THE SOLUBILITY OF BARIUM SULPHATE
IN WATER AT 25°

by

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PART I

A CONDUCTIMETRIC INVESTIGATION OF SATURATED BARIUM SULPHATE SOLUTIONS - THE SOLUBILITY OF BARIUM SULPHATE.

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1. Symbols and Abbreviations

A,B	constants in the Debye-Huckel formula
$a_{Ba^{2+}}$, $a_{SO_4^{2-}}$	activities of barium and sulphate ions
$\underline{a}$	closest distance of approach of barium and sulphate ions
c	molar concentration
D	dielectric constant of water
e	electronic charge
I	ionic strength
K_s	thermodynamic solubility product of $BaSO_4$
K_d	dissociation constant of barium sulphate ion pairs
K_{BaOH^+}, $K_{HSO_4^-}$	hydrolysis constants
k	Boltzmann constant
m	molal concentration
N	Avogadro's number
T	absolute temperature
X_3, Y_3, X_5, Y_5	functions appearing in the "extended terms" for activity coefficient
z_+, z_-	valences of anion and cation $(z = 2)$
α^*, β^*	constants in the Onsager limiting conductivity equation
β	constant in the "extended terms"
$\gamma_{Ba^{2+}}$, $\gamma_{SO_4^{2-}}$	molal ionic activity coefficients of the ions indicated.
$\gamma_{\pm}$	mean ionic mol fractional activity coefficient
κ_{BaSO_4}	measured specific conductance of a saturated barium sulphate solution
$1/\varkappa$	"radius of the ionic atmosphere"

Symbols and Abbreviations (continued)

Λ_c	equivalent conductance of the salt at molar concentration c
Λ^o	limiting equivalent conductance of the salt
λ^o_+, λ^o_-	limiting equivalent conductances of the ionic constituents of the salt
ν_+, ν_-	number of cations, anions produced by the dissociation of one molecule of electrolyte

M	molar
N	normal

1 nm. = 1 nanomho = 10^{-9} reciprocal ohms

nm.cm.$^{-1}$ nanomhos per centimetre

2. Introduction.

Barium sulphate is a widely used analytical precipitate and for this reason its properties have been extensively studied. The variety of results encountered with barium sulphate samples prepared by different methods is an indication of the complex nature of this interesting substance.

A literature survey of the solubility measurements demonstrates the diversity met with in this field. Conductivity measurements provide the most sensitive and precise method for determining the solubility of sparingly soluble salts. It was considered that the use of precision conductimetric apparatus and solvent water of the highest purity would resolve some of the discrepancies in the recorded values, as eventuated in the case of Malan's conclusive work on silver chloride.

As a basis for investigation of this variability two broad modes of barium sulphate preparation can arbitrarily be specified: boiling-point precipitation by dropwise addition of reagents, and formation by diffusion of sulphate- and barium-ion solutions at room temperature. There are commendations for both procedures in attempting to attain the highest purity of precipitate.

In Part II, the effect of incomplete dissociation on the conductivity measurement has been evaluated.

The situation is well summed up by Mattson (43) who states that barium sulphate can be expressed as

(BA)B_z or (BA)A_z (B referring to the cation, A to the anion) where z is very small. The quantity z may be chemically insignificant but is very important as a factor governing the physical character of the material.

3. A Review of Previous Work on Barium Sulphate.

3.1. Solubility Measurements

The first conductimetric measurement of solubility was performed by Kohlrausch, who published a number of values at 18° and 26°C, which he finalised as being 2.4 and 2.77 mg./l. respectively (37).

Hulett (31) obtained the value of 2.29 mg./l. but his results for the solubility of smaller-sized particles were criticised for being taken on a chloride contaminated sample.

Melcher's values (44) of 2.22 and 2.47 mg./l. at 18° and 25°C, are to be regarded with suspicion as his reported resistance readings never stabilised and the selection of any particular value seems quite arbitrary.

Later conductimetric measurements by Kolthoff and Vogelenzang (38) gave various results ranging from 2.07 to 2.53 mg./l. at 18°C, depending on the mode of preparation of the precipitate.

A fairly recent polarographic determination of the solubility of barium sulphate (48) gave the figure 3.37 mg./l. Unfortunately the original

Russian paper was not available for details of preparation. Balarew (4) mentions a "metastable" barium sulphate which has a solubility of 3.3 mg./l. Balarew's value for "normal" barium sulphate at 18 to 20°C is given as 2.3 mg./l. His method was gravimetric and, though less precise than other methods, has the merit of being the least equivocal.

3.2. Factors Influencing the Physical Nature of Barium Sulphate.

Principal desiderata of the precipitate are minimum adsorption of foreign or lattice ions, normal particle size and rapid settling rate. The notoriety of barium sulphate for variability in these respects justifies a broad review of the factors controlling them, viz. pH, temperature, rate and mode of precipitation, concentration of reagents, and age of the barium chloride solution (a factor not found in other cases).

3.2.1. Extraneous Matter in Barium Sulphate.

The literature on this topic is quite voluminous: notable is that by Kolthoff (39). However, these investigations (well summed up by Kolthoff and Sandell (ref. 41, pages 106 to 137 and 322 to 331)) deal with ordinary analytical conditions where fairly concentrated (greater than 0.1 molar) solutions have to be used for precipitation. Although not necessarily applicable to all conditions of precipitation, the Tables on pages 325 and 330 (ref. 41) listing absorbability of ions on barium sulphate provide a guide for the selection of precipitating reagents; there does not seem to be much difference between sodium or potassium sulphates with barium chloride, and others.

Adsorption of lattice ions by barium sulphate (which can be considered a primary step in the adsorption of foreign ions) is shown by pH measurements during precipitation. Caley and Stoffer (9) and Mattson (43) found that if excess barium ion were present in contact with the precipitate the pH of the supernatant solution was appreciably acid, and if excess sulphate ion, the pH was alkaline. Their explanation is that the electrical imbalance caused by barium ion adsorption is countered by adsorption of hydroxyl ion with a resultant lower pH; a similar argument applies for sulphate ion adsorption. When equivalent amounts of both precipitating solutions have been used, the pH is close to neutral.

Water can also be included in the lattice. Balarew's view (3) is that an "inner surface" is thereby formed in the porous particles. The higher the water content, the more foreign ions are contained. Walton and Walden (52) showed, by X-ray studies, that water is present in the lattice actually as a solid solution, a group of three water molecules replacing one barium sulphate. Water may be infixed, if precipitation is performed in acid conditions, as hydrated hydrogen ion. Removal of water is an irreversible process and leaves a hole in the lattice.

Duval (17) by thermogravimetric analysis of a precipitate formed at the boiling point in acid, showed that water was lost on heating up to 1100°C, but that most was removed by 780°C. An important fact emerges from thermogravimetric analysis: barium sulphate formed in the cold without stirring, in a large volume, loses water only up to 180°C, after which the weight remains constant.

Adsorption of lattice ions is demonstrated by electrokinetic potential studies (8). Kruyt and Ruyssen found barium sulphate negative in sulphate solutions and positive in barium ion solutions. Although their findings have been refuted by Buchanan and Heymann (7), they state that mineral barytes (occurring in large crystals and therefore probably more perfect) is negative even in barium ion solution. This is probably due to fewer "active" areas (presumably lattice distortions) on the crystal surface where barium ion adsorption can take place. X-ray examination proved that there was no difference in crystal structure between their various barium sulphate samples and the natural mineral. A later paper by Ruyssen (47) reports that crystals of barium sulphate "with regular walls and even shape remain negative in barium chloride solutions of (low) concentrations". Thus it seems reasonable to infer that regularly-shaped particles have a crystalline perfection approaching that of the natural barytes.

The amount of barium chloride brought down with barium sulphate at different pH's has been studied by Eventov and Patrikeev (18). For their mode of precipitation this was found to be a minimum at pH 3.4.

These considerations suggest that the simultaneous dropwise addition with stirring of barium and sulphate ion solutions to dilute hydrochloric acid, with a constant slight excess of sulphate, will produce the purest barium sulphate. This, however, is not an original idea - it was first proposed by Otto and Hahn (29) but, in the words of Kolthoff and Sandell (ref. 41, p. 324), this procedure "yields a precipitate which is quite impure".

3.2.2. Particle size.

The minimum "normal" particle size for barium sulphate is about 2 to 4 microns (4, 16, 31, 32, 51). Balarew (4) did not find the great dependence of solubility on particle size stated by Hulett (31, 32) and Dundon (16): particles of size 0.2 microns were more soluble by only 3%. Crystals larger than 4 microns are easily obtainable, but not desirable, from the aspect of purity and settling rate.

3.2.3. Settling rate.

Barium sulphate settling rates were measured by Bogan and Moyer (6) and correlated with the age of the barium chloride precipitant solution. They found that, for their mode of preparation (flow-wise addition in the cold of barium chloride solution to acidified sodium sulphate solution) ageing for one week of the barium chloride solution, prior to precipitation, caused an appreciable increase in the particle size of the barium sulphate. Unfortunately a direct correlation is implied between particle size and settling rates, and this has not been proved (50). In fact, Okada and Magari (45) state that the smaller particles settle more quickly. Regardless of this, however, it is noteworthy that there is a difference, at least of texture, with different age of barium chloride solution used.

3.3. Electron Micrography.

Electron micrography provides another useful aspect for consideration. R.B. Fischer (23, 24) obtained silhouette photographs of precipitates prepared at various pH's, rates, temperatures and ages of barium chloride solution. He confirms Bogan's findings that the latter has an effect. Rapidly formed particles of 4 to 51 microns are of no interest due to probable large-scale contamination. Dropwise precipitation caused smaller particles (1 to 5 microns). Significant is the fact that only precipitates prepared by slow diffusion at room temperature of 10^{-3} molar solutions through a parlodion membrane appear "reasonably perfect". These are portrayed in Fig. 5E, ref. 23, but the silhouette nature of the photograph makes the morphology difficult to perceive.

A more systematic and useful morphological investigation by electron micrography is provided by the work of Okada and Magari (45). They used a replica technique whereby impressions of the crystals are made on polyvinyl acetate; shading of these allows the micrographs to manifest the three-dimensional picture of the various crystal habits. The most perfectly crystalline and simplest shape was obtained by dropwise addition of 10^{-3} molar solutions at over 90°C. These crystals are illustrated in Fig. 11, ref. 45: though apparently lens-shaped, on closer inspection each convex surface is seen to consist of four planes. Perfect crystals like these crystallographers call "euhedral" - having the faces belonging to their crystalline form.

Generally from all the illustrations in the latter three papers it is seen that the crystals are cross-shaped, X-shaped, spindle-shaped, butterfly-shaped and approximately rectangularly-shaped when concentrated solutions are used or when precipitation is carried out in the cold. These are "subhedral" - although crystalline in internal structure, the faces are only partly developed. It seems probable that the euhedral crystals are purer; this is the view of Okada and Magari.

4. Theory of the Conductance Method.

The following well-known equations are used for the calculation of the solubility of a sparingly soluble salt:

$$c = \frac{1000\kappa_{BaSO_4}}{2\Lambda_c} \qquad (i)$$

$$\Lambda_c = \Lambda^0 - (\alpha^* \Lambda^0 + \beta^*)c^{\frac{1}{2}} - \frac{c\Lambda_c}{K_d} \qquad (ii)$$

$$\Lambda^o = \lambda^o_+ + \lambda^o_- \qquad \text{(iii)}$$

c	solubility of the salt in gm.moles/l
κ_{BaSO_4}	measured specific conductance of a saturated solution of the salt
Λ_c	equivalent conductance of the salt at concentration c.
Λ^o	limiting equivalent conductance of the salt
λ^o_+, λ^o_-	limiting equivalent conductances of the ionic constituents of the salt.
K_d	dissociation constant of associated barium sulphate ion pairs.
α^*, β^*	constants in the Onsager limiting law for conductivity.

The $\frac{c\Lambda_c}{K_d}$ term in equation (ii) is included to account for the "conductance deficiency" due to ion association in barium sulphate solutions. Equation (ii) may be used only if deviations from the Onsager limiting law are due to incomplete dissociation. The concentration of saturated barium sulphate solution has been assumed to be low enough for this to be true. The results of Deubner and Heise (13) support this; at 10^{-6} molar, conductivities of bi-bivalent sulphate solutions follow the limiting law. The value of K_d is estimated in Part II of this thesis, where ion association is discussed more fully.

Inserting values of $\lambda^o_+ = 63.64$ (49)

$\lambda^o_- = 80.00$ (33)

and $K_d = 0.0043 \pm 0.0005$

equation (ii) becomes

$$\Lambda_c = 143.64 - 510c^{\frac{1}{2}} - 10^4c(3.3 \pm 0.4) \qquad \text{(iv)}$$

The thermodynamic solubility product K_s is calculated from the equation

$$\begin{aligned} K_s &= a_{Ba^{2+}} . a_{SO_4{}^{2-}} \\ &= m_{Ba^{2+}} . m_{SO_4{}^{2-}} . \gamma_{Ba^{2+}} . \gamma_{SO_4{}^{2-}} \qquad \text{(v)} \end{aligned}$$

where $m_{Ba^{2+}}$ and $m_{SO_4{}^{2-}}$ are molalities corresponding to the molar concentration c and $\gamma_{Ba^{2+}}$ and $\gamma_{SO_4{}^{2-}}$ are the activity coefficients. The concentration is low enough for us to interchange the rational and molal activity coefficients without a significant numerical change. For $\gamma_{Ba^{2+}} . \gamma_{SO_4{}^{2-}}$ we substitute $\gamma_{\pm}{}^2$.

In calculating the solubility it is necessary to take <u>all</u> barium sulphate ions into account, whether they are associated or not. Therefore, in calculating the activity coefficient, we use the extended terms of Gronwall, LaMer and Sandved (28) to cover the greater deviation of the electrolyte from the Debye-Huckel expression, instead of the ion association hypothesis. Thus

$$\ln \gamma_{\pm} = -\frac{Az^2 I^{\frac{1}{2}}}{1 + aBI^{\frac{1}{2}}} + \left(\frac{2\beta}{a}\right)^3 \left\{\tfrac{1}{2}X_3(\varkappa a) - 2Y_3(\varkappa a)\right\} + \left(\frac{2\beta}{a}\right)^5 \left\{\tfrac{1}{2}X_5(\varkappa a) - 4Y_5(\varkappa a)\right\} \qquad \text{(vi)}$$

where I = the "ionic strength" of the solution

$$= \tfrac{1}{2}c(\nu_+ z_+{}^2 + \nu_- z_-{}^2)$$

A and aB	constants in the Debye-Huckel expression
<u>a</u>	closest distance of approach of barium and sulphate ions.

$$\beta = \frac{e^2 z^2}{2DkT}$$

$$\varkappa = \left(\frac{8\pi N e^2}{1000DkT}\right)^{\frac{1}{2}} \quad I^{\frac{1}{2}}$$

$1/\varkappa$ = "radius of the ionic atmosphere" at ionic strength I.

$X_3(\varkappa a)$, $Y_3(\varkappa a)$, $X_5(\varkappa a)$ and $Y_5(\varkappa a)$ are the "extended terms".

In calculating A and B we used the latest values of the fundamental constants (10) and of the two values for the dielectric constant of water (14, 53) we chose Wyman and Ingalls' as being the more reliable. From the a values commonly met with for bi-bivalent sulphates (see Part II of this thesis) we considered that (3.7 ± 0.2 Å) would include the value for barium sulphate. Substitution of numerical values into equation (vi) leads to

$$\ln\gamma_{\pm} = -\frac{4.065_4 c^{\frac{1}{2}}}{1 + 0.66(3.7 \pm 0.2)c^{\frac{1}{2}}} - (0.00163 \pm 0.00020)$$

(vii)

5. Description, Calibration and Standardisation of Apparatus.

The conductimetric apparatus was that used by A. Faure and fully described in his Ph.D. thesis (19).

5.1. Temperature Control.

All measurements were carried out in a constant temperature room kept at 24 ± 0.2°C.

The thermostat consisted of two compartments, the outer one filled with water and the inner, in which the conductance cell was immersed, with paraffin, to obviate the Parker effect (36), (a capacitative shunt across the electrode leads). Temperature control at 25.000 ± 0.002°C was achieved using a toluene thermoregulator and Sunvic relay. The water section was stirred mechanically; the paraffin, by bubbling of air which had circulated in heat exchange tubes in the outer section. The absolute temperature was set using a thermometer graduated in 0.01°C, standardised by the British National Physical Laboratories to 0.002°C; temperature fluctuations were observed on a Beckmann thermometer graduated in 0.005°C.

5.2. Conductance Bridge.

The conductance bridge "General Radio" resistances had been checked by P.K. Faure on two occasions and both times were found to vary by less than 0.1% from the nominal values. P.K. Faure's 1953 corrections (21) were used throughout. The bridge was completely overhauled before use, to allow 10,000 ohms to be measured to better than 0.1 ohm. This high precision of resistance reading (and the accurate temperature control) is necessary for the extrapolation procedure used in evaluating conductances. See section 7. (Note: an error has occurred in A. Faure's circuit diagram of the bridge amplifier, Fig. VIII in (19): the condenser C_5 should be shown connected directly to the plate of valve V_1; similarly in the second stage C_9 should be connected directly to the plate of V_2).

Because only high resistances were measured, it was not necessary to apply a polarisation correction, and the only frequency used was 2000 cycles.

5.3. Conductance Cells.

The pyrex conductance cells (see Fig. 1 and Plate 1), first described by Gledhill (25), were of the type which have been in use in this department for several years. The electrode leads are separated as widely as possible by leading each to its electrode on opposite sides of the cell down the axis of half-inch glass tubing. Thus Parker effect is eliminated by spacial separation of leads, an air dielectric surrounding each lead, and the use of paraffin in the thermostat.

In all the runs the cells were shunted with a 10,000 ohm General Radio Company Type 500J resistor (the value of which was checked regularly), as in (26).

Pure nitrogen, heated to 25°C by passage through heat exchange tubes in the thermostat, was bubbled through the cell through the capillary at the bottom, to remove volatile impurities in the conductance solution. This gas escaped through a pinhole in the ground-glass-jointed cap without any back-diffusion of atmospheric carbon dioxide.

Two cells were used: one with bright unplatinised electrodes for measuring the conductance of the water, the other, for conductimetry on barium sulphate solutions, having fairly heavily platinised electrodes.

It was not deemed necessary to re-determine the

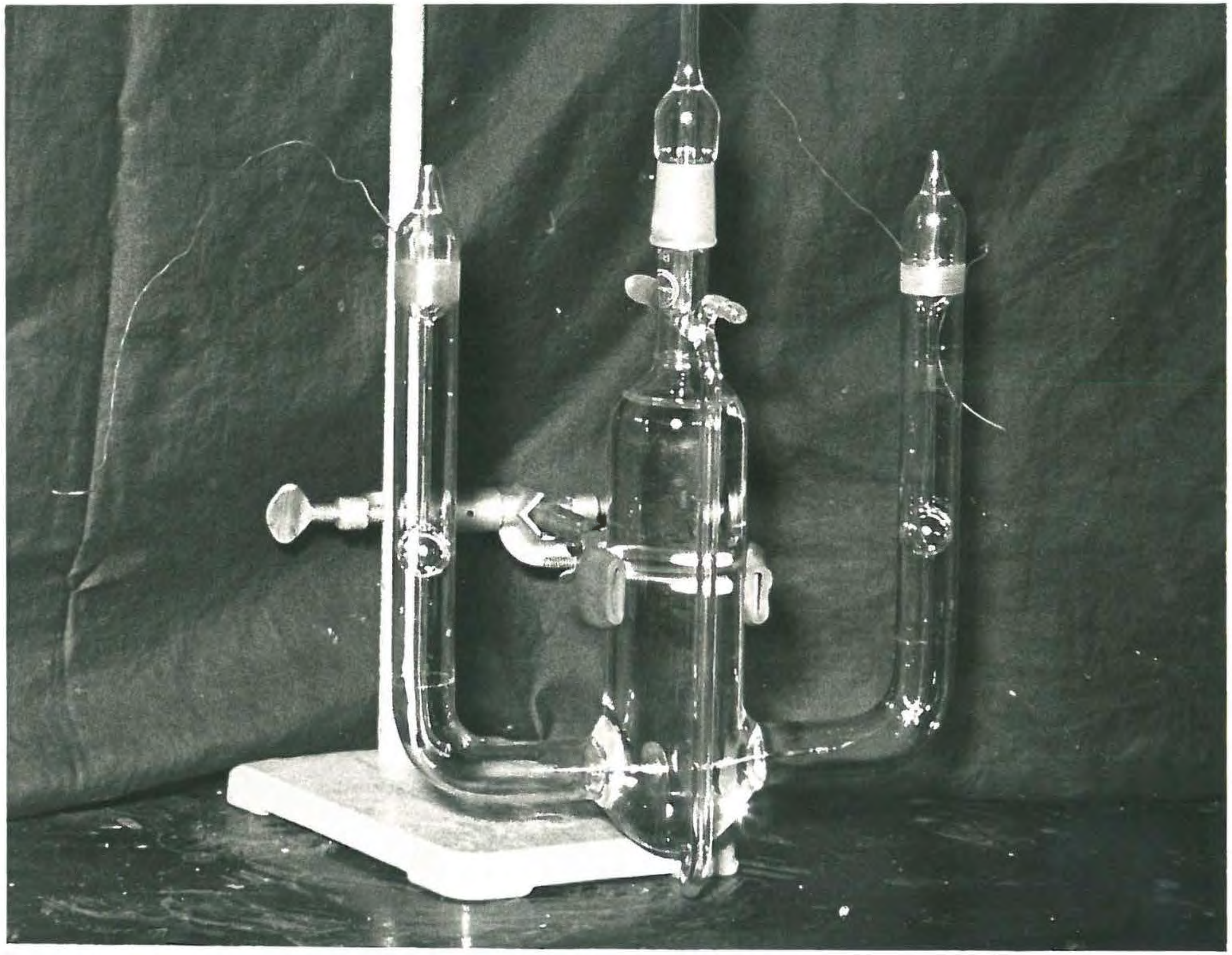
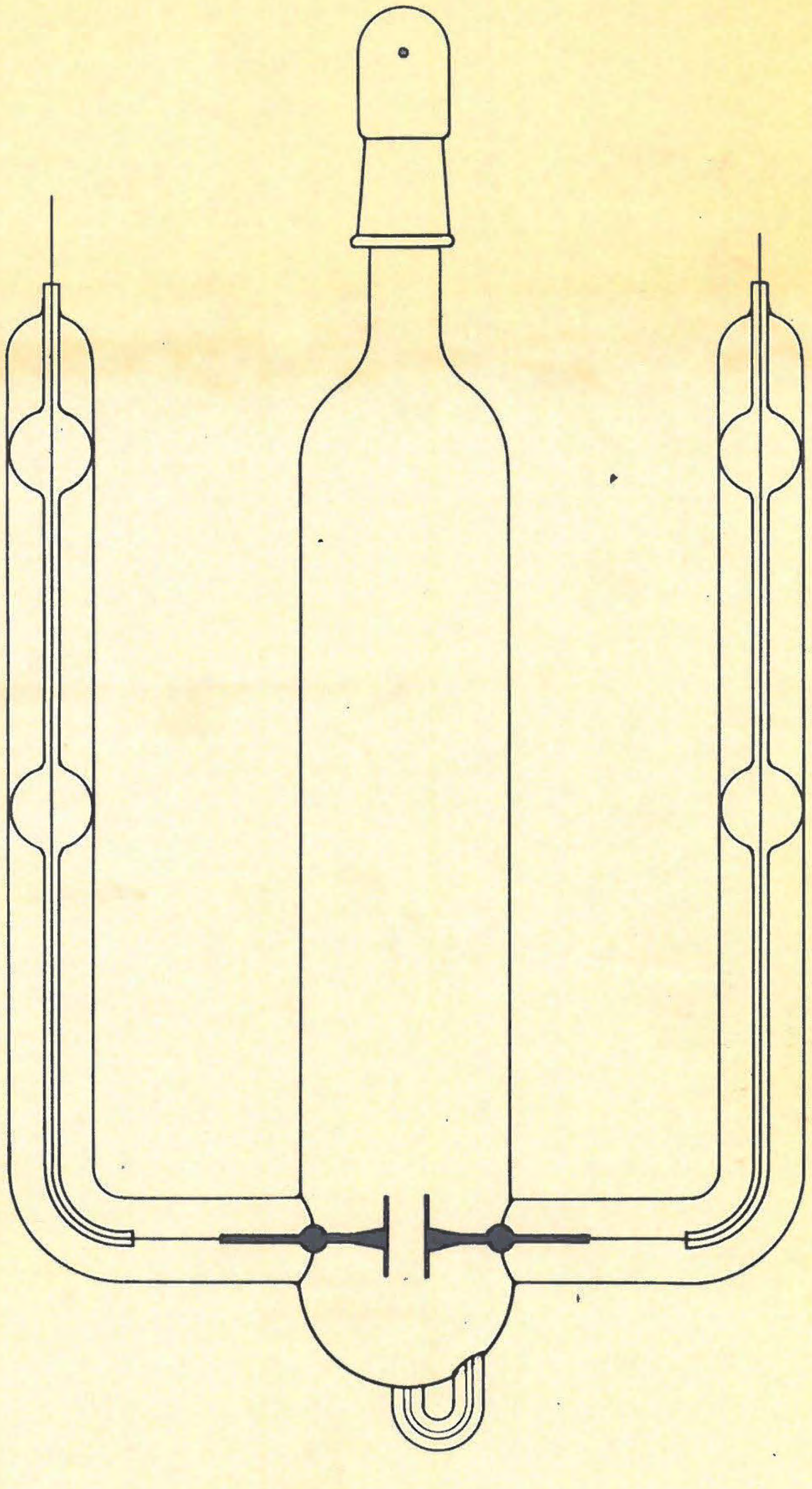


Plate 1.

The Conductance Cell.

FIG. I. THE CONDUCTANCE CELL.



cell constants, because P.K. Faure (21) had shown that these varied only by much less than 0.1%, which is within the experimental accuracy required in this determination. The cell used for barium sulphate solutions had a constant of 0.10892 cm.$^{-1}$ (21). During preliminary runs this cell was used for measuring the conductivity of saturated silver chloride solutions, and the result of Malan (26) was exactly reproduced, thereby confirming that the cell constant had not changed. (This method of measuring cell constants is tentatively suggested by Johnson and Hulett (34)).

5.4. Glassware etc.

All volumetric glassware (Normax grade A burettes, pipettes and volumetric flasks) were standardised by the usual weighing of water procedure.

All other glassware for conductance work was steamed out for at least 12 hours, often longer. 20 litre flasks used in the precipitation of barium sulphate were heated by steambath for 12 hours with concentrated nitric acid (to free the inner surfaces of minute iron particles) and washed by running tap water for 48 hours and then repeatedly shaken with laboratory distilled water and finally, conductance water.

The still for conductivity water is fully described in (20).

An Oertling air-damped balance was used; all riders and box weights were standardised by an intercomparison method, using the chemistry department (corrected) 20 gm. weight as standard.

6. Preparation of Materials.

6.1. Precipitant Solutions, Water, etc.

Water. All water used throughout for preparation of solutions and conductance measurements had a conductivity of less than 100 nm.cm.$^{-1}$, usually between 60 and 80 nm.cm.$^{-1}$

Nitrogen. Commercial nitrogen was passed through a purification train consisting of, in the order given: a bubbler of concentrated sulphuric acid for drying, and removing ammonia, several tubes of soda-lime for CO_2 removal, a U-tube of meta-phosphoric acid for ammonia removal, an 80 cm. silica tube of copper turnings heated to 800°C, to remove oxygen, a sulphuric acid bubbler, soda-lime tubes, a sulphuric acid bubbler and finally through five empty bubblers to act as spray traps. Seeing that the conductance cells contained only water or saturated solutions it was not necessary to saturate the nitrogen with water vapour. Thus all the difficulties encountered with possible spray, described by P. K. Faure (21), are eliminated. All rubber connections were boiled before use with concentrated sodium hydroxide for twenty minutes to remove sulphide from the surface. Tygon tubing is to be avoided - it was found to liberate a large amount of volatile matter.

Barium Chloride and Potassium Sulphate. Merck G.R. grade reagents were twice recrystallised (with all precautions against dust contamination). The barium chloride was dried slowly at 180°C for several hours, and then at 260°C for five days. This removed all water from the hydrated salt. Rapid weighing was necessary to avoid take-up of atmospheric moisture. The potassium sulphate was dried at 260°C for five days. 0.01 and 0.2 molar solutions to be used for the precipitation of barium sulphate were made up exactly by weight, the latter corrected to vacuum. These meticulous precautions were necessary to preclude the slightest possibility of adsorption contamination of the precipitate due to ultimate non-equimolarity of the precipitant solutions.

Sulphuric Acid. B.D.H. A.R. sulphuric acid was used for one precipitate. As solutions of accurately-known concentration could not be made up by weight, alternate methods were sought for standardisation. Barium sulphate precipitation yields results of accuracy about 0.1% only with elaborate analysis (35). Conductimetric titration gives exceedingly poor results, (40). Therefore it was decided that the ordinary acid-base titration was by far the most convenient determination. Recrystallised borax (equilibrated over saturated sugar solution) and sodium carbonate (dried for 24 hours at 250°C) were used. The two determinations were performed at room temperature and boiling point respectively, with an agreement of 0.1%. The mean molarity was corrected to 24°C. The acid was free of sulphite (to a small drop of 10^{-2}M potassium permanganate, added to 10 ml. of acid).

Hydrochloric Acid. A.R. quality acid was twice distilled in an all-glass still.

6.2. Barium Sulphate.

6.2.1. Dropwise Precipitation at Room Temperature. (Precipitate I).

Precipitate I was prepared at room temperature by almost the same method used by Malan (42) for silver chloride: 50 ml. of a 0.01 molar solution of barium chloride was buretted dropwise over 45 minutes into a 300 ml. conical flask containing exactly 50 ml. 0.01 molar potassium sulphate solution and 10^{-3} normal hydrochloric acid, with continuous shaking. The solution was allowed to stand for half an hour and was digested for an hour. The precipitate was then washed 50 times by decantation and kept in the glass covered flask.

This precipitate was seen by microscopy to be subhedral. All the various shapes described in section 3.3 were present.

6.2.2. Diffusion Precipitation at Room Temperature. (Precipitates II to V).

The facts laid out in section 3.2.1 indicated that a precipitate prepared by a diffusion method would have the required purity. Therefore precipitates II and III were prepared by diffusion at room temperature.

50 ml. of 0.2 molar potassium sulphate solution was pipetted into 20 litres of 10^{-3}N hydrochloric acid

(prepared with conductivity water collected directly off the still) and shaken to a uniform solution. Into the surface of this solution (5×10^{-4} molar in sulphate ion) in the neck of the flat-bottom flask (placed on a very stable base) was carefully pipetted 50 ml. of 0.2 molar barium chloride solution. The latter, comparatively highly concentrated, was then able to mix slowly with the sulphate solution by diffusion and the effect of its higher density. After an hour minute crystallites of barium sulphate became visible as a cloudiness; these were allowed to mature slowly overnight and settle. The supernatant solution was siphoned off by vacuum pump, and the residual precipitate was transferred to a glass-covered 300 ml. conical flask. It was washed 60 times, by decantation, with conductance water.

Precipitate IV was prepared similarly but no hydrochloric acid was used.

Precipitate V was prepared similarly to IV but sulphuric acid was used instead of potassium sulphate. Since the acid was not exactly 0.2 molar, an exactly equimolar quantity was buretted in.

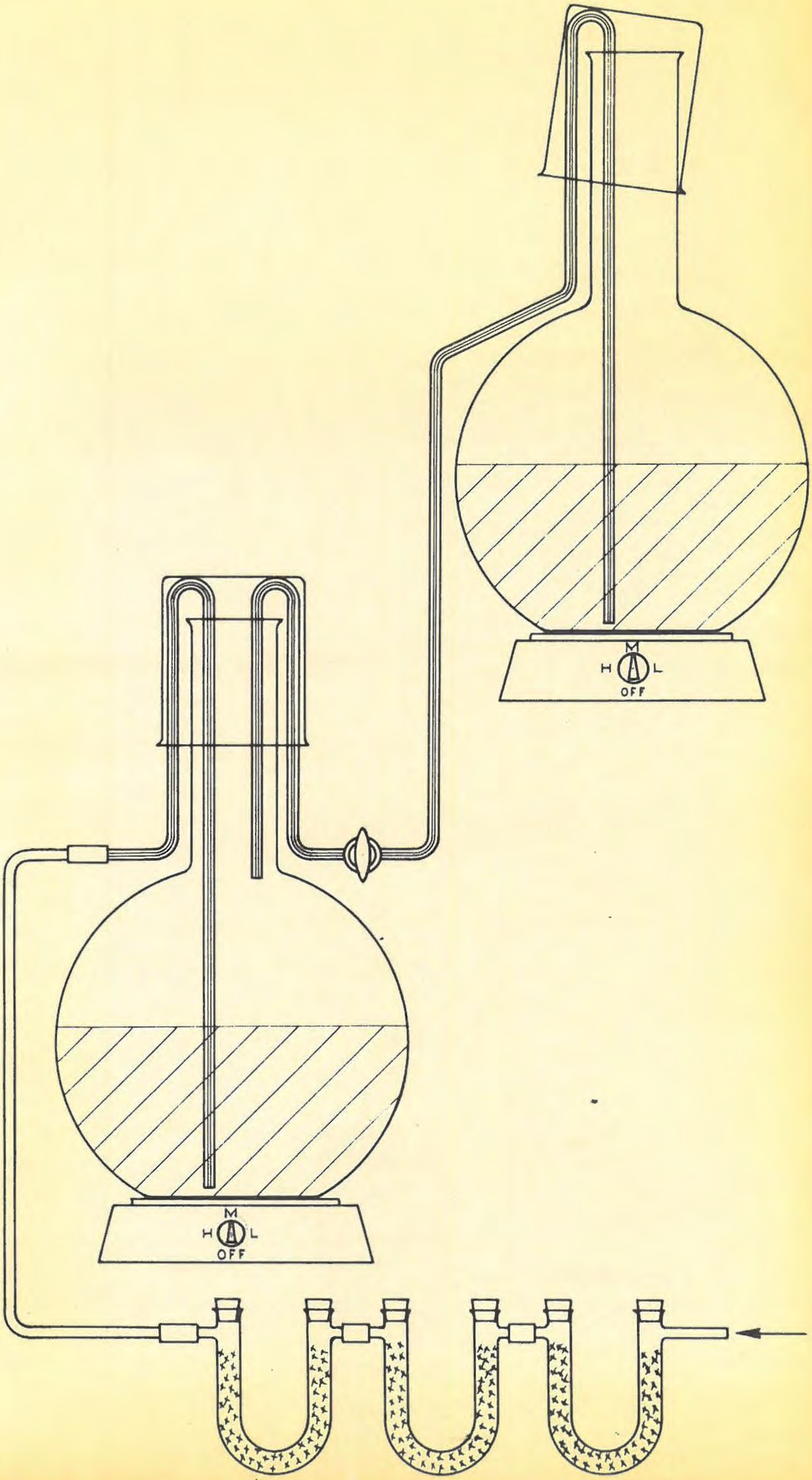
Microscopic examination showed these precipitates to be not quite euhedral. Small imperfections classed them as subhedral.

6.2.3. Dropwise Precipitation at Boiling-point (Precipitates VIa, VIb and VII).

The apparatus for the dropwise addition of hot 10^{-3} M barium chloride solution to boiling 10^{-3} M sulphate solution is depicted in Fig. 2. Into each of the 20 l. flasks, containing 10 litres of conductivity water apiece, was buretted exactly 50 ml. of the standard 0.2M precipitant solutions. The sulphate solution was seeded with a small amount of barium sulphate crystals from a similar smaller-scale preparation. (The efficacy of this procedure later appeared doubtful when the length of time required for saturation became apparent). The siphoning tube was filled with water and placed in position. Both solutions were heated to boiling, a strong flow of nitrogen (after passage through a short train consisting of two large U-tubes of soda-lime and one of metaphosphoric acid) was turned on, for vigorous stirring, and dropwise siphoning of barium solution into sulphate solution was commenced. Inverted beakers effectively covered the mouths of the flasks while allowing steam to escape. "Collars" of filter paper around the necks of the flasks prevented condensed water from running on to the heaters. The rate of flow of the barium solution was controlled by the ungreased tap in the siphoning tube. After about 15 hours most of the barium chloride had siphoned over; the residue was transferred by washing three times with 100 ml. boiling conductivity water, each washing being siphoned over.

Precipitate VI was prepared as described. Portion VIa was decanted into a 300 ml. conical flask, and the residue (portion VIb), which clung tenaciously to the glass surface, was liberated with a few ml. of hot ammoniacal versenate solution (prepared from A.R.

FIG. 2. THE BARIUM SULPHATE PRECIPITATION APPARATUS.



reagents) and poured into another flask. VIa was washed 50 times by decantation. VIb, after 20 washes, was transferred to a carefully cleaned platinum crucible and heated to 700°C for eight hours. After transfer to another flask it was washed a further 30 times.

Unsatisfactory results on VI necessitated the preparation of precipitate VII. The procedure was modified by acidifying the sulphate solution to 10^{-3}M with respect to hydrochloric acid. VII did not adhere to the glass walls. Subsequent treatment of VII is described in Section 7.4.3.

Barium sulphate, prepared by this method, was seen, on microscopic examination, to consist of the apparently lens-shaped crystals described in section 3.3. The particles were smaller than those prepared as in 6.2.1 or 6.2.2.

(Note: During the remainder of this thesis precipitates prepared as described in 6.2.2. are referred to as "cold prep. ppts."; those prepared as in 6.2.3, as "hot prep. ppts.").

7. Experimental Techniques and Results.

7.1. Technique and Extrapolation Procedure.

The technique of the conductance measurements is essentially that described in (15, 26, 27, 42). The cell containing a suspension of solvent and precipitate was placed in the thermostat and nitrogen bubbling was started. (For solvent conductance the separate cell for water was used: measurements were performed in the same way). Resistance readings were taken at regular intervals of between one and two hours, except overnight. When the rate of decrease of resistance eventually became steady (corresponding to a steady rate of solution of glass), the plot of resistance against time over the linear portion was extrapolated back to zero time as described in (27). The shape of each curve is shown in Figs. 4a to 4e. (The units in these are arbitrary and differ between graphs).

7.2. Ppt. I.

Although (not unexpectedly) this sample was grossly contaminated (the conductivity of the saturated solution, corrected for solvent conductance, being 3.5 ± 0.1 micromhos cm.$^{-1}$), the resistance-time graph is included because it shows a minimum. This has not been observed before. After the drop AB, the rise of resistance BC of between 5 and 15 ohms was obtained in all four runs with this precipitate. It is difficult to explain satisfactorily this phenomenon which corresponds to an apparent decrease in the number of ions in the solution, after about one day's stirring. It is probably an adsorption or ion exchange effect involving the cell walls and precipitate. The "slope difference" (vide infra) averaged 0.4 ohms/hr.; the time from B to C was about 50 hours.

7.3. Cold Prep. Ppts., II to V.

Comparison of saturated solution conductivities of II and III with that of IV was necessary to show whether any hydrochloric acid was included in the lattice; comparison of measurements on II and III showed reproducibility between similarly-prepared individual ppts.

The resistance against time curves were all of the form depicted in Fig. 4c. The runs were continued until the length of time BC was about the same as AB; when AB was very long (greater than 30 hours), 24 hours sufficed for BC, to establish linearity and the slope for extrapolation.

The results are recorded in Table 1. A resume of the preparation, and the treatment of the ppt. prior to each run, is included for reference. Tabulated conductivities κ_{BaSO_4} have been corrected for solvent conductance which was in most cases between 60 and 80 nm.cm.$^{-1}$ and always less than 100 nm.cm.$^{-1}$. The column containing "slope differences" records the difference between the final steady slope of the resistance-time graph for the saturated solution, and that for the solvent alone (both measured with the 10,000 ohm shunt). The slopes found for water alone varied between 0.1 and 0.7 ohm/hr. as usual (21). Slope differences thus allow comparison of solution data independently of this variation. It is seen that, with all barium sulphate samples, the slopes are generally somewhat greater than those observed with silver chloride (42); this is attributed to a

TABLE I

Expt. No.	Ppt. No.	Mode of precipitation.	Subsequent treatment of ppt. prior to each run.	Time AS (hours)	Slope difference (ohms/hr.)	K_{BaSO_4} (nn.cm.$^{-1}$)
I	II	Room temp., fresh $BaCl_2$ solution; by diffusion; in 10^{-3}M HCl. Washed 50 times.	Slurry of ppt. poured into cell.	17	0.7	3222
2	II		Solvent in cell was renewed, after careful decantation of saturated solution from previous expt.	24	0.3	3227
3	III	As for II; 2 weeks old $BaCl_2$	Ppt. was shaken vigorously for 5 minutes, with solvent, to aid saturation.	40	0.9	3235
4	III		As in expt. 3	48	1.0	3217
5	III		Solvent was renewed (as in expt. 2)	48	0.3	3275 (x)
6	III		Solvent was renewed.	45	0.5	3217
7	III		Solvent was renewed.	50	0.7	3262 (x)
8	III		New sample of III, washed 90 times.	70	0.9	3238
9	III		New sample, boiled 12 hrs., shaken for two days. Solvent then renewed.	53	0.8	3209
10	IV	As for III, but no HCl. Washed 40 times.	Slurry of ppt. poured into cell.	72	0.7	3227
11	IV		Solvent was renewed.	50	1.0	3218
				MEAN:	0.7	3223.$_3$ ± 7.$_5$

((x) discarded in calculating the mean)

greater rate of solution of, or ion exchange at, the glass walls, in barium sulphate solutions.

One experiment was performed with ppt. V. Temperature control failed during the run and the result is not reported; the specific conductance was approximately within the range of results obtained.

Between runs on different samples, the cell was washed by agitation for several days with several changes of conductivity water. If the ppt. adhered to the wall it was dislodged with warm ammoniacal versenate solution, but if possible this treatment was avoided as it necessitated a long leaching-out period, and the subsequent runs gave uncertain results which had sometimes to be discarded.

Slight irregular departures from linearity of the plotted resistance-time points were provisionally attributed to the leaching-out of local concentrations of impurities in the ppt. The effect could also be due to running back of condensed vapour (as in Malan's measurements at 55°C (42)), or spray (21), from the cell neck and cap. The use of a small heating coil over the cap (as in 42) partially diminished the effect. Changes in bubbling rate (to which resistance readings are very sensitive (21)), and slight variations in temperature were avoided by careful checking.

Recrystallisation of ppt. III, as performed with silver chloride (11), was unsuccessful; no crystals were deposited from the filtered and cooled solution even on seeding. Thus this barium sulphate dissolves only very slowly even on boiling.

Washing of a new sample of ppt. III a total of 90 times i.e. twice the usual number, led to no decrease in the conductance of the solution subsequently (see expt. 8). Any impurity present was thus distributed throughout the lattice.

7.3.1. Alternate Methods of Barium Ion Determination.

A determination of barium ion concentration, independent of the presence of contaminants, seemed desirable, therefore it was decided that a colorimetric method should be investigated. Four methods appeared promising:

(i) a yellow colour is obtained with barium and tannic acid in sodium hydroxide solution (1). The colour was found to be far too transient.

(ii) an intense red colour is obtained with traces of barium ion and tetrahydroxyquinone or rhodizonic acid. These are due to finely divided precipitates and no organic solvent was found for them.

(iii) phthalein purple complexes with barium to give a rose-coloured solution but the optical absorption curve (Fig. 2, ref. (2)) of the uncomplexed indicator is much the same as that for the barium complex, so at low concentrations resolution was impossible.

(iv) Erio Chrome Black T has been used for low concentration colorimetry with magnesium (30). It was found to give a coloured complex with barium at pH 10 which, in preliminary experiments with more concentrated barium solutions, showed an approximate obedience to Beer's law at 560 mμ. However, notwithstanding the use of refinements suggested in (46), the intensity of the colour was too low for quantitative work at the low concentrations desired.

This section was not followed further.

7.4. Hot Prep. Ppts., VIa, VIb and VII.

The shape of the resistance-time graphs for these precipitates is shown in Fig. 4e. It is similar to that obtained with silver chloride (26): the initial rise AB is interpreted as being due to the removal of CO_2, the drop BC corresponding to the solution of ions which takes place at a rate such that the rise of resistance due to CO_2-removal is more than countered by the increased amount of conducting material in the solution. Saturation is represented by point C and portion CD is extrapolated to zero time for resistance R.

7.4.1. Ppt. VI.

The results for ppts. VIa and VIb, although chaotic, are included in Table 2 to illustrate several facts: whether versenate contaminated the precipitate, whether water present in the ppt. affected the readings, and whether heating the ppt. to 700°C caused decomposition.

The randomness of the results might have been due to occluded water (see section 3.2.1), therefore the ppt. was heated to 700°C as described in section 6.3.

TABLE 2.

Expt. No.	Ppt. No.	Mode of precipitation.	Subsequent treatment of ppt. prior to each run.	Time AC (hours)	Slope difference (ohms/hr.)	κ_{BaSO_4} (nn.cm.$^{-1}$)
12	VIa	Boiling solutions, dropwise. (No acid)	Ppt. was shaken vigorously for 5 minutes, with solvent, to aid saturation.	70	1.2	2983
13	VIa		New sample, boiled 12 hrs., shaken for 2 days. Solvent then renewed.	96	1.4	2903
14	VIa		Solvent was renewed.	95	1.8	2967
15	VIa		Ppt. was washed with CO_2-free water, 10 times, for 2 days.	100	2	3200
16	VIb		Washed out with versenate, washed 20 times with water, heated to 700°C, washed again.	45	1.6	2928
17	VIb		Solvent was renewed.	72	1.6	2943
18	VIb		Solvent was renewed.	80	1.6	2770
19	VII	As for VI, but with 10^{-3}M HCl.	After being washed, ppt. was boiled with conc. HCl, washed, heated to 700°C and washed again.	20	0.6	2946.6
20	VII		Solvent was renewed.	19	0.5	2931.2
21	VII		Solvent was renewed.	18	0.4	2925.4 (x)
22	VII		Solvent was renewed.	18	0.6	2985.7 (x)
23	VII		Solvent was renewed.	13	0.6	2944.7
24	VII		Solvent was renewed.	18	0.5	2950.6
25	VII		Solvent was renewed.	8	0.4	2948.2
26	VII		Solvent was renewed.	25	0.7	2944.0
27	VII		Solvent was renewed.	18	0.6	2937.3
				MEAN:	0.6	$2943._3 \pm 5._2$

((x) discarded in calculating the mean)

Although Duval's work (17) shows no decomposition at this temperature, the more sensitive conductance measurement was performed to confirm this.

The same range of results with VIa and VIb showed that the three effects tested for did not take place.

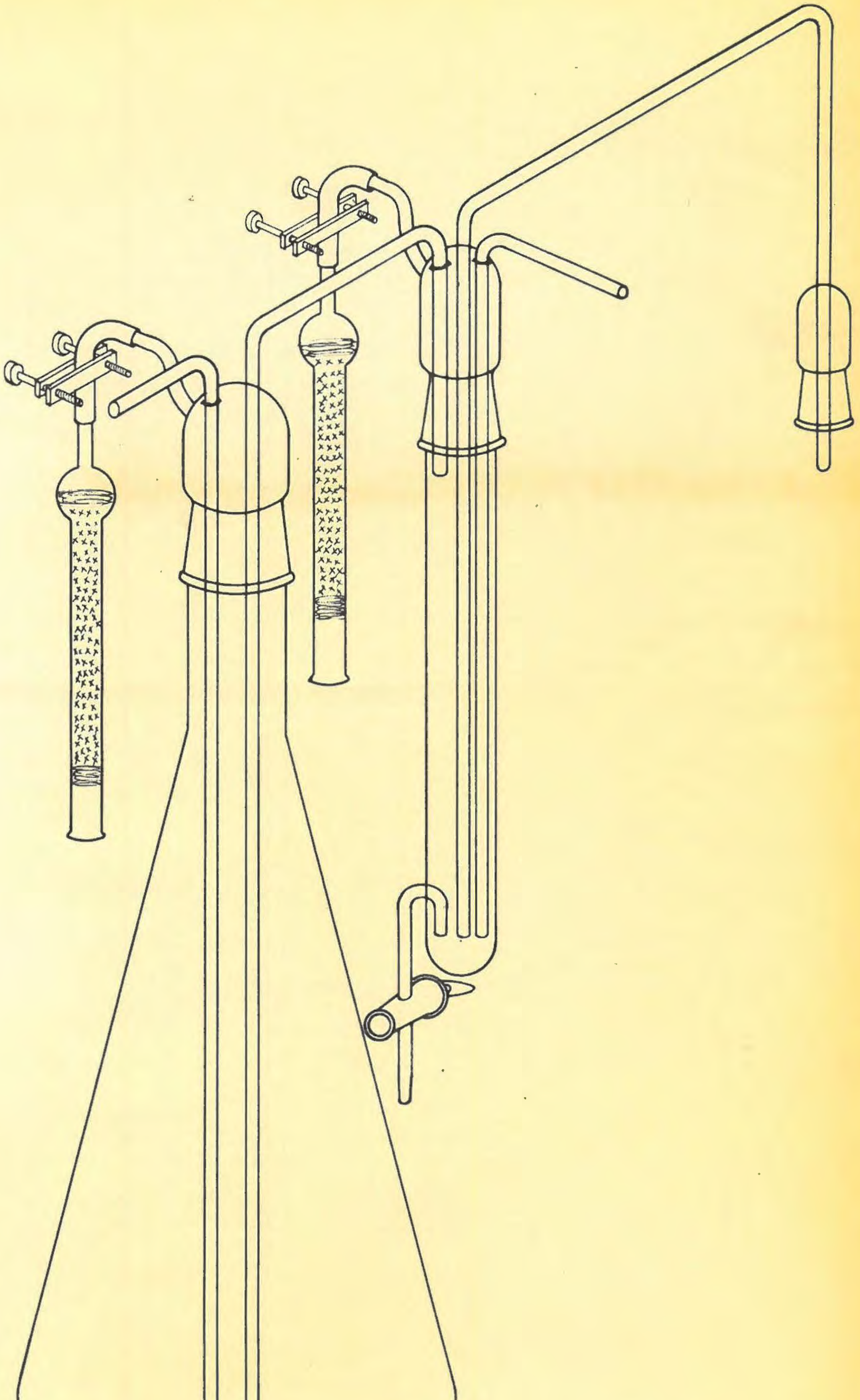
7.4.2. The Effect of CO_2 on the Conductance Measurements.

The comparatively steep slopes obtained with ppt. VIa prompted the idea that CO_2 might affect the measurements. It had been noted that adding CO_2 to water, already freed from CO_2, caused a subsequent steeper slope. To illustrate: in Fig. 4b, the rise of resistance AB is the same as that in Fig. 4a, and to point C. At D a test-tube of pure CO_2 was inverted into the cell, and the resistance naturally dropped. On resuming nitrogen bubbling, the resistance rose to point E and the linear decrease EF is observed. It is important to note that the slope of DEF is greater than that of CD. P. K. Faure (21) obtained a similar curve but the CO_2 in this case was not deliberately introduced. It is therefore tentatively suggested that the increased slope is due to the presence of more sodium bicarbonate in the solution after the addition of CO_2 (sodium bicarbonate probably being the main constituent of the residual water impurity (21)). It is also possible that hydroxyl ion is present - C. Faurholt's studies on the kinetics of hydration of CO_2 (22) show that removal of CO_2 from bicarbonate solution may lead to the formation of hydroxyl ion. The reasoning above is not affected.

Plate 2.

The CO_2-free Washing Apparatus.

FIG. 3. CO_2-FREE WASHING APPARATUS.



Thus to explain a greater slope for barium sulphate VI, the presence of more carbonate was provisionally attributed to greater adsorption of carbonate ion on the larger surface which these precipitates evidently have (section 3.2.1), compared to cold prep. ppts.

However, adsorption of carbonate was proved not to take place, from the result of expt. 15, Table 2, but as the method used is useful, it is therefore described here.

Apparatus and Technique.

The apparatus is shown in Fig. 3 and Plate 2. The large conical reservoir on the left was the ordinary conductance water flask used in the laboratory. The "connecting assembly" consisted of a tube for bubbling nitrogen through the water in the reservoir, and another tube through which, by closing the nitrogen outlet normally guarded with a soda-lime tube, this water could be forced into the middle "precipitate vessel". In the runs with barium sulphate this vessel held the ppt. to be washed with CO_2-free water. Nitrogen could also be bubbled through this vessel, and by closing both nitrogen inlet and outlet tubes on it, the suspension of ppt. could be driven into the cell.

CO_2-free Washing of Barium Sulphate.

A suspension of the ppt. was placed in the ppt. vessel and the whole assembly fitted up as shown in

Plate 2, with the clean empty cell in the thermostat. Nitrogen was passed through the cell, the ppt. vessel and the water in the conical flask, until the latter was CO_2-free. The bubbling through the suspension was stopped for a few seconds until the latter had settled, and the supernatant liquid was drained off through the drainage tube, with ungreased tap. Fresh CO_2-free water was pumped over from the reservoir and the process could be repeated for as many washes as was required. The suspension was then driven over into the cell and the conductance run commenced, with complete absence of CO_2.

Water Conductance.

The solvent correction was obtained by performing a run in the usual manner with the residual water in the reservoir, after completion of the measurement on barium sulphate; deterioration of the water standing in the flask in the meantime was slight.

Prior to use with barium sulphate the dipping assembly was carefully cleaned with nitric acid and alcohol, and washed with tap and distilled water, and finally steamed for several days. Three weeks of trial runs using the apparatus with water alone were necessary for complete leaching-out. These runs showed the same rate of increase of conductance in the flask as took place in the cell, on bubbling nitrogen, viz., about 0.3 ohms/hr. Reproducibility of results with the apparatus was proved by duplication of conductance readings on both the water which had been through the apparatus and that left in the reservoir (the latter measurement being performed in the ordinary manner), to within 1 or 2 mm.cm.$^{-1}$.

Result.

It was unfortunate that the ppt. had become contaminated prior to the CO_2-free washing, as shown by its high conductivity (expt. 15). But the factor under investigation, the resistance-time slope, was conclusively demonstrated to be unaffected by the presence of CO_2, and the carbonate-adsorption hypothesis fell away.

Although a microscopic examination showed no microcrystals, these must have eluded observation; their presence was inferred by elimination. The steeper slopes were therefore interpreted as being due to the continuous slow solution of unwanted small particles without reaching saturation, as was found by Dundon (16). The increasing slopes on consecutive runs with VIa was inexplicable; this was not found with VIb.

7.4.3. Ppt. VII

For the reasons given above ppt. VI was abandoned and ppt. VII prepared as described in section 6.2.3. The presence of 10^{-3}M hydrochloric acid in the sulphate solution lessened the chance of microcrystal formation. Ppt. VII was washed 20 times with conductance water and then boiled with concentrated hydrochloric acid to ensure the complete solution of minute particles. After cooling it was shaken for two days at room temperature. The acid was decanted and, after a

FIG. 4. RESISTANCE AGAINST TIME GRAPHS

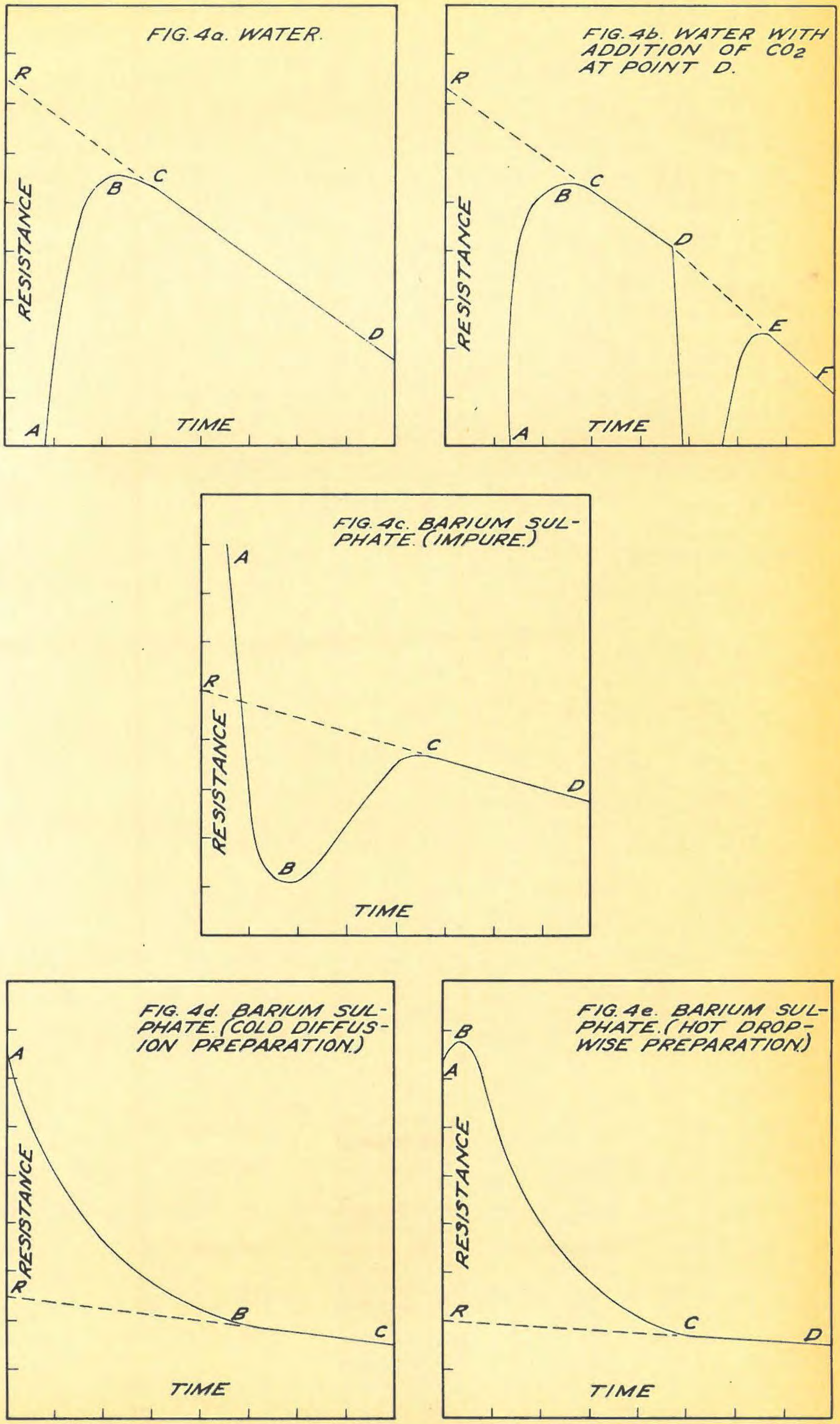


FIG. 4a. WATER.

FIG. 4b. WATER WITH ADDITION OF CO_2 AT POINT D.

FIG. 4c. BARIUM SULPHATE. (IMPURE.)

FIG. 4d. BARIUM SULPHATE. (COLD DIFFUSION PREPARATION.)

FIG. 4e. BARIUM SULPHATE. (HOT DROPWISE PREPARATION.)

further 20 washings, it was heated in a platinum crucible to 700°C for 8 hours to drive off possible water or HCl contamination. After further washing in a 300 ml. conical flask, this sample was considered to be pure. The conductance measurements showed a greater precision than any previously. The linear portion CD of the resistance-time graphs was in most cases almost perfectly linear, indicating a high degree of purity. The slopes were more concordant than before.

7.5. Results. Solubility and Solubility Product of Barium Sulphate.

Substitution of the mean value of the conductance of ppt. VII in equation (i) of section 4 leads to the following value for the solubility:

$$(1.034_6 \pm 0.03_0) \times 10^{-5} \text{ moles litre}^{-1}$$

$$2.415_0 \pm 0.005_0 \qquad \text{mg.litre}^{-1}$$

From this value and equations (v) and (vii), section 4, the thermodynamic solubility product on the molality scale is found to be

$$(1.006_7 \pm 0.003_3) \times 10^{-10}$$

8. Discussion.

8.1. Comparison of Results.

Previous results, and this measurement, are recorded in Table 3.

Table 3

Date	Author	Temp. (°C)	Solubility of $BaSO_4$ (mg. litre^{-1})
1908	Kohlrausch (37)	18	2.4
		26	2.77
1901	Hulett (31)	25	2.29
1910	Melcher (44)	18	2.22
		25	2.47
1919	Kolthoff and Vogelenzang (38)	18	2.07 to 2.53
1927	Balarew (4)	18 to 20	3.3 (metastable)
		18 to 20	2.3
1954	Selivanova and Kapustinski (48)	25	3.37
	This determination	25	$2.415_0 \pm 0.005_0$

In none of the previous conductance determinations was precision conductimetric apparatus used, and the solvent correction, a large possible source of error, was always at least several hundred nm.cm.$^{-1}$. The barium sulphate in this determination (in contrast to the others) was precipitated from exceedingly dilute solutions, and the solvent conductances, about 75 nm.cm.$^{-1}$ formed only 3% of the total conductance of the solution.

This value is thus considered to be least influenced by the three possible sources of error: the resistance measurements, solvent correction, and contamination of the ppt. by precipitant solutions.

8.2. Further Ionic Species in Saturated Barium Sulphate Solution.

Conductance due to the hydrolysis products of the cation and anion, viz., $BaOH^+$ and HSO_4^-, were small.

For the equilibria

$$Ba^{2+} + H_2O \rightleftharpoons BaOH^+ + H^+ \qquad K_{BaOH^+}$$

$$SO_4^{2-} + H_2O \rightleftharpoons HSO_4^- + OH^- \qquad K_{HSO_4^-}$$

the equilibrium constants K_{BaOH^+} and $K_{HSO_4^-}$ were calculated, from the means of the values given by Bell and Prue (5) and Davies, Jones and Monk (12) respectively, to be 4.3×10^{-14} and 10^{-12} respectively. By the use of the conductivity value and the condition of total electrical neutrality of all the ions in solution, it can be shown that the approximate concentration of bisulphate ion is 10^{-10}M and the barium hydroxyl ion, 5×10^{-12}M. These are too low to be significant.

8.3. Time Required for Saturation of the Solution.

Times for saturation for all ppts. (besides II and VII - vide infra) were much longer than those reported in (15), (26) and (42). In the silver chloride experiments, the suspension was heated to 90°C. During the following 120 hours, solid material deposited from the supersaturated solution, either into new crystals or back on the "foundation" of undissolved material. Malan and Gledhill (26) remark that the subsequent quicker saturation was due to the fact that the precipitate was in "a different physical state....probably being more finely divided". It seems likely that the recrystallised material was responsible for the increased rate of solution of the precipitate; presumably a larger surface area was exposed to the solvent.

This method of "recrystallisation" was unsuccessful with barium sulphate (Tables 1 and 2, expts. 9 and 13) due to the exceptionally long time required by the original precipitate to dissolve in pure water; the lack of success in ordinary recrystallisation was also due to this.

Recrystallisation onto the undissolved material could take place more easily in concentrated hydrochloric acid; this explains the comparatively short times required with ppt. VII.

It is noteworthy that, although ppt. II was not subjected to this "recrystallisation" process, the saturation times are much shorter than with the other ppts. prepared in exactly the same manner. The reason was later found in (6): the fresh barium chloride (a few hours) was the only different experimental factor in the preparations. For the later preparations the barium chloride solution was aged at least a few weeks. Thus, besides the changed settling rate observed in (6), ageing of the precipitant barium chloride solution has the effect of increasing the saturation time of the resultant barium sulphate. (The effect would not be shown by hot prep. ppts. because boiling of the barium chloride solution has the same result as ageing it (6).

8.4. Presence of Hydrochloric Acid in the Lattice.

Absence of any discrepancy between readings on cold prep. ppts. II and III indicated that no hydrochloric acid was occluded. It was not possible due to shortage of time to check hot prep. ppts. for this, but it may be taken that no contamination results with these too.

8.5. Comparison of Results on Precipitates Prepared by Different Methods: Exchange between Lattice and Solution Ions.

The solubility results were calculated only from conductance values from hot prep. ppts. It is very probable that the higher conductance of the cold prep. ppts. was due to uniform contamination by either barium chloride or potassium sulphate or both. It could plausibly be argued that the irreversible ejection of foreign ions from the barium sulphate lattice, which would take place continuously with a contaminated sample, would lead to a steeper resistance-time slope; the effect of the contamination would be, partially at least, corrected for. The slopes obtained, with cold prep. ppts. (Table 1), (apart from being rather more random) are very close to those with hot prep. ppts.; the means are 0.7 and 0.6 respectively. The slopes obtained with the highly contaminated ppt. I were less than this.

A comparison of the resistance-time curves (Fig. 4) for cold prep. and hot prep. ppts. is illuminating. During the early stages of each run two processes are taking place: the "CO_2-removal process" and the "solution process" of ions entering the solution from the lattice (we are ignoring the third process of ionic matter leaving the cell walls). The presence of a maximum in the resistance-time graphs for hot prep. ppts. (Fig. 4e) shows that at first the CO_2-removal process is fast enough to eclipse the drop of resistance due to the solution process. This has been observed with silver chloride (26, 42) and mercurous chloride (15). The non-existence of a maximum in the curves for cold prep. ppts. (Fig. 4d) indicates that the solution process predominates. It seems unlikely that the barium or sulphate ions should initially leave the lattice more quickly with these ppts. than with hot prep. ppts., therefore the initial enhanced concentration of ionic matter from the lattice must be due to the liberation of foreign ions during the saturation period. The continued liberation of these foreign ions after saturation would result in a steeper slope. The absence of the latter leads to the reasonable inference that there is very little exchange between lattice and solution ions.

The partial purification, by recrystallising processes, during the digestion of analytical precipitates (39, 41) indicates a large-scale exchange between lattice and solution ions. This is aided by the enhanced solubility of the precipitate due to the mass action effect of other ions in solution, acidity, and high temperatures (and also gross lattice imperfections).

In pure water at room temperature this process has therefore been shown to take place to only a small extent.

9. Conclusions.

1. The solubility and solubility product of barium sulphate have been determined.

2. The effect of carbon dioxide on the measurement has been discussed and investigated.

3. The use of fresh barium chloride solutions in room temperature precipitations has been shown to lead to a precipitate more quickly soluble than a precipitate prepared with aged barium chloride solution. This supports evidence reported elsewhere that the age of barium chloride solution used affects the ultimate nature of the barium sulphate.

4. Evidence has been adduced that there is very little exchange between lattice ions and solution ions after saturation of the solution.

10. Bibliography

(1) G. Ammor and H. Schmitz, Wasser 8, Part II 161 (1934).

(2) G. Anderegg, H. Flaschka, R. Sallmann and G. Schwarzenbach, Helv. Chim. Acta, 37, 113 (1954).

(3) D. Balarew, R. Kaischew, G. Krataschew, Z. Anorg. Chem. 168, 159 (1927).

(4) D. Balarew, Z. Anorg. und Allgem. Ch., 163, 213 (1927).

(5) R. P. Bell and J. E. Prue, J. Chem. Soc., 363 (1949).

(6) E. J. Bogan and H. V. Moyer, Anal. Chem., 28, 973 (1956).

(7) A. S. Buchanan and E. Heymann, Proc. Roy. Soc., 195A, 150 (1948).

(8) J. A. V. Butler, "Electrocapillarity" Chemical Publishing Co., Inc., New York (1940).

(9) E. R. Caley and R. L. Stoffer, Science 118, 749 (1953).

(10) E. R. Cohen, J. W. DuMond, T. W. Layton and J. S. Rollett, Rev. Mod. Phys., 27, 363 (1955).

(11) C. W. Davies and A. L. Jones, Disc. Far. Soc., 5, 103 (1949).

(12) C. W. Davies, H. W. Jones and C. B. Monk, Trans. Far. Soc., 48, 921 (1952).

(13) A. Deubner and R. Heise, Ann. Physik. 9, 213 (1951).

(14) F. H. Drake, G. W. Pierce and M. T. Dow, Phys. Rev. 35, 613 (1930).

(15) M. E. Dry and J. A. Gledhill, Trans. Far. Soc., 51, 1119 (1955).

(16) M. L. Dundon, J. Am. Chem. Soc., 45, 2658 (1923).

(17) C. Duval "Inorganic Thermogravimetric Analysis" Elsevier Publishing Company, Amsterdam, 1953, pp. 395, 396.

(18) L. M. Eventov and V. V. Patrikeev, Chem. Abstr. 42, 3645 (1948).

(19) A. Faure, Ph.D. Thesis, Rhodes University, 1953.

(20) A. Faure, P. K. Faure and J. A. Gledhill, J. S.African Chem. Inst., 4, 19 (1951)

(21) P. K. Faure, Ph.D. Thesis, Rhodes University, 1956.

Bibliography (continued)

(22) C. Faurholt, *J. Chim. Phys.*, *21*, 400 (1924).

(23) R. B. Fischer, *Anal. Chem.* *23*, 1667 (1951).

(24) R. B. Fischer, *ibid.* *25*, 1544 (1953).

(25) J. A. Gledhill, M.Sc. Thesis, Univ. of South Africa (1942).

(26) J. A. Gledhill and G. McP. Malan, *Trans. Far. Soc.* *48*, 258 (1952).

(27) *ibid.* *ibid.* *49*, 166 (1953).

(28) T. H. Gronwall, V. K. LaMer and K. Sandved, *Phyzik. Z.*, *29*, 358 (1928).

(29) F. L. Hahn and R. Otto, *Z. Anorg. und Allgem. Chem.* *126*, 257 (1923).

(30) A. E. Harvey, J. M. Komarny and G. M. Wyatt, *Anal. Chem.* *25*, 498 (1953).

(31) G. A. Hulett, *Z. Phys. Chem.* *37*, 398 (1901).

(32) G. A. Hulett, *Z. Phys. Chem.* *47*, 364 (1904).

(33) I. L. Jenkins and C. B. Monk, *J. Am. Chem. Soc.* *72*, 2695 (1950).

(34) C. R. Johnson and G. A. Hulett, *J. Am. Chem. Soc.* *57*, 256 (1935).

(35) J. Johnstone and L. H. Adams, *J. Am. Chem. Soc.*, *33*, 843 (1911).

(36) G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, *53*, 411 (1931).

(37) F. Kohlrausch, *Z. Phys. Chem.* *64*, 129 (1908).

(38) I. M. Kolthoff and E. H. Vogelenzang, *Z. Anal. Chem.* *58*, 51 (1919).

(39) I. M. Kolthoff and collaborators. A long series of papers in *J. Phys. Chem.* and *J. Am. Chem. Soc.* 1930 - 1940.

(40) I. M. Kolthoff, *Ind. Eng. Chem.* (Anal. Edition) *3*, 129 (1931).

(41) I. M. Kolthoff and E. B. Sandell "Textbook of Quantitative Inorganic Anlysis" The Macmillan Company, New York, 1952.

(42) G. McP. Malan, Ph.D. Thesis, Rhodes University (1953).

Bibliography (continued)

(43) S. Mattson, *J. Phys. Chem.* *32*, 1532 (1928).

(44) A. C. Melcher, *J. Am. Chem. Soc.* *32*, 55 (1910).

(45) S. Okada and S. Magari, *Anal. Chem.* *27*, 1481 (1955).

(46) C. N. Reilly and C. M. Crawford, *Anal. Chem.* *27*, 716 (1955).

(47) R. G. Ruyssen, *J. Phys. Chem.* *44*, 265 (1940).

(48) N. M. Selivanova and A. F. Kapustinski, *Chem. Abstr.* *48*, 7971 (1954).

(49) T. Shedlovsky and A. S. Brown, *J. Am. Chem. Soc.*, *56*, 1066 (1934).

(50) P. Sorgdrager, *Pharm. Weekblad.* *85*, 637 (1950).

(51) H. M. Trimble, *J. Phys. Chem.* *31*, 601 (1927).

(52) G. Walton and G. H. Walden, *J. Am. Chem. Soc.*, *68*, 1750 (1946).

(53) J. Wyman and E. N. Ingalls, *J. Am. Chem. Soc.*, *60*, 1182 (1938).

PART II

A REVIEW OF ION-PAIR FORMATION IN AQUEOUS SOLUTIONS OF BI-BIVALENT ELECTROLYTES. THE DISSOCIATION CONSTANT OF BARIUM SULPHATE.

Contents - Part II

1. Symbols and abbreviations
2. Introduction
    - 2.1 Incomplete dissociation with barium sulphate
    - 2.2 Outline of this work
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1 - Symbols and Abbreviations

A,B	Constants in the Debye-Huckel formula.
<u>a</u>	an interionic distance.
a'_{MSO_4}	parameter in the Bjerrum equation.
$B_o(r)$	the time average probability of finding an oppositely-charged i ion within a shell of thickness dr at a distance r from any j ion at infinite dilution.
$B_c(r)$	the time average probability of finding an oppositely-charged i ion within a shell of thickness dr at a distance r from any j ion, at finite concentration c.
c	molar concentration.
D	dielectric constant of water.
d	an interionic distance.
Ei(x)	integral exponential function of x.
e	numerical value of the electronic charge.
e	base of the natural logarithms.
$f_{\pm}$	mean ionic activity coefficient of the free ions.
G(r)	the probability that an i ion, which has not yet found an oppositely-charged partner for a smaller value of r, will be found in a shell of thickness dr at a distance r from a central j ion.
I	ionic strength of the solution (calculated from the total concentration of all the ions in solution).
I′	ionic strength of the solution due to the free ions alone (calculated from the concentration of the free ions only).

Symbols and Abbreviations (continued)

K	dissociation constant for associated ion pairs.
k	Boltzmann constant.
N'	an arbitrary number of ions.
N	Avogadro's number.
P(x)	function of x, containing Ei(x).
q, q_1..etc.	interionic distances (vide infra).
r	an interionic distance.
T	absolute temperature.
z_i, z_j	valence of an i, j ion ($z = 2$).
α	degree of dissociation.
β	an interionic distance.
$\varkappa$	$= \left(\frac{8\pi N e^2 I}{1000\ DkT}\right)^{\frac{1}{2}}$ where I is calculated for all ions in solution.
Λ_c	equivalent conductance of $BaSO_4$ solution at concentration c.
ψ_j	potential at a distance r from a j ion.

Interionic distances.

r	variable used for interionic distances.
a	closest distance of approach of paired ions.
d	arbitrary closest distance of approach of free ions, at infinite dilution.
q	arbitrary closest distance of approach of free ions, at a finite concentration.

$q = q_1 = 13.87$ Å

$q = q_2 = 6.94$ Å

$q = q_3 = 5.0$ Å

$q = q_4 = 4.0$ Å

β	distance of minimum distribution of ions of the same charge about an oppositely charged ion, at infinite dilution.

Interionic distances (continued)

q_c	distance of minimum distribution of ions of the same charge about an oppositely charged ion, at concentration c.

Dissociation Constants.

K_{MSO_4}	dissociation constant of MSO_4 selected as best.
K_S	dissociation constant found by the Shedlovsky extrapolation.
$K_1 \ldots K_4$	values of K by Brown and Prue's method corresponding to $q_1 \ldots q_4$.

2. Introduction.

2.1. Incomplete Dissociation with Barium Sulphate.

It is well known that bi-bivalent electrolytes exhibit deviations from the Onsager and Debye-Huckel expressions for conductivity and activity coefficients even at very low concentrations. These deviations may be accounted for by extended forms of the two expressions, or by an assumption of the formation of (shortlived) ion pairs; the originator of this concept, Bjerrum, has stated (4) that "the distinction between free and associated ions was not a chemical one, but only a mathematical device making possible an approximate calculation of the effect of interionic forces under conditions where the approximation of Debye and Huckel could not be used". The use of extended terms for the activity coefficient (15) and conductivity (16, p. 148), and the concept of ion pair formation may be accepted as parallel procedures. (The extended conductivity expression contains constants which have not been evaluated theoretically for bi-bivalent electrolytes, but these have been found empirically only for zinc sulphate).

The ordinary Bjerrum treatment of ion-pair formation (3) assumes that two bivalent ions are associated at distances apart of less than 14.3 Å; thus we may safely assume that barium sulphate forms ion-pairs, and will see whether this effect will be appreciable at the concentration of a saturated solution: substitution of numerical values into the conductance equation for "incompletely dissociated" electrolytes,

$$\Lambda_c = 143.64 - 501c^{\frac{1}{2}} - \frac{c\Lambda_c}{K}$$

using an approximate, average value of the dissociation constant $K = 5 \times 10^{-3}$ and concentration $c \sim 10^{-5}$ M, we find that

$$\Lambda_c = 143.64 - 1.58 - 0.29$$

Thus omission of a term for ionic association leads to an error of 0.2% if K = 0.005.

In the absence of an experimental determination of the dissociation constant of barium sulphate a preliminary survey of dissociation constants for all bivalent sulphates (see Table 1) shows a wide range of figures, and the choice of any particular one, or the mean, would require substantial margins of error to be introduced. For example, the extreme values quoted by Brown and Prue (5) are 0.0033 and 0.0100 which introduces a variation of 0.2% in Λ_c, thereby doubling the limits of error in the final solubility calculation.

A suggestion that the dissociation constant should vary regularly with the ionic radii of the cations finds support in the work of Denney and Monk (9) and Money and Davies (21) who stated that "the dissociation constant of the nitrate is smallest for barium and greatest for magnesium, and the same is very possibly true of the sulphates". A plot of

TABLE 1.

	Temp. °C.	Experimental Procedure.	Ref.	Theoretical Procedure.	Ref.	Ref. in which K is quoted.	K x 10^4							
							$CuSO_4$	$ZnSO_4$	$MgSO_4$	$CaSO_4$	$CoSO_4$	$NiSO_4$	$CdSO_4$	$MnSO_4$
1	0	F.p.depression	5	$q_1 = 13.87$ Å	5	5	33	42	41	33	44	41		
2.	0	"	5	$q_2 = 6.94$ Å	5	5	41	55	52.5	43	55	52.5		
3	0	"	5	$q_3 = 5$ Å	5	5	50	73	70	50	73	70		
4	0	"	5	$q_4 = 4$ Å	5	5	66	100	105	54	100	88		
5	0	"	5	C.W.Davies (1938)	8	5	60	90	90	55	90	80		
6	25	Conductance	10	C.W.Davies (1927)	7	10			62					
7	25	"	10	"	7	19			54					
8	25	e.m.f.	19	C.W.Davies (1938)	8	19			44 ± 4					
9	25	Solubility	1	"	8	1				49				
10	25		18			9								52
11	25	e.m.f.	6	C.W.Davies (1938)	8	8		54						
12	25	"	20	"	8	8							51	
13	25	Conductance	22	Shedlovsky	14	22	43	49						

TABLE 1 (continued)

	Temp. °C.	Experimental Procedure.	Ref.	Theoretical Procedure.	Ref.	Ref. in which K is quoted.	$CuSO_4$	$ZnSO_4$	$MgSO_4$	$CaSO_4$	$CoSO_4$	$NiSO_4$	$CdSO_4$	$MnSO_4$
14	25	Conductance	22	Fuoss	14	23		54						
15	25	"	22	C.W.Davies (1927)	7	22		44 to 47						
16	25	"	22	Empirical conductance equation and C.W.Davies (1938)	25) 8)	25	46	53						
17	25	"	22	Empirical conductance equation	22	22		47						
18	25	e.m.f.;a = 3.64	6,3	Bjerrum	3	22		30						
19	25	Conductance	10	Robinson and Stokes	24 (p.401)	24			49.6					
20	25	Conductance	22	"	24 (p.402)	24	42	44						

Brown and Prue's values of the various groups of K against the cationic radii shows that only those values calculated for a distance of closest approach of free ions of 4 Å vary even approximately regularly. In this case the value of K_{BaSO_4} would differ greatly from K for the other sulphates due to the much larger ion size of barium. Thus for our needs it is obvious that an appraisal of the various approaches is necessary.

2.2 Outline Of This Work.

Discrepancies in K (see Table 1) are due not only to different experimental methods (which is to be expected) but also to different theoretical approaches. It is almost true to say that each worker has followed a different theoretical procedure.

First it was necessary to decide whether K was dependent on the crystalline ionic radius of the cation. For this purpose the reasonable assumption was made that **a** (the closest distance of approach of paired ions) for any one substance would remain approximately constant for two different experimental methods of determining K, and at different temperatures, provided consistent theoretical procedures were followed in all cases. For the purposes of comparison, Brown and Prue's results (5) were used as they covered a wide range of bivalent sulphates and were obtained by one experimental method. However, Brown and Prue's **a** values from the Bjerrum equation (see section 3.2.5) were calculated on the assumption that q, the closest distance of approach of free ions, was concentration-invariant; the author has shown, in section 4, that this is not strictly correct. Therefore, an approximate calculation was performed where the <u>a</u> value calculated from the Bjerrum equation did not represent the interionic distance: this value (designated $\underline{a}'$ and considered a parameter) calculated from Owen and Gurry's (22) K_S values for $CuSO_4$ and $ZnSO_4$ (which are free from any assumptions regarding interionic distances), was compared to a'_{CuSO_4} and a'_{ZnSO_4} from the various values of K obtained by Brown and Prue; the latter value having $\underline{a}'$ closest to the $\underline{a}'$ from K_S was considered best. The value so chosen corresponded to q $\sim$ 7 Å; for this q value, <u>the plot of K against the crystalline cationic radius for the various sulphates shows no regular variation at all</u>.

In investigating the status of the various <u>a</u> values obtained as outlined in section 3.2, the concentration dependence of q seemed evident. An expression was derived by the author to describe, albeit qualitatively, the variation with concentration of the distance of minimum distribution of ions of the same charge about an oppositely-charged ion; q will be influenced in much the same fashion.

It is noted that Brown and Prue's "best" K_{CaSO_4} (which may reasonably be supposed to be close to K_{BaSO_4} due to the similarity of the two substances) is also close to K_{CuSO_4}. Therefore we have taken Owen and Gurry's K_S for $CuSO_4$ as being good enough for our purpose to represent the dissociation constant of barium sulphate. As it transpired, this K_{CuSO_4} is nearly the same as K_{CaSO_4} obtained by Bell and George (1), although this was not to be expected, as these authors express no great faith in the activity coefficient equation they used.

3. Critical Review of Previous Work.

3.1. Theoretical Approaches to the Evaluation of Dissociation Constants.

3.1.1 The Bjerrum Method. (3)

This was the original theory which initially suggested the division into two groups, of free and associated ions, of the ions of certain salts.

The time average probability $B_o(r)$ of finding an oppositely-charged i ion within a shell of thickness dr at a distance r from any j ion is given by

$$B_o(r) = 4\pi \frac{N'}{V} \exp -\left(\frac{z_i e \psi_j}{kT}\right) r^2 dr \qquad (i)$$

where N' = total number of i ions in volume V

ψ_j = potential at distance r from the j ion

Bjerrum used this distribution function for the evaluation of the thermodynamic dissociation constant. The effect of the "ionic atmosphere" i.e. the potential due to all ions beside the two under immediate consideration, could be neglected. In these conditions the potential is given by

$$\psi_j = \frac{z_i e}{Dr} \qquad (ii)$$

which gives for the distribution function

$$B_o(r) = 4\pi\frac{N'}{V}\exp\left(-\frac{z_i z_j e^2}{DkTr}\right) r^2\,dr \tag{iii}$$

If there is a minimum in $B_o(r)$ at a distance β, the value of β will obviously be given by differentiating (iii) and equating to zero.

Thus

$$\beta = \frac{z_i z_j e^2}{2DkT} \tag{iv}$$

and its value at 0°C is 13.87 Å and at 25°C, 14.28 Å.

Thus if two ions can approach to a distance of less than β, ion pair formation results. The distance of closest approach of paired ions we denote by <u>a</u>.

The total fraction of ions forming pairs, i.e. the degree of association $(1 - \alpha)$, is given by integration of equation (iii) from the closest distance of approach <u>a</u>, to β, where ions are no longer considered to be paired. (The Fuoss method allows certain of the ions separated by less than β to be classed as free ions, i.e. the limit of the integral is taken as an arbitrary distance d) (vide infra)

$$\text{i.e.}\quad (1 - \alpha) = \int_a^d B_o(r)\,dr \tag{v}$$

On substituting

$$K \sim \frac{c}{1 - \alpha} \quad \text{at low concentrations, where} \quad \alpha \rightarrow 1$$

and integrating explicitly,

$$K^{-1} = \frac{4\pi N}{1000}(2\beta)^3 \left\{P(\tfrac{2\beta}{a}) - P(\tfrac{2\beta}{d})\right\} \qquad \text{(vi)}$$

where

$$P(x) = \frac{1}{6}\left\{Ei(x) - \frac{e^x}{x}\left(1 + \frac{1}{x} + \frac{2}{x^2}\right)\right\}$$

Values of $\left\{P(x) - P(2)\right\}$ are tabulated in (16, p.597) for calculations where the lower limit is taken as 2 (i.e. $d = \beta$) and the integral exponential function $Ei(x)$ in (17) if not.

3.1.2. The Fuoss Distribution Function (12).

Fuoss derived a distribution function $G(r)$ for ion pairs.

The probability $G(r)dr$ that an i ion, which has not yet found an oppositely-charged partner for a smaller value of r, will be found in a shell of thickness dr, at a distance r from a central j ion, is given by

$$G(r) = \frac{4\pi N'}{V} r^2 \exp\left(\frac{2\beta}{r} - \int_a^r B_o(x)dx\right) \qquad \text{(vii)}$$

This function has a minimum, up to a critical concentration which Fuoss has estimated for 1 - 1 electrolytes (13). We have plotted $G(r)$ against r for a 2-2 electrolyte with an arbitrary a value of 3.6 Å and find that the minimum disappears between 10^{-2} and 5×10^{-3} M.

There is a slight increase of the distance of the minimum in $G(r)$ with increasing concentration.

The numerical value is doubtful due to the neglect of an "ionic atmosphere" term in the derivation of (vii).

At zero concentration i.e. in calculating K, $G(r)$ and $B_o(r)$ become the same. The closest distance of approach in this treatment was taken as d, not β, where $d < \beta$. Thus Fuoss' d is almost the same as Brown and Prue's q (see section 3.1.6), but d is "measured" at infinite dilution whereas q is used in activity coefficient calculations, indicating that it is a dimension in a solution of finite concentration.

3.1.3. C.W. Davies (1927) (7) estimated K at each concentration at which measurements were available, using the limiting laws for both activity coefficient and conductivity.

3.1.4. C.W. Davies (1938) (8) defined the mean ionic activity coefficient $f_{\pm}$ of the free unpaired ions by the expression

$$\ln f_{\pm} = - Az^2 \frac{I'^{\frac{1}{2}}}{1 + I'^{\frac{1}{2}}} - 0.20I' \qquad \text{(viii)}$$

where the ionic strength I' is calculated for the free ions only.

3.1.5. Fuoss and Shedlovsky (14) have devised functions to obtain K by the extrapolation to infinite dilution, of conductivity data, where no assumptions about the activity coefficients of the free ions have to be made. The two functions give slightly differing results; the Shedlovsky value (denoted K_s) is preferred because the extrapolation is the more linear.

3.1.6. Brown and Prue, in their highly elucidatory paper (5), have stated that the values of the dissociation constants depend on the distances regarded as the closest distance of approach of the free ions, q. They calculated values of K for $q_1 = 13.87$ Å (i.e. β), $q_2 = 6.94$ Å, $q_3 = 5.0$ Å and $q_4 = 4.0$ Å, the corresponding K being K_1, K_2, K_3 and K_4. These values of q are used in the expression for the activity coefficient of the free ions

$$\ln f_{\pm} = - \frac{Az^2 I'^{\frac{1}{2}}}{1 + qBI'^{\frac{1}{2}}} \qquad \text{(ix)}$$

C.W. Davies' expression (viii) is shown to correspond to the choice q = 4.3 Å.

3.1.7. Robinson and Stokes (24, pp. 401 and 402) modified the C.W. Davies (1927) method by using <u>extended</u> expressions for activity coefficient and conductance, incorporating a closest distance of approach of free ions, which was assumed to be equal to β.

3.2. <u>Calculations Involving the Bjerrum Equation.</u>

As we have seen, the Bjerrum equation may be written

$$K^{-1} = \frac{4\pi N}{1000} (2\beta)^3 \left\{ P\left(\frac{2\beta}{a}\right) - P\left(\frac{2\beta}{d}\right) \right\} \qquad \text{(vi)}$$

The equation may thus be used to calculate K from given <u>a</u> and d values, or to obtain one of the latter interionic distances from the other and an experimentally derived K. These calculations are outlined below, and in subsequent pages each time the Bjerrum equation is used, the method will be indicated.

Method 3.2.1. An a value determined for zinc sulphate from activity coefficient data (6) was used by Owen and Gurry (22) with d = β, to calculate K directly from the Bjerrum equation. Brown and Prue's work shows that the assumption that d = β is dubious. Also it is not certain whether the a value calculated from activity coefficients is the same as that on the Bjerrum model. Dielectric constant effects absorbed in a (11,12) are bound to be different in the two cases.

Method 3.2.2. An a value determined elsewhere may be used to calculate K for various valued of d. This follows the theory of Fuoss (14) where the only change in K would be attributed to the arbitrary change in d.

Method 3.2.3. Dissociation constants obtained by the C.W. Davies method have been used to calculate a values using d = β in equation (vi) (1,2). This has led to results where a is less than the sum of the crystal radii of the two ions, and the paradox, shown by Brown and Prue, of a closest distance of approach of free ions which is less than that of paired ions.

Since q = 4.3 Å (i.e. the closest distance of approach of ions in a solution of finite concentration has been used for the activity coefficient, and β (the corresponding distance at infinite dilution) in the Bjerrum equation, calculations by this method indicate that increasing the concentration from zero up to c has decreased the interionic distance from 13.87 to 4.3 Å.

In view of the inconsistencies quoted above it seems impossible to attribute to a the status of more than a parameter in this calculation.

Method 3.2.4. Dissociation constants from other sources (i.e. where q is not taken as 4.3 Å necessarily) may be used to calculate a as in 3.2.3.

Method 3.2.5. Brown and Prue have calculated from equation (vi) a values using the experimental K values (which are dependent on their arbitrary q distances), and d = q. Although these authors do say of these a values that "their exact physical status is uncertain because of the simplicity of the model", one assumption is implicit in this calculation, viz., that the arbitrary closest distance of approach of free ions in a solution of finite concentration is the same as that at infinite dilution, i.e. that q = d.

They also state that the values of a "are almost independent of q between q = 5 Å and q = 6.94 Å". If we are to choose any particular value of q we should not be influenced by this statement because $\frac{\Delta a}{\Delta q}$ for the range 5 to 6.94 does not differ much from its value for the range

6.94 to 13.87 Å. (It may be significant that the ratio increases greatly for q from 5 to 4 Å.)

$\frac{\Delta a}{\Delta q} = 0$ would indicate that the only difference between K_1 to K_4 would be due to the change in the arbitrary choice of d.

The change of <u>a</u> with d (or q) may be differently illustrated by calculating K for different d values, i.e. method 3.2.2. In Table 2 we take as two examples $a = 3.91$ Å (from K_1 for zinc sulphate) and $a = 3.70$ Å (from K_2 for zinc sulphate), and denote the corresponding dissociation constants by K_1' and K_2'. The bracketed figures are those quoted by Brown and Prue.

TABLE 2

d (Å)	K_1' (a = 3.91 Å)	K_2' (a = 3.70 Å)
13.87	(0.0042)	0.0037
13.2	0.0043	
12.6	0.0044_5	
12.1	0.0046	
11.5	0.0047	
11.1	0.0048	
10.3	0.0050	
9.3	0.0054	
7.9	0.0060	
6.94	0.0067	(0.0055)
5.6	0.0081	

The conclusion to be drawn from these figures is that the assumption made is not correct, i.e. that $q \neq d$. It will be difficult to assess the effect of a finite concentration on an arbitrary q, but we can examine the effect on the distance of minimum distribution β.

4. Variation with Concentration of the Distance of Minimum Distribution of Ions of the Same Charge about an Oppositely-Charged Ion.

The distance β was derived in section 3.1.1. Robinson and Stokes (24, p.384) say of this value "This figure is probably too large because Bjerrum has simplified the treatment by subjecting the ions surrounding the central ion to the potential of this ion alone, whereas allowance for the interionic forces would act in the opposite direction". This statement is not strictly correct because as we have shown β is the value at infinite dilution. Where a distance of minimum distribution is to be estimated for a solution of finite concentration, e.g. in the calculation of activity coefficients, the effect of neglecting the potential due to the ionic atmosphere may be found.

In the Debye-Huckel theory occurs the well-known expression for the potential ψ_j at a distance r from a selected j ion, due to all the ions in solution

$$\psi_j = \frac{z_j e}{D} \frac{e^{-\varkappa(r-a)}}{r(1+\varkappa a)} \qquad (x)$$

where $\varkappa$ is calculated for all the ions in solution.

Thus to obtain the time average probability of finding an oppositely-charged ion at a distance r from the j ion in a solution of total concentration c (from which $\varkappa$ is calculated), we replace ψ_j of equation (ii) with ψ_j of equation (x) in equation (i) to get

$$B_c(r) = \frac{4\pi N'}{V} \exp\left\{- \frac{z_i z_j e^2 \, e^{-\varkappa(r - a)}}{DkTr \;\; (1 + \varkappa a)}\right\} \qquad \text{(xi)}$$

Differentiating and equating to zero gives, for the distance of minimum distribution,

$$q_c = \frac{z_i z_j e^2}{DkT} (\varkappa q_c + 1) \, e^{-\varkappa(q_c - a)} \qquad \text{(xii)}$$

(xii) is to be solved for q_c and this can be done when the exponential term is small, ($c < 0.03$ M approximately, for 2-2 electrolytes). At low concentrations putting β for q_c on the right hand side and using only the first two terms in the expansion of the exponential, (xii) becomes

$$q_c = \beta(1 - \varkappa a) \qquad \text{(xiv)}$$

At 0°C, using a random a value of 3.75 Å, and $\varkappa = 0.1$ Å^{-1} (i.e. $c \sim 0.024$M), we find q_c from (xii) to be 12.8 Å which is 0.92β.

We may now apply this to the calculations outlined previously.

For method 3.2.3, we note that the decrease in β caused by the ionic atmosphere is small, and at low concentrations the distance of minimum distribution is not near 4.3 Å. Therefore, to justify this calculation would invoke the need for phenomena such as dielectric constant changes, ion deformation, etc., to take place.

In Brown and Prue's estimation of K (see section 3.1.6) each q is taken as invariant over the concentration range of their measurements. If we consider that q is affected by the ionic atmosphere as β is, the decrease in q at 0.024M will be approximately to 0.92q. Thus q_3, for example, if taken as 5.0 Å at zero concentration, becomes approximately 4.6 Å at 0.024M. The appreciable difference between K_3, for q = 5 Å, and K_4, for q = 4 Å, demonstrates the effect on the dissociation constant. However, this is merely a qualitative description, because the change in q is not given by (xii) which was derived for β. Also the slight increase in β - section 3.1.2 - has been ignored, and the dielectric constant has been assumed to be that of pure water.

5. Comparison of Dissociation Constants from Different Methods.

Comparison can only be effected by means of **a** values calculated by method 3.2.4 or 3.2.3. As stated there, these **a** values (here denoted by $\underline{a}'$) are to be regarded as parameters. Provided consistent assumptions are made in both cases comparison will be valid.

Thus, from Owen and Gurry's K_s for zinc and copper sulphates (22)

$$a'_{ZnSO_4} = 4.5 \text{ Å} \text{ and } a'_{CuSO_4} = 4.0 \text{ Å}$$

The same calculation for Brown and Prue's K_2 values leads to

$$a'_{ZnSO_4} = 4.4\ \text{Å} \quad \text{and} \quad a'_{CuSO_4} = 3.9\ \text{Å}.$$

This correspondence is close enough for us tentatively to select Brown and Prue's K_2 values as being the best of their figures. Calculation of $\underline{a}$ by method 3.2.5 for $d = 6.94$ Å, from K_3, leads to $a_{ZnSO_4} = 3.8$ Å and $a_{CuSO_4} = 3.67$ Å, which do not agree as well with Brown and Prue's $a_{ZnSO_4} = 3.70$ Å and $a_{CuSO_4} = 3.42$ Å. (This is provisionally attributed to the neglect of the ionic atmosphere term mentioned in the last paragraph, section 4, and its subsequent effect on q).

When the relation between interionic distances in finite concentrations and at infinite dilution has been established more clearly, data from various sources may be compared by this method and a value for Fuoss' d obtained. Thus in principle at least a large variation in the values of K in Table 1 will be eliminated. We may now proceed to estimate a value for barium sulphate.

6. K for Barium Sulphate.

K for calcium sulphate has been assumed to be closest to the value for barium sulphate, as Ca has a large ion size and the sulphate is not very soluble. From K_2 values (for $q = 6.94$ Å) it is seen that K_{CaSO_4} is very close to K_{CuSO_4} and we will assume that this closeness holds at 25°C, so that we may take $K_{BaSO_4} \sim K_{CuSO_4}$ at 25°C. The appreciable difference between the crystal radii of the barium and copper ions need not affect this assumption because dissociation constants are independent of ion size, if $q = 6.94$ Å (as we have decided in section 5).

We thus take $K_{BaSO_4} = 0.0043 \pm 0.0005$ where the limits refer to the uncertainties in the comparison of barium sulphate and copper sulphate dissociation constants.

7. Conclusions.

1. Various theoretical approaches to dissociation constants have been reviewed.

2. The effect of concentration on the distance of minimum distribution, suggested by Robinson and Stokes, has been investigated and found to be small. The effect has been applied qualitatively in a discussion of the uses to which the Bjerrum equation has been put.

3. Dissociation constants measured by freezing point depression, and conductance, have been compared by the use of parameters in the Bjerrum equation, and a tentative choice from Brown and Prue's values has been made.

4. The dissociation constant of barium sulphate was taken as being equal to that of copper sulphate, and limits of error were estimated.

9. Bibliography

(1) R.P. Bell and J.H.B. George, *Trans. Far. Soc.*, **49**, 619 (1953).

(2) R.P. Bell and J.E. Prue, *J. Chem. Soc.*, 363 (1949).

(3) N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No.9 (1926).

(4) N. Bjerrum, *Trans. Far. Soc.*, **23**, 433 (1927).

(5) P.G.M. Brown and J.E. Prue, *Proc. Roy. Soc.*, **232A**, 320 (1955).

(6) I.A. Cowperthwaite and V.K. LaMer, *J. Am. Chem. Soc.*, **53**, 4333 (1931).

(7) C.W. Davies, *Trans. Far. Soc.*, **23**, 351 (1927).

(8) C.W. Davies, *J. Chem. Soc.*, 2093 (1938).

(9) T.O. Denney and C.B. Monk, *Trans. Far. Soc.*, **47**, 992 (1951).

(10) H.S. Dunsmore and J.C. James, *J. Chem. Soc.*, 2925 (1951).

(11) R.H. Fowler, "Statistical Mechanics", Cambridge University Press, London, 1929, p.322.

(12) R.M. Fuoss, *Trans. Far. Soc.*, **30**, 967 (1934).

(13) R.M. Fuoss, *Chem. Rev.*, **17**, 27 (1935).

(14) R.M. Fuoss and T. Shedlovsky, *J. Am. Chem. Soc.*, **71**, 1496 (1949).

(15) T.H. Gronwall, V.K. LaMer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

(16) H.S. Harned and B.B. Owen, "The Physical Chemistry of Electrolyte Solutions", Reinhold Publishing Corpn., 1950, Second Edition.

(17) E. Jahnke and F. Emde, "Tables of Functions", Teubner, Berlin and Leipzig, 1938.

(18) J.C. James, Ph.D. Thesis, London (1947).

(19) H.W. Jones and C.B. Monk, *Trans. Far. Soc.*, **49**, 619 (1953).

(20) V.K. LaMer and W.G. Parkes, J. Am. Chem. Soc., 53, 2040 (1931).

(21) R.W. Money and C.W. Davies, Trans. Far. Soc., 28, 613 (1932).

(22) B.B. Owen and R.W. Gurry, J. Am. Chem. Soc., 60, 3074 (1938).

(23) B.B. Owen, J. Am. Chem. Soc., 61, 1393 (1939).

(24) R.A. Robinson and R.H. Stokes, "Electrolyte Solutions", Butterworths Scientific Publications, London, 1955.

(25) P.A.H. Wyatt, Trans. Far. Soc., 47, 656 (1951).