the rapid formation of the pentasulphide is in this case due to the $C_{(H')}$ then any strong acid which would give as great a $C_{(H')}$ as hydrochloric acid should have a similar effect, providing, of course, the anions occasion no disturbing by-reactions. Neher tried sulphuric acid and found that it acted in a manner analogous to hydrochloric acid. Nitric acid must be excluded but the behavior of other strong acids would prove interesting. There is, however, another way of looking at the matter. Assuming, as we have done, that arsenic acid can act as a very weak base, in the presence of a great excess of such a strong acid as hydrochloric acid, the production of the salt arsenic pentachloride[1] is at least not impossible. It would doubtlessly be formed by stages but the final product of the reaction we may assume to be the pentachloride:

$$AsCl_5 \rightleftharpoons \overset{...}{As} + 5Cl$$

$$2\overset{...}{As} + 10SH' = 2H_3AsS_4 + 2H_2S \rightarrow As_2S_5 + 5H_2S.$$
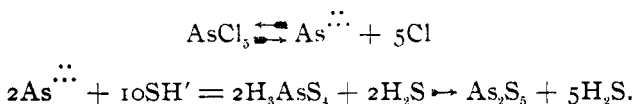
If the train of reasoning above given be correct, the facts cited in my paper in the *Zeitschrift für anorganische Chemie* find a very satisfactory explanation in terms of the electrolytic dissociation theory.

In closing I wish to express my sincere thanks to Dr. George A. Hulett, of the University of Michigan, for his kindness in suggesting to me the possibility of arsenic acid undergoing a slight basic dissociation, as well as for the friendly interest he has shown in my work.

THE SOLUBILITY OF GYPSUM.

BY GEORGE A. HULETT AND LUCIUS E. ALLEN.

ALTHOUGH the solubility of the substance $CaSO_4.2H_2O$ has been the subject of investigation by many careful workers, the results vary widely, while the experimental errors are comparatively small. The cause of these discrepancies was pointed out by Hulett,[2] in the course of an investigation of the influence of

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[1] In this case we would have to assume that the aqueous solution of arsenic acid contains the normal compound H_5AsO_5.

[2] *Ztschr. phys. Chem.*, **37**, 385.

surface-tension on solubility, where it was shown that the energy existing on the surface between a solid and its saturated solution is a measurable factor of the solubility. The concentration of the solution in equilibrium with a curved surface is different from that in equilibrium with a plane surface. Attention was called to a *normally saturated solution; i. e.*, the solution which is in equilibrium with a plane surface of the solid, and it was shown that a convex surface will show greater solubility and a concave one a less solubility than a plane surface; *c. g.*, if the solid is finely divided the solubility will be noticeably greater; in the case of gypsum[1] the solubility was increased 20 per cent. by decreasing the size of the particles to 0.3 micron. When larger pieces of gypsum were placed in a flask with water and rotated in a thermostat—the usual method of saturating a solution—the concentration became 5 per cent. greater than a normally saturated solution at the same temperature, because gypsum is a very soft mineral and is easily ground to powder. It was therefore found necessary to remove all the small particles and then cause the liquid to rotate over the solid, but without disturbing it.

At 25° a normally saturated solution of gypsum contained 15.33 milligram-molecules in a liter (a supersaturated solution was stirred in contact with the gypsum plates at 25° C. and decreased in concentration to 15.33 milligram-molecules to a liter, leaving no doubt as to the question of equilibrium having been established). All previous determinations of the solubility of gypsum vary more or less from the above figure for 25° C., and the results are greater than 15.33 milligram-molecules in a liter, indicating that where care had been taken to avoid supersaturation, the solutions analyzed were still those in equilibrium with more or less convex surfaces, due to the fact that too finely divided gypsum had been used. In view of the above facts and the special importance of the solubility curve of gypsum, a careful determination of the concentrations of normally saturated solutions of gypsum was undertaken.

SOLUBILITY IN GENERAL.

The question as to how solubility should be expressed has received very little attention and with the numerous methods in vogue there is little uniformity in the published results. The densities of

[1] *Ztschr. phys. Chem.*, **37**, 388.

the solutions worked with are seldom given and the lack of these data often excludes comparisons or recalculations.   In the case of a slightly soluble substance like gypsum (2.4 grams per liter) the results are mostly given as parts of water to dissolve 1 part of gypsum, while from the context it appears that the calcium sulphate was determined from a volume of the solution.   The question of the density of the solutions is not mentioned so the results are in reality volumes of solution which contain 1 gram of calcium sulphate, or gypsum, as the case may be.   The error is not negligible and increases with the temperature.

If a quantity of the solution is weighed out in a weighing bottle[1] and the solute (the dissolved substance) is determined gravimetrically, the results are very definite as far as the masses of the solvent and the solute are concerned and the results are to be expressed as parts of solute to 100 parts of solution, or parts of solvent for 1 part of solute, or better still as gram-molecules dissolved by 100 gram-molecules of solvent, but the density is still needed as a control and to allow of comparison with results determined from volume.   The results expressed as parts of solute to 100 parts of solution yield for the temperature curve nearly straight lines,[2] but not in all cases, and while there may be some advantage in locating a break or the appearance of a new phase when the curves are straight lines, still there is so little known at present concerning the relation of solubility to other magnitudes that this choice would be quite arbitrary.

A pipette is an exceedingly accurate instrument if graduated *to volume* (not grams water weighed in air), and the contents rinsed out.   The volume taken is thus diluted by the rinsing water but the mass of the solute is determined gravimetrically.   If the pipette is provided with a ground glass cap for the lower end, it serves at the same time as a pycnometer, or a good-sized pycnometer may be used for a pipette, first determining the density then washing out the solution and determining the solute analytically.   In this manner not only the weight of the solution and solute are obtained but also the volume of the solution and the results can be expressed as gram-molecules of the solute in a liter, or in any manner desired.   Since from the modern standpoint the dissolved substance is regarded as a gas,

1 Van't Hoff : Vorlesungen, p 24.
2 Etard : *Compt. rend.*, 108, 176.

there is much to be said in favor of expressing the solubility results as concentration or gram-molecules in a liter of the solution. A knowledge of the vapor-pressure of the solution is also very desirable as it allows of a calculation of the osmotic pressure and the application of other thermodynamic relations. With electrolytes conductivity is also expressed in terms of concentration, while solutions for volumetric analysis, with which all chemists are familiar, consider only the volume and mass of the solute. Complete data would include a determination of the mass, volume, and concentration of the normally saturated solution; the conductivity, if electrolyte, should be taken as a control and also, if possible, the vapor-tension.

THERMOSTATS.

For temperatures below that of the surroundings, there seems to be no satisfactory device for accurately controlling the temperature. In using the ordinary Ostwald regulator and a cooling tube in the bath, a good deal of tap water is required. This is due to the effect of the small flame, which continually burns beneath the bath. If we do away with this flame and have the bath well covered with felt and the top protected by glass and felt, then a very little ice-water from a convenient tank will keep the temperature down. A short coil of very fine platinum wire is arranged above the mouth of the regulator burner and by means of the second hand of a clock, which makes and breaks an electric current, this platinum wire is made to glow an instant every minute; now the regulator can shut the gas off entirely and when let on again the platinum which glows once every minute will light it. With our large 45-liter bath well protected with felt, the temperature can be maintained quite as accurately below as above room temperature and with very little ice-water dropping into the bath.

The thermostat used at zero consisted of a large tank of 45 liters' capacity, filled with fine cracked ice. The Bunsen flask used for solution was sunk into the ice and stood on a tripod. The bath was covered on all sides with a thick layer of felt and the ice kept for fully twenty-four hours without replenishing, the temperature remaining almost absolutely constant.

For all temperatures above room temperature, except at 100° C., a large bath was used which was covered on the sides with

several thicknesses of asbestos, the bottom being also covered, with the exception of a small circular place in the center for the flame, and the top was covered with glass plates and asbestos. The thermostat was let into a table so that it projected about 10 cm. above the top. Below, and extending from the table to the floor, four large sheets of asbestos enclosed the lower part of the bath, thus preventing draughts, etc., from effecting the temperature. This bath enabled us to keep within 0.1° even at 75°.

Jena flasks, Erlenmeyer form, were used, the flask being immersed to the neck in the bath and covered so that there was no distillation and condensation in the neck. The temperature was controlled to within 0.1 or 0.05 of a degree during saturation. A Shultz stirrer was used in the flask and the height of the stirrer was so regulated that the arms did not disturb the gypsum plates, but kept the solution in a slow but steady motion over them, the stirrer running about 50 revolutions per minute.

The bath used for 100° C. was much smaller than those used for the other temperatures, being of about 7 liters' capacity. The bath was filled about a third full of water so that the flask was not immersed in the boiling water, but was completely surrounded with steam. A long-necked Florence flask (Jena) was used and to prevent evaporation, a test-tube which fitted nicely into the neck of the flask, was provided with a short tube below for the passage of the stirrer-rod; the stirrer-rod was supported also by the cork in the upper part of the test-tube. The flask was thus closed off at the point where the neck joined the flask and was so full of water that there was little free surface for evaporation; this scheme effectually prevented distillation from the solution even at 100°.

All density determinations were made with a Sprengel-Ostwald pycnometer, capacity 25 cm³. The end of the capillary arm of this pycnometer was provided with a ground-on cap to prevent loss by evaporation or in handling. As a control, the density of water was determined at the temperature of the experiment, and then the gypsum solution, under exactly the same conditions. The results were calculated to weight in vacuum and from the known density of water, the density of the solution was calculated to $\frac{mass}{cm^3}$, that is, referred to water at 4° C. Duplicates agreed to the fifth decimal place, leaving the sixth uncertain.

ANALYTICAL METHODS.

The analytical results were based on the amount of anhydrous calcium sulphate in 100 cm³ (volume) of the gypsum solution saturated at a given temperature. The samples for analysis were taken from the solution flask while still immersed in the constant water-bath, by filling an accurately standardized 100 cm³ (volume) pipette and at once allowing the solution to run into a weighed platinum dish, thoroughly rinsing the pipette with distilled water. The duplicate samples were then evaporated to dryness on water-baths, using condensing funnels to exclude dust. When evaporated to dryness the platinum dishes were placed in a specially constructed glowing oven, made as follows : A cylindrical sheet-iron or tin jacket was covered with asbestos, the seams of the asbestos being cemented together with a little sodium silicate. A conical cover was made, covered in the same manner, and having a small hole in the apex to allow of the escape of the gases of combustion. Within the jacket and about in the center was supported a casserole in which the platinum dish was placed, standing on three small pieces of porcelain. The casserole was then covered with an inverted evaporating dish. The whole apparatus was supported on a ring stand and heated from underneath with a Detroit burner. In this way the samples of gypsum could be carefully heated and the temperature within the casserole was sufficient to completely dehydrate the gypsum, but too low to decompose the calcium sulphate as the following experiment showed.

A known weight, 0.8788 gram, of the gypsum plates were placed in a weighed platinum dish and put in the glowing oven. After glowing for one and three-quarter hours, the platinum dish was cooled and weighed, giving the following weight—51.5600 grams ; the dish was replaced in the oven and glowed for two hours under the same conditions and again cooled and weighed, giving the same weight as before—51.5600 grams. The loss of water was within 0.1 per cent. of the theoretical. It was noticed that the weight of the calcium sulphate would increase if left for a little time in the air ; hence, it seems to be slightly hygroscopic and the weighings were made *rapidly*. The first heating gave the approximate weight and, having this, the second and following heatings could be done so rapidly that the error was entirely negligible. The residue of the above experiment was digested with a

little water but showed no suggestion of an alkaline reaction, while the weight indicated that it had not lost sulphur trioxide, nor did it lose weight on continued heating.

The gypsum used in this work was the same as that used in the previous work on gypsum.[1] It was from a very large and perfectly clear crystal from Wyoming. Analysis of a saturated solution of this gypsum showed no trace of chlorine. The gypsum was broken up into thin plates of 1.0 to 0.5 mm. thickness, and all fine particles were removed by repeated washing and decantation with distilled water. The water used was obtained by redistilling distilled water after addition of barium hydroxide,[2] only water having a conductivity of less than 1.5×10^{-6} being used for the solution of the gypsum. The capacity of the cells used in this work was determined by a N/50 potassium chloride solution, using the above water and carefully purified and fused potassium chloride. The results represent the conductivity of a cubic centimeter of the solution compared to a solution, 1 cc. of which has a resistance at the temperature of 1 ohm ($106.3 \frac{cm.}{mm.^2}$ Hg at 0°) (Kohlrausch unit).

The following table (I) gives the results obtained in this investigation; column II gives the actual weights, in duplicate, of the calcium sulphate (heated to constant weight as above described) from 100 cm³ of the solution measured at the temperature of the experiment. Column III gives the calculated milligram-molecules in a liter at the temperature of the experiment. The result for 107°, 11.39 milligram-molecules in a liter, is exterpolated, and the course of the curve I (Fig. I) is so uniform that this figure is probably correct to the first decimal place. This point is the end of the gypsum curve since van't Hoff and Armstrong[3] have shown that at this temperature the vapor-pressure of gypsum equals that of water and (since the vapor-pressure of the gypsum solution varies so slightly from that of water) this is the temperature at which gypsum turns to halfhydrate. At 107°, under normal conditions, there is a break in the curve, and the continuation is the curve which is in equilibrium with $CaSO_4.\frac{1}{2}H_2O$.

Column IV gives the density $\frac{mass}{cm^3}$ at the temperature of the experiment; these data allow of a recalculation of the concentra-

[1] *Loc. cit.*

[2] Hulett : *Ztschr. phys. Chem.*, **21**, 297.

[3] *Sitz. Ber.*, (1900), p. 559.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII.
Temperature.	Grams CaSO$_4$ in 100 cm³ solution. Duplicate.	Millimolecules for 1 liter.	Density of solution. $\frac{\text{Mass}}{\text{cm}^3}$ For T°C.	λ for T°C.	λ for 25° C.	Time for conductivity to become constant. Minutes.
0°	{0.1760, 0.1758}	12.926	1.001970	0.000945	0.001958	..
10°	{0.1931, 0.1926}	14.177	1.001727	0.001486	0.002080	90
18°	{0.2017, 0.2015}	14.817	1.000590	0.001830	...	80
25°	{0.2083, 0.2078}	15.295	0.999109	0.002206	0.002206	75
30°	{0.2092, 0.2089}	15.361	0.997891	0.002445	...	60
35°	{0.2096, 0.2096}	15.405	0.996122	0.00268	0.002226	50
40°	{0.2097, 0.2097}	15.413	0.99439	0.002845	0.002232	45
45°	{0.2086, 0.2081}	15.310	0.992370	0.003045	0.002264	60
55°	{0.2012, 0.2007}	14.765	0.98796	0.003375	...	40
65.3	{0.1934, 0.1930}	14.200	0.98256	0.003603	...	45
75°	{0.1851, 0.1844}	13.575	0.977724	...	...	40
100°	{0.1624, 0.1615}	11.900	...	...	...	..
107°	...	(11.390)	...	...	...	..

tion to any other standard. The weights are all corrected to vacuum. The densities differ rather uniformly from water by $+ 0.002$. At 25° C. for example, from the density and the mass of solute (regarding it as calcium sulphate and specific gravity 3), we find the density of the solvent slightly greater than water (0.99773) instead of (0.99710), that is, the condensation of the solvent is very slight, only 0.00063.

Columns V and VI give the electrical conductivity in the standard unit. These were taken primarily to determine when the solution was saturated. Into a 1½ liter Erlenmeyer flask with the bottom covered 1 cm. deep with small gypsum plates was brought about 1 liter of conductivity water, all at the temperature of the bath, and the liquid rotated about fifty times per minute, and since the gypsum plates were not disturbed the solution above was always

clear. From this every five or ten minutes (at first), 10 cm³ was removed and its conductivity determined. Under these conditions, which could not be regarded as overfavorable for rapid saturation, it was found that saturation took place in from forty to ninety minutes, depending on the temperature, as can be seen in column VII. Of course the rate of solution depends on several factors, but in the case of gypsum it seems to be fairly rapid, and this agrees with the observations of Bruner and Tallocyko.[1]

Temperature C.
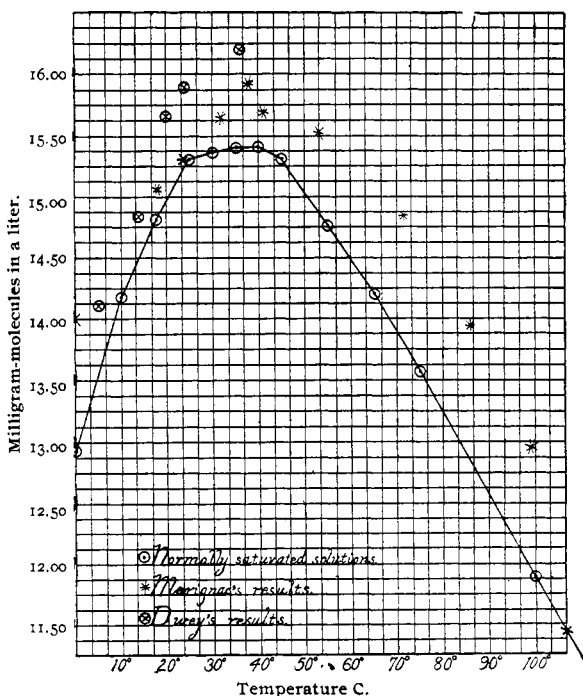
○ "Dwey's results" in diagram should read "Droez's results."

Cameron[2] assumes that the rate of solution is very slow and endeavors to explain the discrepancies in the published solubility results as due to undersaturated solutions, whereas the results generally are on the other side of normally saturated solutions.

The preceding table gives the results of normally saturated solutions starting from water and gypsum and assuming that equilibrium was reached when the conductivity of the liquid was

[1] Ztschr. anorg. Chem., **28**, 320.
[2] J. Phys. Chem., **5**, 567.

constant, although in all cases the liquid was rotated over the gypsum plates for an extra hour or two before the analysis was made. A solution saturated at $25°$ C. (or which from conductivity showed 15.29 milligram-molecules per liter) was brought to $0°$ and rotated in contact with the gypsum plates. The conductivity slowly decreased but it required two days, or forty-eight hours to become constant, and analysis gave for 100 cm³ 0.1758 gram calcium sulphate, whereas the solution starting from water and gypsum at $0°$ C. gave 0.1760 and 0.1758 gram while the conductivity of the two solutions was the same.

At $25°$ C. the system water-gypsum showed a constant conductivity of 0.002206 in seventy-five minutes, while the previous work[1] showed that a solution saturated at $35°$ C. and brought to $25°$ C. gradually decreased in conductivity, and after twelve hours reached the normal value $\lambda = 0.002208$. These results show that our method gave us equilibrium, but it was deemed advisable to test this point above the change in the solubility curve at $40°$ C., so $50°$ C. was the temperature selected; first a saturation was made at $38°$ C.; then the system was brought to $50°$ C., where it was found that the solubility slowly decreased and next morning had already become constant. An analysis of the solution gave per 100 cm³ 0.2049 gram and 0.2045 gram calcium sulphate respectively. Water and gypsum plates were brought together at $50°$ C., and in about forty minutes the conductivity had become constant, and an analysis showed 0.2040 gram calcium sulphate in 100 cm³. In these experiments evaporation from the solution was prevented in the same manner as in the experiment at $100°$ C.

These experiments seem to settle conclusively the question of equilibrium. Above $50°$ the conductivity seems to indicate that the glass of the flask was slightly attacked, although not enough to sensibly affect the solubility results.

The early works on the solubility of gypsum have only a historical interest, although the result given by Giese[2] of 380 parts of cold water to dissolve 1 gram of gypsum is not far wrong for room temperature; but 388 parts of boiling water to 1 of gypsum is quite wrong. Tipp[3] also gives 388 parts of water to 1 of gypsum at $15°-20°$ C.

¹ *Ztschr. phys. Chem.,* **37,** 391.
² **Auflage Gmelin's Handbuch,** Vol. V., 183.
³ *Jahresbericht,* (1864), **5,** 325.

Marignac[1] showed that it was exceedingly easy to obtain a supersaturated solution of gypsum and that such a solution was very slow to come to equilibrium, even in the presence of an excess of the solid gypsum. Marignac made determinations between 0° and 100°, taking care to have an excess of finely divided gypsum uniformly distributed through the solution, and the system was undoubtedly in equilibrium before a part of the clear solution was analyzed. He was able to show that the results of his predecessors were affected by the phenomena of supersaturation.

Droez[2] confirmed Marignac's results and added several of his own. He especially showed that the equilibrium could be reached from either side, emphasizing the necessity of an excess of the finely divided gypsum and constant agitation. Droez also took account of the density of water in his calculations. He assumed the density of his solution to be the same as that of water at the same temperature, and gave a table of solubilities from 0° to 100° C. from a curve of his and Marignac's results. Both of these workers avoided supersaturation in the sense that their solutions were in equilibrium with the solid present. . Still, from the method of these experiments and the results, the solid must have

TABLE II.

	I.	II.	III.	IV. Normally saturated solutions.
T°.	Poggiale.	Marignac.	Droez.	
o	15.06	14.00	...	12.91
5.5	...	...	14.11	13.56
14.2	...	...	14.83	14.50
18	...	15.06	...	14.81
19.5	...	...	15.66	14.88
20	17.72	...	...	14.95
24	...	15.30	15.87	15.23
32	...	15.64	...	15.38
35	18.75	...	...	15.40
36	...	...	16.19	15.41
38	...	15.79	. .	115.41
41	...	15.71	...	15.39
53	...	15.52	...	14.85
72	...	14.86	...	12.70
86	...	13.94	...	12.70
99	...	12.89	...	11.95
100	...	...	...	11.90

[1] *Ann. chim. phys.*, (5) 1, 274 (1874).
[2] *Ber. d. chem. Ges.*, (1877), p. 330.

been very finely divided, that is, having some particles less than 2 microns in diameter since their solutions were about 5 per cent. more concentrated than normally saturated solutions. The results of these two workers have been accepted as the most reliable, so they have been calculated to millimolecules per liter and given in Table II (preceding page), together with the concentrations of normally saturated solutions taken from the curve of our results.

Kohlrausch and Rose[1] give results of conductivity of solutions saturated at various temperatures. A comparison of these data with the conductivity of known solutions[2] shows that their solutions were some 4 per cent. too concentrated. There are a great many determinations of the solubility of gypsum or crystallized $CaSO_4.2H_2O$ by various workers, and even where care was taken to avoid supersaturation, the results generally distinctly show the influence of surface-tension. There are two exceptions, Cossa and Church, who made determinations at about 20° and 13°; their results are 10.5 per cent. and 12 per cent. respectively *below* the normally saturated solutions. We have not been able to consult the original publications so we cannot judge of the material or the method used. The previous work[3] showed that in the case of gypsum the surface-tension plays a decided rôle in the solubility, for it was found possible to increase the solubility (at 25°) 20 per cent. by grinding the gypsum powder in an agate mortar, but the system so obtained was not in final equilibrium, since the smaller particles grew smaller and disappeared while the larger ones grew in size. This is, however, a slow process[4] with gypsum and does not reach final equilibrium (the normally saturated solution) in five days, while if the stirring is too rapid, the abrasion from the soft gypsum continually yields a fine powder, and a normally saturated solution is never attained. Plates of gypsum rotated with water in a flask, as is ordinarily done in solubility determinations, will easily yield a 5 per cent. too great solubility. On the other hand the results here obtained show that slowly rotating a liquid over the plates will give a saturated solution in about an hour's time. These facts give a satisfactory explanation of the irregularities in the published determinations.

[1] *Ztschr. phys. Chem.*, **12.**
[2] *Ibid.*, **37**, 371.
[3] *Ibid.*, **37**, 392.
[4] *Loc. cit.*, p. 394.

The solubility curve of gypsum is of special interest on account of the change in the direction of the curve. This fact was discovered by the early workers, and from Marignac's and Droez's results the maximum solubility is given at 38° C. while the curve of the results here obtained indicates 40° C. as the temperature at which there is the greatest concentration. From here the concentration decreases with the temperature and at 90° is the same as at 0°, while at 107° it has decreased some 12 per cent. further. There seems to be no break in the curve at 40° as we had expected to find, while the vapor-pressure curve of water compared to that of gypsum, plotted from the interesting results of van't Hoff and Armstrong,[1] show a perfectly uniformly increasing difference from 0° to 85°, where the vapor-pressure of water is some 85 mm. greater than that of gypsum. At 40° the difference is 29 mm. From 85° on the difference decreases, and at 107° the lines cross and the half hydrate appears (a saturated solution of gypsum must have a vapor-pressure that is only a few hundredths of a millimeter less than that of pure water). The uniformity of the vapor-pressure curve of gypsum excludes the idea of explaining the change at 40° (from increasing to decreasing solubility) by assuming the appearance of a new phase. Thermodynamics connects this change at 40° with the change of the sign of the heat of solution. This question has been thoroughly discussed by van't Hoff[2] where the case of gypsum is considered. It is to be noted that this is a thermodynamic relation and while it is experimentally supported by the observations of Berthelot on the heat of precipitation of $CaSO_4.2H_2O$ above and below 40°, we are still in the dark as to why the curve takes a downward curve at 40°.

In the case of slightly soluble substances the effect of the dissolved substance on the solvent can be neglected, while in the case of more soluble substances the nearly saturated solution is a quite different agent from the pure solvent,[3] so it seems probable that general relations will first be found in connection with less soluble substances and the results of this paper indicate that there is need of a careful redetermination of such data with due regard to the influence of surface-tension.

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March, 1902.

[1] *Sitz. Ber.* (1900), p. 559.
[2] Vorlesungen, p. 31.
[3] Nernst: "Theoretische Chemie," p. 445.