SOLUBILITY OF GYPSUM IN AQUEOUS SOLUTIONS OF CERTAIN ELECTROLYTES¹

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The results obtained in the study of the solubility of gypsum in aqueous solutions of sodium chloride² were of such a character as to make it appear desirable to obtain data for other solutions of a similar kind. The work was therefore continued and a description of the investigation is here recorded. The solubility of gypsum was therefore determined in solutions of magnesium chloride, calcium chloride, sodium sulphate, and in solutions of sodium chloride when calcium carbonate in the solid phase was also in contact with the solution.

All these determinations were made at temperatures from 23° C to 26° C. The temperature of the laboratory held quite constantly within these limits and, as slight changes of temperature were found to affect the solubility of gypsum in these solutions but very little, it was not deemed necessary to use a constant temperature bath.

It is desirable, for some reasons, both scientific and technical, that determinations should be made at other temperatures, especially above 40° C; but the exigencies of the public service hardly seemed to warrant their being made at this time.

Instead of gypsum, precipitated calcium sulphate, obtained from The Baker and Adamson Chemical Co. and labeled c. p., was used in these experiments. It was found by examination of a few solutions that, as was the case in sodium chloride solutions described in the preceding paper, the same results were obtained with gypsum and with precipitated calcium sulphate; but that the solutions came to equilibrium more rapidly when the latter was used. The other salts used in the investigation were chemically pure materials obtained from the same firm.

¹ Published by permission of the Secretary of Agriculture. See Bul. 18, Division of Soils, U. S. Department of Agriculture.

² Jour. phys. Chem. 5, 556 (1901).

The general method of procedure was the same in all cases. A series of solutions of various concentrations with respect to the readily soluble salt was prepared, and enough calcium sulphate added to insure an excess of this substance in the solid phase. The solutions were then set aside for periods of from one to six weeks, with occasional vigorous shaking.

The solutions were generally of about 700 cc volume and were contained in liter Florence flasks fitted with rubber stoppers, to prevent evaporation of the solvent. When ready for analysis, they were allowed to settle, and appropriate portions of the clear supernatant solutions were drawn off with a pipette, and whenever this procedure seemed advisable, they were fil-

Fig. 1

tered. The analytical operations were conducted according to the conventional methods and call for no special comment. The amount of calcium sulphate which had dissolved was calculated from the amount of sulph-ions found in the solution. The results obtained are presented graphically in Fig. 1, the ordinates represent reacting weights per liter of calcium sulphate, and the abscissas represent reacting weights per liter of the more soluble salt used.

For some reasons it seemed more advisable to give the results in terms of calcium sulphate found in the solution rather than in amounts of gypsum found to be soluble. These latter can always be readily obtained by multiplying the given results by the factor 1.2647.

Although the temperature was not quite the same for these different series of determinations, in all these series it was found that such small differences of temperature as are involved here have such a small influence on the solubility of the calcium sulphate that these curves may fairly be considered as entirely comparable.

Solubility of calcium sulphate in magnesium chloride solutions

It was found that the curves illustrating this case showed unusually well-marked maximum points. Therefore it was deemed advisable to determine the curve with reference to a constant weight of the solvent water as well as to a constant volume of the solution. The data obtained at 26° C are given in the accompanying table, which is self-explanatory. The results, referred to a constant volume of solution, are presented graphically.

TABLE I.

Solubility of calcium sulphate in aqueous solutions of magnesium chloride at 25° C

H ₂ O (grams per liter)	CaSO ₄		MgCl ₂	
	Grams per liter	Reacting wts. per liter	Grams per liter	Reacting wts. per liter
997.924	2.082	0.0154	0.000	0.0000
996.520	4.258	0.0315	8.501	0.0900
994.489	5.692	0.0421	19.175	0.2030
989.143	7.588	0.0561	46.640	0.4938
972.218	8.622	0.0638	121.381	1.2850
949.950	6.567	0.0486	206.985	2.1912
908.678	2.774	0.0205	336.986	3.5674
878.588	1.385	0.0102	441.128	4.6699

TABLE I.—(Continued).

CaSO ₄		MgCl ₂	
Grams per 1000 grams of water	Reacting weights per 1000 grams of water	Grams per 1000 grams of water	Reacting weights per 1000 grams of water
2.086	0.0154	0.000	0.0000
4.273	0.0316	8.531	0.0903
5.724	0.0423	19.860	0.2102
7.674	0.0568	47.170	0.4993
8.867	0.0656	124.800	1.3212
6.913	0.0511	217.900	2.3068
3.553	0.0263	370.900	3.9265
1.577	0.0116	502.000	5.3144

By interpolation on the curves it appears that the maximum solubility for calcium sulphate is about 8.8 grams per liter in a solution containing about 105 grams per liter of magnesium chloride. In this solution, therefore, there is more than four times as much calcium sulphate as in a saturated solution of this substance alone. Calculated as gypsum, this maximum solubility is 11.129 grams per liter, or 4.23 times as much as is soluble in pure water. Beyond the maximum point the solubility of the calcium sulphate decreases quite rapidly as the concentration with respect to magnesium chloride increases, this decreasing solubility being much more rapid than in the corresponding curve for the solubility of gypsum in sodium chloride solutions. This decrease in solubility continues until in a solution containing about 370 grams magnesium chloride per liter the solubility of gypsum is the same as in pure water. Therefore, even in the presence of this salt, which does not yield a common ion, the solubility of gypsum is less at high concentrations than in pure water.

The curve plotted from the data obtained on the basis grams of salt per 1,000 grams of the solvent is of the same general nature as the curve plotted on the basis of a constant volume of solution, and shows about equally well the character of the phenomena involved. The former lies slightly above the

latter, and it does not seem worth while to chart it here. Attention is called to it for it also shows, in a most striking way, the real existence of a maximum point on the solubility curve. It would seem that this pair of electrolytes may be particularly well adapted to the further study along the general lines indicated by the investigation here described.

Another point of interest in the curves for this pair of electrolytes is the wavy character for the higher concentrations with respect to magnesium chloride. To what this may be due can not be said at present, but it shows that in all probability complex molecular or ionic changes must take place in the solution at these higher concentrations and that the subject is much in need of further investigation.

By referring to Fig. 1 it will be observed that the maximum point on the curve for magnesium chloride occurs at about half the concentration that it does on the curve for sodium chloride; that is, at about the same concentration for chlorine in the two cases, since a reacting weight of magnesium chloride contains twice as much chlorine as does a reacting weight of sodium chloride. But the total amount of calcium sulphate is different in the two cases, showing that magnesium and sodium have markedly different properties, at least in degree, under such circumstances.

Solubility of calcium sulphate in calcium chloride solutions

In the preparation of the calcium chloride solutions for this series of experiments it was found that the solutions were more or less turbid, due to undissolved calcium hydrate originally present in the supposed chemically pure calcium chloride used. A few drops of methyl orange solution were therefore added in each case, and then hydrochloric acid, until the indicator showed the solutions to be neutral. The solutions became perfectly clear and free from suspended matter. The calcium sulphate was then introduced and the usual procedure followed.

In this case the two salts will yield a common calcium ion, and in consequence the solubility of the calcium sulphate will

be much decreased by the presence of the calcium chloride. This is shown by the accompanying table of results, obtained on a series of experiments made at 25° C. It is even more strikingly brought out by the graphical representation of the results. The observations on this pair of electrolytes made by Tilden and Shenstone¹ and by Lunge² agree in general with the results given here.

TABLE II.

Solubility of calcium sulphate in aqueous solutions of calcium chloride at 25° C

CaSO ₄		CaCl ₂	
Grams per liter	Reacting weights per liter	Grams per liter	Reacting weights per liter
2.056	0.01521	0.000	0.00000
1.244	0.00921	7.489	0.06801
1.181	0.00874	11.959	0.10860
1.096	0.00811	25.770	0.23401
1.080	0.00799	32.045	0.29100
1.016	0.00752	51.530	0.46794
0.841	0.00622	97.023	0.88106
0.465	0.00344	192.705	1.74996
0.203	0.00150	280.303	2.54543
0.032	0.00024	367.850	3.34045

The solubility of the calcium sulphate decreases very rapidly as the concentration with respect to calcium chloride increases, until a concentration of about 20 grams per liter of this latter salt is reached. From this point the solubility of the calcium sulphate decreases more slowly, but steadily, until by extrapolation on the curve it would seem that the solution containing 375 grams per liter of calcium chloride would dissolve practically no calcium sulphate.

Just why there should be so marked a change in the solubility of the calcium sulphate in solution concentrations of about 2 percent calcium chloride does not admit of explanation as

¹ Proc. Roy. Soc. 38, 335 (1885).

² Jour. Soc. Chem. Ind. 4, 31 (1885).

yet. It is possible that at concentrations above this the calcium chloride may partially dissociate in such a way as to form complex ions containing both calcium and chlorine,¹ and thus diminish the proportional effect of calcium as ions in the solutions forcing back the dissociation of the calcium chloride, and consequently the retarding effect upon the solubility of the calcium sulphate. It seems probable, however, that the density of the solvent itself may have an important rôle in this connection.

The solubility of calcium sulphate in sodium sulphate solution

In this case it is to be expected that the two electrolytes would yield the common sulph-ion, therefore the solubility of gypsum should decrease as the concentration with respect to sodium sulphate increases. Such was found to be the case up to a concentration of about 17.5 grams per liter of sodium sulphate, when the solubility of the calcium sulphate was about 1.38 grams per liter, or 1.745 grams per liter of gypsum. At this point, as the concentration with respect to sodium sulphate increases, there is a sudden change in the direction of the curve and the solubility of the calcium sulphate steadily increases until, in a liter of solution containing 230 grams of sodium sulphate, there will be dissolved 2.5 grams of calcium sulphate — a quantity markedly larger than will be dissolved by pure water. The data obtained for this pair of electrolytes are given in Table III.

Apparently we have to deal with two solubility curves which intersect at the minimum point. Possibly at concentrations with respect to sodium sulphate greater than that at the minimum point the dissociation of the sodium sulphate takes place in part according to the scheme :

rather than entirely as indicated thus :

¹ Noyes. Phys. Rev. 12, 15 (1901) ; Jour. Am. Chem. Soc. 23, 37 (1901) ; Zeit. phys. Chem. 36, 61 (1901).

If this be so, it is tantamount to introducing a substance into the solution which does not yield a common ion with calcium sulphate, and which therefore may be expected to increase the solubility of the latter. We thus have the sodium sulphate exerting two effects on the solubility of the calcium sulphate, depending on the way in which it dissociates. These two effects are opposite in direction, and in consequence the resulting effect will be dependent on the relative amounts of the dissociation in the two different ways, which is dependent in turn upon the concentration of the solution with respect to the sodium sulphate itself.

TABLE III.

Solubility of calcium sulphate in aqueous solutions of sodium sulphate at 22° C

CaSO ₄		Na ₂ SO ₄	
Grams per liter	Reacting weights per liter	Grams per liter	Reacting weights per liter
2.084	0.0154	0.000	0.0000
1.583	0.0117	2.771	0.0196
1.433	0.0106	13.820	0.0979
1.408	0.0104	16.360	0.1159
1.569	0.0116	39.310	0.2786
1.841	0.0136	77.320	0.5480
2.185	0.0162	133.000	0.9425
2.414	0.0178	193.800	1.3734
a2.578	a0.0190	a222.580	a1.5773

From this point of view one would expect the existence in the solution of a double salt, possibly of the composition $\text{Ca}(\text{NaSO}_4)_2$. Such a salt is, probably, the mineral glauberite, found in nature. Fritzsche¹ describes a hydrated double sulphate ($\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$), obtained by heating gypsum with a small amount of water and a large excess of Glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). The substance was a well characterized one,

¹ Jour. prakt. Chem. **72**, 291 (1857).

a Both calcium sulphate and sodium sulphate as solid phases were in contact with the solution.

crystallizing in fine needles, which, on heating, quickly lost the water it contained, yielding the anhydrous double salt. It was expected, therefore, that this salt, or its hydrate, might be obtained by evaporating solutions of sodium sulphate saturated with respect to calcium sulphate. Such solutions were prepared and allowed to evaporate spontaneously at room temperature. No evidence of the presence of the double salt, however, could be detected in the residue after evaporation of the water. It should be remembered that in those areas where this double calcium sulphate has been observed in nature, the ground temperatures are frequently very high and the equilibrium condition of the solution may well be very different from those obtaining at 25° C.¹

An experiment was then made to see if the composition of the solid phase would affect the composition of a solution in contact with both salts in the solid phase. Four vessels were prepared. In each was placed 100 cc of water and 40 grams of sodium sulphate and 1, 2, 5, and 10 grams of calcium sulphate, respectively, insuring the presence of both salts in the solid phase. The vessels were then placed in a shaking apparatus and shaken constantly for four days. The contents were allowed to settle and the supernatant solutions quickly decanted upon folded filters. Aliquot portions of the filtrates were analyzed for calcium and sulphates. It was found that the composition of the solid phase apparently did not effect the composition of the solution, practically identical results being obtained in all four analyses. The solution in contact with both salts in the solid phase was found to contain 222.5810 grams per liter of sodium sulphate and 2.5783 grams per liter of calcium sulphate. It is desirable that some one, with time and opportunity for it, should

¹ van 't Hoff and Chiaraviglio [Sitzungsber. Akad. Wiss. Berlin, 1899, 810] have shown that gypsum and the decahydrate of sodium sulphate will form glauberite at 25° C. if the solution be saturated with respect to both these salts and sodium chloride as well. This last substance is commonly, though perhaps not always, found in those areas from which glauberite has been reported as occurring in nature. These authors have also shown that glauberite and gypsum exist together as solid phases only when solid sodium sulphate, decahydrate, is not also present.

take this matter up and investigate the system throughout a range of temperature. It is a subject of considerable practical importance in several technical operations, as well as in geological and soil studies.

It follows from these experiments that, considerable amounts of sodium sulphate being in the solution, the solubility of calcium sulphate or gypsum may be relatively great, instead of falling to a very small figure; and the amount of gypsum in contact with the solution in the solid phase will not have any effect in determining the amount that will go into solution at ordinary temperatures, even though sodium sulphate also be present in the solid phase.

Solubility of calcium sulphate in aqueous solutions of sodium chloride and in the presence of solid calcium carbonate

In order to obtain light on some problems which had been referred to this laboratory for explanation, it was determined to study the solubility of calcium sulphate in sodium chloride solutions when calcium carbonate in the solid phase was also in contact with the solution. The solubility of this latter salt is dependent upon the partial pressure of the carbon dioxide in the gaseous phase in contact with the solutions. Therefore, air which had been previously washed in dilute sulphuric acid was bubbled through the solutions for fifty-one days, or until they came to equilibrium.¹ The addition of phenolphthalein to the solution did not show the presence of normal carbonates in any of the solutions. The amounts of bicarbonates found, in the equivalents of calcium hydrogen carbonate dissolved, are given in Table IV.

The variation in the solubility of the calcium carbonate in the solutions of sodium chloride when gypsum was also present in the solid phase will be discussed in more detail in a following paper. The effect of the presence of the calcium carbonate upon the solubility of the calcium sulphate is most strikingly

¹ It is very probable that these solutions had come to final equilibrium within eighteen days, but the passage of air through them was continued to make certain that such a condition had been reached.

brought out in the graphic presentation of the results. From a point representing no sodium chloride in solution up to a concentration for this latter salt of somewhat more than 80 grams per liter, the curve follows very closely the curve representing the solubility of calcium sulphate in the presence of sodium chloride alone. The solubility of calcium sulphate steadily increases with increasing concentration of sodium chloride, but at a somewhat diminishing rate from that which obtains when no calcium carbonate was present. As the amount of sodium chloride increases beyond 80 or 100 grams to the liter, the solubility of the calcium sulphate steadily decreases and apparently follows a new curve, the two curves probably intersecting as charted and not forming a continuous curve with a maximum point, as in the case when there is no calcium carbonate present.

TABLE IV.

Solubility of calcium sulphate in aqueous solutions of sodium chloride in contact with solid calcium carbonate

CaSO ₄		Ca(HCO ₃) ₂		NaCl	
Grams per liter	React'g wts. per liter	Grams per liter	Reacting wts. per liter	Grams per liter	Re'c'g wts. per liter
1.9298	0.0143	0.0603	0.000375	0.000	0.0000
2.7200	0.0201	0.0724	0.000450	3.628	0.0625
3.4460	0.0255	0.0885	0.000550	11.490	0.1979
5.1560	0.0381	0.1006	0.000625	39.620	0.6824
6.4240	0.0475	0.0603	0.000375	79.520	1.3696
5.2720	0.0390	0.0563	0.000350	121.900	2.0995
4.7860	0.0354	0.0482	0.000300	193.800	3.3379
4.4620	0.0330	0.0402	0.000250	267.600	4.6090

It thus appears that while the solubility of gypsum in solutions of sodium chloride would be but little affected by the presence of calcium carbonate up to 8 or 9 percent solutions, beyond this point its solubility would be considerably diminished. But in solutions nearly saturated with respect to sodium chloride the gypsum would be about twice as soluble as in pure water, even though calcium carbonate be present.

It is interesting to note that while the solubility of calcium sulphate is only about 2.1 grams per liter in pure water, it reaches a maximum solubility of about 7.5 grams per liter in solution containing 140 grams per liter of sodium chloride. But this solubility would be reduced to about 5 grams per liter if calcium carbonate were present, and in the presence of this latter substance the maximum solubility of calcium sulphate is about 6.35 grams per liter in a solution containing only about 80 to 90 grams per liter of sodium chloride.

Summary

By reference to Fig. 1 it will be seen that up to the tenth-normal solution the solubility curves in all cases follow, qualitatively at least, the direction indicated by an application of the mass law to the hypothesis of electrolytic dissociation. This is still true for calcium chloride solutions at high concentrations, but in the other cases here recorded it is not true, and it would have been quite impossible to have predicted the character of these solubility curves *à priori*.

The phenomena which have been described in this paper lend support to the view that ionic complexes are formed in solutions of high concentration. Noyes,¹ in a recent publication, has brought forward evidence to show that such ionic complexes are probably in solutions of the chlorides of the alkaline earths, even at quite high dilutions. The investigations in recent years lend much evidence pro and con to the view that such complexes exist, not only in aqueous solutions, but in other solvents.² Of great interest in this connection is the fact brought out by Walden³ that binary electrolytes in general dissociate much more readily than do ternary or quaternary electrolytes. Since it is to be presumed that ternary electrolytes were present in all the solutions studied in this investigation, it is not so surprising, therefore, that abnormal results were observed at the higher concen-

¹ loc. cit.

² See Jones. Am. Chem. Jour. **25**, 232 (1901).

³ Zeit. anorg. Chem. **25**, 209 (1900).

trations. It seems most probable that all these facts are dependent upon, or at least causally connected with, the considerable condensation of the solvent which takes place when solutes, especially electrolytes, go into the solution; and that much of interest for the general theory of solutions could be obtained by a systematic investigation from this point of view.

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