In conclusion we are glad to express our gratitude to the Carnegie Institution of Washington, for generous pecuniary assistance.

Summary.

1. The method of Berthelot and Kahlenberg for determining heats of vaporization has been modified in such a way as to diminish greatly the errors inherent in the experimentation. A Dewar vessel was used as a vaporizer and the calorimetric work was strictly adiabatic.

2. A serious persistent disturbing effect, amounting to about 0.1 per cent. of the total per minute, was eliminated by conducting experiments at different speeds and extrapolating the results to a hypothetical instantaneous experiment from which the disturbing effect may be supposed to be eliminated, because this was found to depend essentially upon time. The disturbing effect was probably premature condensation in the very narrow zone between the vaporizer and the condenser.

3. The heat of vaporization of a true gram of water was found by this method to be 538.9 $\text{cal.}_{21}{}^\circ$ or 2.251 kilojoules per gram. A gram molecule therefore requires 9.707 $\text{cal.}_{21}{}^\circ$ or 40.54 kilojoules, when the vaporization is conducted at 100° ($O = 16.000$, $1\ \text{cal.}_{21}{}^\circ = 4.177$ kilojoules).

4. Comparison of this figure with the results of others shows that the method is trustworthy and suitable for general use.

5. Numerous other liquids also have been used in the apparatus, and consistent results with them have been obtained. These will be communicated in a future paper, when the specific heats of the liquids have been determined.

CAMBRIDGE, MASS.

THE POSSIBLE SOLID SOLUTION OF WATER IN CRYSTALS.

BY THEODORE W. RICHARDS.

Received April 25, 1911.

In a recent paper Perdue and Hulett[1] have published the results of several careful analyses of cadmium sulfate, which deserve an adequate explanation. According to these determinations the amount of cadmium both in the hydrated sulfate and in the anhydrous sulfate is less than that required by the usually accepted atomic weight of cadmium, sulfur, oxygen and hydrogen, and the formulas $3CdSO_4.8H_2O$ and $CdSO_4$ respectively.

The determination of the cadmium seems to have been well executed; the experimenters adopted two well known and long tested methods, namely, the use of mercury as a receptacle for the electrolytic precipitate

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[1] Perdue and Hulett, *J. Physic. Chem.*, 15, 147 (1911).

on the one hand[1] and the method of washing the deposit while it is still a cathode[2] on the other hand.

Perdue and Hulett evidently believe that their results are best explained by assuming an error in the accepted atomic weight of cadmium, but this atomic weight rests on the very careful work of Baxter[3] carried out by methods quite as well tested and trustworthy as those used by Hulett; and while no work of this sort even in the very most experienced hands can be considered as quite wholly final, the presumption is decidedly in favor of the accuracy of the generally accepted value for cadmium.

Here is a definit contradiction. An explanation of the inconsistency is important, not only to those interested in the atomic weights, but also to physical chemists, especially those concerned with the causes which lie back of the difficulties of analytical chemistry. I shall endeavor to show that in all probability both sets of data are correct, and that the difficulty lies solely in the interpretation.

If the fact discovered by the Princeton investigators stood alone, an attempt at explanation might be hazardous; but their results are wholly in line with many other observations made in recent years concerning the amount of water in crystallized salts. Over two decades ago it was shown in the Chemical Laboratory of Harvard College that crystallized copper sulfate also contains an excessive amount of water, about 36.11 per cent., instead of the theoretical quantity 36.07.[4] Moreover, the salt still retained after drying to constant weight at 400° about 0.12 per cent. of this quantity, as nearly as could be estimated at that time. This water only escaped when the salt itself was decomposed. Finely powdering the salt and using very clear crystals did not seem to diminish very greatly the excess of water. Many other similar cases might be cited.

In a more recent paper, read at the meeting of the American Philosophical Society in 1903,[5] I took occasion to point out that included solvent is a great source of error in dealing with crystals obtained from solutions, quoting many well-recognized cases, such as for example the inclusion of solvent in crystallized silver, first noticed by Lord Rayleigh, later verified in the Chemical Laboratory of Harvard College, and recently confirmed by Hulett himself. It was made clear that this cause of error must be taken into account whenever a crystallized salt is weighed. Yet

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[1] W. Gibbs, *Am. Chem. J.*, 13, 571; Luckow, *Z. anal. Chem.*, 26, 113; Vortmann, *Ber.*, 24, 2749; E. F. Smith, "Electro-analysis," p. 58. This method Perdue and Hulett improved by using an amalgamated platinum receptacle.

[2] See for example, Classen, *Ausgewählte Methoden der analytischen Chemie*, 1, 112 (1901).

[3] Baxter, *Pub. Car. Inst.*, 135, 3–26 (1910).

[4] Richards, *Proc. Am. Acad.*, 26, 267 (1891); also, *Z. anorg. Chem.*, 1, 179 (1892).

[5] Richards, "The Inclusion and Occlusion of Solvent in Crystals," *Proc. Am. Phil. Soc.*, 42, 28 (1903); *Z. physik. Chem.*, 46, 189 (1903).

another point was emphasized in this paper, namely, the frequent presence of adsorbed moisture in the surface of crystals. This increases, of course, as the surface is increased; therefore the act of powdering, in order to break up the cells containing mother liquor, increases the adsorption.

Nevertheless for the recent work of Hulett and the old work on copper sulfate neither of these explanations seems to be wholly sufficient, although probably explaining a part of the discrepancy as regards the crystallized salt. The crystals employed in both cases were clear and transparent, and (at any rate in the case of copper sulfate) probably enough crushing was effected to open most of the objectionable cells. If any considerable amount of enclosed mother liquor had been present in enclosed cells, the crystals would have been expected to appear slightly cloudy in places; but as far as appearances went they were homogeneous. One is inclined therefore to search for a superposed effect which might account for this apparent homogeneity.

At the close of the previously mentioned paper on inclusion and occlusion of solvent in crystals[1] a hint is given of a possible explanation for the existence of a surplus of water in crystals; and because, as time goes on, this explanation seems more and more probable to me, I venture to amplify it now.

May it not be that crystals formed from aqueous solution have power to *dissolve* water in the form of a solid solution? In his interesting and conclusive paper on solid solutions van't Hoff[2] showed that solid substances may dissolve not only isomorphous substances, but also in greater or less amounts almost any sort of material; and he pointed to the colors of gems and to a great variety of other well known phenomena as examples.[3] He did not suggest that a solvent also might thus be dissolved by the crystal in the act of crystal formation from a solution; but why should the solvent, so available for this purpose, be overlooked by the crystal? Indeed, the conditions of the formation of a crystal from an aqueous solution suggest that every such crystal should be a saturated solid solution of water in the crystallized salt; and the extent to which the water would thus be dissolved by the crystals must, of course, depend upon the specific nature of the substances concerned.

This hypothesis that crystals contain not only included and adsorbed but also *dissolved* water in the form of solid solution receives striking support from a recent paper by D. Gernez, "The Nature of the Change in Crystals of Sodium Sulfate Heptahydrate in Contact with Crystals of the Decahydrate."[4] Gernez points out that metastable crystals such

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[1] Richards, *Loc. cit.*

[2] van't Hoff, *Z. physik. Chem.*, 5, 322 (1890).

[3] Attention may be called to the adsorption of coal-tar colors by crystals, Marc, *Z. physik. Chem.*, 75, 710 (1911).

[4] Gernez, *C. r.*, 149, 77–84 (1909).

as the heptahydrate of sodium sulfate, while forming traces of the higher hydrate (in this case the decahydrate) within themselves, on being inoculated with another crystal of this substance, show no evidence of the formation at the same time of the hydrate poorer in water

Gernez supposed that the extra water necessary to form this decahydrate came from included water contained in imprisoning cells, but this seems to me to supply only a partial explanation. The appearance of such a changed crystal suggests a more intimate distribution of the change than would be possible according to this suggestion. On the other hand, if water were dissolved in the form of solid solution, the result would be expected to be just that which is actually observed. The dissolved water together with some of the heptahydrate might form crystals of the decahydrate throughout the mass, enough to render it opaque, but leaving the remainder of the heptahydrate unchanged.

The recent revival of the discussion concerning the loss of superfluous water (not water of crystallization) occasioned by powdering crystals has offered no valid argument in disagreement with the idea that water may be dissolved in solid solution by the crystals. The work of Baker and Adlam[1] confirms the existence of superfluous water in crystals and confirms also the fact noticed by the author twenty years ago that this water is partially but not wholly lost upon powdering. This could have happened from a solid solution almost as easily as from included cells of mother liquor. The amount of water dissolved by a crystal at the moment of formation must be a function of the aqueous vapor pressure of the mother liquor at that moment. Such a crystal could lose water from its surface, into an atmosphere which contained less aqueous vapor pressure. The greater the surface the more chance there would be for the loss of water, because water cannot escape from the interior of the crystals.

All these considerations taken together present a striking argument for the asssumption of the solid solution of water in crystals; and the hypothesis seems to have very little against it. The existence of too much water and therefore too little cadmium and copper in their respective crystallized sulfates becomes from this point of view an entirely reasonable phenomenon. The lack of numerical consistency is then to be traced to the nature of the crystallized salt rather than to an error in any of the accepted atomic weights, or in the analytical results of either Baxter or Perdue and Hulett.

If this is the case, probably different amounts of water are dissolved by crystals at different temperatures. Thus $3CdSO_4.8H_2O$ would probably dissolve different amounts of water at 70° and at 0°. The presence of

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[1] H. B. Baker and G. H. J. Adlam, *J. Chem. Soc.*, **99**, 507 (1911). See also Richards, *Z. anorg. Chem.*, 1, 79 (1892); Richards, *Z. physik. Chem.*, 46, 189 (1903).

alcohol or other miscible liquid together with the water would diminish the water dissolved by the crystals at the moment of their formation. This difference in aqueous content would probably affect slightly all the properties of the crystals. Moreover, in a l probability water is dissolved by salts without water of crystallization, as well as by hydrated salts.

All these points are interesting, and will be studied in the near future at Harvard University.

Baker and Adlam in the paper already mentioned describe experiments wherein dried salts were allowed to regain their water of crystallization in a somewhat moist atmosphere, and were found actually to absorb almost exactly the theoretical amount. Under these conditions the hydrated salt would be formed in the presence of an atmosphere less nearly saturated with aqueous vapor than if it were formed from a solution. Therefore the absence of dissolved water is exactly what would be expected. There is, of course, always some doubt in such cases as to whether every innermost pore has been reached by the aqueous vapor. Possibly the agreement with the theoretical was due to the balancing of a slight deficiency of water in the innermost pores with a slight excess adsorbed on the surface. It is evident, however, that these observations cannot be used as an argument against the assumption of the existence of water in solid solution within the crystals formed from an aqueous mother liquor.

One of the phenomena noticed by the author long ago, and more recently by Perdue and Hulett, thus seems to be easily explicable. It remains only to discuss the other, namely, the deficiency of metal in a dried sulfate, due to traces of water held by the salt.

The retention of small amounts of water or other volatil substances by the solid cadmium and copper sulfate at high temperatures may also be examples of solid solution, or these phenomena may be caused merely by the mechanical imprisonment of some traces of the substance by the solid. Many cases of the latter sort are known.[1] Taken together, these two possible sources of error form quite explanation enough to account for the inadequate cadmium content of metal in Perdue and Hulett's ignited sulfate; and of course the per cent. of water found from the loss on ignition would be a variable quantity without much significance, depending upon the relative amounts of the residual water in the dried salt and the crystals.

These considerations reinforce the conclusion italicized in the paper already referred to on the inclusion and occlusion of solvent in crystals, namely, "*it seems to be impossible to determine with the exactness demanded in the most accurate work the true weight of any salt containing water of crystallization.*" The reason for this is because all solids, in the condition

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[1] See for example Richards, "On the Occlusion of Gases by Copper Oxide," *Proc. Am. Acad.*, 26, 28 (1891); 28, 200 (1873).

in which they have been separated from media containing other substances, very likely contain "included" and "occluded" or dissolved impurities.

As has been repeatedly emphasized in papers concerning atomic weight from this laboratory, a solid should be first prepared in such a way as to include or occlude only volatil impurities, and subsequently fused (thus forcing the escape of these volatil impurities), in order to attain purity worthy of serious quantitative consideration in exact work.

Summary.

In this brief paper it has been pointed out that not only inclusion but also *solid solution* of solvent in crystals is to be feared in precise quantitative work. Such solid solution could neither be easily detected nor easily eliminated. The conclusion is reiterated that the solids obtained from an environment containing other substances, such as a solution, are not safely available for exact quantitative work without further treatment. It is pointed out that these considerations afford an adequate explanation for the anomalous results concerning cadmium sulfate obtained by Perdue and Hulett. Therefore no reason for suspecting an error in the accepted atomic weight of cadmium seems to be indicated by these results.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE REFRACTIVE INDEX OF WATER.

BY GREGORY PAUL BAXTER, LAURIE LORNE BURGESS AND HERBERT WILKENS DAUDT.

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Investigations in this laboratory upon the refractive indices of salt solutions and the refractive constants of dissolved salts,[1] have made desirable an exact knowledge of the index of refraction of water at 25°, a temperature for which this constant has never been accurately found, although many determinations have been made at temperatures somewhat above and below this point. In the following investigation determinations were made not only at 25° but also, for purposes of comparison, at one higher and at one lower temperature.

The accuracy of a determination of the index of refraction of any liquid depends not only upon the sensitiveness and accuracy of the measuring instrument, but also very largely upon the purity of the liquid and the careful regulation of its temperature. It is in the last two respects that many previous investigations have been faulty. In this research these two points received special attention.

The Spectrometer.—The spectrometer was of the Meyerstein type, manufactured by Max Wolz. Its divided circle was graduated in ten-

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[1] See following paper.