitive hydrometer, whose scale is represented jointly by the weights and the balance pointer scale. A change of temperature of one degree is accompanied by an alteration of as much as ten to fifteen milligrams in buoyancy. This change is of course neutralized to the nearest milligram by the addition or removal of weights, the fractional milligram being then read off as a slight deflection on the pointer scale from the known sensibility constants. The rider has not been resorted to in any of the work, except as a means of adjusting the pointer to zero at the outset of each experiment. The pointer has to be read stationary, not by oscillations, as the viscosity of the solution quickly damps out the oscillations.

The sinker, like the pyknometer, has been accurately calibrated for dilatation by immersing in pure water of varying temperature. The standardization presently to be explained may possibly render this unnecessary, but it has been thought best to make the secondary method as nearly absolute as practicable without sacrificing its convenience.

A more immediate reason, even than that of labor-saving, for adopting the secondary method, was the fact that it involves much less disturbance of the liquid under examination, and is therefore better adapted to use with supersaturated solutions, which are likely to begin crystallizing out if agitated. The sinker hangs very quietly in the liquid, which is examined at short intervals in a strong beam of light; and when crystals begin to form, they are immediately detected and the work stopped.

The principal sources of discrepancy between the secondary and absolute measurements lie (1) in the impossibility of double weighings in the former, and hence the entrance into the results of the balance arm-ratio (which differs on different days and often shows a slow progressive variation even in the course of a few hours' work); and (2) in the un-

certain capillary force acting upon the platinum suspension wire at the surface of the liquid. It is also difficult to get the depth of solution above the sinker quite constant, so that the amount of the fine wire immersed is slightly variable in different experiments.

The reduction of the secondary results to absolute measure is made by means of corresponding values of the specific volume *of the solution*, this being the first stage reached in common by the two methods. This process may be illustrated by the following example.

A near-saturated solution of potassium chlorate was being experimented upon. The specific volumes of the solution obtained from a typical series of sinker observations are here tabulated along with corresponding pyknometer determinations for certain temperatures.

Temp.	Sinker Method.	Pyknometer Method.	Calculated Absolute.
°			
23.0	0.952750		0.952839
23.5	0.952879		0.952982
24.0	0.953003		0.953121
24.5	0.953177	0.953322	0.953316
25.0	0.953339	0.953488	0.953497
25.5	0.953505		0.953683
26.0	0.953678		0.953876
26.5	0.953840	0.954059	0.954057
27.0	0.954012		0.954249
27.5	0.954187		0.954446
28.0	0.954366		0.954646
28.5	0.954526		0.954824
29.0	0.954701		0.955020
29.5	0.954872		0.955212
30.0	0.955075		0.955438
31.0	0.955426		0.955831

The values in the second column constitute the secondary series of specific volumes taken with the sinker, and involve all the persistent errors inherent in the method. Each of the three determinations in the third column is the mean of three careful measurements with the pyknometer, and these may be considered as "tie points," to be used in reducing the secondary series to absolute measure. This "tying in" process is as follows.

Let X = a secondary result at any temperature,

Y = the corresponding absolute result desired.

Assume the simple linear relation $Y = AX + B$ as the basis of the observation equations which are to connect the series. There will be as many of these equations as there are absolute data available, in this case three.

Least square adjustment (which need be here applied only to the last four decimal places), now gives the constants A and B , and the transformation formula with these values inserted becomes for this case

$$Y = 1.1183 X - 0.112622.$$

The adoption of such a simple linear relation is justified by the small values of the discrepancies to be eliminated. The absolute specific volumes thus calculated are given in the last column of the table, and the whole process is shown graphically on the accompanying diagram, Fig. 3. The "tie points" in this particular case were taken too near

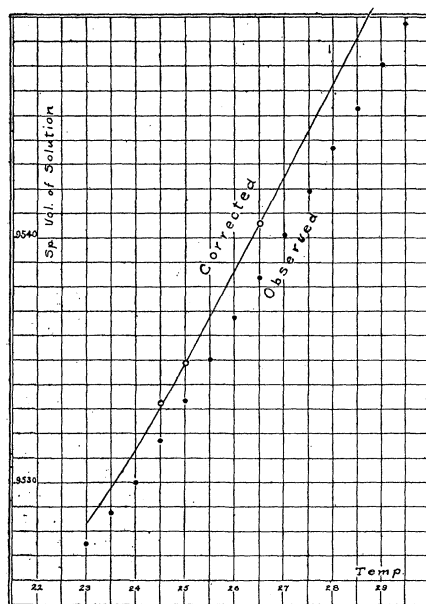


Fig. 3.

together. They have usually been chosen as far apart as possible, but they cannot enter the region of supersaturation on account of the formation of crystals in the pycnometer.

For the study of the behavior of Δ at given concentration over any particular temperature range, several such series as the above may be made in a short time (each series taking but one specimen from the stock solution), the series weighted, averaged and standardized, and the corresponding Δ series then calculated from the known concentration and the known specific volumes of pure water.

III. RESULTS WITH POTASSIUM CHLORATE.

The only substance with which complete series have been obtained up to the present time is potassium chlorate, but experiments are now in progress along similar lines, in which copper sulphate, sodium carbonate, sodium sulphate and possibly other solutes are to be examined, the results to be published later in a separate paper. The results with potassium chlorate are, however, in certain respects so singular, as to lead the writer to present them at this stage.

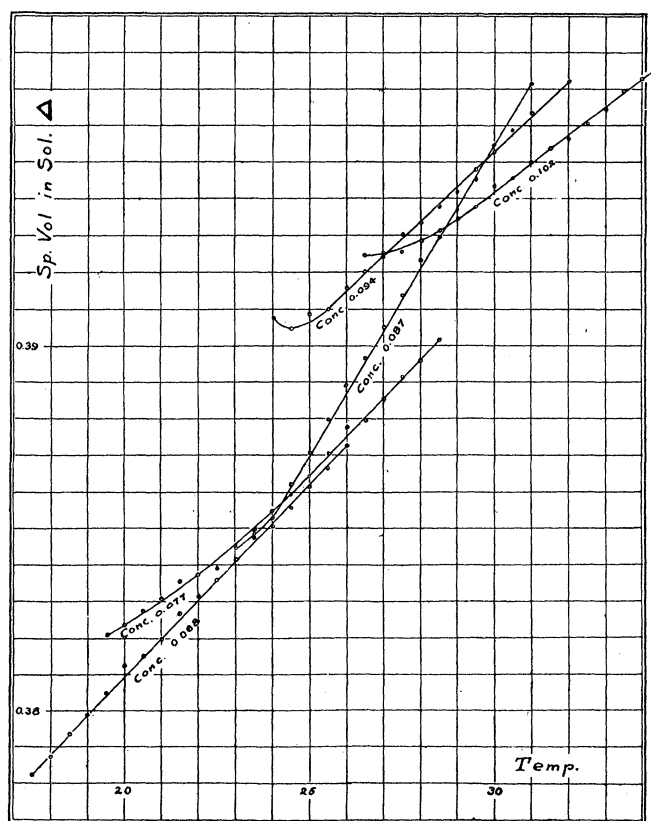


Fig. 4.

Potassium chlorate is rather sparingly soluble in water, about 7 per cent. dissolving at 20° C. The solubility rapidly increases with temperature, the heat of solution and hence the constant *B* of the solubility equation being large. This gives a sharply defined saturation, which is advantageous in some ways and in others not so. The other salts mentioned are much more soluble and saturation is less distinct.

In Fig. 4 are shown typical curves for potassium chlorate, in which abscissas represent temperature and ordinates the apparent specific volume in solution, Δ . The concentration is indicated for each curve. Concentrations are expressed in grams of solute per gram water.

In each of the curves except that for the most dilute solution, there is a distinct upward concavity and an unmistakable suggestion of approaching a minimum as the temperature is lowered. A minimum actually appears in the curve for concentration 0.094, and there is indication that it would be reached in the others if the experiment could be extended far enough into the region of supersaturation, which was successfully accomplished only in the one case. The saturation temperature for this concentration is about $27^{\circ}.5$, or three degrees above the minimum indicated by the curve.

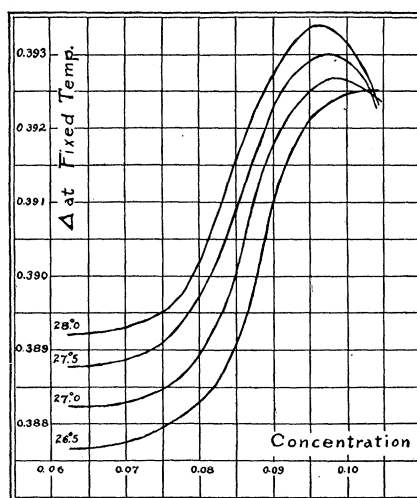


Fig. 5.

The significance of this concavity in the curves, and of the minimum if it really exists, is very interesting, for it suggests at once the behavior of pure water just before it crystallizes on cooling, and of impure water (as a weak solution of salt) when supercooled. It is well known that the minimum volume point, which is at 4° for pure water, is lowered by the addition of a solute, and soon passes below the freezing point of the solution, so as not to be attained except by supercooling. Now if we could interchange the relations of solute and solvent, and regard a concentrated solution as merely a mixture of two substances both in the fused condition (though below their pure melting points), we might regard this observed behavior of potassium chlorate mixed with water as

analogous to that of water mixed with salt, and explain it by something akin to Roentgen's ice molecule hypothesis. This would also be in agreement with the fact that, the more impurity (water) there is mixed with the substance under examination (potassium chlorate), the farther below the crystallizing (saturation) point of the latter does the minimum specific volume appear to be, which is evident from an examination of the curves.

The second interesting feature of these results is the variation of Δ with concentration at a fixed temperature, obtained from the same series of experiments. This is shown typically by the curves in Fig. 5, each of which pertains to a single temperature.

It was expected that there would be, for each temperature, a more or less uniform change in Δ with concentration. On the contrary, we observe at 26°.5, for example, a sudden increase in the neighborhood of

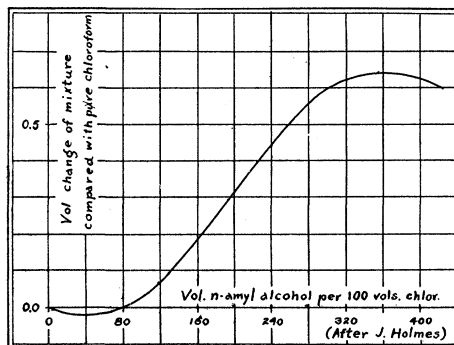


Fig. 6.

concentration 0.087, giving a point of inflection; while for the higher temperatures, furthermore, Δ goes through a very pronounced maximum for concentrations between 0.095 and 0.100. For this phenomenon the writer has, as yet, no explanation to suggest. It is interesting to compare these results with those obtained by J. Holmes¹ on the volume of a mixture of *n*-amyl alcohol in chloroform. As the percentage of the alcohol, as compared with the chloroform, increases, the volume of the mixture goes through a minimum and then a maximum with a point of inflection between (Fig. 6), the curve being somewhat suggestive of some of the curves of Fig. 5. Probably a separate research, arranged along somewhat different lines of procedure, might be profitably directed toward this question.

¹ J. Holmes, Intermiscibility of Liquids, Chem. Soc. Jour., 103, Dec., 1913.

In conclusion, attention may be called to the very large apparent coefficient of expansion of potassium chlorate in solution, that is, the rapid fractional increase of Δ with temperature, as indicated by the slopes of the curves in Fig. 4. This is seen to be especially large for concentration 0.087, and the average apparent volume coefficient per centigrade degree for all the concentrations tested, taken outside the neighborhood of the minimum volume, is about 0.0029, a value more than fifteen times the volume coefficient of expansion of mercury and about four-fifths that of a perfect gas.

Very little physical significance can, however, be attached to these latter figures, inasmuch as the quantity Δ is defined in an arbitrary manner, without any reference to the possible shrinkage of the water itself when the salt is dissolved in it,¹ which would make the actual value of the volume of the salt in solution larger than Δ by an unknown amount. The point is that, while Δ itself represents something quite uncertain, the *changes* in Δ here observed undoubtedly do represent some physical process peculiar to the solute and probably connected with its molecular structure. In what manner this process depends upon the dissolved substance, may appear more clearly when other substances have been similarly experimented upon.

I desire to acknowledge my indebtedness to Mr. M. H. Teeuwen, of the University of Iowa, for assistance in constructing certain parts of the apparatus, and to several of my students, whose painstaking co-operation proved very helpful in the experimental work.

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¹ W. F. Magie, PHYS. REV., Vol. 18, p. 449.