A STUDY OF PRECIPITATION FROM SUPERSATURATED SOLUTIONS OF STRONTIUM SULPHATE

by

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Being a Thesis
Submitted to the Committee on
Post-Graduate Studies of the
University of Manitoba in par-
tial fulfilment of the require-
ments for the Degree of
Master of Science.

April 1934

To Dr. A. N. Campbell

Who has directed and very kindly

assisted in this work, the thanks of

the writer are most gratefully

offered.

CONTENTS

INTRODUCTION

A system comprising one salt and water is, by the phase rule, a two-component system, and when there are two phases present, there are two degrees of freedom. Therefore at constant temperature and pressure (atmospheric) the amount of salt in solution should be constant. This however would hold only as long as no variable other than pressure, temperature and concentration come into play, because the phase rule considers only these three factors as governing equilibrium. If then, another factor which might be expected to affect the equilibrium, such as surface energy, appears, we should expect the predictions of the phase rule to be no longer valid.

All liquids and presumably all solid substances possess a certain surface energy, that is, a tendency to reduce their total surface to a minimum. The surface energy associated with massive solid is small, however, and would have no effect on the equilibrium. But the surface energy increases with degree of subdivision so that below a certain magnitude the surface energy of the solid particles should be great enough to affect the equilibrium, and should result in an increase in solubility of the solid.[1]

For a given quantity of precipitate there is a maximum of common surface for a minimum of particle size and a minimum of common surface when the precipitate forms a single

sphere. If the solid body forms two equal spheres the total surface is 26% greater, while a reduction to one hundred spheres would cause an increase in total surface of 364%. Bearing in mind the enormous number of particles involved, this might serve to give some idea of the extensive surface of a precipitate.

Many solid bodies when freshly precipitated pass through a filter, but if they are allowed to stand for some time in the liquid, the precipitate can readily be separated from the liquid by filtration. If precipitation takes place in hot solution, filtration can usually take place immediately. In the latter case the precipitate is probably just as fine at first, as in the cold, but at the higher temperature coarse formation takes place more rapidly. In a finely divided precipitate the surface energy tends to produce a diminution of total surface. This means an increase of particle size. By chance all the particles in the precipitate are not of the same size. This being the case the solution is not saturated with respect to both large and small particles. If it is saturated re the large it is less than saturated re the smaller and the latter will dissolve making the solution supersaturated re the coarser particles. This results in a deposition of solid on the larger particles and, as it is usually expressed, the larger grow at the expense of the smaller. The same process takes place if the solution is at first supersaturated with respect to the coarser particles because, as is obvious,

this condition is one stage of the cycle described above. These processes of solution and reprecipitation occur simultaneously and continue till the surface energy of the system has become a minimum. Then, and they only, is the system in equilibrium and the solution is said to be normally saturated.

By definition a normally saturated solution is one in contact with a plane surface of the solute. Theoretically if the surface were convex the concentration would be greater, and would be less if the surface were concave. Practically there is no difference in concentration between a normally saturated solution and one that is in contact with coarsely crystalline particles of solute.

Van't Hoff has shown that with allotropic modifications of the same substance, the metastable form, that is, the form with the greater free energy, has the greater vapor pressure and the greater solubility in all liquids. Otherwise from thermodynamical considerations, it would be possible to establish a perpetum mobile. The finer particles possess the greater free energy and are therefore unstable and hence will dissolve, to reprecipitate on the coarser particles and thus establish equilibrium.

On this reasoning it should be possible to obtain a permanently superaturated solution by dissolving extremely small particles of uniform size. But this is obviously experimentally improbable if not impossible. Starting from the other end of the scale, that is from molecular size, it should

be possible to build up enormous degrees of supersaturation. If there is a definite relation between solubility and particle size, it should be possible to follow the growth of the particles as the metastability of the supersaturated solution destroys itself, provided of course crystallization sets in. Subsequently this point will be discussed more fully in connection with some data obtained.

In view of the evidence in the literature, discussed later, it was decided to deal more especially with the metastable states which must exist as solid precipitates from a supersaturated solution. The best opportunity for such an investigation occurs with substances of small solubility, in which case equilibrium comes about with such slowness that it can be followed conductometrically. Such solution equilibria, must however, be easily attained and continued hydrolysis or other decomposition in solution must not occur. For these reasons we chose to work with strontium sulphate.

An additional problem presented itself just after the work commenced. Careful persual of the literature failed to reveal any record of the ionic conductivity of strontium at 30° C., and since this value was needed in calculations it was determined experimentally. This work was carried out prior to commencing the problem proper and, due to unforseen experimental difficulties, it occupied several months. This of course reduced the time allotted for the thesis work, but the consistent results finally obtained afford some compensation for the time involved.

OUTLINE OF PREVIOUS WORK

The effect of increased subdivision of particles on the solubility was investigated by Hulett[2]. Working with gypsum, he found that with increasing degree of fineness, the solubility was greater. He prepared normally saturated solutions of pure gypsum, determined their conductivity, then introduced finely ground gypsum, shook and determined conductometrically the change in solubility. Particle size of the power was determined with a microscope before introducing it into the solution. He observed a definite increase in solubility which, however, decreased as the particles grew in size, and the solution tended to return to normal.

Dundon and Mack[3] continued the investigations of Hulett on gypsum. They carried numerous experiments, using similar technique, and reached the conclusion that the increased solubility, which they confirmed was due principally to the dehydration of the gypsum during the grinding process. They decided that the increase in solubility actually due to particle size was small. It might be noted here that since the partially dehydrated gypsum is the metastable form it would have the greater free energy and therefore the greater solubility.

Dumdon[4] in a further paper continues his investigations, and for a number of salts he finds that solubility increase with greater subdivision of particles. From his data he calculates the surface energy of the solids in

question by substituting in the Ostwald--Freundlich equation which was first derived in its general form by Willard Gibbs[5].

In the case of strontium sulphate he finds an increase in solubility but no tendency to return by more than about 2% from a maximum increase of 26%. This he attributes to the formation of a positive colloid and concludes that the solution is permanently supersaturated. He obtained similar results with barium sulphate.

Bigelow and Trimble[6] worked on the analogous phenomenon of enhanced vapor pressure of very small droplets of liquid, and of small crystals. They point out that the assumptions of the well known Thomson equation are unreliable, and that the equation is applicable only within narrow limits and only to bodies that are experimentally measurable.

Sir William Thomson[7] predicts that for a radius of curvature of less than 0.0012 m.m. an effect on the vapor pressure should be observed.

From the equation, the effect increases for more curved surfaces and becomes enormous when the radius of the drop approaches molecular magnitude.

They quote papers of several workers[8] in favor of a positive effect for enhanced vapor pressure of small drops and crystals, and increased solubility of small particles.

Bigelow and Trimble investigated a large number of substances and obtained no definite quantitative results.

Indeed mercury was the only substance which yielded positive results, and these were only qualitative because distillation of the smaller to the larger drops ceased before the smaller had disappeared. They suggested that the substances wet the surface on which they were deposited, and therefore the droplets are in equilibrium with the film thus formed and no distillation can take place.

Ostwald's[9] sulphur experiments were repeated carefully, but in a closely regulated thermostat no distillation from the smaller to the larger could be observed. Growth of the larger drops at the expense of the smaller was seen to take place when not in the thermostat, so that Bigelow and Trimble concluded that Ostwald's observations must have been due to temperature differences. Moreover when distillation did take place the centre of the large drop was always crystalline.

No sublimation took place between small and large crystals of iodine, camphor and naphthalene, indicating that the vapor pressure difference must be very small, even for minute crystals.

Dundon considers the Ostwald--Freundlich equation,

$$\frac{RT}{M} \log \frac{S_2}{S_1} = \frac{2\theta}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

where R is the gas constant, T the absolute temperature, M the molecular weight of solid, θ the surface energy per unit common surface, ρ the density of solid and S_2 and S_1 are the solubilities of particles of radii r_2 and r_1 respectively.

and on it he bases his calculations of surface energy of solids, admitting that the necessary assumptions are questionable. He introduces the van't Hoff factor "i" so as to cover dissociated particles.

When one particle has a plane surface (normally saturated solution) r becomes infinity and that term vanishes. The equation is, by substituting vapor pressure for solution pressure (solubility) then the same as that of Thomson, which is discussed by Bigelow, viz.,

$$\log_e \frac{P}{P_o} = \frac{2M\gamma}{rsRT}$$

where R is the gas constant, M the Molecular weight, T the absolute temperature, S the density, γ the surface tension, P_o the vapor pressure of liquid with plane surface and P the vapor pressure of liquid with surface curvature r. The assumption made are the same as for the other equation.

Dundon assumes that the equation holds, and indeed, there is no doubt as to the veracity of the thermodynamic considerations leading up to it. Bigelow, while not doubting the soundness of the thermodynamic reasoning of the Thomson equation, which he says: "with suitable modifications holds quite as well, theoretically, for vapor pressure of solid particles, and for the solution pressure of solid and liquid particles, as for vapor pressure of liquid bodies, "has not in", --persistent efforts extending over several years, been successful in finding any quantitative experimental data supporting the Thomson equation." He concludes that, "---the

causes and effects formulated by the Thomson equation are so small that they are usually obscured or oblitered by other causes and effects always simultaneously present."

His results by analogy cast some doubt on those of the other workers.

It seemed to us, at the time, that some ambiguity was introduced by an incomplete definition of equilibrium. Equilibrium is defined as the state at which a system will eventually arrive spontaneously, given, if necessary, infinite time. This once postulated there can be only one conception of solubility equilibrium and this, as the phase rule requires, will be fixed and definite at any given temperature and pressure. Admitting the small particle effect, and seeming persistence of metastability of some such solutions, there can be no doubt that the solutions will eventually arrive at the condition of a saturated solution in contact with coarse particles, that is, a normally saturated solution.

It appeared therefore, of greater interest to leave open the question of increased solubility caused by the introduction of small particles into an already saturated solution and rather to follow the various metastable states through which a supersaturated solution passes as the salt precipitates. In this connection it might be well to mention Von Wiemarn's[10] conception of precipitation of a salt. His view seems inherently probable and according to him the process consists of five stages:

1. Collision of ions to form molecules.
2. Aggregation of these molecules to form disperse systems.
3. Precipitation of the colloid (from sol to gel sometimes) affected and effected by ions remaining in the mother liquor.
4. Further aggregation of the colloid to form visible particles of the solid.
5. Changes of solid particles owing to contact with the mother liquor, e.g. into a more stable form, and growth of crystals.

Lambert and Hume-Rothery[11] investigated effects of variations in concentrations, temperature, cation and anion of precipitationg solutions and their results bear out Von Wiemarn's conception of precipitation. But they worked with comparitively strong solutions of strontium sulphate and consequently the metastable conditions were of short duration. They observed a time effect which varied with the anion and cation. They also observed two types of crystals, needles and rhombs, the latter appearing in the more dilute solutions, while the former precipitated at first in the stronger solutions, but changed to rhombs on standing or when the temperature was raised. These workers, however, give no quantitative results. Their "time" factor is presumably the length of time till visible precipitation.

Their observations of the effect of various anions and cations must be remembered in connection with this work,

because of the continous presence of ions other than those of the salt under investigation.

EXPERIMENTAL METHOD

Supersaturated solutions of $SrSO_4$ were prepared by mixing equivalent quantities of solutions of $SrCl_2$ and $K_2\ SO_4$ and the spontaneous behavior of these solutions, with respect ro conductivity and particle size, was followed in the thermostat. Separate samples of these solutions were placed in conductivity cells and their conductivities measured immediately before mixing. The mixing device is described later with a diagram in (Fig.2.) After mixing the stirrer was removed, replaced by electrodes and the conductivity measured at once. The gradual decrease in concentration of the $SrSO_4$ solution was determined by the fall in conductivity. But, as will be shown subsequently, the danger of contamination from the atmosphere was always great. It was desirable that this possible source of error be reduced to a minimum, and for this reason a series of experiments were attempted under reduced pressure. They did not, however, prove entirely satisfactory. Since the amount of air in the flask, at normal pressure, could not materially affect the conductivity, the flask was sealed with paraffin but was not evacuated.

From time to time small samples were taken from the cell, placed on a slide, and examined under the microscope for determination of particle size. Other samples were examined for the Tyndal cone effect. The process of removing successive samples from the cell was subsequently deemed unsatisfactory and the method was changed.

Samples were removed immediately after mixing and were sealed in small cells, whose description is to follow. This necessitated opening the conductivity cell only once. The cells were of such dimensions that they could be placed under the microscope and their whole contents examined. But even this was later considered unsatisfactory and a third method was devised.

A sample of the prepared solution was placed in the cell as before. Another large sample was placed in a drying bottle to whose inlet a stop-cock had been fused and turned down. This was protected from the atmosphere by a ground glass cap and the bottle placed in the thermostat. From time to time a few drops were blown over by specially purified air, which had been passed through large U-tubes of soda-lime and cotton-wool and finally bubbled through conductivity water in the thermostat, and examined under the microscope and ultra-microscope. This was the method used when the cell was sealed in a flask, as mentioned above.

The method of determining the ionic conductivity of strontium, the specific conductivity and normal solubility of strontium sulphate appear in the sections under those respective headings.

All work was carried out in a laboratory used solely for this investigation. Fumes from outside sources were excluded as far as possible.

APPARATUS

All work, except measurement of particle size, was carried out in an electrically controlled and heated thermostat. The regulator was of the usual mercury-toluene type, operated through a transformer on a 110 volt A. C. circuit, and maintained a temperature of 30° ± .02° C. A few drops of light machine oil on the surface of the water prevented too much evaporation overnight. The thermometer was checked by comparison with two standard thermometers.

Silica cells of the usual Kohlrausch type were used and the electrodes were platinized.

All flasks in which the solutions remained for more than a few seconds were of fused silica, and were plugged with corks which had been immersed in hot paraffin for several minutes and then covered with tinfoil.

All volumetric apparatus was calibrated by weighing.

Vessels were well steamed each time before use.

Measurments of conductivity were made by the well known modified Wheatstone-bridge method devised by Kohlrausch [12]. The connections for this apparatus are shown diagramatically in Fig.1. All leads were of heavy insulated copper wire, suspended in air or in glass tubes. H, the source of alternating current is a microphone hummer by the General Radio Co., placed fifteen feet from the bridge, and delivering a frequency of 1000 cycles. High frequency is necessary to overcome polarization effects. K is a slide wire of the Kohlrausch circular

type, by Leeds and Northrup. T is the telephones and R_1 a resistance of 1000 ohms placed across them. R is the variable resistance, consisting of three Leeds and Northrup resistance boxes, two of 1 to 11.110 ohms and one of 0.1 to 111.0 ohms. S is a variable air condenser by the General Radio Co., placed in parallel with R to balance the capacitance of the cell C, which contains the solution whose conductivity is to be measured, and to permit of absolute silence being obtained at the point of balance. The plugs in the resistance boxes R were kept bright by cleaning with fine emery cloth and wiping with alcohol from time to time.

For the detection of the first sign of precipitation, that is the colloidal stage, an ultramicroscope was devised on the principle of Zsigmondy[13] using a microscope objective as a condenser with an ordinary microscope placed at right angles to the beam. With a carbon arc lamp as a source of light, fairly good sensitivity was obtained. For the examination of particles in the visible region, a microscope with a maximum magnification of x 2500, and fitted with an ocular micrometer by Zeiss, was used.

The cells in which the solutions were placed for microscopic examination, were constructed by sealing a sheet if mica, with a suitable hole in it, on an ordinary slide glass. By smearing the surface of the mica round the hole with a little vaseline and covering the solution with a cover-glass, a quite effective seal was obtained.

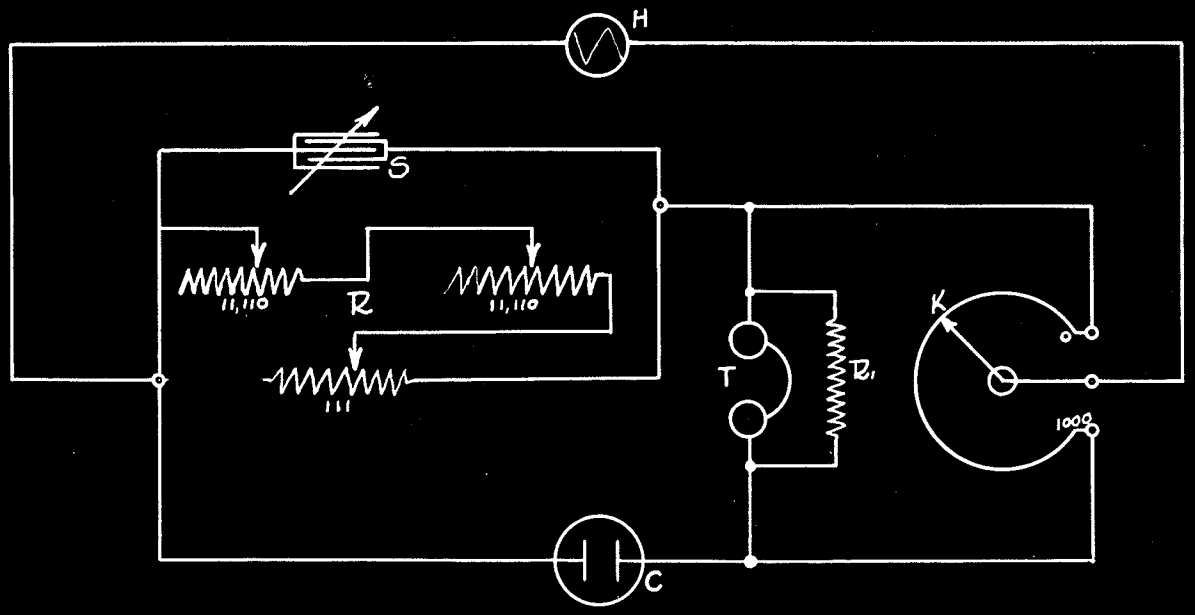

Fig Nº 1

The mica cells varied in depth from the thickness of a cover-glass to about three times that amount. Some were made by sealing a glass tube to a slide with Canada balsam and grinding down to a suitable depth. The cell used in detecting the Brownian movement was constructed in this manner and was about one centimeter deep. The use of these cells was continued after the method had been changed, but the liquid was not sealed in them, and since the examination took only a few minutes, and a new sample was examined each time.

The device for mixing the solutions in preparing the supersaturated $SrSO_4$ solutions is shown diagramatically in Fig.2. Purified air enters under pressure at A and forces the solution in B into the cell D via the capillary tube C, where it is rapidly and effectively mixed by the mercury-seal screw-type stirrer E, mechanically operated at high speed. F is a very fine capillary to permit air to escape. The efficiency of this apparatus was demonstrated by mixing a solution of potassium permanganate into pure water. The spread of color through the water was instantaneous. This rapid mixing was necessary in order to overcome local superaturation as one solution was added to the other.

For experiments under reduced pressure a specially ground stop-cock was sealed to the side-arm of a large suction flask. Platinum leads were sealed into glass tubes and passed through a rubber stopper so that the platinum made contact with the mercury leads of the electrodes of the cell which was placed

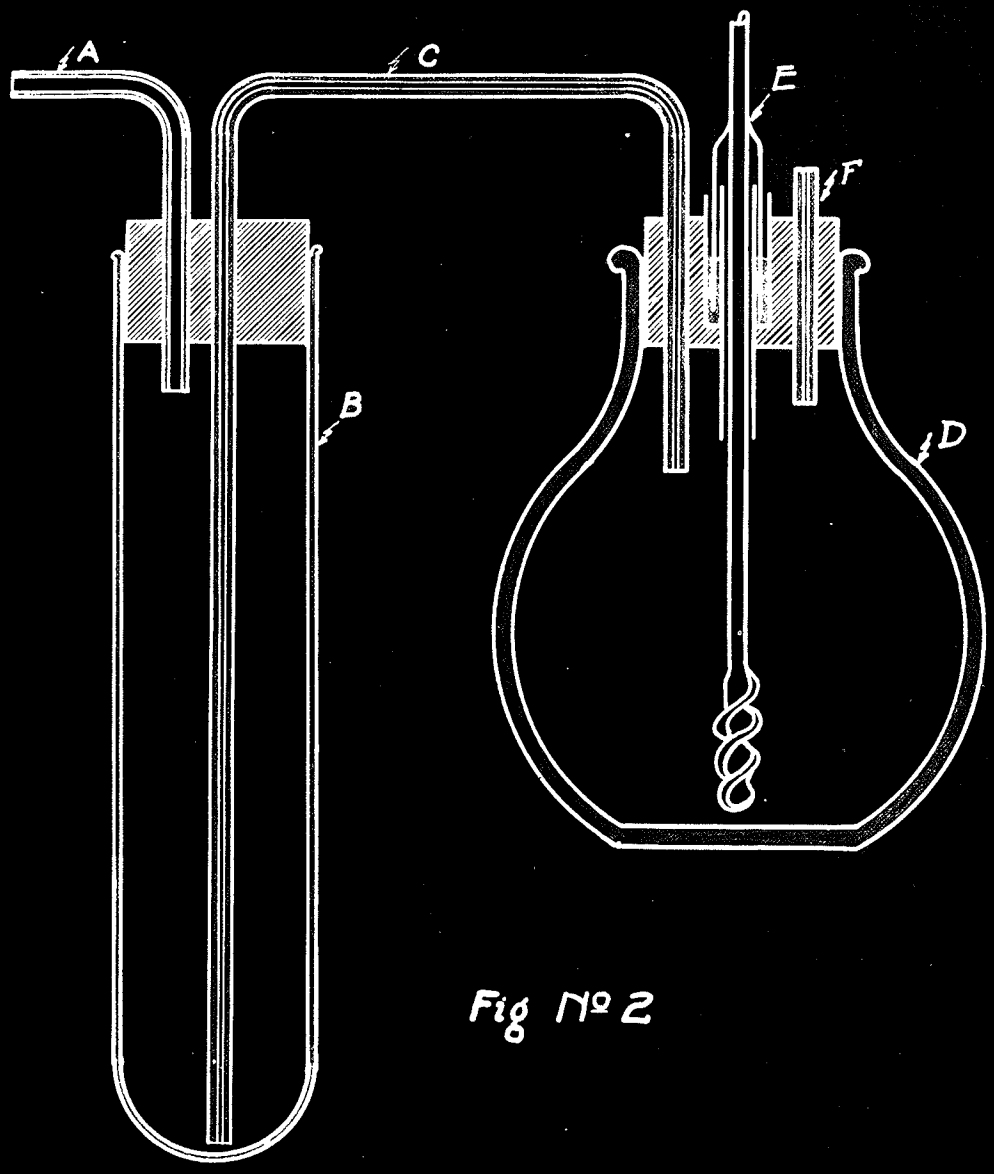

Fig Nº 2

in the flask, and the flask evacuated. Conductivity water was placed in the flask in order to compensate for evaporation from the solution. This apparatus however, did not give satisfactory results, due probably to the evacuation process, and so the experiments were repeated in the same apparatus, unevacuated. The rubber stopper was covered with melted paraffin and the flask completely immersed in the thermostat.

CONDUCTIVITY WATER

Conductivity water was prepared in large quantities and was used in the preparation of all solutions.

Ordinary distilled water was redistilled three times;

(1) From alkaline potassium permanganate.

(2) From baryta.

(3) Through block tin condenser into a large silica receiving flask.

(1) and (2) were distilled from monax flasks through glass condensers, into monax receivers and were allowed to stand overnight before distillation. (2) and (3) were protected from the atmosphere by soda-lime tubes. The water was drawn from the silica flask in (3) through a siphon so that the flask was never opened. This water, tested frequently, had a specific conductivity of 3 to 5 x 10^{-6} mhos, and in calculations this was taken into consideration where necessary.

EQUIVALENT CONDUCTANCE OF STRONTIUM SULPHATE SOLUTION AT INFINITE DILUTION AT 30° C

In calculating the amount of strontium sulphate in solution we considered it desirable to know the equivalent conductivity of this salt at infinite dilution. This value can be calculated by the well known law of Kohlrausch;

$$\Lambda_\infty = l_c + l_a$$

or in words, the equivalent conductivity at infinite dilution of any electrolyte is equal to the sum of the conductances of the cation and anion (l_c and l_a respectively). Moreover, l_c and l_a are independent of each other and have constant values at a given temperature, regardless of the electrolyte from which they originate. If, therefore, we know $l_{\frac{1}{2}Sr^{++}}$ and $l_{\frac{1}{2}SO_4^{--}}$ the desired value will be the sum of these two. But there was no record in the literature of the ionic conductivity of strontium at 30° , and for this reason it was determined experimentally, using solutions of strontium chloride.

Considering the time spent on this part of the work it might have been wiser merely to calibrate conductivity against analytically determined amounts of strontium sulphate. But we were finally rewarded with consistent results, in spite of the fact that the salt used ($SrCl_2$) was of necessity a uni-bivalent electrolyte. This type of electrolyte possesses a greater degree of electrostriction at measurable dilutions than does one of the

uni-univalent type, and considerable difficulty is encountered in arriving at infinite dilution, that is, the point at which all the ions participate in conducting the electric current.

(a) EXPERIMENTAL

A complete description of the conductivity apparatus used is given in the section headed "Apparatus". A diagram of the electrical connections is shown in Fig.1.

Two pipettes were calibrated, one to deliver exactly fifty c.c.'s and the other to withdraw exactly that volume.

The general method was simply that outlined in any good text on practical physical chemistry, as for instance, in Daniels, Matthews and Williams[14] .

To avoid cumulative errors which might have arisen from the method of dilution, (successively withdrawing a volume of solution from the cell and replacing it with the same volume of conductivity water,) solutions were made up down to a concentration of $\frac{N}{100}$ and these were diluted in turn. The determinations were continued till consistent results were obtained, and it might be noted here that such results were not forthcoming till the experiments were carried out in a laboratory used for nothing else, where the air could be kept relatively pure. Throughout these investigations the greatest source of error seemed to be the atmosphere. To keep a check on any error due to contamination by the atmosphere, a cell similar to the one containing the solution under investigation, was filled with conductivity water, placed in the thermostat alongside the other and a "blank" was run in conjunction with the experiment proper.

The solutions used in the earlier determinations were

checked by analysis, but since the results were well within the limits of experimental error, this was deemed unnecessary in subsequent work.

The cell constant was determined with exactly $\frac{N}{50}$ KCl and $\frac{N}{10}$ KCl. The specific conductivities of these solutions used in evaluating the cell constant were those given by Kohlrausch. By using two standard solutions, instead of only one, as is customary, a good check was made.

The potassium chloride used was Mallinckrodt's "Analytical Reagent" quality. This was placed in an oven at 90° C. overnight and solutions were made up by weighing.

The strontium chloride was purchased as $SrCl_2 \cdot 6H_2O$, the quality being B.D.H. "Certified Chemical." This appeared to effloresce during weighing and so was completely dehydrated in an oven at 90° C, and solutions made up from the dried salt.

(b) CONDUCTIVITY DATA

The data obtained in the above experiments is contained in the tables below. The figures in Tables 2 and 3 were calculated from those in Table 1.

The graph in Fig.3 was obtained by plotting equivalent conductivity against dilution, that is, the number of litres containing one equivalent weight of salt ($SrCl_2$). These figures are listed in Table 1. On a large scale graph the curve, when produced, appeared to approach Λ_v-150 asymptotically, indicating that Λ_∞ lies very close to 150.

TABLE 1

Equivalent Conductivity of Strontium Chloride Solutions at 30° C.

Concentration in equivs. per litre.	Dilution in litres.	Λ_v
1.0000000	1.0	87.30
0.5000000	2.0	95.70
.2500000	4.0	102.30
.1250000	8.0	107.60
.0625000	16.0	115.30
.0312500	32.0	122.52
.0156250	64.0	128.70
.0078150	128.0	133.40
.0099300	100.7	131.21
.0049650	201.4	135.38
.0039060	256.0	137.67
.0024820	402.8	139.80
.0019580	512.0	141.07
.0009765	1024.0	144.17
.0004882	2048.0	146.67
.0003107	3222.4	148.04
.0000777	12889.6	149.00

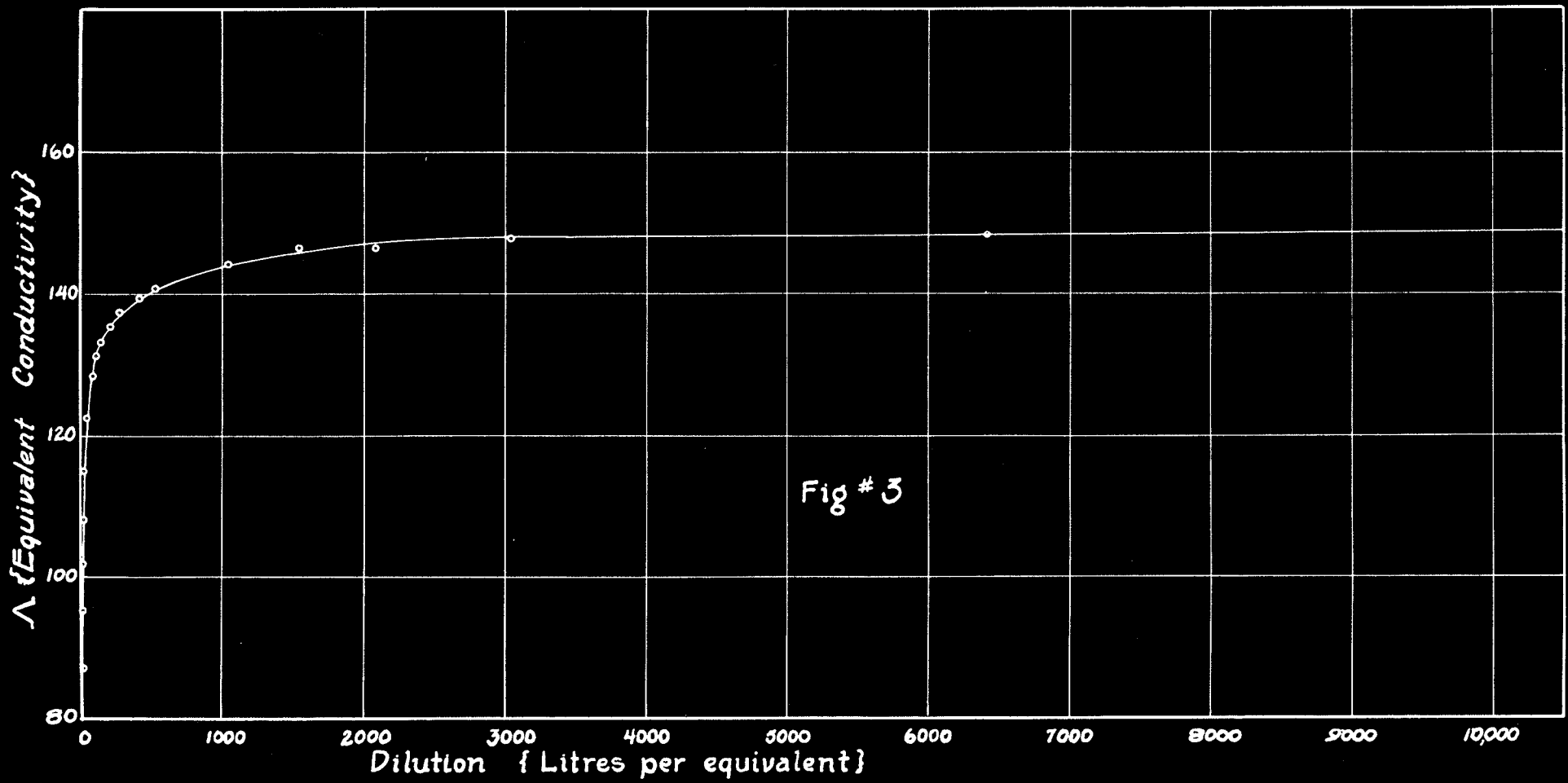
160
140
120
100
80
Λ {Equivalent Conductivity}
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10,000
Dilution {Litres per equivalent}

Fig # 3

A closer approximation to Λ_∞ can be obtained by plotting Λ_v against $\sqrt[3]{C}$, as is suggested by Kraus[15], where C is the concentration in equivalents per litre. Extrapolation of the curve, thus obtained, to $\sqrt[3]{C}=0$ gives a very close approximation to Λ_∞ since the curve has to be produced only a comparitively short distance. It will be noted that the curve in Fig.4 has the general shape of those pictured by Kraus.

Λ_∞ obtained in this manner is 149.8.

TABLE 2

Data for Curve in Fig.4.

$\sqrt[3]{C}$	Λ_v
1.00000	87.30
0.79370	95.70
.63000	102.30
.50000	107.50
.39650	115.30
.31500	122.52
.25000	128.70
.21500	131.21
.19840	133.40
.17060	135.38
.15750	137.67
.13550	139.80
.12510	141.07
.09921	144.17
.07874	146.67
.06773	148.04
.02495	149.00

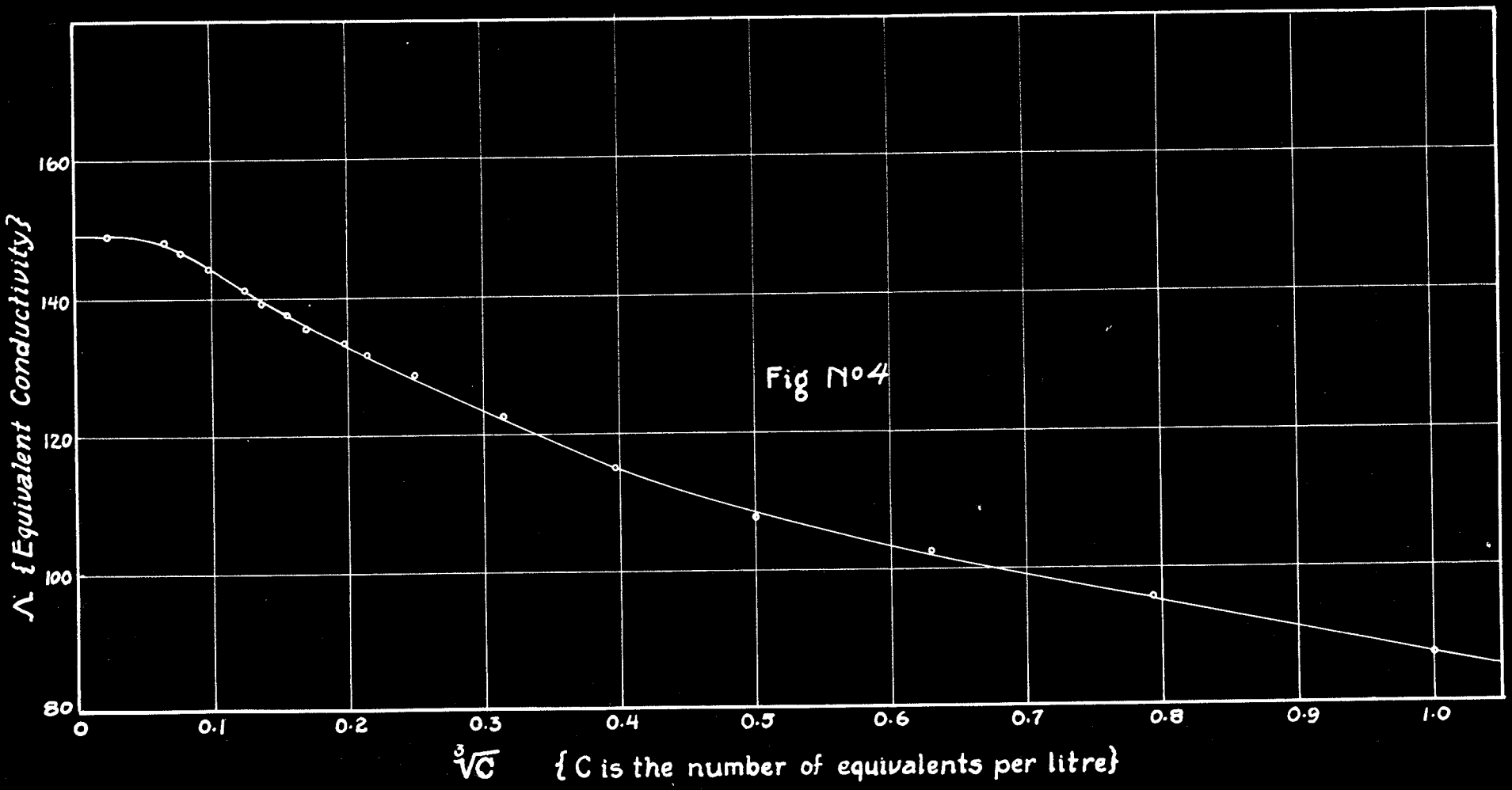
160
140
120
100
80
Λ {Equivalent Conductivity}
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
∛C {C is the number of equivalents per litre}

Fig No 4

A third graph was plotted with γC as abscissa and $1 - g$ as ordinate, where γ is the number of ions into which the molecule dissociates (3 for $SrCl_2$), C is the number of equivalents of salt ($SrCl_2$) per litre, and g is the osmotic coefficient, defined as the ratio of the actual osmotic pressure to the ideal pressure which would exist if the solute were completely dissociated and no interionic attraction existed. Then

$$g = \frac{P}{\gamma P_0} = \frac{1}{\gamma} \cdot i \text{ where i is the van't Hoff factor}$$

$$\frac{1}{\gamma}\left(1 + 2\frac{\Lambda_v}{\Lambda_\infty}\right)$$

The advantage of this method is that it requires the assumption of the value for Λ_∞ obtained from the preceding graphs, and for the correct value of Λ_∞ the curve must pass through the origin. This is obvious from the definition of g. At infinite dilution $\frac{\Lambda_v}{\Lambda_\infty}$ becomes 1 and g is therefore zero; also at infinite dilution C is zero.

This curve was plotted on a large scale and a smaller reproduction of it is shown in Fig.5, and the data calculated on the assumption that $\Lambda_\infty = 149.8$, is contained in Table 3. The curve supports the assumption.

TABLE 3

Data for Curve in Fig. 5.

δ_c	1 - g
3.000000	0.2780
1.500000	.2404
0.750000	.2107
.375000	.1877
.187500	.1533
.093750	.1207
.046875	.0937
.029790	.0817
.023430	.0727
.014895	.0633
.011700	.0537
.007447	.0442
.005858	.0375
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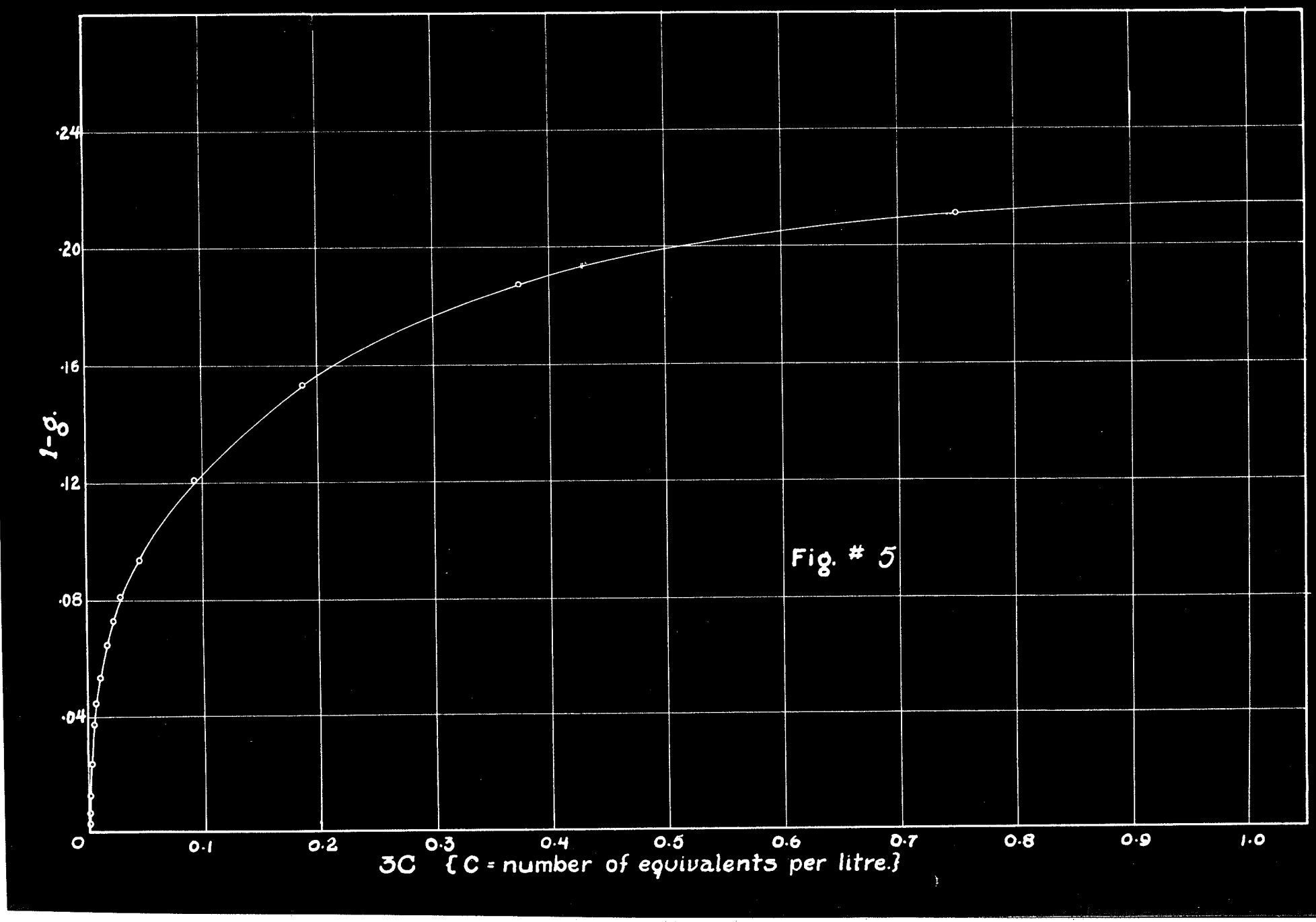
.001464	.0133
.000930	.0067
.000232	.0033


·24
·20
·16
·12
·08
·04
0
1-σ.
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
3C {C = number of equivalents per litre.}
Fig. # 5

Hence the equivalent conductivity of strontium chloride at infinite dilution is 149.58, at 30° C.

The ionic conductivity of strontium at 30° C was calculated, by the Kohlrausch law, mentioned previously. The ionic conductivity of Cl^- at 30° was obtained by interpolating the plots of the figures taken from the Smithsonian Physical Tables, and the value so obtained was, $l_{Cl^-} = 84$.
From this it was calculated that $l_{\frac{1}{2}Sr^{++}}$ at 30° is 65.58
$l_{\frac{1}{2}SO_4^{--}}$ was determined in a manner similar to that for l_{Cl^-} and was found to be 88.

The equivalent conductivity of strontium sulphate, then, is

$$l_{\frac{1}{2}SO_4^{--}} + l_{\frac{1}{2}Sr^{++}} = \Lambda\infty_{\frac{1}{2}SrSO_4} \qquad 153.58$$

at 30° C.

SPECIFIC CONDUCTIVITY OF NORMALLY SATURATED STRONTIUM SULPHATE SOLUTION AT 30° C

The value for the specific conductivity of normally saturated strontium sulphate solution was essential in the calculation dealing with the decreasing concentration of strontium sulphate in the supersaturated solutions. This was determined experimentally.

Strontium sulphate was prepared by precipitation from hot solutions of strontium chloride and potassium sulphate, using a slight excess of the chloride. The strontium salt used was the same as that described previously (B.D.H. Certified Chemical). The sulphate was Malinkrodt's C.P. quality and was crystallized twice from conductivity water and only the second crop of crystals used.

The precipitate was washed several times by decantation, transferred to the filter and washed with hot conductivity water till the filtrate gave no cloudiness when tested with silver nitrate. Excess of this $SrSO_4$ was placed in the cell with conductivity water, stirred for about two hours in the thermostat, allowed to stand for some time and then the conductivity was taken. The solution was then poured off, fresh conductivity warer added and the process repeated. This resulted in a large drop in conductivity and as the process was continually repeated the drop became less each time.

Eventually when only a small decrease was observed a variation in method was adopted. This consisted of stirring the solution rapidly while keeping the temperature just below boiling, then allowing to cool in the thermostat without stirring, and measuring the conductivity after the solution had stood for some time. By alternating these processes a constant value was obtained. As a final test, excess strontium sulphate which had been treated no less than twenty-seven times in the above manmer was added to conductivity water and stirred through a mercury seal overnight in the thermostat. After standing for several hours the conductivity was found to be in excellent agreement with the results obtained in the above.

As a result of these experiments the specific conductivity of normally saturated strontium sulphate was found to be

$$K = 162.6 \times 10^{-6}$$

Kohlrausch[16] gives K (specific conductivity) for saturated solutions of strontium sulphate for various temperatures ranging from 0° to 32.26° C. Interpolation from the plots of these points indicates a value of

$$K = 163.1 \times 10^{-6}$$

at 30° C.

NORMAL SOLUBILITY OF STRONTIUM SULPHATE AT 30° C

The literature reveals figures for the solubility of strontium sulphate in water that are somewhat discordant. Fresenius[17] gives 0.0146 grams $SrSO_4$ per 100 grams of water. Wolfmann[18] quotes a number of other determinations from previous workers, all discordant, and he himself carried out a number of determinations; his figure for 30° is 0.016 grams $SrSO_4$ per 100 grams of water. Kohlrausch's[19] figure for 32.5° is 0.01143 grams $SrSO_4$ per 100 c.c.'s solution, and at 0° is 0.0114.

This determination was repeated by evaporation of some of the solution prepared as described in the preceding section. 50 c.c.'s of the supernatant liquid were evaporated in an ignited platinum dish and afterwards heated to dull redness. This gave 0.0128 grams per 100 c.c.'s of solution.

Assuming as a first approximation that the strontium sulphate possesses its maximum equivalent conductivity, viz., 153.8 mhos, as determined by us, we obtained 944 litres as the volume containing one gram-equivalent weight, by dividing the specific conductivity of normally saturated $SrSO_4$, also obtained by us, into the equivalent conductivity. This works out to 0.0097 grams $SrSO_4$ per 100 c.c.'s solution. The equivalent conductivity, however, is undoubtedly less than this, due to the very nature of a bi-bielectrolyte, and hence the amount of $SrSO_4$ in 100 c.c.'s of solution must be somewhat greater than 0.0097 grams.

RESULTS

The results of the series of experiments on precipitation from supersaturated solution of strontium sulphate are summarized in Table 4. The headings of the columns are self-explanatory except perhaps, column five. This column gives the degree of supersaturation in per centage. "Actual $SrSO_4$" is the specific conductivity of the solution minus the specific conductivity of KCl at that concentration and temperature. "Normal $SrSO_4$" is the specific conductivity of normally saturated strontium sulphate solution. This method of calculation is permissible on the assumption that for small changes in concentration the degree of dissociation is constant. The third column gives the specific conductivity x 10^6 of the supersaturated solution.

Table 4.

Supersaturation Experiments.

Expt. No.	Time after mixing.	Sp. Cond. x 10^6	Mean Cond. of unmixed solutions x 10^6	Actual $\frac{Sr\ SO_4}{Normal\ Sr\ SO_4}$ x 100	Particle size.	Observations.
1	0	436.7	439.7	28.4		no change after 19 hours.
2	0 19½ hrs. 13 days	478.1 483.0 599.0	473.9	42.1		Increase in conductivity after 20 hrs. due to atmospheric CO_2
3	0 20 hrs.	467.5 471.5	485.8	21.9		
4	0 19 hrs. 66 hrs.	489.9 489.9 492.0	506.3	35.3		
5	0 15 days 22 days	560.7 488.6	586.05	53.65 9.35	 .3μ and less to a few about 10μ	No Tyndalbeam after 30 hrs. On innoculation Tyndal beam immidiately appeared and particles appeared to increase as they fell thru solution.

Table 4. (cont'd)

Supersaturated Experiments.

Expt. No.	Time after mixing.	Sp. Cond. x 10^6	Mean Cond. of unmixed solutions x 10^6	Actual $\frac{SrSO_4}{Normal\ SrSO_4}$ x 100	Particle size.	Observations.
6	0	644.3	663.7	73.5		
	18 hrs.	650.0				
	45 hrs.	652.0				
	20 days	636.0			up to 4μ	Spontaneous crystallization at free surface
7	0	891.6	929.75	135.6		
	18¾ hrs.	892.0				
	41 hrs.	892.0				
	18 days	722.4		31.6	0.2μ to 4.0μ. On surface 7.0μ to 10.0μ	Crystals formed on surface.
8	0	1327	1409	228.4		
	17½ hrs.	1198		148.0		Spontaneous crystallization.
	21½ "	1175		133.7		
	24¼ "	1157		122.7		

(over)

Table 4. (cont'd)

Supersaturated Experiments.

Expt. No.	Time after mixing.	Sp. Cond. x 10^6	Mean Cond of unmixed solutions x 10^6	Actual $\frac{SrSO_4}{Normal\ SrSO_4} \times 100$	Particle size.	Observations.
8 (cont'd)						
	42 hrs.	1103		89.50		
	46½ "	1093		83.35	4.5 μ to	Cell opened. Scum
	65½ "	1070		69.20	4.8 μ.	on surface. Removed sample of this and under microscope found to be crystalline particles (rhombs) measuring 4.5 μ to 4.8 μ. Conductivity taken after closing cell and found to have increased by 1.5 mm on bridge -- due to atmospheric contamination.
	90½ hrs.	1059		62.43		Cell opened -- more
	141½ "	1041		51.35	7 μ -- 8 μ.	scum -- Sample examined -- perfect
	167 "	1050				little crystals
	29 days	1070				10 μ -- 15 μ. Majority about 7 μ -- 8 μ

Table 4. (cont'd)

Supersaturated Experiments.

Expt. No.	Time after mixing.	Sp. Cond. x 10^6	Mean Cond of unmixed solutions x 10^6	Actual $\frac{SrSO_4}{Normal\ SrSO_4}$ x 100	Particle size.	Observations.
						Thought possible that crystals had formed on surface because of nuclei in atmosphere. Tried adding toluene
9	0	1403	1405.5	264.1		
	30 mins.	1353		243.5		Introduced toluene immediately after first reading.
	18¾ hrs.	1240		174.0		
	24 "	1220		161.7		
	41½ "	1167		128.8		
	90 "	1106		91.33		
	114½ "	1091		85.15		
						Removed electrodes -- no visible crystals at interface. Replaced electrodes and shook well.
	138 hrs.	1084		77.8		
	165 d"	1061		63.65		
	20 days	1051		57.4	2μ to 8μ.	Crystals deposited on walls of t.t. Some crystalline aggregates.

Table 4. (cont'd)

Supersaturated Expiriements.

Expt. No.	Time after mixing.	Sp. Cond. x 10^6	Mean Cond. of unmixed solutions x 10^6.	Actual $\frac{SrSO_4}{Normal\ SrSO_4} \times 100$	Particle size	Observations.
10	0 hrs.	549.0	560.8	51.6		Cell in sealed flask.
	24 "	548.0		51.0		Vivid Brownian movement observed.
	96 "	535.5		43.3		No visible particles to date.
	112 "	529.5		39.6		

DISCUSSION

With the lower degrees of supersaturation no change in conductivity was observed after a period of two days. These solutions were assumed to be truly metastable (not labile) as in the case observed by Dundon[20]. They were stored away in silica test tubes, stoppered in the manner described under "Apparatus". At the end of several weeks these solutions were examined and the conductivity was found to have fallen almost to that of a normally saturated solution, the difference being due probably to contamination. They also exhibited a pronounced Tyndal beam, and crystals found at the bottom and adhering to the sides of the test tubes, when examined under the microscope, were found to be distinctly crystalline (rhomic) and of magnitude varying from 4μ to 10μ.

For the more concentrated solutions growth of crystals at the surface is mentioned. This was considered due to innoculation at the surface by nuclei in the air, and one experiment was carried out with the surface of the solution covered with toluene. Crystals, in this case, did not appear at the interface but they appear at the bottom of, and adhering to the sides of the test tube. The rates of fall of conductivity for the two solutions (with and without toluene) are the same. This would indicate that innoculation from the air does not materially affect precipitation, (as indicated by the fall in conductivity), at the higher concentrations.

But such well develop crystals as those formed on the surface were not observed in the body of the solution.

It will be noted that in every case the specific conductivity of the mixed solutions is less than the mean of the specific conductivities of the unmixed solutions. This may possibly be connected with the higher electrostriction of an electrolyte like strontium sulphate. It will be noted further, especially for the solutions of lower concentration, that a slight rise in conductivity is shown during the course of, in some cases, several days. This was attributed to contamination; and to eliminate this it was proposed to repeat the experiments at the lower concentrations with the cell in a sealed flask. The experiments in a vacuum were intended to overcome this also but, as mentioned before, these were unsuccessful due to evaporation of the solvent, and therefore are not recorded in the Table.

Lack of time prevented complete investigation of the lower concentrations with the cell in a sealed flask, but the experiment recorded as no. 10 in the Table, although incomplete, appears to be progressing favorably, and there seems to be prospects of successfully following the course of precipitation essentially as outlined by von Wiemarn[22]. After a period of apparent metastability the conductivity decreased slightly and a well defined Brownian movement could then be observed. At the time of writing no microscopic particles have appeared but should do so in the course of a short time.

Although the work on spontaneous crystallization is not yet complete the following considerations emerge.

Slightly supersaturated solutions, after a period of apparent metastability, eventually crystallize spontaneously. This may be due either to the region of true metastability having been exceeded and that of spontaneous crystallization entered, or it may have been due to accidental innoculation. In connection with this point, Ostwald has shown how very difficult it is to obtain, and maintain an atmosphere entirely free from nuclei, either of the substance crystallizing or of some isomorphous substance. By now the atmosphere of the laboratory is doubtless impregnated with strontium sulphate nuclei.

Immediate spontaneous crystallization set in at a degree of supersaturation of about 75%. Even then the crystallization was very slow and normal saturation was not attained after eighteen days. This is no doubt connected with the comparatively high degree of dilution of all solutions used(maximum concentration used was 0.005 N.). Under such circumstances, impacts between Sr^{++} and SO_4^{--} ions will be relatively rare. When the fall of conductivity is plotted against time a smooth curve is obtained which approaches normal concentration asymptotically.

As far as the gradual growth of particles with a decreasing degree of supersaturation is concerned (cf. von

Weimarn's hypothesis), no evidence of this has been found in the more concentrated solutions. We have always observed that solutions of a still comparatively high degree of supersaturation develop large crystalline rhombs, of magnitude about 4μ, unaccompanied by very small particles. Neither have the needle forms recorded by Lambert and Hume-Rothery[21] been observed. This however, is probably due to the low concentration of solutions used. The process of precipitation in our more concentrated solutions appeared to proceed by the continued growth of a relatively few large particles.

To complete this investigation further work should be directed towards the less supersaturated solutions where spontaneous crystallization appears to set in only after a period of induction. It might be possible to obtain a slightly supersaturated solution whose period of induction extends over several months or even years. Unfortunately, lack of time prevented further experiments along these lines.

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