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A Study of Precipitation from Supersaturated Solutions of Strontium Sulfate

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It has long been known on theoretical grounds that the solubility of a solid in a very fine state of subdivision should be greater than its solubility in the coarsely crystalline state.[1] The experimental work in this field reveals considerable doubt as to the magnitude of the effect and even, perhaps, as to its existence, at such degrees of subdivision as are obtainable by grinding.[2]

Marc[3] has carried out an extended investigation of the process of crystallization from supersaturated solutions, in most cases, however, of very soluble substances. In so far as in all his experiments crystallization was brought about by inoculation most of his observations have no immediate bearing on the present work; one important exception to this statement is considered in the discussion.

It seemed to us more practicable to leave open the question of enhanced solubility brought about by bringing an already normally saturated solution in contact with fine particles, and rather to follow the successive labile or metastable states through which an originally supersaturated solution passes. We chose to work with strontium sulfate, on account of its appreciable solubility and freedom from hydration.

Briefly, our plan was to mix together solutions of potassium sulfate and strontium chloride of such strength as to produce a desired degree of supersaturation, and then to follow in a thermostat the spontaneous behavior of such solutions with regard to conductivity and particle size. The view of von Weimarn[4] on the nature of precipitation seems inherently probable. According to this view, the stages of precipitation are: 1, collision of ions to form neutral molecules; 2, aggregation of molecules to form a disperse system; 3, precipitation of colloid by residual ions in solution; 4, further aggregation of these particles to form visible particles; 5, further changes in these particles, *e. g.*, growth to larger particles, or transformation of metastable to stable forms.

In the latter connection it is worthy of note that Lambert and Hume-Rothery[5] find that strontium sulfate is first precipitated in the form of needles, presumably a metastable form, from which it passes into rhombic crystals. These workers also note that the time of precipitation, presumably the time required for visible precipitation, varies with the nature of the residual ions left in solution. This is what would be expected on the basis of von Weimarn's conception, and must be taken into account in all such work as the present.

Experimental

All work, except the determination of particle size, was carried out in a thermostat whose temperature was 30.0

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(1) Thomson, *Proc. Roy. Soc. Edin.*, **7**, 63 (1870).

(2) Hulett, *Z. physik. Chem.*, **37**, 385 (1901); Bigelow and Trimble, *J. Phys. Chem.*, **31**, 1798–1816 (1927); Dundon and Mack, THIS JOURNAL, **45**, 2479 (1923); Dundon, *ibid.*, **45**, 2658 (1923).

(3) Marc, *Z. physik. Chem.*, **61**, 385 (1908); **67**, 470 (1909); **68**, 104 (1909); **73**, 685 (1911); **75**, 710 (1911); **79**, 71 (1912).

(4) Von Weimarn, *Kolloid-Z.*, **5**, 221 (1909).

(5) Lambert and Hume-Rothery, *J. Chem. Soc.*, 2637 (1926).

± 0.02°. Conductivity water was used throughout: specific conductivity = 5 to 3 × 10^{-6} mhos. To avoid chance inoculation, the work was done in a laboratory not used for any other purpose. All measuring and containing flasks were of silica, plugged with corks which had been immersed in melted paraffin and wrapped in tin foil. The measuring vessels were calibrated by weighing. The method of determining conductivity was the ordinary bridge method using, however, a microphone hummer and applying all the refinements mentioned in Ostwald–Luther ("Physicochemische Messungen," 4th ed., 1924).

For the first detection of precipitation (colloidal region) an ultra-microscope was devised, on the lines of the original device of Zsigmondy. For the determination of particle size in the ordinary visible region, a microscope with a screw micrometer eyepiece was used, by means of which particles as small as 0.096 μ could be measured.

In order to evaluate observed decreases in conductivity in terms of concentration, we considered it desirable to know the equivalent conductivity at infinite dilution of strontium sulfate. This occupied several months and we should perhaps have been wiser merely to calibrate conductivity against an analytically determined content of strontium sulfate. However, as the result of our work, we have obtained a consistent value for the ionic conductivity of strontium ion at 30°, despite the fact that the electrolyte used, strontium chloride, was necessarily of the unibivalent type, where the electrostriction at measurable dilution is greater than is the case with a uniunivalent electrolyte. The strontium chloride was purchased in the form of the hydrated salt $SrCl_2 \cdot 6H_2O$ (B. D. H. certified chemical). The potassium chloride used in determining the cell constant was only C. P. purity, but it was recrystallized twice from water before use, and only the first crop of crystals used. The strontium chloride was dehydrated by heating at 90° and solutions made up from this by weighing. The earlier solutions were also analyzed, but as no difference was apparent, this was deemed unnecessary in subsequent work. Dilution was carried out in the ordinary way, but to avoid, as far as possible, cumulative errors, solutions of different concentrations were made up, down to 0.01 *N*, and these diluted in turn. To correct for variation in the conductivity of the water, due to absorption of carbon dioxide, a duplicate flask containing the electrodes and conductivity water, and stoppered in the same way, was kept in the thermostat, and determinations of conductivity of the water made from time to time. In this way the following figures were obtained.

TABLE I

EQUIVALENT CONDUCTIVITY OF STRONTIUM CHLORIDE SOLUTION AT 30°

Dilution in liters	Λ_v	Dilution in liters	Λ_v	Dilution in liters	Λ_v
1	87.30	64	128.70	512	141.07
2	95.70	100	131.21	1024	144.17
4	102.30	128	133.40	2048	146.67
8	107.50	201	135.38	3222	148.04
16	115.30	256	137.67	12889	149.00
32	122.52	402	139.80		

The results were treated graphically by the three common methods, *viz.:* 1, Λ_v plotted against dilution; 2, Λ_v plotted against cube root of equivalent concentration; 3, $(1 - g)$ plotted against γc where $\gamma = 3$ for a ternary electrolyte and $g = P/\gamma P_0 = 1/\gamma \times i = 1/\gamma\,(1 + 2\Lambda_v/\Lambda_\infty)$.

The third method requires the assumption of the value of Λ_∞, which was obtained from the preceding methods. The correct value of Λ_∞ causes the graph to pass through the origin.

All three methods of treating the data agreed in yielding 149.58 as the value of Λ_∞ (equivalent conductivity at infinite dilution) for solutions of strontium chloride in water at 30°. The ionic conductivities of Cl^- and $^1/_2\ SO_4^=$ at 30° were obtained by interpolation from the plots of the figures in the Smithsonian Physical Tables, as $l_{Cl^-} = 84.0$, $l_{1/_2SO_4^{--}} = 88.0$. From this we deduce $l_{1/_2Sr^{++}} = 65.58$, $\Lambda_{\infty\,1/_2SrSO_4} = 153.58$ at 30°.

Previous figures for the normal solubility of strontium sulfate in water are somewhat discordant. Fresenius[6] gives 0.0146 g. of $SrSO_4$ per 100 g. of water. Wolfmann[7] quotes a number of other determinations from previous workers, all discordant, and himself carried out a number of determinations; his figure for 30° is 0.016 g. of $SrSO_4$ per 100 g. of water. Kohlrausch's figure[8] for the solubility at 32.5° is 0.01143 g. of $SrSO_4$ per 100 cc. of solution. We repeated this determination in the following way.

Strontium sulfate was prepared by precipitating a hot solution of strontium chloride (in slight excess) with potassium sulfate solution. The precipitate was well washed with hot conductivity water until no cloudiness was produced with silver nitrate. Excess of this strontium sulfate was placed in the conductivity cell with conductivity water and stirred at intervals for two hours in the thermostat. A determination of conductivity was then made, the solution poured off, and fresh conductivity water added. This process was repeated until the conductivity showed only a small decrease. The procedure was then varied by boiling the strontium sulfate and water with rapid stirring and then allowing to cool in the thermostat. Conductivity readings were taken as soon as temperature equilibrium was established. The procedure was now repeated with fresh conductivity water on the same strontium sulfate. In the final test, strontium sulfate which had been treated in the above way twenty-seven times was stirred through a mercury seal overnight in the conductivity vessel. The conductivity determined next day showed no change. Our final result for the specific conductivity at 30° of saturated strontium sulfate solution is 1.626 × 10^{-4} mhos. Assuming as a first approximation the strontium sulfate to possess its maximum equivalent conductivity, *viz.*, 153.58 mhos as determined by us, we

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(6) Fresenius, *Ann.*, **59**, 121 (1846).

(7) Wolfmann, *Z. Zuckerindustrie und Landwirtschaft*, **25**, 986 (1896).

(8) Kohlrausch, *Z. physik. Chem.*, **64**, 129 (1908).

obtain 944 liters as the volume containing 1 equivalent, or 0.0097 g. of $SrSO_4$ per 100 cc. of solution. As the equivalent conductivity at 944 liters is undoubtedly less than its maximum value the solubility must be somewhat greater than this. A direct determination of solubility by evaporation of some of the above solution in a weighed platinum dish, followed by ignition at a dull red heat, gave 0.0128 g. of $SrSO_4$ per 100 g. of water.

The supersaturated solutions were prepared by mixing solutions of strontium chloride and of potassium sulfate of equivalent concentration. The concentrations were such that on mixing equal volumes a definite degree of supersaturation with respect to strontium sulfate would be produced. Silica vessels were used throughout. Before mixing the solutions the conductivity of each was determined in a separate conductivity cell. The potassium sulfate solution was then driven over into the strontium chloride solution by means of purified and dried compressed air. Correction was made for the volume of potassium sulfate left adhering to the walls. The contents of the receiver were stirred during this process with a small stirrer, operating through a mercury seal. The stirring device was then removed, the electrodes replaced, and a determination of conductivity made immediately. In all cases it was found that the conductivity of the mixed solutions was less than the mean of the two before mixing. This may possibly be connected with the higher electrostriction of an electrolyte like strontium sulfate.

With the solutions of lower concentration, up to 50% supersaturation, no fall in conductivity was observed after the initial fall mentioned above, during a period of two days. It was assumed that these solutions were truly metastable (not labile) as in the case observed by Dundon.[2] These solutions were stored away in stoppered silica test-tubes. When these were examined some weeks later, however, they were found to exhibit a pronounced Tyndall beam, while the conductivity had fallen. Particles of strontium sulfate were also found at the bottom of the test-tubes. These, when examined under the microscope, were found to be highly crystalline (rhombic) and of magnitude varying from 4 to 10 μ. The further course of experiments is indicated graphically in Fig. 1, where specific conductivity is plotted against time.

The results of the above experiments indicated that immediate spontaneous crystallization sets in at 75% original supersaturation. Below this concentration, crystallization eventually took place, but whether or not this was due to chance inoculation remained undecided. Moreover, during the earlier prolonged experiments, absorption of carbon dioxide from the atmosphere rendered the quantitative interpretation of the conductivity figures impossible. Accordingly, for experiments V and VI, an apparatus was built up in which the solutions after mixing were placed in a sealed glass vessel, containing electrodes, in the thermostat. This vessel was not opened throughout the experiment so that conductivity determinations were unaffected by atmospheric pollution. In order to make simultaneous determinations of particle size, some of the identical mixed solutions were simultaneously placed in a separate apparatus in the same thermostat. This apparatus consisted of a carefully steamed-out gas washing bottle, connected, through guard-tubes containing soda-lime, glass wool and cotton wool, at one end with the compressed air. The delivery tube of the gas washing bottle was drawn to a point and fitted with a ground glass cap. Determinations of particle size were made immediately after a conductivity measurement. These were carried out by applying air pressure to the second apparatus and driving over about 1 cc. of liquid for examination. Two lengthy runs were carried out with this apparatus. The original supersaturation was in both cases 50%, since we wished to know whether precipitation from this concentration was truly spontaneous, and also because in this region of relatively low supersaturation and consequent slow precipitation, it was expected that von Weimarn's consecutive stages of precipitation might more readily be observed.

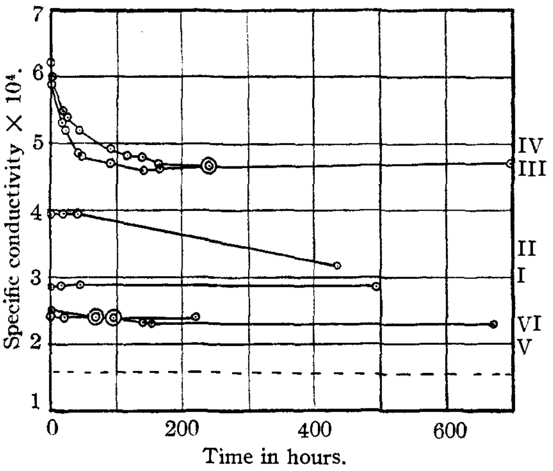

Fig. 1.—Dotted line shows normal saturation.

NOTES TO CURVES

No.	Mean sp. cond. of unmixed solns. × 10^{-4}	(Actual $SrSO_4$/normal $SrSO_4$ − 1) × 100 at start	Notes
I	2.92	75.0	Spontaneous crystn. at free surface. Particle size up to 4 μ
II	4.05	142.0	Crystals formed on surface. Particle size 0.2 to 10 μ
III	6.20	265.0	Spont. crystn. Surface crystals rhombic, meas. 4.5 to 4.8 μ (after 48 hours); 7 to 15 μ (after 29 days)
IV	6.25	284.0	Toluene on free surface, large clear crystals growing from points on wall 2 to 8 μ
V	2.50	49.0	Brownian movt. obsd. after 95 hours. Very few visible particles after 153 hours, 0.8 to 1.5 μ. After 28 days many particles avg. 4 to 8 μ
VI	2.72	54.0	Vivid Brownian movt. after 95 hours. No small particles obsd., few aggregates of 15 to 25 μ obsd. at end

Discussion

It appears that true spontaneous crystallization sets in at 50% supersaturation, and presumably with even lower supersaturation, given time. Prior to the formation of visible (microscopic) particles, von Weimarn's colloidal zone is observed. All these colloidal particles cannot, however, function as nuclei, since we have found it very difficult to observe the occurrence of particles less than 1 μ, that is, the number of those present at any moment in the solution is very small. Nevertheless, after the elapse of a certain period of time, the occurrence of fairly large crystalline fragments, typical of strontium sulfate, is common. It would appear that, to use Tammann's phraseology, the nuclear number of such a solution as this is small, but that once developed, the nuclei grow rapidly to considerable magnitude (say 5 μ). The most remarkable observation, confirming that of Dundon,[2] is that after the degree of supersaturation has fallen to 40–50%, further precipitation appears to stop or become very slow. Our longest experiment ran for twenty-eight days only, but if it is true that there is no further precipitation, the observation becomes incomprehensible, for, although the tendency to spontaneous formation of nuclei might be zero, that is, a 30% supersaturated solution of strontium sulfate might be expected to be indefinitely metastable, in the absence of inoculation, in the experiments under consideration large crystals of the solid phase are present, which nevertheless, do not appear to grow further. We are inclined to take the view that crystallization is still continuing, albeit very slowly.

Marc,[3] in his work on crystallization, found that crystallization from supersaturated solutions after seeding could be slowed down and brought to a standstill, before normal solubility was attained by addition of certain substances (dyes for the most part). His curves expressing degree of supersaturation against time are strikingly like ours. Marc's explanation of their behavior, based on experimental work, is that the true process of crystallization is preceded by a rapid adsorption of solute molecules on the surface of the inoculating solid, the subsequent relatively slow process being the arrangement of these molecules in the form of the crystal lattice. The slowing down or inhibition of the crystallization process by addition of certain anticatalysts is due to their adsorption and displacement of solute molecules from the surface of the crystalline seed. Such an explanation, however, can hardly apply to the case considered here. The only possible anticatalyst in solution is the relatively low concentration of potassium chloride molecules, produced by the double decomposition. Marc has shown in the cases studied by him that potassium chloride does not exert an appreciable anticatalytic effect and that strontium sulfate is a poor adsorbent. We think it more probable that in solutions of strontium sulfate of 50% or less supersaturation, spontaneous formation of nuclei is very slow as, indeed, our early experiments showed while the growth of the comparatively large crystalline fragments is also slow because of the low total concentration of strontium sulfate molecules in solution.

In no case was the occurrence of Lambert and Hume-Rothery's[5] needle-like form of strontium sulfate observed.

Summary

1. The equivalent conductivity of strontium chloride at infinite dilution for the temperature 30° has been determined and the ionic conductivity of strontium ion for that temperature evaluated.

2. The fall in conductivity of supersaturated solutions of strontium sulfate produced by mixing potassium sulfate and strontium chloride, has been followed. Solutions down to and including 50% supersaturation crystallize spontaneously, but the conductivity never falls to normal. The solutions appear to be permanently supersaturated at 30–40% supersaturation, despite the presence of large particles.

3. Von Weimarn's hypothesis of the mechanism of precipitation receives support, with slight modification.

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