An Electrochemical Study of the Kinetics of Crystallisation and Dissolution of Sparingly Soluble Salts

A Thesis by

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PREFACE

This work was done from October, 1960 to September, 1963 at the University of Glasgow, in the Department of Physical Chemistry, which is under the supervision of Professor J. Monteath Robertson, F.R.S.

Thanks are due to the Department of Scientific and Industrial Research for a maintenance grant during the three years of this work. I am also indebted to Mr. J. Leslie and Mr. T. Pitt for the construction of the conductivity cells.

Above all, I should like to record my sincere gratitude to Dr. G.H. Nancollas for the interest, encouragement and patience shown throughout the work.

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Kinetic Studies of the Precipitation and Dissolution of Sparingly Soluble Electrolytes.

GENERAL INTRODUCTION.

Crystallisation has been studied quantitatively since the 18th century, when it was appreciated that the normal solubility of a salt in solution could be exceeded without crystallisation taking place. A great amount of research led to many contrasting theories and no real advance was made until the work of Ostwald[1], who proposed that the region of supersaturation in a solution was composed of a 'metastable' and a 'labile' portion. Immediately above the normal solubility curve was a metastable zone in which crystallisation could occur only if induced by mechanical shock or inoculation of the solution. If seed crystals were added to such a solution, all the growth took place on the crystals and no additional nuclei were formed. This region was followed at a sharply defined concentration by a region of labile solutions which would crystallise spontaneously.

There was much support for this concept of a rigid boundary between the regions and Miers found that it could be represented by a definite temperature-concentration curve. Criticism however, notably by de Coppet[2], who argued that any supersaturated solution would crystallise in time or with the application of sufficient mechanical energy, led to the metastable limit being regarded as unreal. It was modified to that concentration range over which the formation of nuclei of sufficient size to act as growth sites changed from being negligible to become rapid.

More recently Davies and Jones[3] studied the crystallisation of supersaturated solutions of silver chloride in the absence of seed crystals, and they found that the solutions did not precipitate spontaneously unless the concentration product was almost double the solubility product. From measurements of the initial fall in conductivity of slightly supercritical solutions, they obtained a value for the critical concentration and established that the boundary was fairly sharp.

In terms of the Gibbs-Thomson relationship, the growth of crystal nuclei was favoured compared to their rate of solution as the concentration of the unseeded solution increased, until, at the critical concentration, the nuclei were able to act as centres of further growth. A slight increase in concentration gave a very rapid rise in the number of nuclei of critical size and a rapid reduction in the minimum size of the stable nucleus, so the number of nuclei attaining a given size varied greatly with small changes in concentration. The critical supersaturation was therefore identified with the narrow concentration range in which stable nuclei arose in significant numbers. Davies and Jones found that the value of the critical supersaturation increased as the silver to chloride ionic ratio diverged from unity.

LaMer and Dinegar[4] studied the spontaneous precipitation of sparingly soluble sulphates by generating sulphate ions by a chemical reaction in the presence of a soluble barium or strontium salt. They postulated the formation of complexes of $(MSO_4)_x$ of various sizes in statistical equilibrium with M^{2+} and SO_4^{2-}, and they designated $(MSO_4)_x$ an embryo. When the ionic product was less than the solubility product, all embryos dissociated, and although the average value of <u>x</u> increased as the concentration of sulphate ion increased, even with the ionic product greater than the solubility product, the overwhelming majority of the embryos were still unstable with respect to the ions and redissolved. Only when the solubility was exceeded by a certain critical amount did formation of the stable macro phase proceed at a measurable rate. The nuclei, as these critical embryos were named, corresponded to a complex of maximum Gibbs free energy in respect to particle size, and they differed from embryos in that addition of MSO_4 reduced the free energy and further growth was spontaneous.

LaMer and Dinegar concluded that the critical concentration was actually a very narrow region and that the concentration of nuclei present at a given time was determined not only by the concentration of dissolved material but possibly also by the length of time the concentration had exceeded the saturation value. Although remarkably constant critical supersaturation values were obtained, the nucleation appeared to have been heterogeneous rather than homogeneous, since it has been found that the critical concentration was strongly dependent on the purity of the reagents[5,6].

Precipitation from the labile region was considered by von Weimarn[7] to be initiated by the collision of ions to form neutral molecules, aggregation of which gave a disperse system. The residual ions in the solution caused precipitation of the colloid, and this further aggregated to form visible particles on which additional growth occurred. He concluded that the velocity of precipitation and the number of particles formed were functions of the degree of supersaturation and even the absolute magnitude of the concentration.

Gibbs[8] suggested that the growth of a perfect crystal should proceed by continuous two-dimensional nucleation on the crystal surface providing growth steps which would grow laterally by the incorporation of solute molecules at their leading edges. Energy considerations thus require that there should be a critical supersaturation below which no crystal growth can occur, but this limit has been found to be absent in a number of systems[9]. It was proposed that a mobile self-adsorbed layer in thermodynamic equilibrium with the crystal surface provided the possibility of growth without surface nucleation. This was opposed by Frank[10], who suggested that the surfaces of crystals were imperfect and contained dislocations, most of which were caused by impurities in the crystal[11]. A screw dislocation at a crystal surface offered a perpetual growth step, at the kinks on which solute could be assimilated, and this view is supported by much experimental evidence[12,13,14]. The necessity for two-dimensional nucleation at low supersaturations was therefore removed, and Burton, Cabrera and Frank[15] stated that for solutions less than 50% supersaturated, screw dislocations should be the only source of growth steps.

The rate of growth in many cases is much slower than predicted by this theory, and it appears that there may often not be sufficient dislocations on the crystal. Diffusion in the solution is also an important factor in crystal growth and since the concentration of solute is not uniform over the crystal surface, nucleation can occur, particularly at the corners and edges of the crystal. A two-dimensional mechanism has been proposed by Nielsen[16] and O'Rourke and Johnson[17] for the growth of barium sulphate, and in studies of the growth of near perfect crystals, Sears[18] observed that growth could occur by surface nucleation and screw dislocations on different planes of the same crystal.

In a study of crystal growth, kinetic factors must be considered as well as surface energy factors and these involve a knowledge of the mechanism of growth. Crystallisation and dissolution are both heterogeneous reactions and the problem of the kinetics may vary from being a purely chemical one to being entirely non-chemical.

Bircumshaw and Riddiford[19] discussed systems in which the observed rate of reaction is either wholly or partly determined by the rate of a transport process. These authors consider that for the general case of a reaction between a solid and a solution, resulting in soluble products, the overall process may comprise five primary steps :-

1. Transport of solute molecules to the interface.
2a. Adsorption of solute at the surface.
2b. Chemical reaction at the surface.
2c. Desorption of products from the surface.
3. Transport of solute from the interface to the bulk of the solution.

Steps 2a, 2b and 2c represent the interaction between the solid and the solute and can be combined to give an overall interface step, step 2. Crystallisation will therefore be interface controlled if step 1 is much faster than step 2, and diffusion controlled if step 2 is faster than step 1, and the situation is analogous for dissolution if steps 2 and 3 are compared.

Nernst[20] suggested that the interface processes were always very much faster than either of the transport processes, so that unless a slow process occurred within the bulk of one of the phases, the observed rate was transport controlled. His diffusion theory of heterogeneous reactions was based on the study of many dissolution reactions. Noyes and Whitney[21] had found that the dissolution of benzoic acid and lead chloride followed the first order equation

$$\frac{dm}{dt} = k\ (m_o - m_t) \qquad . \quad . \quad . \quad . \qquad (1)$$

where m_o is the solubility concentration, m_t the concentration at time t, and k the rate constant. Similar results for the dissolution of metals in acid led to the picture of a stationary layer, the Nernst layer, at the interface, efficient stirring being considered to exist down to this layer with a linear concentration gradient across it. Nernst assumed that equilibrium was established almost instantaneously at the solid surface, and the rate of dissolution was determined by the rate of diffusion of the solute across the layer.

Employing Fick's law this can be written as

$$\frac{dm}{dt} = \frac{Ds}{\delta}\ (m_o - m_t)$$

where D is the diffusion coefficient, s the surface area, and δ the thickness of the diffusion layer. Nernst believed that crystallisation and dissolution were strictly reciprocal processes and that crystal growth could also be represented by a first order equation.

On this theory, for a constant geometry of system, an increase in the rate of stirring should be accompanied by an increase in the observed velocity, and many workers[22,23,24] have confirmed this for dissolution experiments, usually expressing their results in the form

$$k_d \propto (\text{r.p.m.})^a$$

where a varied from 0.56 to 1. However, from a study of the solution of calcium carbonate in acetic acid and hydrochloric acid, although the rate of solution increased with stirring speed up to 7000 r.p.m., King and Liu[25] considered that it would tend to reach a maximum at even higher speeds.

For a particular stirring rate and geometry of system, Nernst proposed that if the thickness of the adhering layer was obtained for one reaction, the velocity constant of others could be predicted. This was done with reasonable success by Brunner[22], but the values obtained for δ were improbable, and this and other factors[26] led to the picture of a stationary layer being modified to that of a much more mobile one.

Energies of activation for dissolution reactions have been obtained[27] by applying the Arrhenius equation

$$k_d = A.e^{-E/RT}$$

and the values, approximately 4 kcals.mole^{-1}, are comparable to the energy of activation for diffusion. Davies and Nancollas obtained a similar result for the dissolution of silver chloride[28], but they found for crystallisation that the energy of activation was zero.

Although there is little doubt that dissolution of an electrolyte is very often governed by the rate of diffusion of solute away from the crystal face, the idea of there being strict reciprocity between growth and dissolution was disproved by Marc[29] and Leblanc and Schmandt[30]. Marc observed very small rates for the crystallisation of supercooled melts and thought it improbable that the rate should be greater in solutions. In experiments on crystallisation from seeded supersaturated solutions, the rate of growth was much slower than for dissolution and was independent of the rate of stirring if the latter were sufficiently vigorous. Marc observed that the kinetics of crystal growth was in many cases second order, and he interpreted this in terms of the adsorption of a thin layer of the solute at the crystal face. He thus laid the foundations of the adsorption layer theories of crystal growth, and established the technique of studying the growth of seed crystals.

Most of the work however has involved spontaneous crystallisation from supercritical concentrations, since such precipitation is so important in quantitative inorganic analysis. These crystallisation experiments have often exhibited induction periods, during which it was assumed that nuclei were being formed, and most theoretical analyses regarded the formation of a critical nucleus as a steady state process. It has been shown[31,32] that delays in nucleation may be anticipated on the basis of the relaxation time required for the steady state concentrations of the embryo to be attained, but calculations have proved prohibitively difficult. Collins[33] however obtained a lower limit for the time required to build up a steady state concentration of embryos which was independent of the free energy of formation of the critical nucleus.

Christiansen and Nielsen[32] adopted a simple kinetic approach and considered that the induction period was the time required to build up clusters of size X_p by a steady state process. These differed from smaller clusters in being more likely to gain another ion than to lose one. The time of crystallisation varied inversely as some significant power of the initial concentration

$$k = c_o^p.t$$

where t is the duration of the induction period and k and p are constants, the latter being identified with the number of ions required to form the critical nucleus. This theory differs from earlier theories in that the nucleation rate is almost independent of the supersaturation, and the size of the nucleus is constant. Values obtained for p are 8 for barium sulphate, 6 for silver chromate and 9 for calcium fluoride, corresponding to equivalent molecular units of 4, 2 and 3 respectively[34]. Klein, Gordon and Walnut[35], using a similar relationship, found that a nucleus of 5 ions was indicated for silver chloride.

The above theory contrasts with the views of Volmer[36] and Becker and Doring[37], who considered that the supersaturation was built up slowly and homogeneously until a critical supersaturation was reached, at which point the nuclei would be fairly large. Duke and Brown[38] considered that a nucleus of sufficient size to be stable in contact with a supersaturated solution should contain several tens of ions.

Homogeneous nucleation is extremely irreproducible and

Fischer[39] goes so far as to suggest that it can never be achieved. Even if we consider spontaneous crystallisation to occur by homogeneous nucleation and growth, there is still the problem as to whether nucleation has ceased before growth commences or whether both take place concurrently. Collins and Leinweber[5] and Turnbull[40] both favour consecutive processes with nucleation occurring in an initial burst, followed by subsequent growth. Other workers believe that nucleation and crystal growth occur simultaneously and Johnson and O'Rourke[41] derived equations for the two processes in the crystallisation of barium sulphate. The experimental data for the first few minutes of the precipitation fitted a relationship which accounted for simultaneous nucleation and growth, and the remainder agreed well with a rate equation derived on the assumption that nucleation had by this time become negligible. Kolthoff[42], in a study of the growth of lead sulphate, observed that nuclei formed in the initial stages of the precipitation promoted the formation of new nuclei before nucleation was completed.

In growth experiments involving spontaneous nucleation, the assumption can be made that all nuclei are formed in a short initial period[43], but it is extremely difficult to determine the instant at which growth predominates. It is moreover virtually impossible to reproduce the results of such experiments, and therefore work in which a controlled and reproducible amount of growth is allowed to occur is of considerable value. This was achieved by Davies and

Jones[44], who prepared supersaturated solutions of silver chloride which remained stable until inoculated with seed crystals. All growth took place on these crystals and the crystallisation was followed conductimetrically. This technique has since been used to study the crystal growths of silver chromate[45], magnesium oxalate[46], barium sulphate[47] and lead sulphate[48], as well as being employed in the present work.

This thesis is in three parts. The first part deals with the growth and dissolution of a silver chloride electrode, and the second and third parts with the crystal growth of strontium sulphate and silver iodate respectively. The experiments were done initially using solutions prepared with deionised conductivity water, but it was eventually realised that the results had been affected by traces of impurity in the conductivity water, and the series were repeated using distilled water. The crystal growth of strontium sulphate was also examined in the presence of small concentrations of condensed phosphates to study the effect of adsorbates on the rate of growth.

APPARATUS AND EXPERIMENTAL TECHNIQUE

The rates of crystallisation of some sparingly soluble salts have been studied conductimetrically in order to determine the kinetics and obtain information about the mechanism of crystal growth from solution. The growth of silver chloride from supersaturated solutions onto a silver-silver chloride electrode, and the dissolution of this electrode into water and subsaturated solutions have been followed by observing the decrease and increase of conductivity respectively on the immersion of electrode into the solution in a conductivity cell. The crystallisation and dissolution of crystals of silver iodate and strontium sulphate have also been examined by the same conductivity technique.

Measurement of Resistance.

Resistances were measured with an a.c. screened Wheatstone bridge of the type described by Jones and Joseph[49] and Shedlovsky[50], incorporating the recommended modifications to minimise inductance and capacitance effects of various parts of the bridge circuit, shown in Figure 1.

R_1 was the conductivity cell and R_2 a Sullivan non-reactive resistance box reading from 0.1 to 10,000 ohms. The ratio arms R_3 and R_4 were supplied by a 100 ohm Sullivan non-reactive slide resistance, and the total resistance was subdivided into 10^5 parts by two concentric dials. The output from the bridge was amplified

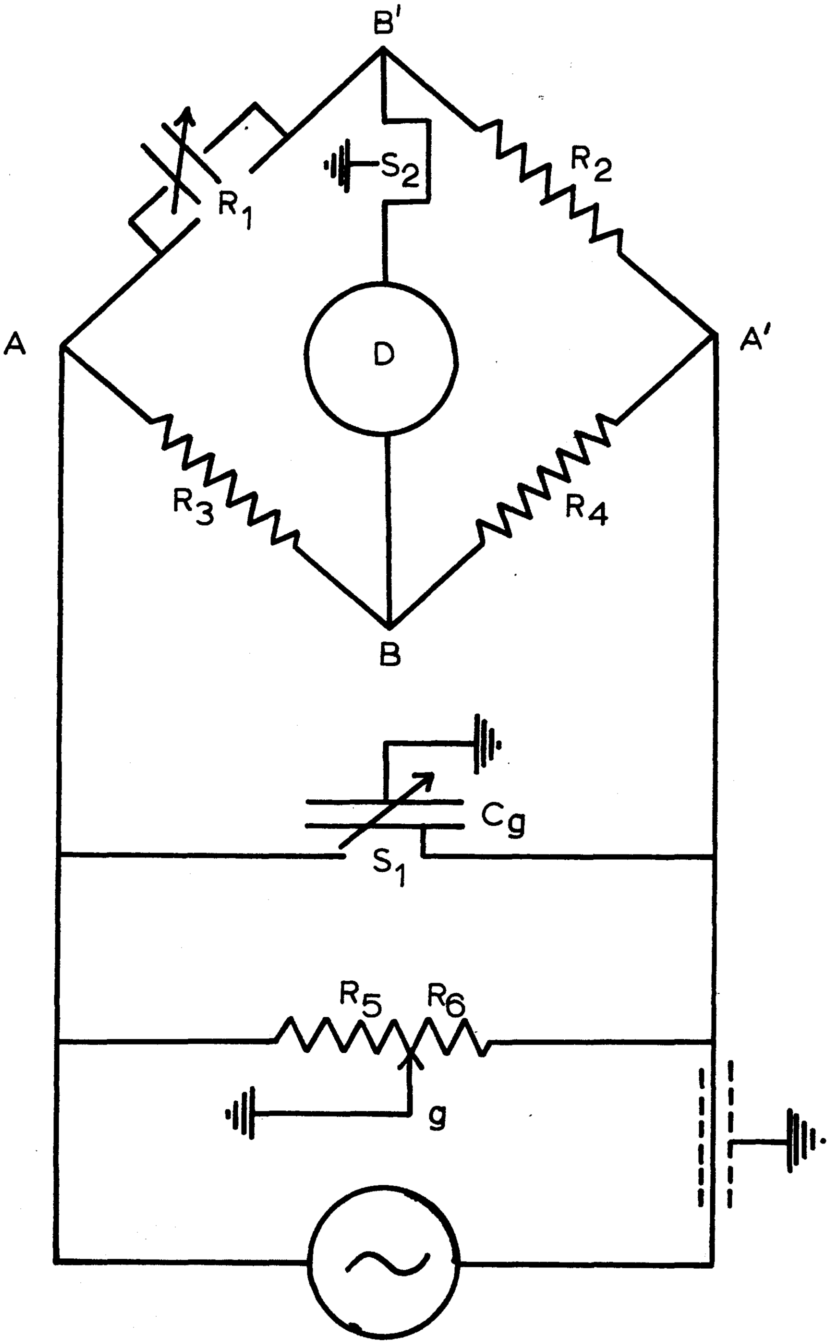


Figure 1.

before passing to the earphones by a two-stage high gain mains operated Sullivan amplifier. The oscillator, a mains operated Advance model H-1 giving frequencies from 15 to 15,000 cycles per second, was placed about five feet from the bridge to reduce the possibility of its inducing currents in the bridge circuit. Measurements were taken at a frequency of 1000 cycles per second, the optimum for aural detection.

Screened and grounded leads connected the oscillator to the bridge via a Sullivan balanced and screened transformer, designed to screen effectively the supply source from the bridge without upsetting the balance of the latter to earth. The sharpness of the sound minimum in the detector was improved considerably by earthing the bridge.

A modified Wagner earth described by Jones and Joseph[49] ensured the telephone earpiece being maintained at ground potential, thus eliminating any leakage of current due to capacity between the telephone coils and the operator. The Wagner earth is represented by the resistances R_5 and R_6, in parallel with the bridge proper, the contact g, which was connected to earth, and a variable condenser C_g. One side of this condenser was connected to earth and and the other side was connected through a switch S_1 to either A or A', whichever proved to be necessary. An approximate adjustment of the bridge proper was first made, and the detector D was then brought to ground potential by means of the switch S_2. B was then brought to ground potential by adjusting the contact g and the variable condenser C_g. The detector D was restored to its original position from B to B' by switch S_2 and the bridge was again balanced. This process was repeated until no change was observed in the position of balance between successive measurements.

The cell itself behaved as a condenser, and capacity effects arising from interaction between the electrodes, and between the electrodes and the cell wall were eliminated by balancing out against a Sullivan decade stable mica condenser, reading from 0 to $1\mu F$, connected across R_2.

The cell was brought into circuit via two copper leads from the platinum-mercury contacts of the electrodes to mercury cups supported in the thermostat to keep them at the same temperature as the cell. These copper leads were of equal lengths to compensate for resistance effects, as were the leads from the mercury cups to the resistance box R_2. The connections to the cell and the resistance box could be made by means of a mercury commutator of the rocking type. This was later replaced by a low contact-resistance multi-brush potentiometer switch.

In practice when measurements were taken, the Wagner earth was balanced as described above and the capacity and resistance R_2 were varied until the bridge position was determined corresponding to a minimum of sound in the earphones. It was found that the setting of the Wagner earth could now be kept constant, any slight deviation being easily compensated for by the mica condenser. The thermostat stirrer motor was switched off while a reading was being taken.

When water or solutions of high resistance were being measured, a 10,000 ohm, non-reactive standard resistance was connected in parallel with the cell.

The amplifier and earphones system used to find the position of balance of the bridge was replaced during this work by a General Radio Company Tuned Amplifier and Null Detector, Type 1232-A. This instrument proved to be extremely sensitive and under favourable conditions the balance point could be determined with a resolution of 2 parts in 10^6. It was a low-noise, transistor amplifier, which tuned continuously from 20 cycles per second to 20 kilocycles, with additional fixed-tuned frequencies at 50 kilocycles and 100 kilocycles. The circuit consisted of a low-noise preamplifier, followed by a frequency-selective stage and an amplifier-compressor stage. The three amplifier stages each supplied about 40 db. of gain, making the total gain of the amplifier about 120 db. After amplification, the signal could be fed either to a meter, the scale of which could be linear or compressed as controlled by a panel switch, or to earphones. In practice, the meter was used as a logarithmic amplifier and balance was determined visually by minimum deflection. The power supply of this instrument was 12 volts d.c., obtained from nine mercury (M 72) cells in series.

At one stage in the work, a transformer ratio arm bridge[51] (henceforth referred to as a "T.R.A. bridge") was substituted for the apparatus described above. The basic circuit of the T.R.A. bridge is shown in Figure 2:

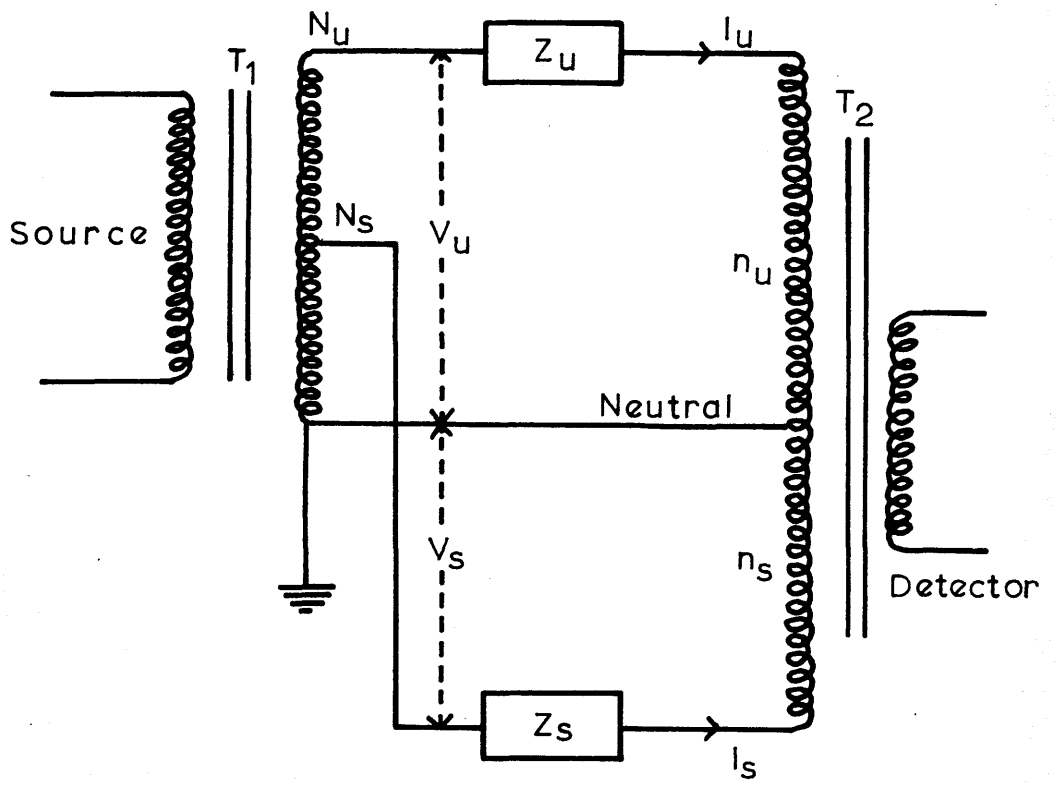


Figure 2.

$\underline{z}_u$ and $\underline{z}_s$ are the unknown and standard impedances respectively. $\underline{T}_1$ is a voltage transformer, to the primary of which the source of a.c. is connected. The secondary winding is tapped to give $\underline{N}_u$ and

$\underline{N_s}$ turns. $\underline{T_2}$ is a current transformer, whose primary is tapped at $\underline{n_u}$ and $\underline{n_s}$ turns, the secondary coil being connected to the detector.

Assuming that the transformers are ideal, if impedance $\underline{z_s}$ is adjusted to give a null indication on the detector, zero flux is produced in the current transformer and there is therefore no voltage drop across its windings. The detector sides of both the unknown ($\underline{z_u}$) and standard ($\underline{z_s}$) impedances are therefore at neutral potential.

If the voltage across the unknown and standard sides are $\underline{V_u}$ and $\underline{V_s}$ respectively, then the currents through them are given by

$$I_u = \frac{V_u}{z_u} \qquad ; \qquad I_s = \frac{V_s}{z_s} \quad .$$

For zero core flux in $\underline{T_2}$, the algebraic sum of the ampere turns must be zero :

$$\text{i.e.} \quad I_u.n_u = I_s.n_s$$

$$\text{or} \quad \frac{V_u.n_u}{z_u} = \frac{V_s.n_s}{z_s} \ ,$$

$$\text{and hence} \quad z_u = \frac{V_u}{V_s}.\frac{n_u}{n_s}.z_s \quad .$$

For an ideal transformer, the voltage ratio is equal to the turns ratio, and therefore :

$$z_u = \frac{N_u}{N_s}.\frac{n_u}{n_s}.z_s.$$

Thus by suitable tappings on the two transformers, a wide range of measurements can be carried out. Although in practice transformers are not ideal, transmission losses merely reduce the sensitivity. Provided that the coils are precision wound, and that their effective self-resistance is small compared with that of $\underline{z}_u$ and $\underline{z}_s$, all the turns embrace the same flux and hence the ratio of induced voltages is accurately equal to the turns ratio.

Standard impedances are divided into resistive and reactive components. At balance it is necessary for both the "in phase" and "quadrature" ampere turns to sum algebraically to zero, and thus the resistive and reactive standards must be capable of being connected to different tappings to balance out the currents of the unknown impedance. The independance of components is useful in that impurities in the standards can be balanced out by compensating trimmers in the unknown side of the bridge. Thus an impure capacitor is equivalent to a pure capacitance shunted by a resistance. The effect of the latter can be cancelled by feeding a current, equal to that produced by the resistance impurity, through a fixed trimming resistor into the opposite side of the transformer.

In the Wayne Kerr B 221 Universal Bridge, used in the present work, transformer tappings are arranged to give two decades, each requiring one resistive and one reactive standard. With a T.R.A. bridge it is possible to add continuously variable controls without detracting from the accuracy of the decade standards. A continuously variable reactance and a continuously variable conductance are provided in this instrument. Although one resistive and one reactive standard is required per decade, the transformer ratio may be used to set those in one decade against those in another, so that only one resistive and one reactive fixed standards of known accuracy are required. Also, in a similar method to that whereby the standards are purified, compensation can be made for any impedance in the external test leads. An excellent feature of the Wayne Kerr bridge is the "set zero" controls which enable small external impedances in series with the unknown to be trimmed out. The detector is a tuned two-stage amplifier incorporating a sensitivity control, with a double-shadow "magic eye" associated with each stage. Balance is indicated by maximum shadow.

The conductivity cell is brought into circuit with the T.R.A. bridge by two screened coaxial cables which dip into the mercury cups suspended in the thermostat. Balance is obtained by moving the decade and variable resistances and capacitances until maximum shadow is seen in the two "magic eyes". The bridge gives the impedance of the cell as a parallel combination of resistance and capacitance.

Thermostat and Temperature Control

The thermostat was a large, earthed and heat insulated metal tank, which contained transformer oil to prevent capacity errors[49]. The oil was stirred efficiently by an electrically operated paddle stirrer. The conductivity cell was supported on a perforated metal tray, and a similar tray carried a metal box containing water in which the pyrex bottles with the various seed suspensions were equilibrated. The temperature of the tank was maintained at 25° ± 0.005°C by a mercury-toluene regulator, connected in series with a 60 watt red bulb through a simple vacuum relay. This was later replaced by a Sunvic Electronic Relay, Type EA4. Temperatures were continuously checked on a Beckmann thermometer which had been standardised against a calibrated platinum resistance thermometer[52]. A booster heater was provided for rapid heating of the oil when necessary and a water cooling system was also included. The experiments were carried out in a constant temperature room, thermostated to 24.5°C, the air circulation being maintained by two large fans. This effectively prevented condensation taking place inside the cell cap, although in exceptional cases a red bulb, placed some distance from the cap, was used to keep it at the optimum temperature.

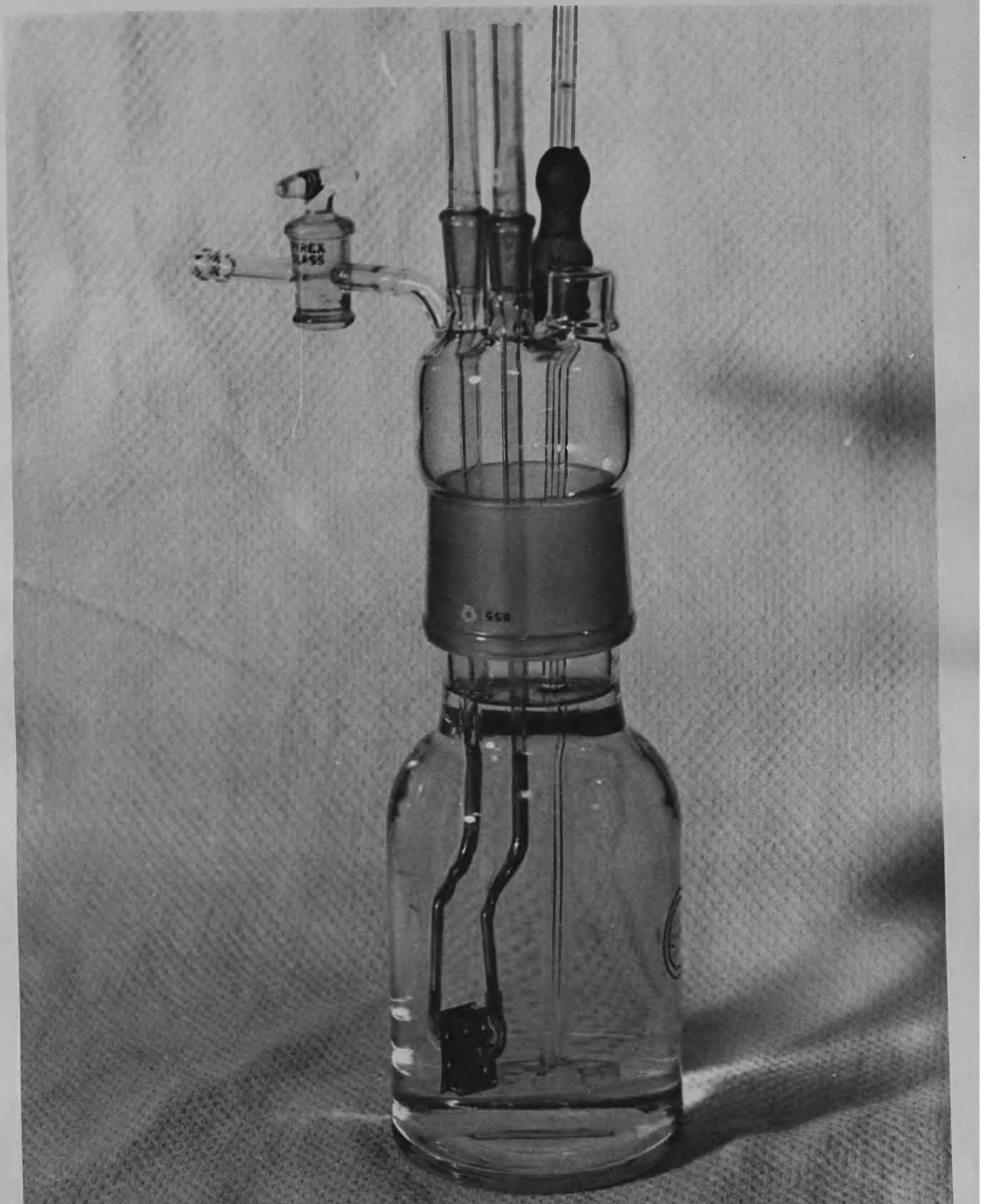
The thermostat was operated continuously so that the seed crystals could age at the temperature at which they would subsequently be used.

The Conductivity Cell

The cell was of the Hartley-Barrett type[53] and was constructed of pyrex glass (Plate 1). The cap was fitted to the pot by a lightly

PLATE 1

The Conductivity Cell



greased B.55 Quickfit joint, and carried the electrodes, apertures to accomodate the stirrer and entry tube, and a horizontal side-arm fitted with a three-way stopcock. The electrodes were of greyed platinum and were situated near the wall of the cell. They were held apart at a fixed distance by four small pyrex glass rivets, and each had six or eight small holes in it to improve the circulation of the solution between the electrodes. They were carried by platinum wires which were fused into glass supports, and since it is not possible to seal platinum into pyrex glass, a little powdered Araldite epoxy resin was set in the bottom of each support. After fusing and curing at 60° overnight, and then allowing to cool slowly, a permanent seal was obtained. The electrode supports were fixed to the cap by two B.10 Quickfit joints and sealed in position with Araldite epoxy resin. The cap was placed in the same position relative to the pot for every experiment by aligning scratches on the edge of the cap and the neck of the flask.

The cell solution was stirred by a vibratory stirrer. This consisted of a circular glass disc, perforated with conical holes, fused to a glass rod, the whole being driven by a vibromix motor (Shandon Scientific Co.). The maximum amplitude of the oscillations was 0.03 inches and the extent of stirring could be varied widely. This type of stirring was preferred to rotary stirring because the blades of the latter cut the lines of force from the electrodes and introduced errors in the measured resistance[54]. The errors varied depending upon the position of the stirrer blades relative to the electrodes. The vibrating stirrer did not suffer from this disadvantage since it was fixed in position with respect to the electrodes. The vibromix motor also appeared to induce no appreciable current in the bridge, and it did not require therefore to be turned off while a reading was being taken. The stirring rod entered the cell via a tight rubber membrane which excluded dust particles. The additions of solution and seed suspension were made by pipette through a short tube in the cell cap which was fitted with a dust cap. The side-arm was used to introduce a stream of carbon dioxide-free air into the cell.

The Carbon Dioxide-Free Air Supply

The compressed air supply was first filtered by passing it through a jar of cotton wool, and then passed through 2N sulphuric acid to remove ammoniacal vapours. Carbon dioxide was removed by passing the air stream through 30% potassium hydroxide in three tubes and two towers packed with glass beads. These were followed by a water scrubber, a filter, and a column of distilled water. Before entering the cell, the air bubbled through conductivity water, a preheating tube and a glass wool pad, all supported in the thermostat. In some experiments, pure presaturated nitrogen was used.

Preparation of Conductivity Water

In the early experiments, conductivity water was prepared by passing distilled water over a mixed bed resin[55]. This consisted of an intimate mixture of Amberlite IRA 400 basic resin and Amberlite IR 120(H) acid resin, mixed in a proportion of 2:1 by volume. Any cation impurities were replaced by hydrogen ions from the strong acid resin, and these were immediately neutralised by hydroxyl ions from the basic resin. Anions were removed by the strong base resin in the same way. The specific conductivity of the product at 25°C was about 0.1×10^{-6} ohms^{-1}.

Before use, the Amberlite IR 120(H) was washed with 2N sodium chloride, and then with 2N hydrochloric acid, before being washed free from chloride ions. After conversion to the chloride form, the Amberlite IRA 400 was treated with carbonate-free sodium hydroxide and washed to pH 7-8.

The above resins were later replaced by a Permutit "Bio-Deminrolit" mixed bed resin. The water collected from the ion-exchange columns was stored in pyrex flasks fitted with soda lime guard tubes. For each experiment, the conductivity cell was filled directly from the resin column, as a stream of purified air was blown through it.

As described later, the conductivity water prepared by ion-exchange columns was eventually found to contain traces of impurities, which greatly affected some experiments, and a Bourdillon Still[56] was therefore substituted. The still was filled with distilled water to which a few grams of potassium hydrogen sulphate had been added, and on preparation, the conductivity water was collected in a large pyrex glass receiver, fitted with guard bottles of conductivity water and potassium hydroxide to exclude carbon dioxide. Two to three litres of conductivity water, of specific conductivity 0.35×10^{-6} $ohms^{-1}$; could be prepared per hour.

The Bourdillon still has recently been replaced by a still of similar design, which is, with the exception of a copper boiler, all pyrex glass. Conductivity water of specific conductivity 0.3×10^{-6} $ohms^{-1}$ has been obtained.

Preparation of Stock and Cell Solutions

All glassware used in the preparation of solutions was pyrex. Pipettes and burettes were grade A standard. The flasks used in the preparation of stock and dilute solutions were cleaned with chromic acid and steamed out before use. If stored, they were filled with distilled water.

The cell solution was prepared by weight from dilute solutions which would give the desired subsaturated or supersaturated solution concentrations in the cell. These dilute solutions were prepared immediately before addition to the cell from stock solutions, and their concentrations were such that 10ml. added from a calibrated pipette to about 400gms. of conductivity water in the cell, would give the predetermined cell solution concentration. All solutions were made up by weight from conductivity water using a Sartorius balance of 2kg. capacity, and weights which had been calibrated by the method of Kohlrausch[57]. The balance was sensitive to 0.005gm.

Analar salts were used throughout. Solids were weighed in pyrex sample tubes, using a Stanton Model S.M.1 balance and platinum plated weights, calibrated as above[57]. All weights were vacuum corrected[58]. Details of the preparation of silver chloride, silver iodate and strontium sulphate solutions are given in the appropriate sections.

A typical example of the preparation of the cell solution for an experiment would be as follows. The cell was cleaned, weighed empty, and then weighed again, filled with conductivity water. It was then placed in the thermostat and allowed to come to equilibrium with a stream of purified air or nitrogen blowing over the stirred solution. The weight of conductivity water in the cell allowed the required concentration of the dilute solutions to be evaluated. 10ml. of stock solution was added to the calculated weight of conductivity water to prepare each dilute solution. These were then added to the cell individually, the second one being added very slowly over a period of from five to ten minutes to prevent spontaneous nucleation of crystals from high local concentrations of the added electrolyte..The cell solution was again allowed to reach equilibrium. Carbon dioxide was meanwhile removed from the seed suspension before addition to the cell by passing a rapid stream of nitrogen over it for almost an hour. Rapid additions of seed were made from a pipette with a sawn-off tip, and the time of half-delivery of the suspension was taken as the zero time for the experiment.

Determination of the Cell Constant

The cell constant was determined by the method of Fraser and Hartley[59]. The cell was dried, weighed, rinsed several times with conductivity water, and then, with a stream of purified air blowing over it, filled with about 400gms. of conductivity water. After weighing again, it was allowed to reach carbon dioxide and temperature equilibrium in the thermostat. Equilibrium was attained in about three hours, and tests showed that resistance readings would then stay steady for at least six hours. Analar potassium chloride was recrystallised four times from conductivity water. The crystals were then placed in a platinum dish and dried in an electric oven. Just before use, samples were heated to dull red heat for several minutes and allowed to cool in a dessicator. A few grams were added to conductivity water to prepare an approximately 5×10^{-2} normal solution of potassium chloride, and about 2gms. of this stock solution was then added to the water in the cell from a weight burette. Resistances were measured when equilibrium had been reached, usually 15-30 minutes after the addition. The resistance box R_2 was adjusted until the bridge readings for both positions of the commutator were close together. A slightly different value of R_2 gave a further two readings on the ratio arms. The average conductivity value was now obtained from the two pairs of ratio arm readings. Further additions from the weight burette were made until the concentration of potassium chloride in the cell reached about 0.001N. The cell was then removed from the thermostat and, after cleaning and drying its outer surface, it was weighed full and then again, after emptying and drying with acetone. Evaporation during the run was invariably found to be negligible. The weight of solution in the cell for each concentration was calculated from the known weights of potassium chloride added.

The conductivity of the water was corrected for the interionic attraction effects of increasing potassium chloride concentrations on dissolved carbon dioxide[60], and these amended solvent corrections were subtracted from the average conductivity values of the cell solutions, obtained as described above. The cell constant was then calculated by comparing these measured values with the conductivity values at the same concentrations, derived by Shedlovsky[61], and corrected by Jones and Bradshaw[62]. For this, the interpolation formula of Davies[63]:-

$$\Lambda_c = 149.92 - 93.85c^{\frac{1}{2}} + 50c$$

was employed.

The cell constant of cell C was evaluated from sixteen determinations (four series), and a mean value of 0.09311 ± 0.05% was obtained. After a short period in use, trouble with a leak at the platinum-glass-araldite seal led to the pair of electrodes being remounted. A series of twelve determinations (three series) on this cell, cell C', resulted in a mean value of cell constant of 0.09358 ± 0.03%. Another cell was later introduced, and again twelve determinations (three series) were carried out, giving 0.07000 ± 0.07% as the cell constant of cell A.

PART 1

Crystallisation and Dissolution of the Silver Chloride Electrode in Aqueous Solutions.

Introduction

Crystal growth can generally be represented by an equation of the form

$$\frac{dm}{dt} = ks\ (m_t - m_o)^n \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k is the rate constant and s is a surface area function. Values of n of 2,3,4 and as high as 8 have been reported, but the higher values have been obtained in studies of nucleation rather than growth.

In a study of the growth of silver-chloride seed crystals, Davies and Jones[44] found a value of $n = 2$, and proposed that the reaction was interface controlled. The adsorption layer theory of growth[29] postulated an adsorbed monolayer of ions at the crystal surface, and Davies and Jones developed this on the following two assumptions :

(1) A crystal in contact with an aqueous solution always tends to be covered with a monolayer of hydrated ions, and secondary adsorption on this monolayer is negligible.

(2) Crystallisation occurs through the simultaneous dehydration of stoichiometrical proportions of cations and anions.

A saturated solution exists when the rate of adsorption of ions from the solution becomes just sufficient to maintain the monolayer of hydrated ions intact, and it is considered that every ion striking the surface enters this mobile adsorbed layer. Then the rate of adsorption of cations $= k_1 s \left[C_o{}^{c+}\right]$, and of anions $= k_1 s \left[A_o{}^{a-}\right]$, the subscript zero indicating the solubility value of each ion species. In an unsaturated solution, ions leave the surface faster than they are replaced, whereas in a supersaturated solution, not all the ions reaching the surface enter the monolayer, those which do not, $([C_t{}^{c+}] - [C_o{}^{c+}])$ for cations and $([A_t{}^{a-}] - [A_o{}^{a-}])$ for anions, being available for deposition. These ions either suffer elastic collisions at the surface of the monolayer, or, when the ions arrive simultaneously in stoichiometric proportions at sites suitable for growth, the underlying ions may become dehydrated and incorporated into the crystal lattice. For a symmetrical electrolyte, <u>c</u> = <u>a</u>, and the rate equation becomes

$$
\begin{aligned}
-\frac{dm}{dt} &= k\,([C_t{}^{c+}] - [C_o{}^{c+}])([A_t{}^{a-}] - [A_o{}^{a-}]) \\
&= k\,(m_t - m_o)^2 \qquad . \quad . \quad . \quad . \quad . \qquad (3)
\end{aligned}
$$

A similar rate equation has been derived by Walton[64], who considered that the adsorption of ions upon sols of the same material followed the Gibbs Adsorption Isotherm

$$\Gamma_{C^+} = k_1.\ln\,[C^+] + \text{constant}_1 \qquad . \quad . \quad . \qquad (4)$$

where ${}_{C^+}$ represents the total concentration of adsorbed cations. A similar expression holds for anions

$$\Gamma_{A^-} = k_2.\ln\,[A^-] + \text{constant}_2 \qquad . \quad . \quad . \qquad (5)$$

The rate of surface reaction per unit area may be expressed as

$$J = -k \; (C^{+} + A^{-}) \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

By substitution from equations (4) and (5), equation (6) becomes

$$J \simeq \frac{k \, . k_1 . k_2}{c_o^2} \; (c_t - c_o)^2 \quad . \quad . \quad . \quad . \qquad (7)$$

in the special case where the ionic concentrations are equivalent and $c_t \rightarrow c_o$. Similar expressions can be derived for non-equivalent ionic concentrations, and non-symmetrical electrolytes.

On the basis of assumptions very similar to those of Davies and his co-workers, Doremus[65] has suggested two mechanisms by which the ions adsorbed on the crystal surface may combine stoichiometrically and be incorporated into the crystal lattice. In the first, the adsorbed ions combine in the surface layer to form neutral salt molecules, which diffuse over the crystal surface until they reach a suitable growth site. To explain certain third order dependencies for 1:1 electrolytes, he assumed, by analogy with gas phase reactions, that an additional ion stabilises the surface molecule as it is formed by removing some of the hydration from the combining ions. In the second model, the adsorbed ions collide directly with a kink in the growth step, resulting in the alternate incorporation of cations and anions into the crystal lattice.

Doremus proposed that for the first model, the rate of precipitation should be proportional to $(m_t - m_o)^3$ for 1:1 and

2:2 electrolytes, and to $(m_t - m_o)^4$ for 2:1 electrolytes. With the alternate mechanism however, the rate of growth should vary with the second power of the solute concentration for symmetrical electrolytes, and with the third power for 2:1 electrolytes. At high supersaturations therefore, conditions should favour the first model and, at lower concentrations, the second should apply.

Results of experiments on the spontaneous crystallisation of barium sulphate[40,41] and silver chromate[66] are in agreement with the first mechanism. On the other hand, the crystallisations on added seed crystals of barium sulphate[47], silver chloride[44] and silver chromate[45] have been shown to fit the second model. The initial supersaturations in the spontaneous crystallisation experiments, however, were much higher than those used in the seeded growth experiments, and Doremus considered that this explained the apparently conflicting results. It is also possible to explain the concentration dependencies in terms of the first model only. For the seeded growth experiments, the rate determining step may be the formation of an ion pair or neutral molecule in the monolayer, and the presence of a third particle need not be assumed.

In the above theories of growth, it was assumed that the adsorbed monolayer contained equal numbers of positive and negative ions, but this will rarely be so. If one ion is adsorbed more strongly than the other, due to differences in the adsorption energies, the surface will assume an electrical charge, and an electrical double layer will be set up around the particle. For concentration ratios equal or almost equal to the stoichiometric one, the effect of this selective adsorption will be negligible.

A different situation holds when the ionic concentrations are non-equivalent. When seed crystals are added to a solution in which $[C^{x+}] : [A^{x-}] = \underline{r}$, where $\underline{r} > 1$, more C^{x+} ions will be adsorbed and a potential difference ψ will be set up between the crystal and the solution. An electrical double layer now surrounds the crystals, and the value of ψ is such that cations and anions can enter the adsorbed layer in equal amounts.

The availability of cations at the surface $= k_1 s[C^{x+}] \exp.(-\psi/RT)$ and the availability of anions at the surface $= k_2 s[A^{x-}] \exp.(\psi/RT)$.

These are equal and therefore

$$\begin{aligned}\exp.(\psi/RT) &= [C^{x+}]^{\frac{1}{2}}/[A^{x-}]^{\frac{1}{2}}\\ &= r^{\frac{1}{2}}\end{aligned}$$

The number of ions of each kind entering the monolayer is, as before, m_o, and the rate of crystallisation is

$$\begin{aligned}-\frac{dm}{dt} &= ks\ (\ [C^{x+}]r^{-\frac{1}{2}} - m_o\ )(\ [A^{x-}]r^{\frac{1}{2}} - m_o\ )\\ &= ks\ (\ [C^{x+}]^{\frac{1}{2}}.[A^{x-}]^{\frac{1}{2}} - m_o\ )^2 \qquad . \quad . \quad . \quad (8)\end{aligned}$$

With equivalent ionic concentrations, this equation reduces to equation (3). The crystallisation of symmetrical electrolytes should therefore be a second order reaction, even when the initial concentrations are non-equivalent, and this has been shown to be the case with silver chloride[44]. The crystal growth of magnesium oxalate[46] and barium sulphate[47] also followed the second order rate equation, but if insufficient seed crystals were added, the initial growth was complicated by nucleation effects. Additional growth sites were provided by spontaneous nucleation in the bulk of the solution in the magnesium oxalate experiments, and by two-dimensional nucleation on the surface of the barium sulphate seed crystals. The crystallisation of lead sulphate[48] was similar to that of barium sulphate except that the growth was not second order with non-equivalent initial ionic concentrations.

It has been shown above (page 6) that dissolution can generally be regarded as a diffusion-controlled reaction, and can be represented by the first order equation

$$\frac{dm}{dt} = ks\ (m_o - m_t).$$

Although the dissolutions of silver chloride and silver chromate[45] into subsaturated solutions follow this equation, the solution of sparingly soluble salts is not always a straightforward diffusion-controlled process. Little has shown that the dissolutions of barium sulphate and lead sulphate are second order reactions[48], and suggests that a step occurring at the crystal surface is rate determining. The lattice energy of silver chloride is much less than for the 2:2 electrolytes, and therefore much less energy is required to remove the ions from the crystal, and the subsequent diffusion of hydrated ions away from the surface will be the slowest step. For the 2:2 electrolytes, the reaction at the surface may be slower than the rate of diffusion, resulting in the observed second order kinetics.

Burton, Cabrera and Frank[15] proposed that dissolution should occur by monomolecular steps retreating across the crystal surface as individual molecules are removed from kinks in the surface. Gilman, Johnston and Sears[67] have stated that the dissolution of a perfect crystal in a solvent begins by the creation of unit pits, one molecule deep, which grow as above. On a real crystal, dislocations are likely to be preferred sites for the initiation of such unit pits, and it may be assumed that dissolution proceeds from these sites of localised high energy on the crystal faces.

The energy of the dislocation will be lowered, however, by the presence of impurity molecules, since these will adsorb at the active sites, and the rate of formation of unit pits, and hence the rate of solution, will be reduced. In the dissolution of lithium fluoride crystals[67,68], etch pits were formed due to traces of ferric ions, and when this was complexed by the addition of ammonium hydroxide, uniform dissolution with few etch pits was obtained. Sears proposed that the formation of such etch pits at a dislocation occurred by the generation of loops, of step concentric with the dislocations, and these could not be formed unless an impurity was present. Etch pits become deeper as the concentration of impurity increases, since the poison inhibits the movement of monomolecular steps, and solution therefore proceeds faster into the crystal than over its surface.

Crystal growth is also affected by the presence of impurity, and Sears considered that small molecules tend to be adsorbed at kinks on the growth steps[69], monostep coverage being necessary to cause an appreciable reduction in the rate of step motion[70]. Further advance of a growth step, once poisoned, can only occur by nucleation of a new step of substrate atoms at the affected step. Adsorption of impurity at a step should reduce the critical energy for two-dimensional nucleation and result in an increase in the rate of surface nucleation, and this has been observed[71] with lithium fluoride, where traces of ferric ions hindered step motion and caused an appreciable increase in two-dimensional nucleation on perfect crystal surfaces.

The crystallisation of a silver chloride electrode from solutions of equivalent initial ionic concentrations has been shown to follow a second order rate law, although an induction effect was observed when traces of impurity were present. The dissolution of an electrode into water and non-equivalent solutions has also been studied, and it has been found to be a first order reaction throughout.

Experimental

Preparation of the Silver Chloride Electrode

The silver-silver chloride electrode was prepared electrolytically by the deposition of both silver and silver chloride[72]. Potassium argentocyanide, used for silver plating, was prepared as follows. A slight excess of 0.8N silver nitrate was added to 400ml. of 0.8N potassium cyanide, and the precipitate of very insoluble silver cyanide was thoroughly washed about twenty times with distilled water, and left as a damp slurry. The whole operation was carried out in complete darkness, since silver cyanide proved to be extremely light sensitive. A slight excess of silver cyanide was added to 50ml. of a hot 20% solution of potassium cyanide and, after stirring for 30 minutes, the excess was filtered off. The solution was boiled to concentrate and, when chilled in ice, white crystals of potassium argentocyanide separated out and were filtered off in a sintered glass filter. The product was recrystallised from water and dried in a dessicator; it appeared to be completely insensitive to sunlight.

The silver-plating solution was prepared by dissolving 5gms. of potassium argentocyanide in 500ml. water. Free cyanide was removed by adding sufficient dilute silver nitrate solution to produce a faint cloud of silver cyanide, which was allowed to settle, and the clear solution decanted. It was necessary to reduce the free cyanide in the solution to a minimum each time before use, since cyanide ion adsorbed on the silver plated electrode can lead to reduction of the silver chloride prepared in the following stage[73].

The electrode base was prepared from a platinum sheet, 4cm. by 1cm. in area, which was bent into a half-cylindrical shape. The sheet was spot welded to a platinum wire, which was sealed into a glass tube, araldite being used as a final seal. The platinum sheet was cleaned in boiling concentrated nitric acid, and made the cathode in the silver-plating solution, the anode also being of platinum. The electrolysis was carried out for 24 hours at a current of 2 milliamperes, and the electrode, which was off-white in colour, was carefully washed and left overnight in distilled water.

The sheet was chloridised by electrolysis for 5 hours using a platinum cathode in 0.1N hydrochloric acid solution at a total current of 2 milliamperes. The electrode, which was purplish brown in colour and unaffected by sunlight, was washed thoroughly and stored in distilled water. Eleven electrodes were prepared by this method, and they were all similar in colour and behaviour, the greyish patches reported by Brown[72] on chloridising at a lower current density than 0.6 milliamperes per square cm. never being present.

Preparation of Seed Suspension

Silver chloride was prepared by mixing equivalent amounts of analar silver nitrate and analar potassium chloride solutions, the precipitate being washed free from chloride ions with distilled water. An excess was added to distilled water and the solution was boiled for about two hours and rapidly filtered into preheated flasks, lagged with cotton wool. Crystallisation of silver chloride occurred on cooling slowly, and the crystals were washed twelve times with distilled water and eight times with conductivity water. They were transferred to a blackened and waxed pyrex stock bottle, and the suspension was allowed to age for at least one month before use. All the above operations were carried out under photographic safety lamps.

Concentrations of seed in the suspensions were directly determined to within 1% by filtering the cell solutions through small, weighed sinter-glass filter tubes, and drying to constant weight at 120°C[74]. It was normally about 0.5 mg. $ml.^{-1}$, and the crystals were all in the size range 2 - 7 microns, the average of a hundred measurements being 5 microns.

Preparation of Cell Solutions

The cell solution was prepared by the addition of 10ml. portions of the dilute solutions of silver nitrate and potassium chloride. The solution was allowed to come to temperature and carbon dioxide equilibrium, and the silver chloride electrode or 5ml. of seed crystals in suspension were introduced. Growth commenced and the reaction was followed by measuring the conductivity at suitable time intervals.

The Solubility of Silver Chloride

The solubility of silver chloride in water has been determined by many workers and early published data showed a wide range of values. Not only did values obtained by the conductimetric and potentiometric methods disagree, but independent investigators using the same method obtained results which differed by as much as 15%. It was suggested[75,76] that the discrepancies were largely due to a real difference in solubility between samples of silver chloride prepared by different methods. Recent results obtained by different techniques with samples prepared in a variety of ways, however, show a remarkable consistency. Owen[76], using potentiometric methods, found the solubility at 25° to be 1.334×10^{-5} mole.litre^{-1} for silver chloride prepared by chloridising silver oxide. Gledhill and Malan[77], investigating the relationship between the solubility and the physical state of silver chloride, found the solubility to be $(1.334 \pm 0.005) \times 10^{-5}$ mole.litre^{-1}, and the thermodynamic solubility product

$$K_o = [Ag^+][Cl^-].f_1^2$$
$$= (1.774 \pm 0.010) \times 10^{10} \text{ mole}^2.\text{litre}^{-2}.$$

Both conductimetric and potentiometric techniques were used on precipitated and electrolytic silver chloride respectively, and the results were found to agree to within the limits shown. It was also discovered that the solubility did not vary significantly with age of precipitate. Later values in excellent agreement with the above are those of Guggenheim and Prue[78], who found the solubility, corrected to zero ionic strength, s_o, to be 1.327×10^{-5} mole.litre^{-1}, giving $K_o = 1.761 \times 10^{-10}$ mole^2.litre^{-2}. Davies and Jones[44] obtained $s_o = 1.334 \times 10^{-5}$ mole.litre^{-1} and $K_o = 1.765 \times 10^{-10}$, and these values were used in the present work.

In the experiments, the solubility was calculated at each Ionic Strength, using activity coefficients obtained from the Davies' equation[79]:

$$-\log f_z = 0.5092\ z_1.z_2\left[(I^{\frac{1}{2}}/1+I^{\frac{1}{2}}) - 0.2I\right] \quad . \quad . \quad . \quad (9)$$

where $I = \frac{1}{2}\sum m_i.z_i^2$ is the Ionic Strength.

Conductivity Equations and Equivalent Conductivity

Concentrations were calculated from the observed conductances using the equation :

$$m = \frac{10^3 \times \text{cell constant} \times R^{-1}}{\Lambda} \quad . \quad . \quad . \quad (10)$$

Λ, the equivalent conductivity at the ionic strength of the experiment, was obtained from the Onsager equation[80] which, for an electrolyte in water at 25°, may be written :

$$\Lambda = \Lambda_o - \left[\frac{0.5527 \; |z_1 . z_2| \; q}{1 + q^{\frac{1}{2}}} \Lambda_o + 21.29 \; (|z_1| + |z_2|) \right] \Gamma^{\frac{1}{2}}$$

where Γ, the ional concentration, $= \sum m_i . z_i^{\;2}$, and

$$q = \frac{|z_1 . z_2| (\lambda_1^{\circ} + \lambda_2^{\circ})}{(|z_1| + |z_2|)(|z_1| \lambda_2^{\circ} + |z_2| \lambda_1^{\circ})} \qquad (= \tfrac{1}{2}, \text{ for}$$

symmetrical electrolytes.)

z_1 and z_2 are the valencies of the two ions, and λ_1° and λ_2° are their limiting ionic conductivities. The constants in this equation incorporated the values recommended in 1952[81] for the fundamental physical constants, and the values of dielectric constant and viscosity of water, 78.54[82] and 0.008949[83] respectively.

$\lambda^{\circ}_{Ag^+}$ and $\lambda^{\circ}_{Cl^-}$ are respectively 61.92[84] and 76.34[84,85,86], and therefore

$$\Lambda_{AgCl} = 138.26 - 91.85m^{\frac{1}{2}}.$$

During an experiment, the ionic concentrations of silver and chloride changed by less than 0.1%, and the equivalent conductivity was therefore effectively constant. Experimental conductances of the cell solutions always agreed with those calculated on the basis of strict additivity of conductivities to better than 0.5%.

Results

In the crystallisation experiments, smooth curves were obtained relating the reciprocal of resistance with time, and these are shown in Figures 3 and 4 for the experiments with equivalent initial concentrations of silver and chloride ions. The change in ionic concentration was obtained from equation (10), and the concentration of either ion at any stage in an experiment was given by $m_t = m_i - \Delta m$, where m_i was the initial concentration of the silver and chloride ions. The rate of fall of conductivity at any instant, and therefore the rate of crystallisation, was determined from measurements of the slope of the conductivity-time curve. From these $-\Delta R^{-1}/\Delta t$ values, the rate of crystallisation, expressed as the rate of change of concentration of silver chloride in the supersaturated solution, was calculated using equation (10).

The experiments are summarised in Table 1, and plots of the rate of crystallisation, $\Delta m/\Delta t$, against $(m_t - m_o)^2$ are shown in Figure 5. The integrated form of the second order equation :

$$-\frac{dm}{dt} = ks\ (m_t - m_o)^2 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

may also be used to test the kinetics, and Figures 6 and 7 show $\{(m_t - m_o)^{-1} - (m_i - m_o)^{-1}\}$ plotted against t. In all the crystal growth experiments, after an initial induction period, equation (11) was followed for at least 51% of the reaction.

The factor s, in equation (11), is some unknown function of the surface area, but since the change in surface area of a silver chloride electrode during crystallisation or dissolution was negligible, any variation in s has been disregarded in the present work, and it has been incorporated in the rate constant. The rate constant, ks, is obtained from the gradients of the straight lines in the above graphs, and the values are given in Table 1.

Figure 5 shows the reproducibility of the results for Experiments 22 and 23. In this graph, the induction period, which is in any case very short, has been omitted. Linear second order plots for Experiments 11, 21 and 24 are shown in Figure 6. Experiment 24 was done using an electrode less than two days old, whereas Experiment 11, which showed a more pronounced induction effect, involved the use of an electrode which had aged for 30 days. Experiment 21 was seeded with silver chloride seed crystals, aged for many months.

The rate constants for Experiments 5, 11, 22 and 23 agree well, and $\underline{ks}$ = 1340 ± 50 litre.mole^{-1}.min^{-1}. In each of these cases, the electrodes had been allowed to age for at least 10 days before use. In Experiment 24, where a fresh electrode, less than two days aged, was used, the significantly higher $\underline{ks}$ value of 1950 litre.mole^{-1}.min^{-1}. was obtained.

5 ml. of seed suspension (containing 0.5 mg.ml.$^{-1}$) was used in Experiment 21, and the rate constant, $\underline{ks}$, was 4970 litre.mole^{-1}.min^{-1}. Assuming the seed crystals to be regular cubes, their actual surface area can be estimated from the mean crystal size of 5μ and the density of silver chloride of 5.6[87]. The result is 1.06 cm^2 per ml. suspension, and when this value is assigned to $\underline{s}$, k equals 930 litre.mole^{-1}.min^{-1}.cm^{-2}. This result is in good agreement with the value of approximately 900 litre. mole^{-1}.min^{-1}.cm^{-2}. reported by Davies and Jones[44]. The silver

chloride electrode has a surface area of 8 $cm.^2$, and consequently **k** = 170 $litre.mole^{-1}.min^{-1}.cm^{-2}$. These values indicate that the number of growth sites per unit area of electrode surface is much less than for the same surface area of seed crystals.

An outstanding feature of crystallisation on an electrode was the initial induction period, the duration of which increased with the age of the electrode. In some experiments the induction period accounted for as much as 20% of the total silver chloride to be deposited (Experiment 5). The average amount was less than 10%, or about 0.02×10^{-5} $mole.litre^{-1}$. Repeated use of an electrode greatly increased the induction effect, and in Figure ~~5~~7, crystal growth on electrodes which were being used for the first and third times, is compared (Experiments 22 and 5 respectively). Moreover after a third use, no crystallisation occurred in the first two hours after inserting the electrode.

At this stage of the work, the method of preparing the conductivity water was changed. The use of a mixed bed ion exchange resin column was discarded in favour of conductivity water prepared in a Bourdillon Still. In Figure 8, conductivity vs. time curves are given for Experiments 27 and 30. Experiment 27 was made using a fresh electrode prepared just over a day previously, and Figure 9 shows that no induction period was present and second order kinetics were followed for as much as 70% of the reaction. The inoculating electrode used in Experiment 30 had been fully aged, and Figure 10 shows that there was no appreciable delayed crystallisation effect. It is very probable

TABLE 1

Crystallisation of Silver Chloride

Experiments in Deionised and Distilled Waters.

Expt No.	$m_i \times 10^5$ moles/l.	$[Ag^+][Cl^-] \times 10^{10}$ $(\text{moles}/l)^2$	Electrode		ks $\times 10^{-3}$ $l.\text{mole}^{-1}.\text{min}^{-1}$.
			No.	Age (days)	
5	1.588	2.522	2	13	1.390
11	1.588	2.522	3	30	1.290
21	1.541	2.375	5ml.	Seed a	4.970
22	1.524	2.324	4	20	1.300
23	1.524	2.324	4	24	1.335
24	1.524	2.324	5	2	1.950
27	1.482	2.196	6	2	6.250
30	1.524	2.324	7	7	2.690

Solubility = $1.336_5 \times 10^{-5}$ moles/l.

Solubility Product = 1.786×10^{-10}

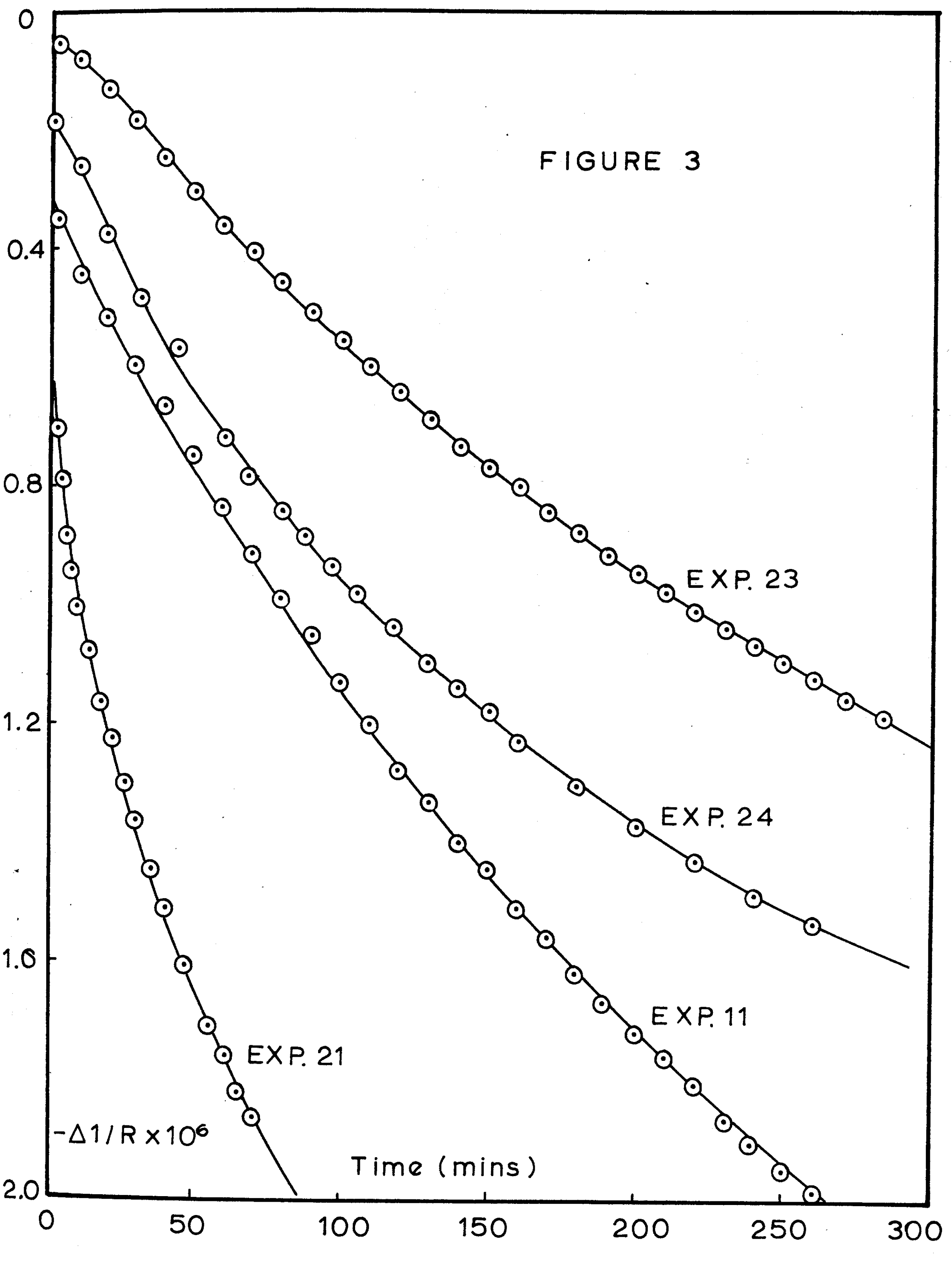


FIGURE 3
EXP. 23
EXP. 24
EXP. 11
EXP. 21
$-\Delta 1/R \times 10^6$
Time (mins)
0
0.4
0.8
1.2
1.6
2.0
0
50
100
150
200
250
300

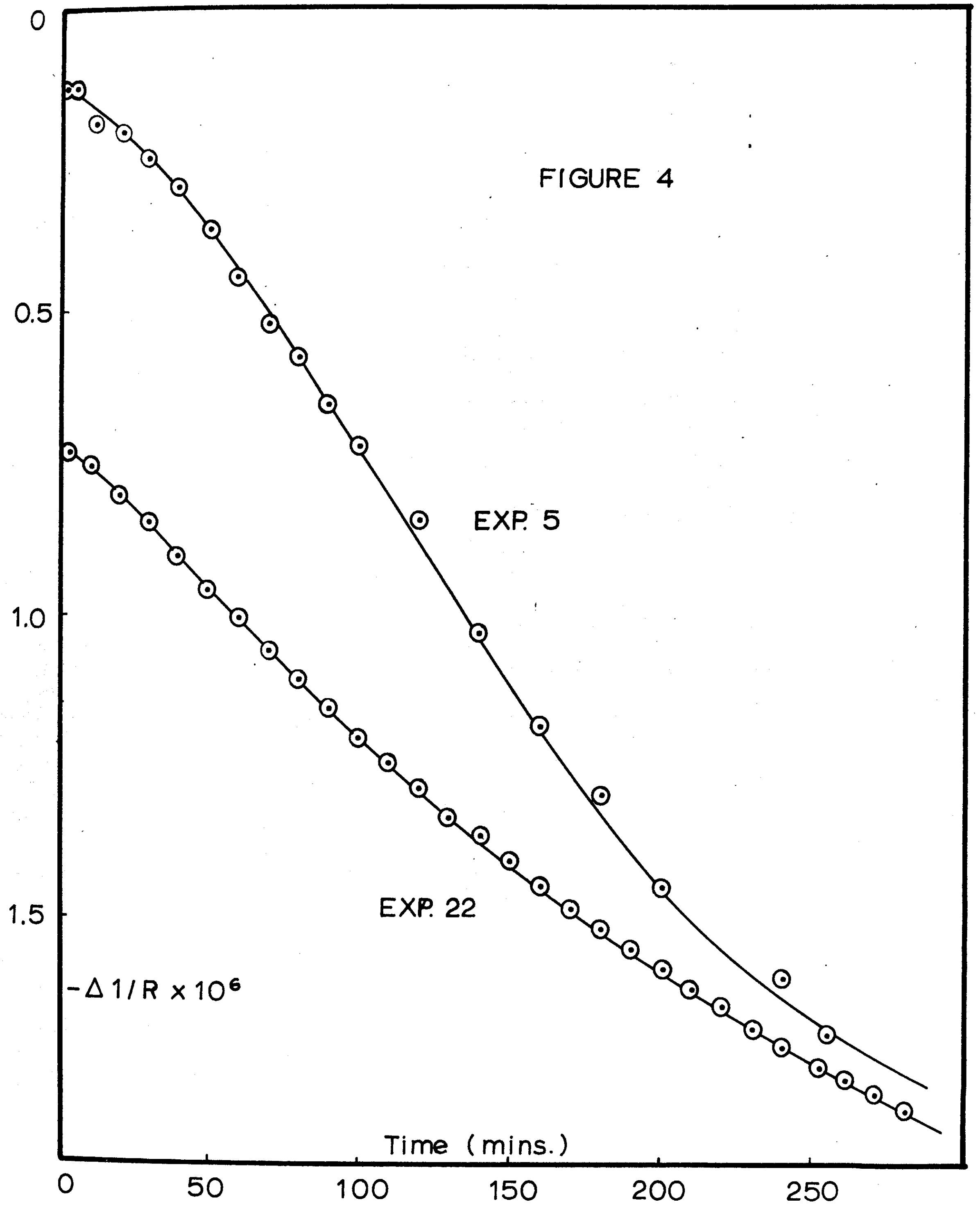


FIGURE 4
EXP. 5
EXP. 22
-Δ 1/R x 10⁶
Time (mins.)
0
0.5
1.0
1.5
0
50
100
150
200
250

TABLE 2

Crystallisation of Silver Chloride

$1/R$ $\times 10^5$ ohm^{-1}	$-\Delta m$ $\times 10^6$ mole/l	m_t $\times 10^5$ mole/l	$(m_t - m_o)$ $\times 10^6$ mole/l	$(m_t - m_o)^2$ $\times 10^{12}$ mole^2/l^2	$-\Delta\frac{1}{R}/\Delta t$ $\times 10^9$ m/l/min	$-dm/dt$ $\times 10^9$ m/l/min
Experiment 22.						
4.8575	0.000	1.5244	1.879	3.531	--	--
4.8250	0.221	1.5023	1.658	2.749	4.99	3.39
4.8100	0.322	1.4922	1.557	2.424	4.50	3.05
4.7950	0.424	1.4820	1.455	2.117	4.06	2.75
4.7800	0.526	1.4718	1.353	1.831	3.40	2.31
4.7650	0.628	1.4616	1.251	1.565	3.08	2.09
4.7500	0.729	1.4515	1.150	1.323	2.51	1.70
Experiment 23.						
4.7650	0.000	1.5244	1.879	3.531	--	--
4.7300	0.237	1.5007	1.642	2.696	5.20	3.53
4.7150	0.339	1.4905	1.540	2.372	4.60	3.12
4.7000	0.441	1.4803	1.438	2.068	4.10	2.78
4.6850	0.543	1.4701	1.336	1.785	3.63	2.46
4.6700	0.644	1.4600	1.235	1.525	3.00	2.04
4.6550	0.746	1.4498	1.133	1.284	2.61	1.77

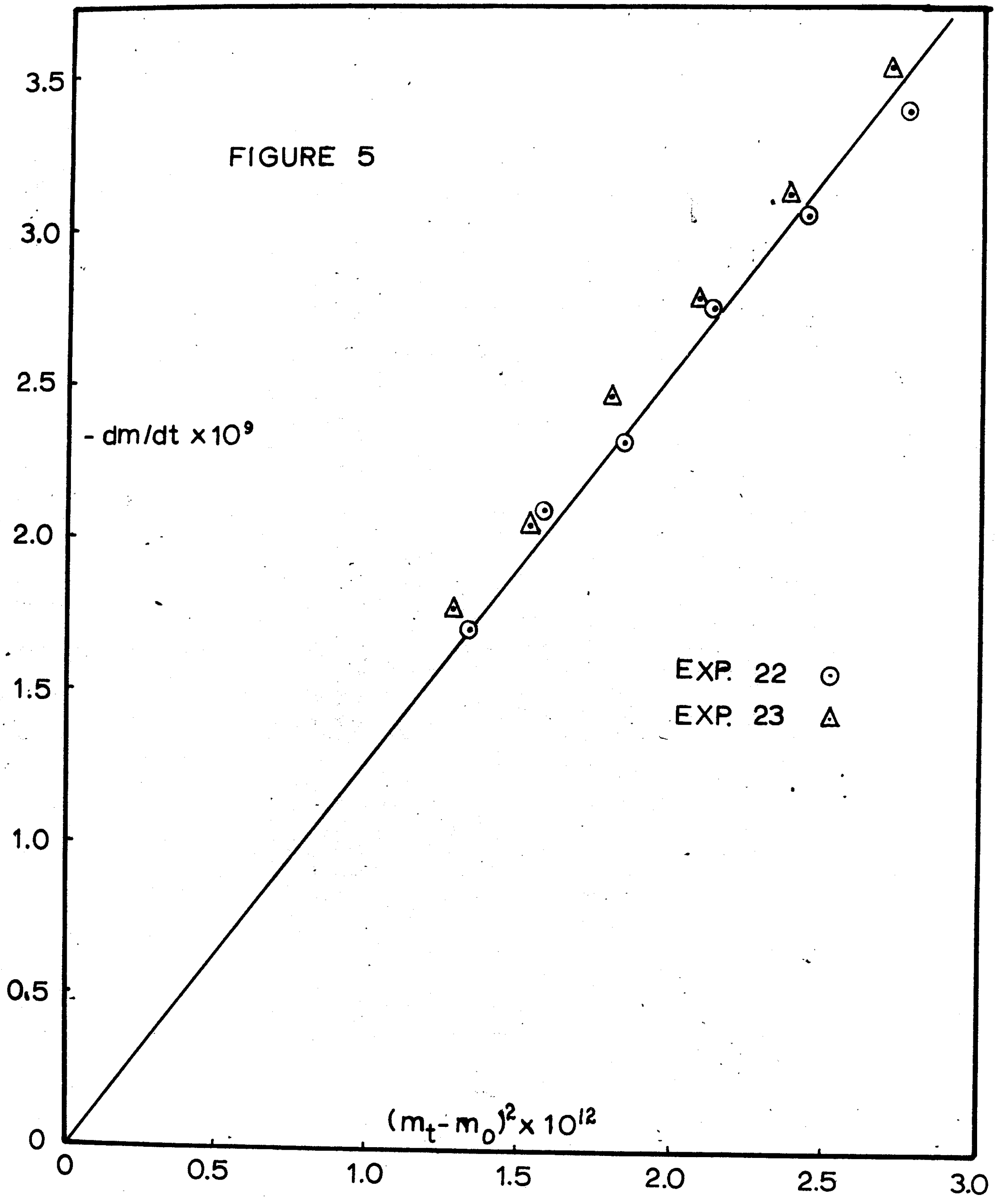


FIGURE 5

- dm/dt × 10^9
$(m_t - m_0)^2 \times 10^{12}$
EXP. 22 ⊙
EXP. 23 △
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
0.5
1.0
1.5
2.0
2.5
3.0

TABLE 3

Crystallisation of Silver Chloride

t mins	$1/R$ $\times 10^{5}$ ohm^{-1}	$-\Delta m$ $\times 10^{6}$ mole/l	m_t $\times 10^{5}$ mole/l	$(m_t - m_o)$ $\times 10^{6}$ mole/l	I* $\times 10^{-5}$ (mole/l)$^{-1}$
Experiment 11.					
0	5.159	0.000	1.588	2.519	0.00
40	5.124	0.236	1.565	2.283	0.41
80	5.091	0.455	1.543	2.064	0.88
120	5.063	0.650	1.523	1.869	1.38
160	5.040	0.806	1.508	1.713	1.87
200	5.018	0.950	1.493	1.569	2.40
240	5.000	1.076	1.481	1.443	2.96
280	4.984	1.182	1.470	1.337	3.50
Experiment 21.					
0	4.820	0.000	1.541	2.046	0.00
10	4.780	0.271	1.514	1.775	0.73
20	4.762	0.390	1.502	1.656	1.14
30	4.746	0.502	1.491	1.544	1.59
40	4.731	0.604	1.481	1.442	2.05
50	4.718	0.694	1.472	1.352	2.51
60	4.706	0.775	1.464	1.271	2.98
70	4.695	0.848	1.456	1.198	3.46
80	4.686	0.912	1.450	1.134	3.93

$$* \; I = (m_t - m_o)^{-1} - (m_i - m_o)^{-1}$$

TABLE 3 cont.

t mins	$1/R$ $\times 10^5$ ohm^{-1}	$-\Delta m$ $\times 10^6$ mole/l	m_t $\times 10^5$ mole/l	(m_t-m_o) $\times 10^6$ mole/l	I* $\times 10^{-5}$ $(\text{mole/l})^{-1}$
Experiment 24.					
0	4.772	0.000	1.524	1.879	0.00
10	4.764	0.055	1.519	1.824	0.16
20	4.753	0.132	1.511	1.747	0.40
40	4.735	0.252	1.499	1.627	0.83
60	4.719	0.358	1.489	1.521	1.25
100	4.695	0.524	1.472	1.355	2.06
150	4.671	0.682	1.456	1.197	3.03
200	4.653	0.805	1.444	1.074	3.99
260	4.637	0.916	1.432	0.963	5.06

$* \; I = (m_t-m_o)^{-1} - (m_i-m_o)^{-1}$

FIGURE 6

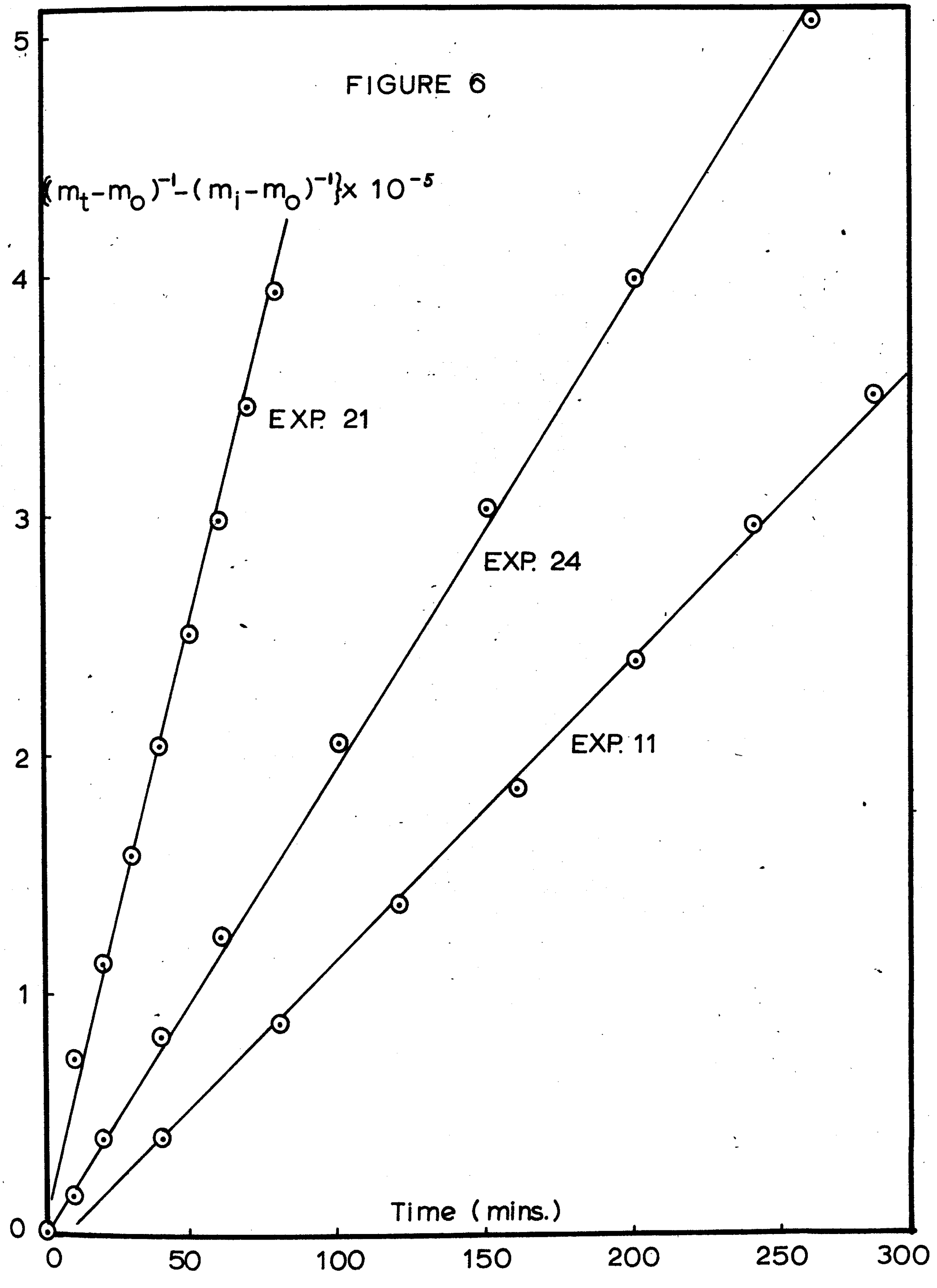

$\{(m_t-m_o)^{-1}-(m_i-m_o)^{-1}\}\times 10^{-5}$
5
4
3
2
1
0
EXP. 21
EXP. 24
EXP. 11
Time (mins.)
0
50
100
150
200
250
300

TABLE 4

Crystallisation of Silver Chloride

t mins	$1/R$ $\times 10^5$ ohm^{-1}	$-\Delta m$ $\times 10^6$ mole/l	m_t $\times 10^5$ mole/l	$(m_t - m_o)$ $\times 10^6$ mole/l	I* $\times 10^{-5}$ $(\text{mole/l})^{-1}$
Experiment 5.					
0	4.987	0.000	1.588	2.519	0.00
10	4.983	0.026	1.586	2.493	0.04
20	4.979	0.054	1.583	2.465	0.09
40	4.970	0.118	1.577	2.401	0.19
60	4.958	0.199	1.568	2.320	0.34
100	4.928	0.397	1.549	2.122	0.74
150	4.889	0.667	1.522	1.852	1.43
200	4.856	0.886	1.500	1.633	2.15
250	4.833	1.048	1.483	1.471	2.83
Experiment 22.					
0	4.858	0.000	1.524	1.879	0.00
10	4.854	0.022	1.522	1.857	0.06
20	4.850	0.052	1.519	1.827	0.15
30	4.845	0.084	1.516	1.795	0.25
40	4.840	0.121	1.512	1.758	0.37
60	4.829	0.192	1.505	1.687	0.61
100	4.810	0.323	1.492	1.556	1.11
150	4.789	0.462	1.478	1.417	1.74
210	4.768	0.605	1.464	1.274	2.53
280	4.748	0.743	1.450	1.136	3.48

$$* \; I = (m_t - m_o)^{-1} - (m_i - m_o)^{-1}$$

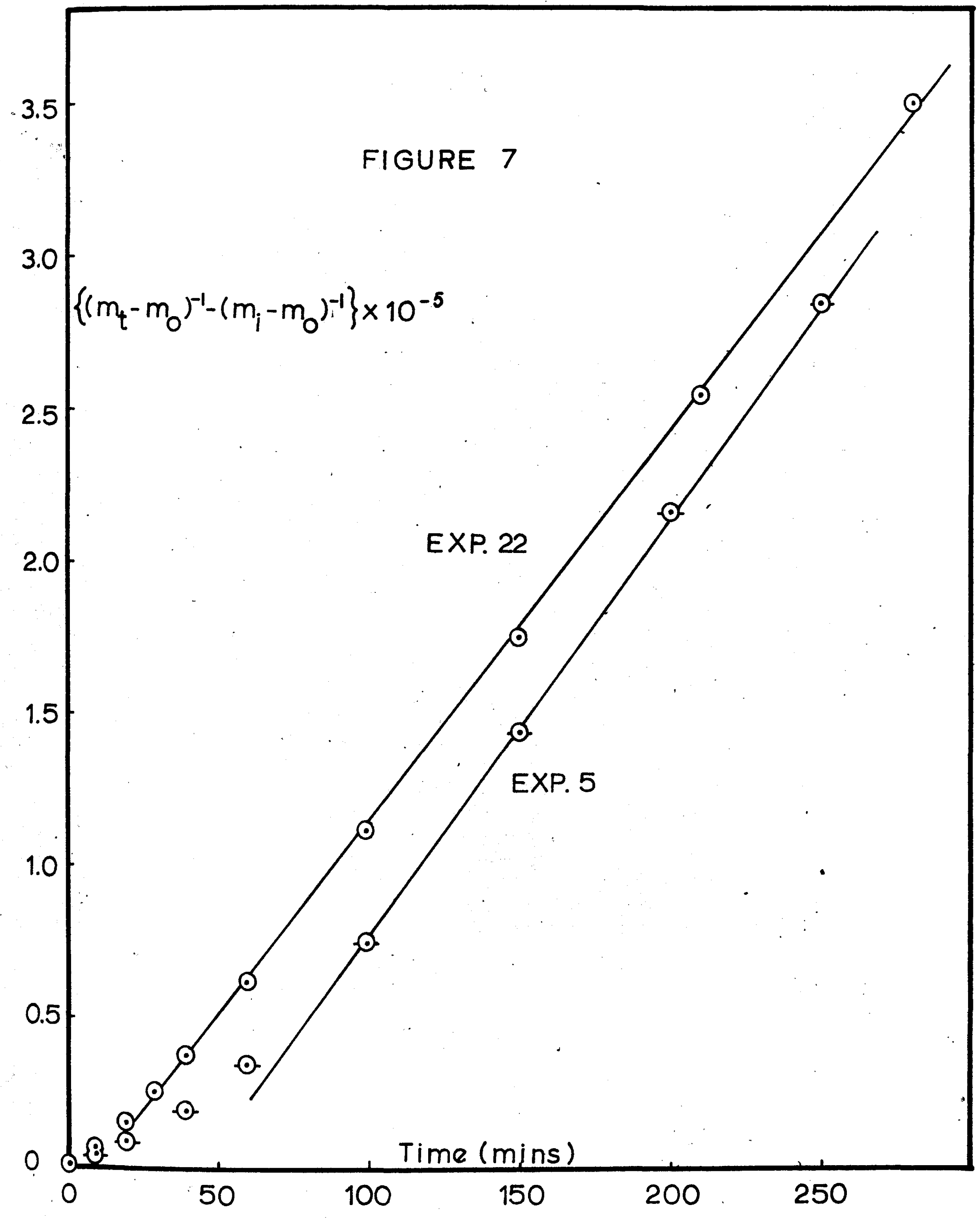


FIGURE 7

$\{(m_t - m_o)^{-1} - (m_i - m_o)^{-1}\} \times 10^{-5}$
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
EXP. 22
EXP. 5
Time (mins)
0
50
100
150
200
250

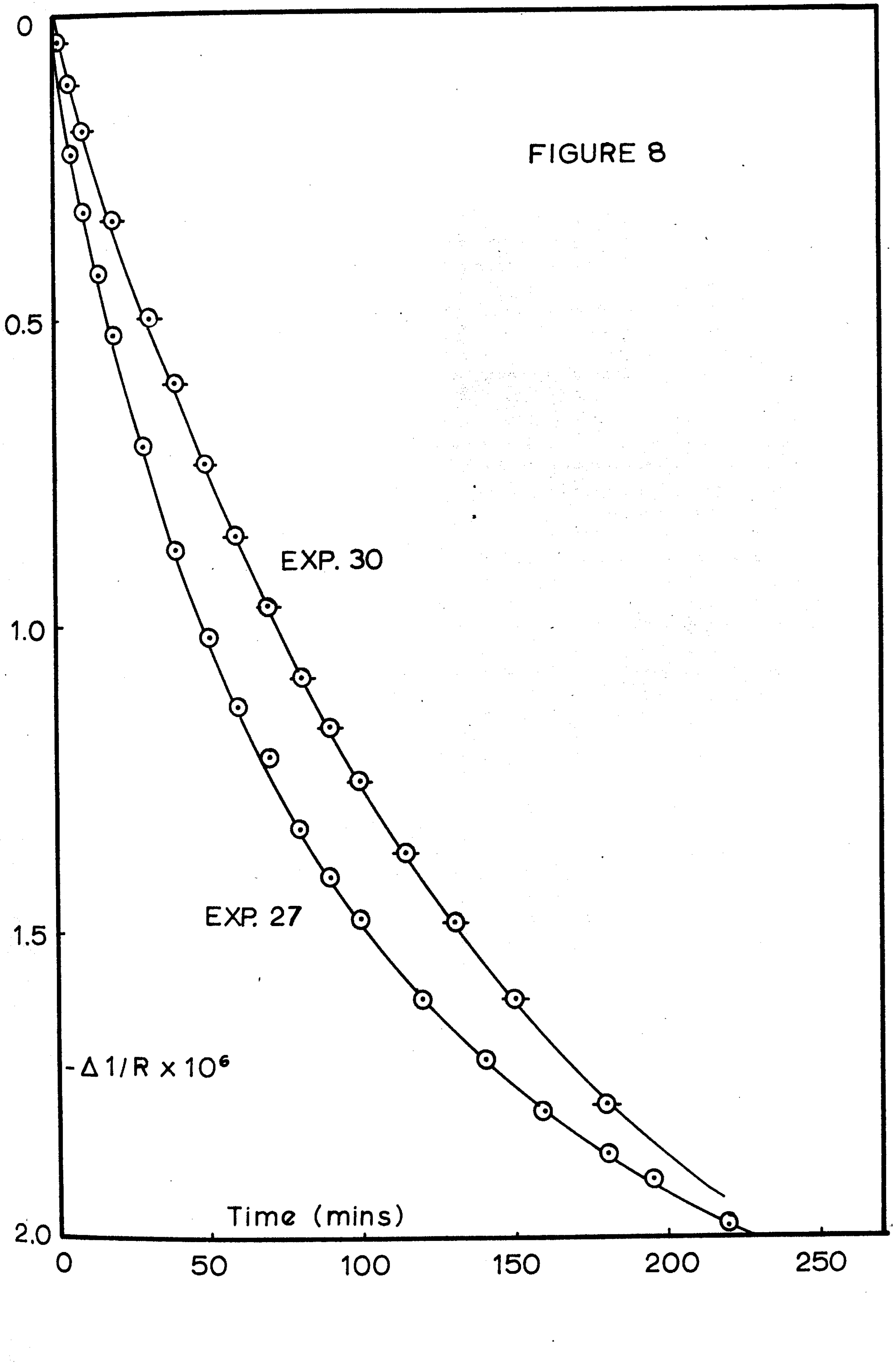


FIGURE 8
EXP. 30
EXP. 27
- Δ 1/R x 10⁶
Time (mins)
0
0.5
1.0
1.5
2.0
0
50
100
150
200
250

TABLE 5

Crystallisation of Silver Chloride

$1/R$ x 10^5 ohm^{-1}	$-\Delta m$ x 10^6 mole/l	m_t x 10^5 mole/l	$(m_t - m_o)$ x 10^8 mole/l	$(m_t - m_o)^2$ x 10^{12} $mole^2/l^2$	$-\Delta\frac{1}{R}/\Delta t$ x 10^8 m/l/min	$-dm/dt$ x 10^8 m/l/min
Experiment 27.						
6.360	0.000	1.482	1.456	2.120	--	--
6.340	0.101	1.472	1.355	1.836	2.27	1.152
6.320	0.203	1.462	1.253	1.570	1.84	0.934
6.300	0.305	1.452	1.151	1.325	1.66	0.843
6.280	0.406	1.441	1.050	1.102	1.48	0.751
6.260	0.508	1.431	0.948	0.900	1.13	0.574
6.240	0.609	1.421	0.847	0.717	0.90	0.457
6.220	0.711	1.411	0.745	0.555	0.65	0.330
6.200	0.812	1.401	0.644	0.415	0.46	0.233
6.180	0.914	1.391	0.542	0.293	0.34	0.173
6.160	1.015	1.380	0.441	0.194	0.26	0.132

TABLE 6

Crystallisation of Silver Chloride

t mins	$1/R$ $\times 10^5$ ohm^{-1}	$-\Delta m$ $\times 10^6$ mole/l	m_t $\times 10^5$ mole/l	(m_t-m_o) $\times 10^6$ mole/l	I* $\times 10^{-5}$ $(mole/l)^{-1}$
Experiment 30.					
0	6.716	0.000	1.524	1.879	0.00
2	6.713	0.013	1.523	1.866	0.04
4	6.710	0.029	1.521	1.850	0.08
6	6.707	0.045	1.520	1.834	0.13
8	6.704	0.060	1.518	1.819	0.18
10	6.701	0.076	1.517	1.803	0.22
25	6.679	0.186	1.506	1.693	0.59
50	6.646	0.353	1.489	1.526	1.23
90	6.603	0.571	1.467	1.308	2.32
115	6.583	0.676	1.457	1.203	2.99
130	6.572	0.731	1.451	1.148	3.39
150	6.559	0.797	1.445	1.082	3.92
180	6.542	0.884	1.436	0.995	4.73

* $I = (m_t-m_o)^{-1} - (m_i-m_o)^{-1}$

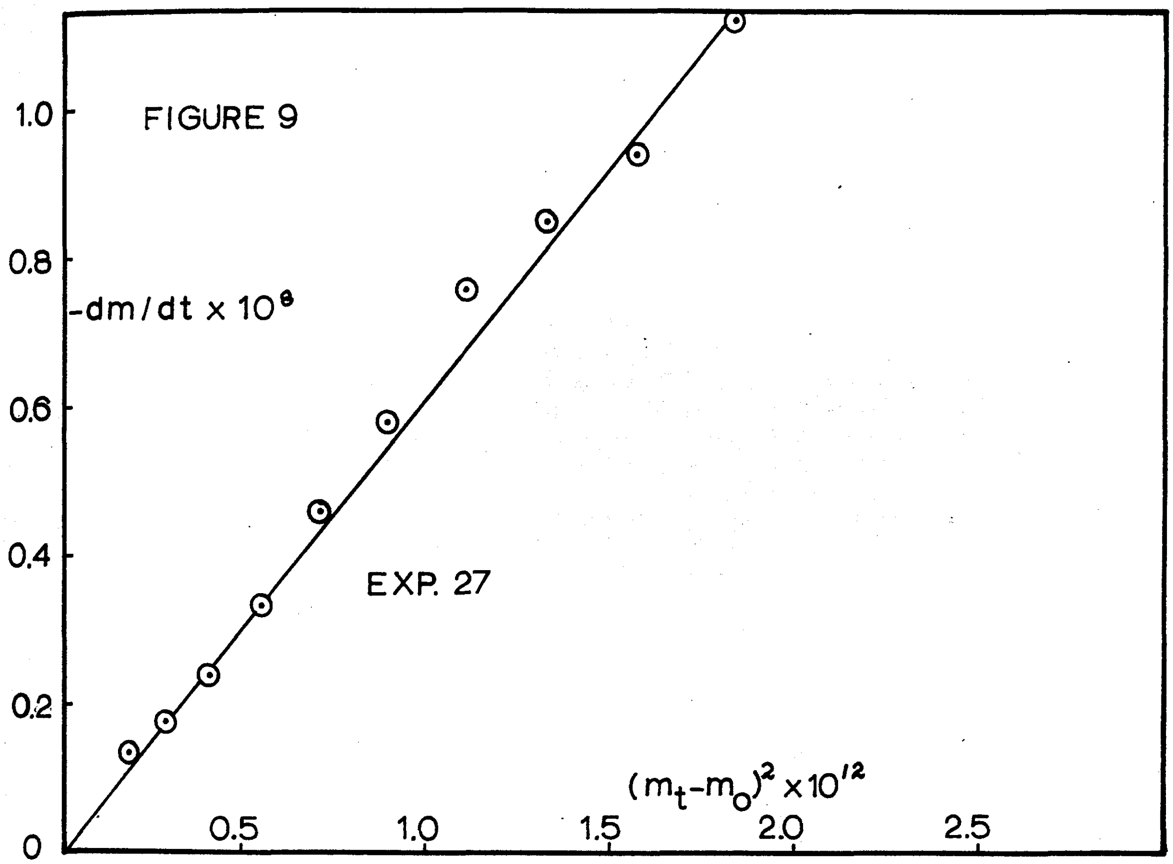


FIGURE 9

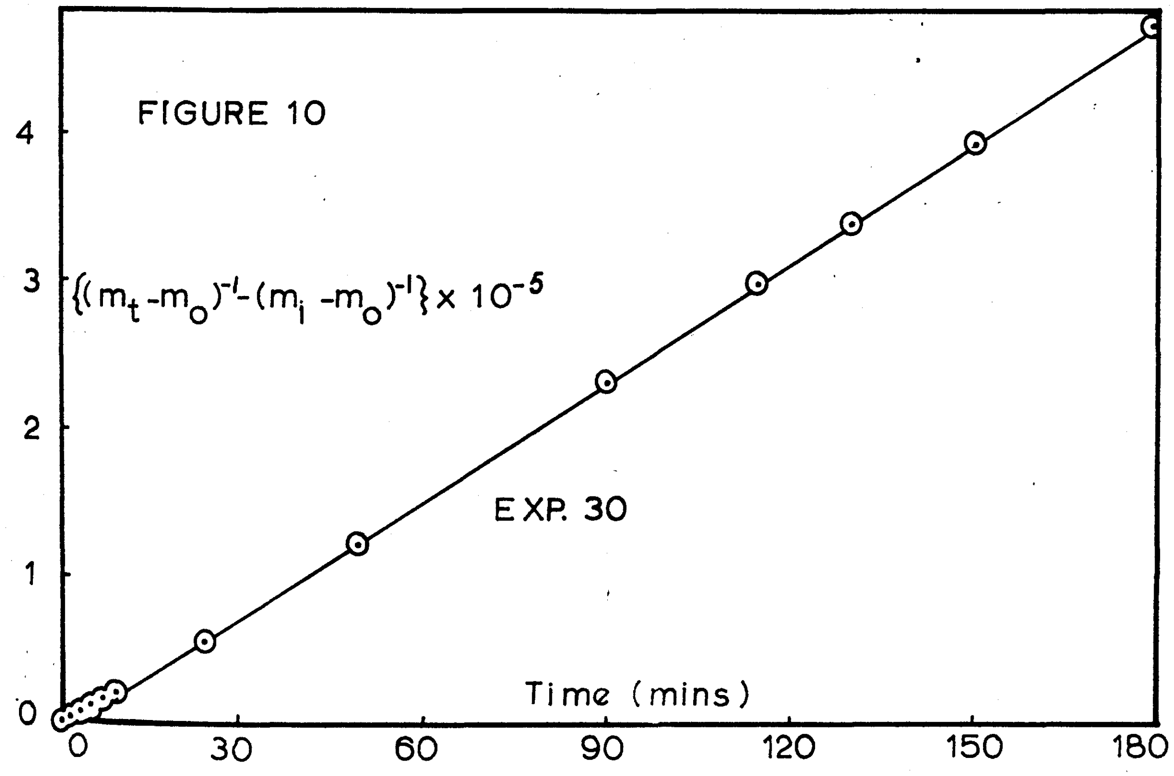


FIGURE 10

that the induction effects observed with deionised water were due to an impurity in the water itself. This impurity was adsorbed at many of the growth sites on the electrode surface, giving values of <u>ks</u> which were considerably smaller than those from conductivity water prepared by distillation. The rate constants are compared in Table 1, and it can also be seen that in distilled water too, the values fell off with age of electrode over the first few days after its preparation.

Experiments were also made in solutions containing non-equivalent concentrations of silver and chloride ions. Conductivity vs. time plots are given in Figure 11, and the results are summarised in Table 7.

Concentrations at time <u>t</u> were calculated from

$$[Ag^+]_t = [Ag^+]_e + \Delta \text{ and } [Cl^-]_t = [Cl^-]_e + \Delta ,$$

where $\underline{\Delta}$ was the amount of silver chloride to be deposited before equilibrium was reached, and $[Ag^+]_e$ and $[Cl^-]_e$ were the equilibrium ionic concentrations which satisfied the solubility product relationship

$$[Ag^+]_e . [Cl^-]_e = K_s = (1.336_5 x10^{-5})^2 (\text{mole.litre}^{-1})^2$$
$$= 1.786 \times 10^{-10}$$

$$\text{Therefore } \{[Ag^+]_t - \Delta\}\{[Cl^-]_t - \Delta\} = K_s .$$

When initial values of $[Ag^+]$ and $[Cl^-]$ were inserted in this equation, the amount of silver chloride to be deposited was obtained. From changes in the conductivity values during the experiment, $\underline{\Delta}$ was calculated using equation 10.

TABLE 7

Crystallisation of Silver Chloride

Experiments in Distilled Water.

Expt No.	$[Ag^+]_i$ x 10^5 mole/l	$[Cl^-]_i$ x 10^5 mole/l	$[Ag^+][Cl^-]$ x 10^{10} $(mole/l)^2$	Electrode No.	Electrode Age (Days)	Init. ks $l.mole^{-1}.min^{-1}$
31	1.072	2.144	2.298	8	7	1100
38	1.072	2.144	2.298	11*	16	1090
39	2.144	1.072	2.298	11*	18	1350

Solubility Product = 1.786 x 10^{-10} $(mole/l)^2$

* Smaller electrode :- ks values corrected.

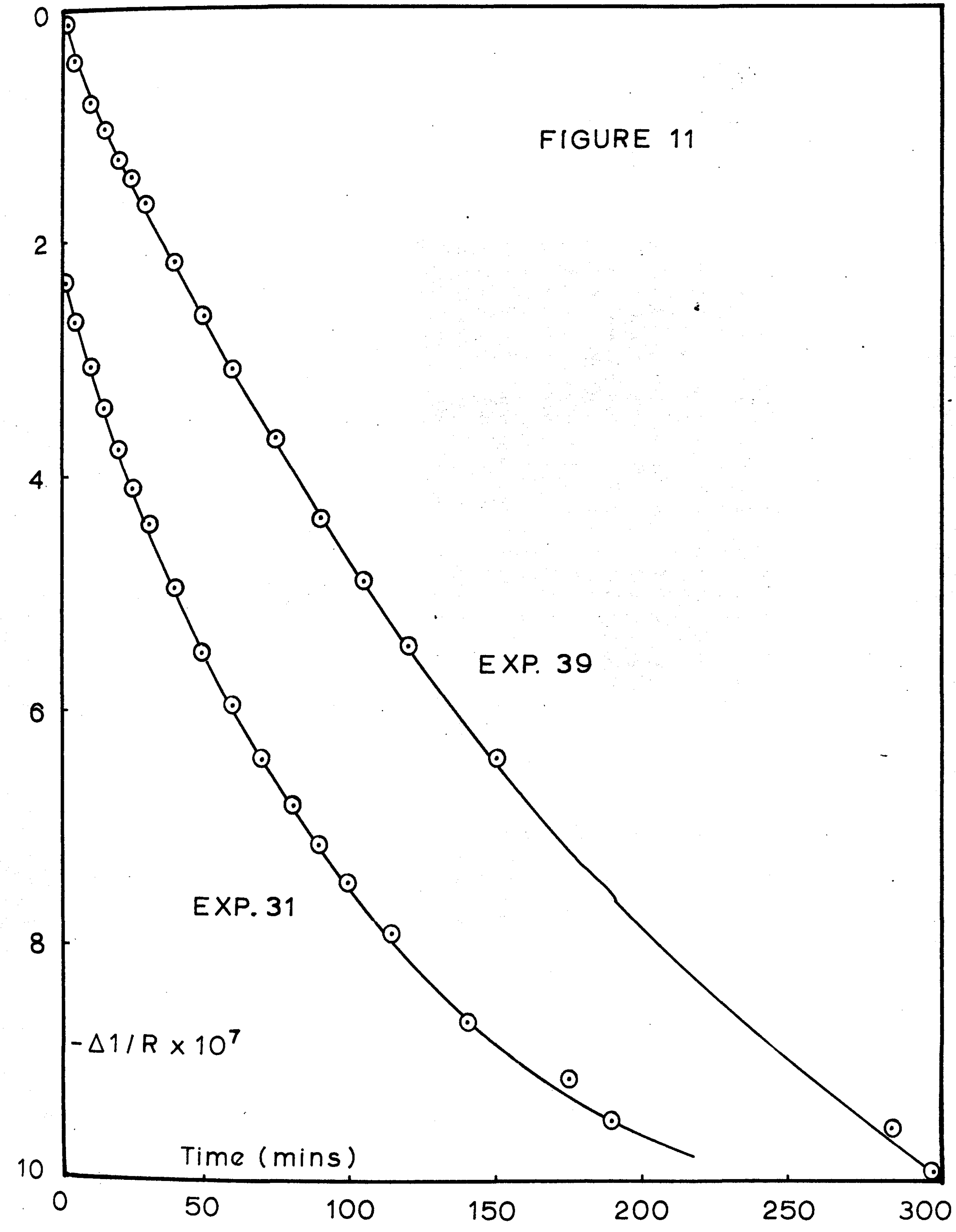


FIGURE 11
EXP. 39
EXP. 31
$-\Delta 1/R \times 10^7$
Time (mins)
0
2
4
6
8
10
0
50
100
150
200
250
300

TABLE 8
Crystallisation of Silver Chloride

t mins	$1/R$ $\times 10^5$ ohm^{-1}	$-\delta(\Delta)$ $\times 10^6$ mole/l	$[Ag^+]$ $\times 10^5$ mole/l	$[Cl^-]$ $\times 10^5$ mole/l	Δ $\times 10^6$ mole/l	I* $\times 10^{-5}$ $(m/l)^{-1}$
Experiment 31.						
0	7.112	0.000	1.072	2.144	1.700	0.00
10	7.104	0.041	1.068	2.140	1.659	0.14
20	7.097	0.076	1.064	2.136	1.624	0.27
40	7.086	0.136	1.058	2.130	1.564	0.51
60	7.076	0.186	1.053	2.125	1.516	0.71
80	7.067	0.231	1.049	2.121	1.469	0.92
100	7.061	0.263	1.046	2.118	1.437	1.08
140	7.049	0.324	1.040	2.112	1.376	1.38
190	7.040	0.366	1.035	2.107	1.334	1.61
Experiment 38.						
0	7.191	0.000	1.072	2.144	1.700	0.00
10	7.185	0.027	1.069	2.141	1.673	0.09
30	7.178	0.066	1.065	2.137	1.634	0.24
50	7.170	0.108	1.061	2.133	1.592	0.40
65	7.165	0.130	1.059	2.131	1.570	0.49
155	7.137	0.271	1.045	2.117	1.429	1.12
190	7.128	0.320	1.040	2.112	1.380	1.36
240	7.118	0.367	1.035	2.107	1.333	1.62
290	7.110	0.411	1.031	2.103	1.289	1.87

* $I = (\Delta^{-1} - \Delta_i^{-1})$

TABLE 8 cont.

t mins	1/R $\times 10^5$ ohm^{-1}	$-\delta(\Delta)$ $\times 10^6$ mole/l	$[Ag^+]$ $\times 10^5$ mole/l	$[Cl^-]$ $\times 10^5$ mole/l	Δ $\times 10^6$ mole/l	I* $\times 10^{-5}$ $(m/l)^{-1}$
Experiment 39.						
0	8.260	0.000	2.144	1.072	1.700	0.00
10	8.252	0.040	2.140	1.068	1.660	0.14
20	8.247	0.065	2.137	1.066	1.635	0.23
40	8.238	0.110	2.133	1.061	1.590	0.41
60	8.229	0.155	2.128	1.055	1.545	0.59
90	8.217	0.221	2.122	1.050	1.479	0.88
150	8.197	0.322	2.112	1.040	1.378	1.37
285	8.165	0.485	2.095	1.023	1.215	2.35

* $I = (\Delta^{-1} - \Delta_i^{-1})$

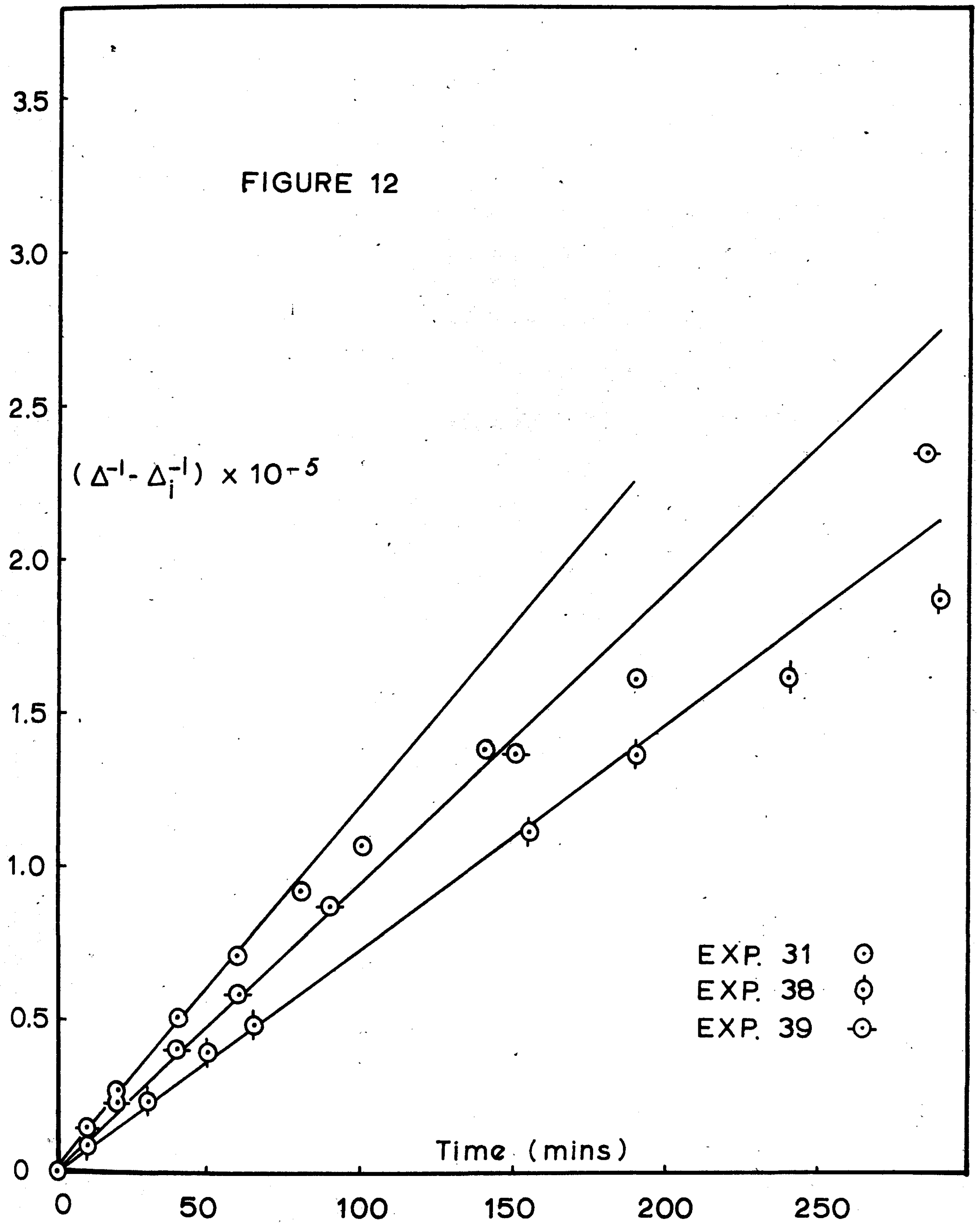


FIGURE 12
$(\Delta^{-1} - \Delta_i^{-1}) \times 10^{-5}$
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Time (mins)
0
50
100
150
200
250
EXP. 31 ⊙
EXP. 38 ⊙
EXP. 39 -⊙-

Graphs of $\{\Delta^{-1}-\Delta_i^{-1}\}$ vs. t for Experiments 31, 38 and 39 are shown in Figure 12, and it is seen that the equation used by Davies and Jones[44] in experiments with silver chloride seed crystals,

$$\frac{dm}{dt} = ks(\Delta)^2,$$

was not obeyed in any case for more than 20% of the reaction. The initial rates were much smaller than those with equivalent ionic concentrations. A smaller electrode was used in Experiments 38 and 39 than in the earlier experiments, and the ks values have been corrected on the assumption that they were proportional to the surface area of the electrode. It is clear that the rate constant was less with the chloride ion in excess (Experiments 31 and 38) than with silver ion in excess (Experiment 39).

The dissolution of the silver chloride electrode into conductivity water has also been studied. The smooth curves of conductivity against time, shown in Figure 13 for Experiments 28 and 29 indicate the good reproducibility. One advantage over the use of seed crystals was that the apparent surface area remained constant during a dissolution. Table 9 summarises the experiments, and the straight lines obtained by plotting $\{\log(m_o-m_t)-\log(m_o-m_i)\}$ vs. t, the integrated form of the first order rate equation, are shown in Figure 14. The equation

$$\frac{dm}{dt} = ks(m_o-m_t)$$

was obeyed to 97% completion.

Experiments were also made on dissolution into subsaturated solutions containing non-equivalent concentrations of silver and chloride ions. These are also summarised in Table 9, and the conductivity vs. time plots are given in Figures 15 and 17. The first order graphs and rate constants for these experiments provide a self-consistent picture. Figure 18 shows that in Experiments 36 and 37, which had one ion in an excess of over 2:1, first order kinetics were obeyed for at least 69% and 82% of the reactions respectively. Plots of $(\log\Delta - \log\Delta_i)$ vs. t for Experiments 34 and 35, which initially contained only one type of ion, are seen in Figure 16. In neither case can any significant divergence from the straight line be observed, even with the last points, both of which correspond to 90% of the reaction.

The rate constants for the dissolution experiments into equivalent concentrations of silver and chloride ions agreed very well, but the average value of $0.42\times10^{-3}\text{min}^{-1}\cdot\text{cm}^{-2}$. was much smaller than 1.3×10^{-2} $\text{min}^{-1}.\text{cm}^{-2}$. obtained with seed crystals. The ks values shown in Table 9 have been corrected for the different sizes of the electrodes.

Discussion

In the crystallisation of silver chloride onto seed crystals, Davies and Jones[44] observed that second order kinetics were followed for at least 75% of the reaction. A similar result was obtained at temperatures of 15°, 25° and 35° by Davies and Nancollas[28], who also found that the rate constant was independent of temperature. The present experiments on the crystal growth of silver chloride onto an electrode show that with equivalent silver and chloride ion concentrations the reaction is again second order, with the exception of an initial

TABLE 9

Dissolution of the Silver Chloride Electrode

Experiments in Distilled Water.

Expt No.	$[Ag^+]_i$ x 10^5 mole/l	$[Cl^-]_i$ x 10^5 mole/l	$[Ag^+][Cl^-]$ x 10^{10} $(mole/l)^2$	Electrode No.	Electrode Age (Days)	ks min^{-1}
28	0.000	0.000	0.000	6	8	3.24
29	0.000	0.000	0.000	6	10	3.62
34	1.334	0.000	0.000	10*	5	1.20
35	0.000	2.104	0.000	10*	7	1.30
36	0.596	1.582	0.944	10*	14	2.07
37	1.582	0.791	1.252	10*	16	1.83

Solubility Product = 1.786 x 10^{-10} $(mole/l)^2$

* Smaller electrode :- <u>ks</u> values corrected.

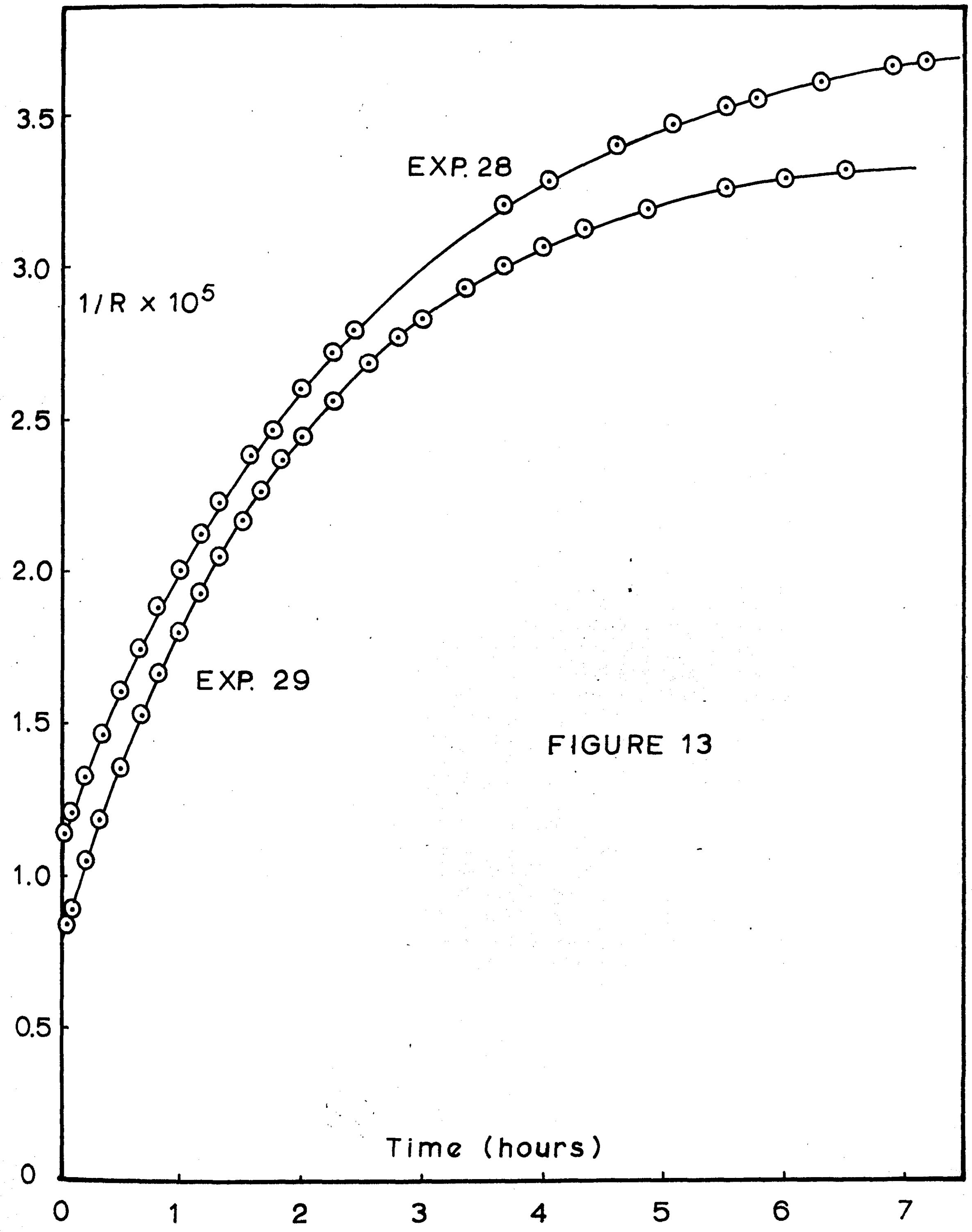


FIGURE 13

TABLE 10 Dissolution of Silver Chloride

t mins	$1/R \times 10^5$ ohm^{-1}	$\Delta m \times 10^5$ mole/l	$m_t \times 10^5$ mole/l	$(m_o-m_t) \times 10^5$ mole/l	I*
Experiment 28.					
0	1.125	0.000	0.000	1.334	0.000
10	1.293	0.085	0.085	1.249	0.029
20	1.455	0.167	0.167	1.167	0.058
30	1.607	0.245	0.245	1.089	0.089
45	1.818	0.352	0.352	0.982	0.133
60	2.011	0.450	0.450	0.884	0.178
90	2.337	0.615	0.615	0.719	0.268
120	2.603	0.750	0.750	0.584	0.359
180	3.000	0.952	0.952	0.382	0.542
240	3.280	1.094	1.094	0.240	0.744
300	3.470	1.190	1.190	0.144	0.967
360	3.575	1.243	1.243	0.091	1.168
Experiment 29.					
0	0.790	0.000	0.000	1.334	0.000
11	1.013	0.113	0.113	1.221	0.038
20	1.183	0.199	0.199	1.135	0.070
30	1.359	0.289	0.289	1.045	0.106
45	1.596	0.409	0.409	0.925	0.159
60	1.804	0.515	0.515	0.819	0.212
91	2.176	0.703	0.703	0.631	0.325
120	2.447	0.841	0.841	0.493	0.432
180	2.836	1.038	1.038	0.296	0.655
240	3.074	1.159	1.159	0.175	0.882
291	3.198	1.222	1.222	0.112	1.076
330	3.264	1.255	1.255	0.079	1.230
360	3.300	1.274	1.274	0.060	1.345
390	3.325	1.286	1.286	0.048	1.448

* $I = \text{Log}(m_o-m_t) - \text{Log}(m_o-m_i)$

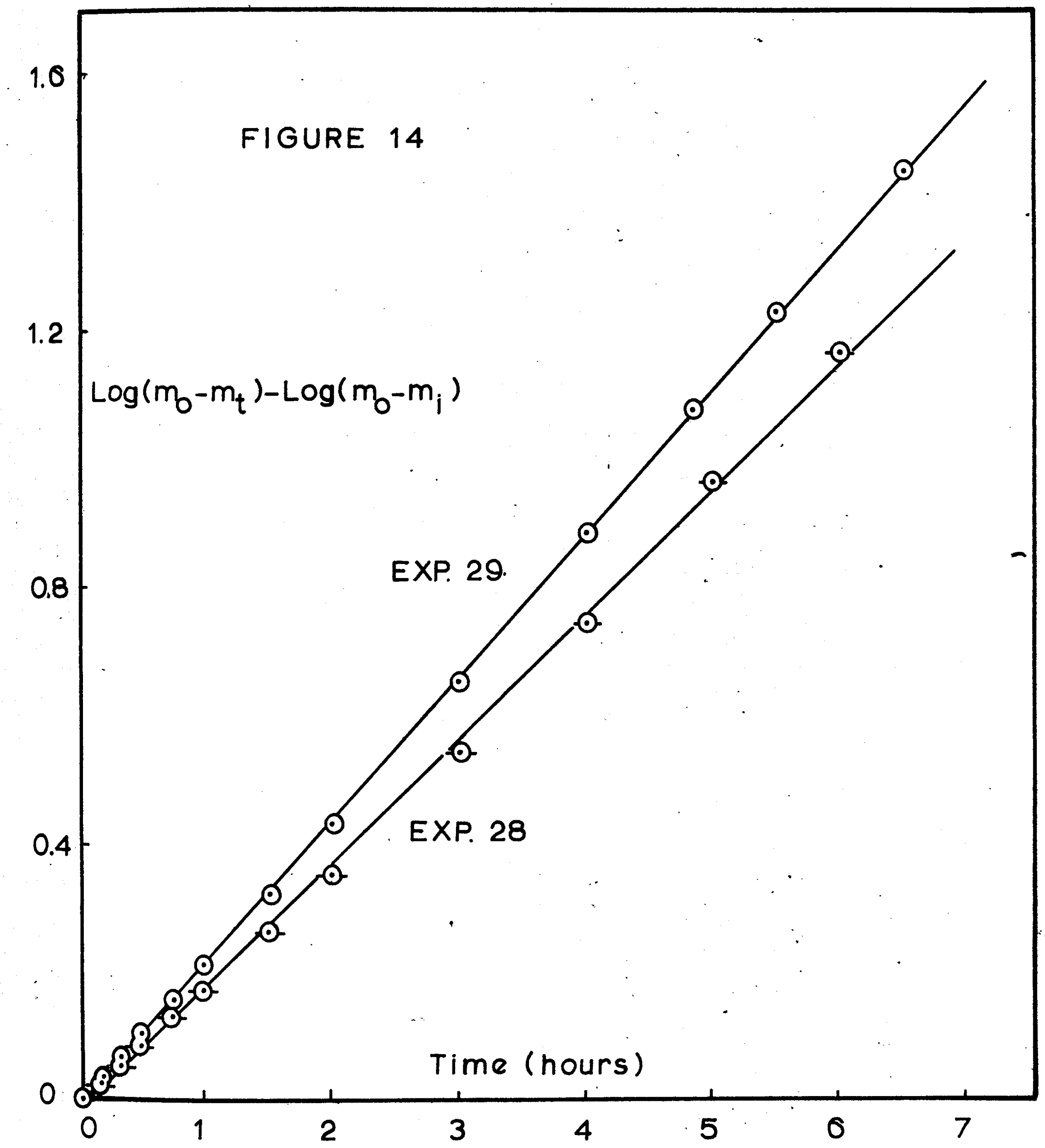


FIGURE 14
1.6
1.2
0.8
0.4
0
Log(m_o-m_t)-Log(m_o-m_i)
EXP. 29
EXP. 28
Time (hours)
0
1
2
3
4
5
6
7

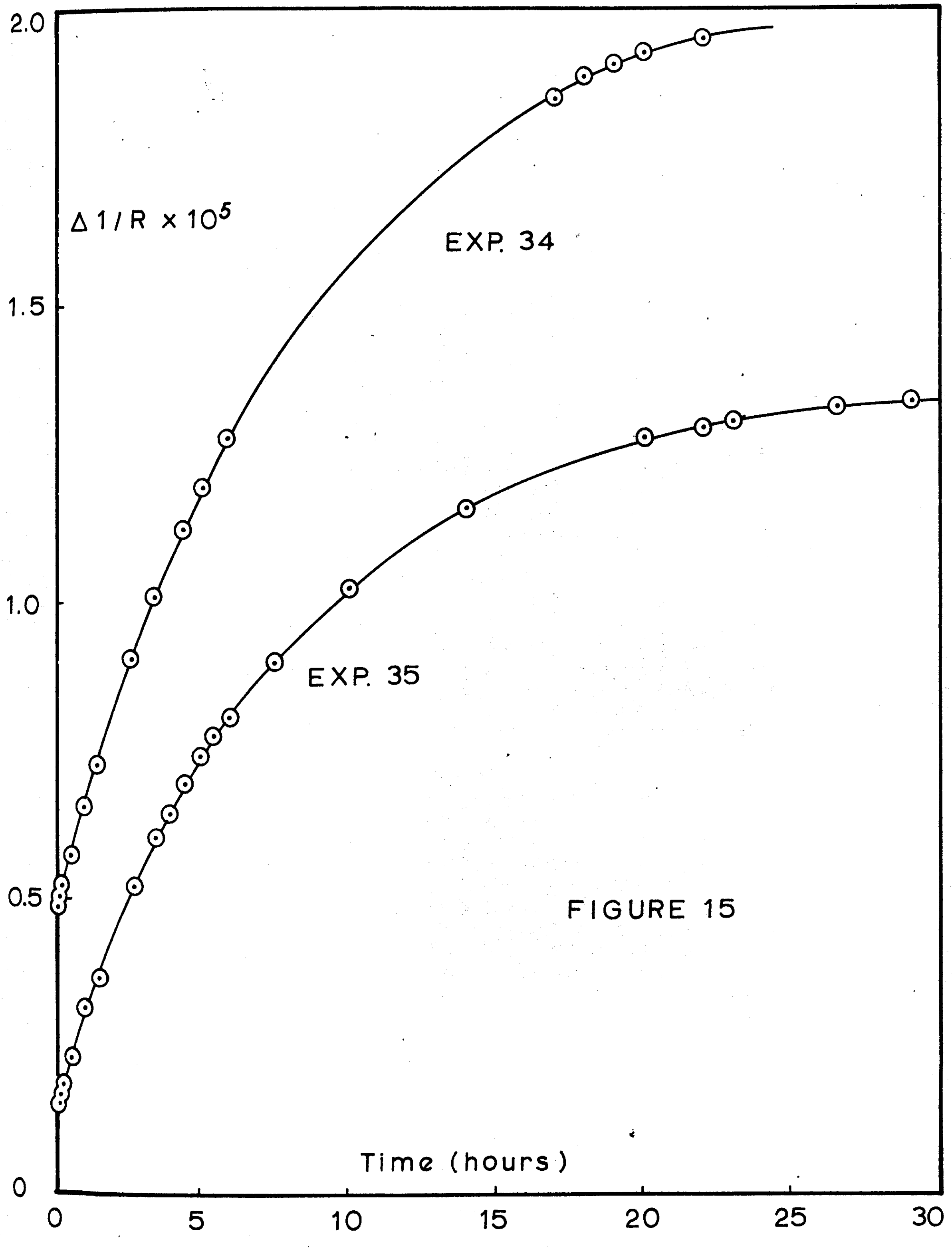

2.0
1.5
1.0
0.5
0
$\Delta 1/R \times 10^5$
EXP. 34
EXP. 35
Time (hours)
0
5
10
15
20
25
30

FIGURE 15

TABLE 11

Dissolution of Silver Chloride

t hours	1/R x 10^5 ohm^{-1}	$\delta(\Delta)$ x 10^5 mole/l	$[Ag^+]$ x 10^5 mole/l	$[Cl^-]$ x 10^5 mole/l	Δ x 10^6 mole/l	I*
Experiment 34.						
0	3.384	0.000	1.334	0.000	8.244	0.000
0.5	3.472	0.045	1.379	0.045	7.795	0.024
1.0	3.558	0.088	1.422	0.088	7.362	0.049
2.0	3.706	0.163	1.497	0.163	6.610	0.096
3.0	3.843	0.233	1.567	0.233	5.915	0.144
4.0	3.968	0.296	1.630	0.296	5.280	0.193
6.0	4.179	0.403	1.737	0.403	4.210	0.292
10.0	4.470	0.551	1.885	0.551	2.733	0.479
14.0	4.662	0.649	1.983	0.649	1.758	0.671
18.0	4.782	0.709	2.043	0.709	1.149	0.856
22.0	4.850	0.744	2.078	0.744	0.804	1.011
Experiment 35.						
0	6.348	0.000	0.000	2.104	6.468	0.000
0.5	6.431	0.042	0.042	2.146	6.046	0.030
1.0	6.516	0.085	0.085	2.189	5.615	0.062
1.5	6.567	0.111	0.111	2.215	5.354	0.082
2.75	6.721	0.189	0.189	2.293	4.575	0.151
3.5	6.804	0.231	0.231	2.335	4.156	0.192
4.5	6.896	0.278	0.278	2.382	3.689	0.244
6.0	7.008	0.335	0.335	2.439	3.116	0.318
10.0	7.223	0.444	0.444	2.548	2.025	0.504
14.0	7.359	0.513	0.513	2.617	1.338	0.684
20.0	7.478	0.573	0.573	2.677	0.734	0.945

* $I = \text{Log}\Delta - \text{Log}\Delta_i$

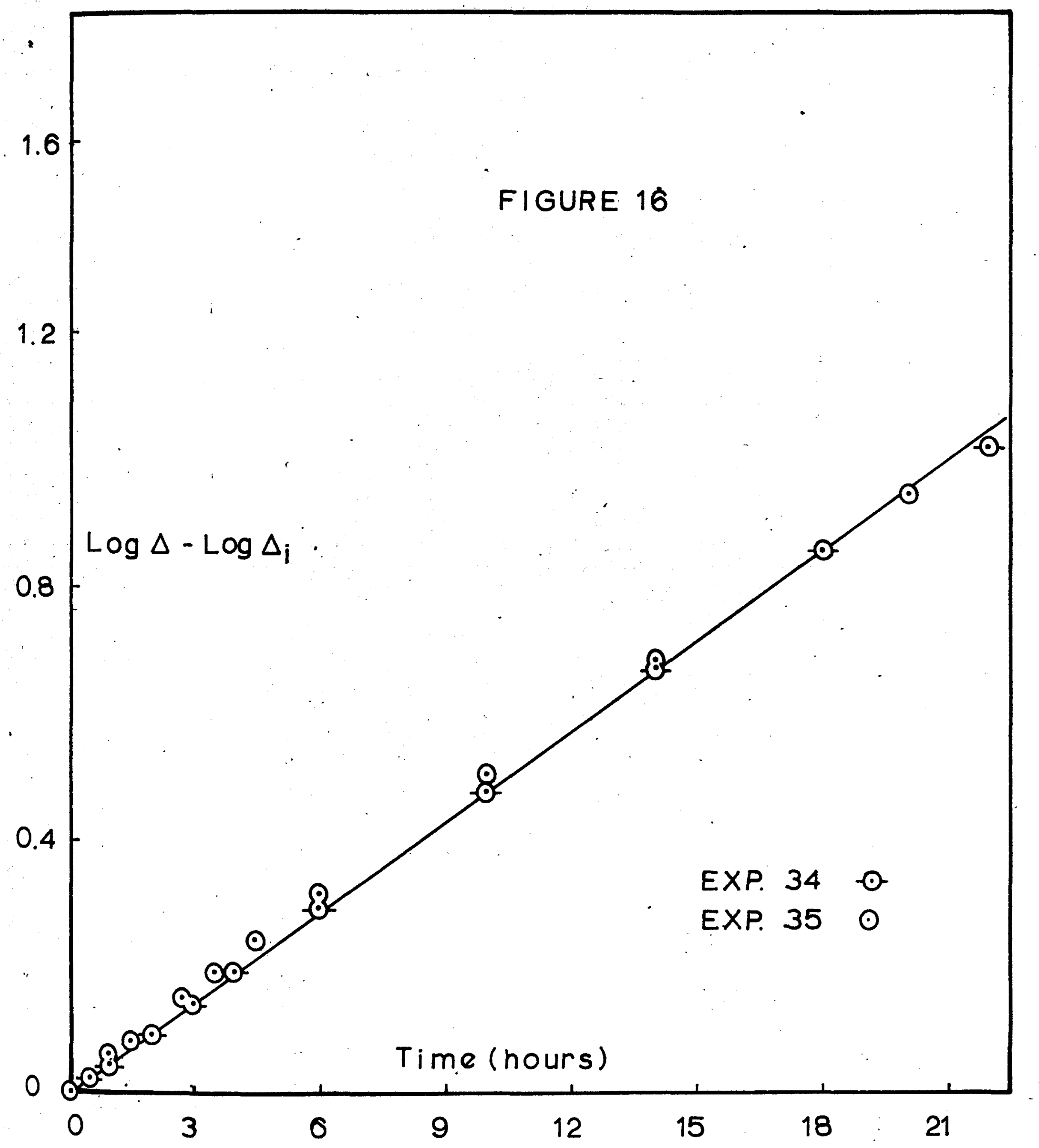


FIGURE 16
Log Δ - Log Δ$_i$
1.6
1.2
0.8
0.4
0
Time (hours)
0
3
6
9
12
15
18
21
EXP. 34 -⊙-
EXP. 35 ⊙

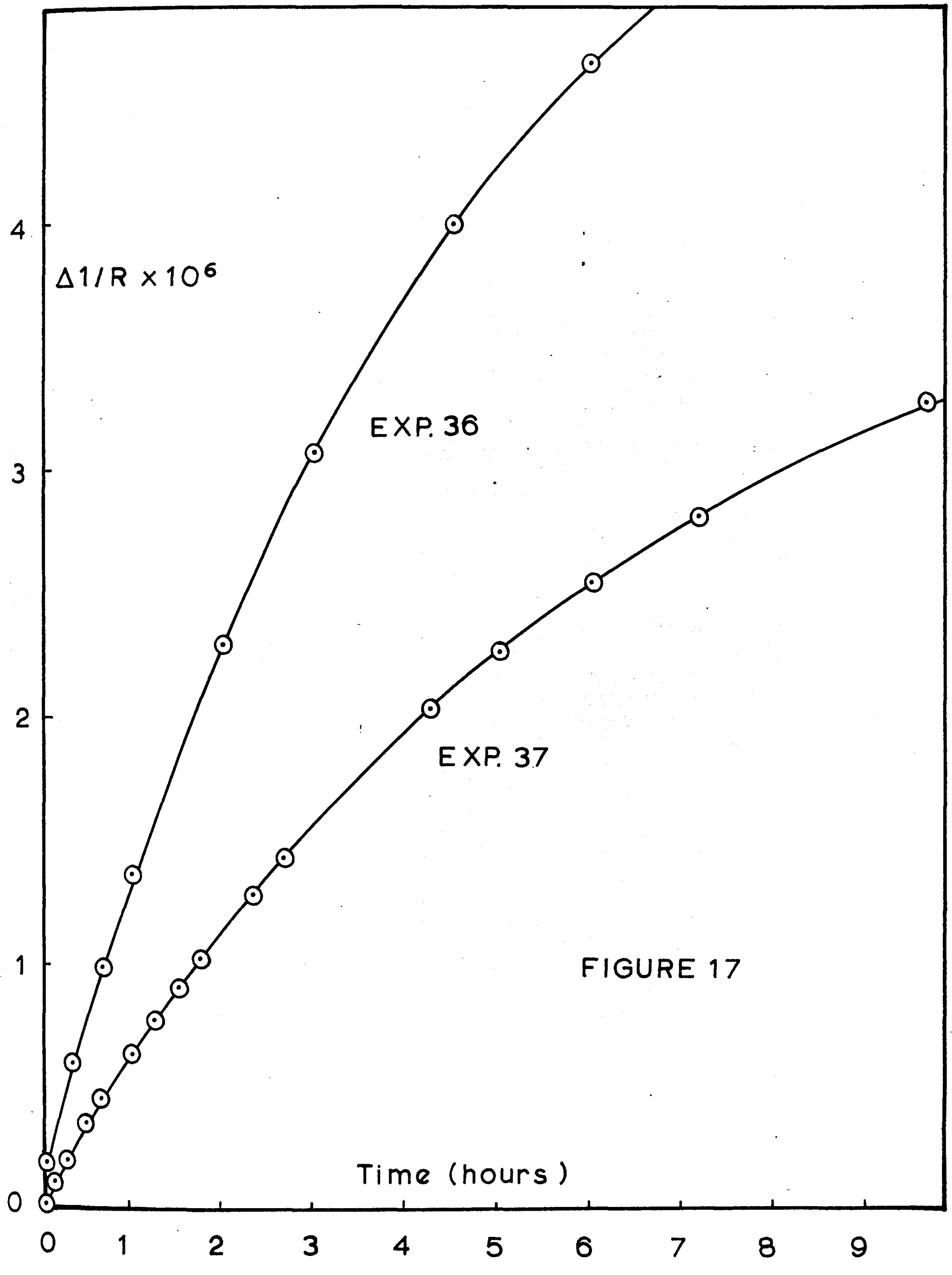


FIGURE 17

TABLE 12
Dissolution of Silver Chloride

t mins	$I/R \times 10^5$ ohm^{-1}	$\delta(\Delta) \times 10^6$ mole/l	$[Ag^+] \times 10^5$ mole/l	$[Cl^-] \times 10^5$ mole/l	$\Delta \times 10^6$ mole/l	I*
Experiment 36						
0	5.144	0.000	0.5964	1.5824	3.328	0.000
20	5.185	0.209	0.6173	1.6033	3.119	0.028
40	5.224	0.404	0.6368	1.6228	2.924	0.056
60	5.262	0.599	0.6563	1.6423	2.729	0.086
120	5.355	1.069	0.7033	1.6893	2.259	0.168
180	5.433	1.466	0.7430	1.7290	1.862	0.252
270	5.525	1.932	0.7896	1.7756	1.396	0.377
360	5.590	2.266	0.8230	1.8090	1.062	0.496
Experiment 37						
0	6.225	0.000	1.582	0.791	2.046	0.000
20	6.250	0.126	1.594	0.804	1.920	0.028
30	6.260	0.179	1.600	0.809	1.867	0.040
60	6.289	0.324	1.615	0.824	1.722	0.075
90	6.315	0.457	1.628	0.837	1.589	0.110
120	6.340	0.582	1.640	0.849	1.464	0.145
180	6.382	0.797	1.662	0.871	1.249	0.214
240	6.420	0.989	1.681	0.890	1.057	0.287
360	6.480	1.293	1.712	0.920	0.753	0.434
480	6.523	1.515	1.734	0.943	0.531	0.586
600	6.554	1.670	1.749	0.958	0.376	0.736

* $I = \text{Log}\Delta - \text{Log}\Delta_i$

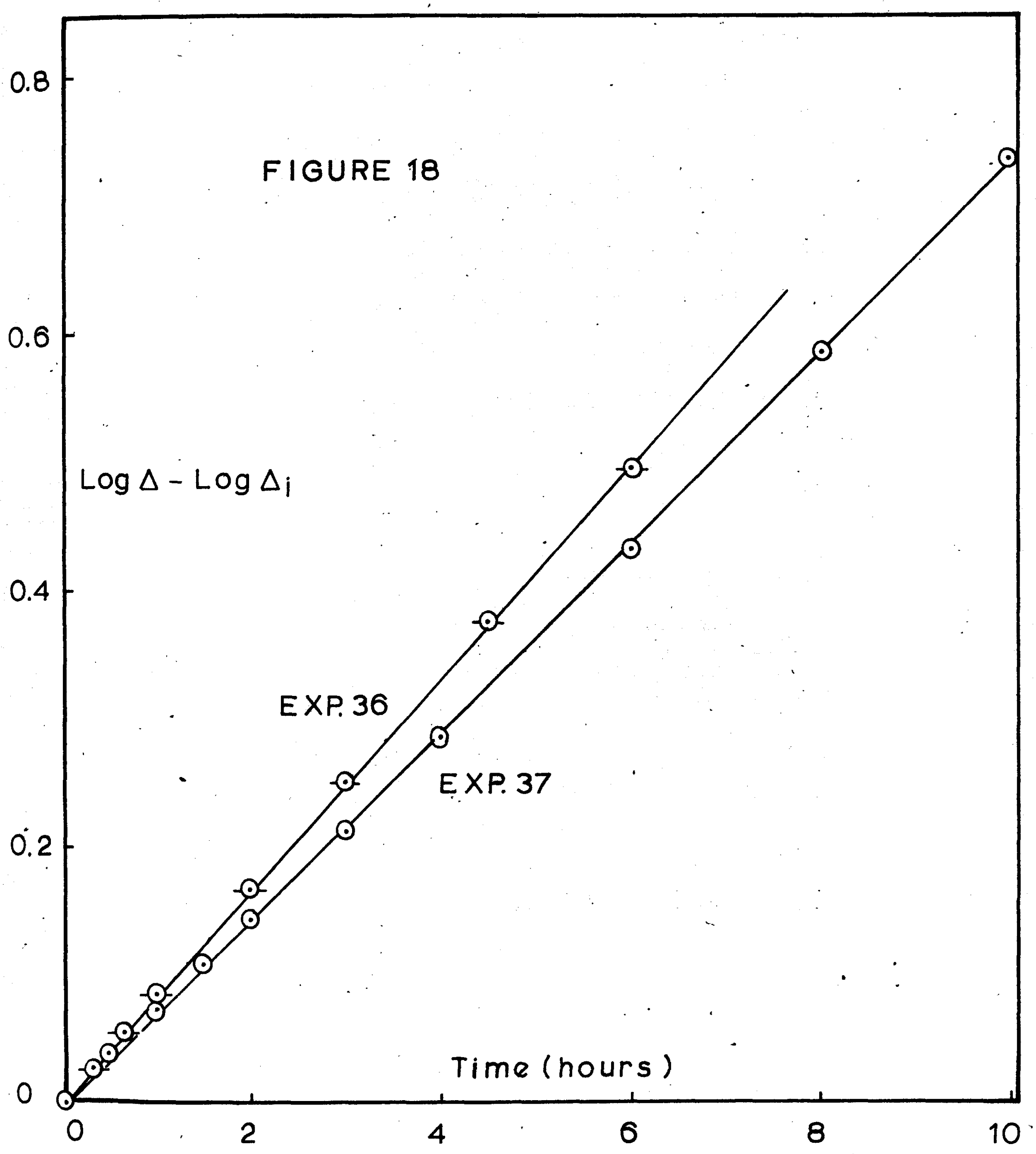


FIGURE 18

induction period in experiments using deionised water.

The ks value for the reaction is constant when a fully aged electrode is used, but an appreciably higher value is obtained when the electrode is only a few days old. This suggests that the ageing effect is similar for both an electrode and seed crystals. Kolthoff and Yutzy[88] studied the ageing of freshly precipitated silver chloride by measuring the amount of dye adsorbed upon crystals of various ages. This gave a measure of the external surface and it was observed that, upon ageing, a very pronounced reduction in the total surface occurred. Davies and Nancollas[89], in a study of the influence of foreign ions on the crystallisation of silver chloride concluded that the adsorption characteristics were constant after an ageing period of two months. It is evident that the number of sites available for growth on the electrode surface decreases during the first few days after preparation, and remains constant after about ten days.

Crystallisation onto an electrode differs from that onto seed crystals in that in experiments using deionised water, the second order growth is preceded by an induction period which increases with the age of the electrode. With a freshly prepared electrode the delayed crystallisation is scarcely significant, but it becomes pronounced when the electrode has aged fully. Davies, Jones and Nancollas[90] found that when silver chloride seed crystals had been aged in dilute solutions of various adsorbates, induction periods were observed in crystal growth experiments using the seeds. The initial slow portions ranged from a few minutes to over two hours, depending on the concentration of adsorbate. The effect was explained as being due to a complete adsorption layer covering the surface at the start of a run. Desorption then proceeded, and the induction period ended when the rate of crystallisation had attained a definite, detectable value. In the present series of experiments, the initial rates of crystallisation were rarely zero, but they were much slower than required by the rate law. This indicates that a complete adsorption layer was not present and that only certain growth sites were blocked.

Van Hook found that when seed crystals of silver chromate were added to its supersaturated solutions[66], induction periods were obtained whose lengths were inversely proportional to the volume of added seed. He associated these induction periods with the formation of fresh nuclei, but Howard and Nancollas[45] showed that they were due to contamination of the crystal surface by a hydrolysis product.

The work of Nancollas and Purdie on magnesium oxalate[46], however, showed that fresh nuclei could be formed during an induction period in the presence of seed crystals. Whenever the initial ionic concentration product exceeded a well-defined value spontaneous nucleation was observed, and the subsequent growth occurred on both the original seeds and the fresh nuclei. This was considered as being due to the number of available growth sites on the added seed crystals not being sufficient to accomodate the large amount of material to be deposited. Although the supersaturation of silver chloride is much less than that of magnesium oxalate, the density of growth sites on a silver chloride electrode has been shown to be low compared with seed crystals. With the number of such sites further reduced by the adsorption of impurity, a situation similar to that existing with magnesium oxalate can occur. Conversely when the density of growth sites is relatively large, as with a freshly prepared electrode or when distilled water is used instead of deionised water, the induction effect is negligible.

The rate constants in distilled water were found to be much larger than for similar experiments using deionised water. This confirms earlier observations[89] that the presence of a small concentration of impurity decreases the rate of crystallisation, but does not influence the kinetic order of the reaction.

In experiments on the crystal growth onto an electrode from non-equivalent initial concentrations of silver and chloride ions, the second order kinetic law was not followed, and the initial rates were much smaller than for the corresponding equivalent concentration experiments. Davies and Jones[44] found that when solutions of non-equivalent ionic concentrations were inoculated with seed crystals, straight lines were obtained in plots of

$$-\frac{dm}{dt} = ks\,\Delta^2,$$

and the rate constant <u>ks</u> was independent of the ionic ratio. Davies and Nancollas[28] however observed that as the ratio increased, <u>ks</u> decreased and was much lower with the chloride ion in excess than with the silver ion. Similar results have been obtained for silver chromate[45], magnesium oxalate[46], and barium sulphate[47].

Silver halide particles acquire a positive charge when silver ions are present in excess, and the electrical double layer which surrounds each crystal results in a decrease in the rate of crystallisation. An equal excess of halide ions exerts an even greater effect, as has been found by Kolthoff and Lingane[91] for silver iodide and Basinski[92] for silver bromide, and the present results show that this also applies to silver chloride. A change in the potential difference between the adsorbed layer and the solution due to an increase in the ionic ratio as crystal growth proceeds, can affect the equilibrium and cause a premature falling off in rate. This effect is likely to be more pronounced with the low density of growth sites on the electrode surface.

The dissolution of a silver chloride electrode into conductivity water has been shown in the present work to be a first order reaction throughout. This agrees with the widely accepted theory that dissolution is diffusion controlled. Davies and Nancollas[28] studied the dissolution of silver chloride seed crystals into conductivity water and found that the order of the reaction varied with temperature, being 3/2 at 25°, and it was therefore not a simple diffusion controlled reaction. Howard, Nancollas and Purdie[93] continued this work by examining dissolution into solutions up to 30% subsaturated. They observed that when $[Ag^+] = [Cl^-]$, first order kinetics were followed for at least 96% of the available reaction. With one ion in excess however, the rate of dissolution fell off too rapidly to satisfy a first order equation, and this was more pronounced when silver ion was in excess. Strong confirmation of the diffusion theory was however afforded by the value of 5 kcals., obtained for the activation energy, this being very close to the activation energy for diffusion of 4.5 kcals.

The 3/2 order kinetics found in the earlier experiments were interpreted as being due to the thickness of the double layer surrounding the seed crystals being a significant fraction of the mean distance between crystals. It was found that when the initial subsaturation was increased to almost 70%, the process tended to follow a higher kinetic order than unity,and therefore the magnitude of the concentration gradient would appear to be critical. This effect should theoretically be eliminated by the use of a mounted crystal, or an electrode, which was considered by Jones to be equivalent[94]. He followed the dissolution of a silver chloride electrode into water by a radioactive tracer technique, and obtained first order kinetics and the same rate constant for both equivalent and non-equivalent ionic concentrations. His results also differed from the earlier ones in that in dissolution into silver nitrate solution, no divergence from the first order law was observed up to 75%, whereas with potassium chloride solutions, this law was not followed above 65% reaction.

The present results show that in the dissolution of an electrode into solutions containing either silver or chloride ions, the deviation from a first order reaction is negligible. The rate constant for the dissolution of an electrode is much smaller than for the equivalent surface area of seed crystals, and this indicates a smaller concentration gradient, which allows the rate controlling step to be purely diffusion. Purdie observed that in the dissolution of seed crystals[95], excess of either ion caused a decrease in ks, silver ion having the greater effect. The same result has been obtained in the present series of experiments, and suggests that some surface effect is retarding the dissolution. Adsorption of either ion in excess will begin immediately on adding the electrode to the subsaturated solution, and the electrode surface may therefore not be allowed to reach the adsorption equilibrium for maximum release of equivalent amounts of silver and chloride ions.

PART 2

Crystallisation of Strontium Sulphate in Aqueous Solution

Introduction

The crystallisation studies have been extended to a sparingly soluble 2:2 electrolyte, strontium sulphate. Experiments were made initially using supersaturated solutions of strontium sulphate prepared with deionised conductivity water, but the work had to be repeated with water prepared by distillation in order to achieve reproducible results. Crystal growth was studied from solutions containing equivalent and non-equivalent initial concentrations of strontium and sulphate ions, and the inhibiting effects of adsorbates on the growth was also examined.

The crystallisation of strontium sulphate has been studied by many workers on account of its fairly high solubility and freedom from hydration. Lambert and Hume-Rothery[96] carried out a systematic study of the effects of conditions of precipitation on the nature and size of precipitated particles of strontium sulphate, and found that two different types were produced, depending on the solution concentrations and temperature. A needle-shaped form and a rhombic form were obtained, but the former which was identified as a hydrated form, was unstable and underwent a transformation to the latter. The rhombs, which varied greatly in shape, consisted of anhydrous strontium sulphate.

Campbell and Cook[97] attempted to distinguish the successive labile or metastable states through which a supersaturated solution passes during crystallisation, and found that strontium sulphate began to crystallise spontaneously in 50% supersaturated solution, producing rhombic crystals, up to 10μ in size. They made the remarkable observation that when the degree of supersaturation had fallen to around 40%, i.e. a concentration of approximately $8.5\text{x}10^{-4}$ mole.litre^{-1}, further precipitation appeared to cease, and no more crystal growth was observed, even when inspected 28 days later. Since large crystals of the solid phase were present in the solution, this behaviour was most irregular. Marc had shown that dyes could inhibit growth by adsorption on the crystal surface, but potassium chloride, which was the only other substance present, did not exert an appreciable anti-catalytic effect. No explanation could be given, but the results had confirmed the observations of Dundon[98], who had earlier attempted to calculate surface energy by adding finely ground crystals to a saturated solution containing large crystals. Measurements were made of the initial increase in solubility and the consequent fall to the original value, as the small crystals dissolved and recrystallised on the larger. With strontium and barium sulphates however, he found that although the initial increase was as large as 25%, there was never more than a 2% return from the maximum. This was considered to be due to either a very slow solution rate or the acquisition of a charge on the small particles. A similar effect has been reported for gypsum, $CaSO_4.2H_2O$[99].

The solubility of strontium sulphate was examined by Emustun and Turkevitch[100] using radioactive tracer methods, and it was found to be dependent on the size of the smallest particles present. All the strontium sulphate particles in the suspension were in the form of aggregates, which indicated that there was no electric charge on the crystals to affect the solubility, as had been suggested by some authors. Over a period of two months, the crystals in a stirred solution showed a significant increase to a larger size in the particle size distribution, with a corresponding decrease in solubility. The solution was in equilibrium with the smallest particles rather than any larger ones, and this was considered to be due to a low rate of crystallisation compared to the rate of solution, as was shown by a very slow 'Ostwald ripening'. The low rates of crystallisation for both strontium and barium sulphates differed considerably from the rapid crystal growth of gypsum, and was attributed to the strontium and barium salts having no water of crystallisation. The hydrated ions in the solution would then require a high activation energy to free them from all solvated water molecules, before they could be accomodated in the crystal lattice.

The presence of foreign substances affects the crystal growth and crystal habit of strontium sulphate very considerably, and the effect on spontaneous crystallisation has been extensively studied by Otani[101,102]. He showed that the problem of habit modification was very complicated and related to the nature and degree of adsorption on particular crystal faces, which was in turn dependent on the crystal structure of the substance to be crystallised and the molecular or ionic structure of the adsorbate. Sodium citrate and EDTA, for example, were found to give thin ellipsoids and aggregates of two-dimensional spherulites respectively, in place of rhombs. Traces of sodium triphosphate and sodium hexametaphosphate had a very great influence on the rate of deposition and the crystal habit, which became spherulitic. Crystal growth from a 2×10^{-2} mole.litre^{-1} solution of strontium sulphate was completely inhibited by a 3×10^{-5} mole.litre^{-1} solution of sodium triphosphate and smaller adsorbate concentrations gave steps on the crystallisation rate plot, corresponding to the deposition of spherulites and then single crystals. Dissolution was also hindered and finally completely inhibited as the phosphate concentration increased. The amount of adsorbed sodium triphosphate tended to reach saturation at the same concentration as retardation of crystallisation and dissolution became significant.

A comparison of the effects on the precipitation of strontium sulphate of some condensed phosphates was made by Muira, Otani, Kodama and Shinagawa [103]. Whereas the effect of sodium trimetaphosphate and sodium orthophosphate on the crystal habit was insignificant in concentrations up to 10^{-2}M., sodium pyrophosphate and sodium triphosphate gave spherulites having either irregular or spherical shapes at concentrations as low as 5×10^{-6}M. A similar trend was observed with their effect on the rate of crystal growth, for 5×10^{-6}M. sodium triphosphate and 7×10^{-6}M. sodium pyrophosphate inhibited precipitation from 10^{-2}M. strontium sulphate solution, while approximately 100 times this amount was required merely to retard crystallisation with sodium trimetaphosphate and sodium orthophosphate. The large differences in adsorption were correlated with the solubilities of the strontium phosphate salts and the ability of the phosphates to form complexes with strontium. In the case of sodium triphosphate, the amount adsorbed tended to reach a saturation value at 1.3×10^{-6} moles per gm of adsorbent. In the presence of even relatively low concentrations of triphosphate therefore, the surface of the strontium sulphate crystals could be regarded as covered with a monomolecular adsorbed layer, and deposition of strontium sulphate onto such a surface would be strongly inhibited. With sodium trimetaphosphate and sodium orthophosphate, the adsorbate must cover merely a fraction of the crystal surface, even at the comparatively high concentrations used. The difference in the behaviour of the sodium trimetaphosphate was partially ascribed to the rigidity of its ionic structure, which could prevent its adaptation to the crystal lattice of strontium sulphate. The stability constants of the strontium complexes with these phosphates have been determined[103], and the values of 6.1 for the triphosphate and 1.52 for the orthophosphate confirm the expected relationship between complexing ability and adsorption.

The crystallisation studies described above have concerned precipitation from supercritical solutions, the results of which are difficult to reproduce. In a study of the crystallisation of barium sulphate, Nancollas and Purdie[47] used seed crystals to initiate growth, which followed the equation:-

$$-\frac{dm}{dt} = ks(m_t - m_o)^2,$$

after an initial fast period of from 2 to 60 minutes, corresponding to 1 to 25% of the reaction. Crystal growth from non-equivalent initial concentrations also followed a second order equation. The kinetics were consistent with the theory of Davies and Jones[44], the rate of growth being controlled by an interface process involving the formation of an adsorbed surface layer of hydrated barium and sulphate ions. The presence of other ions, such as chloride, was found to be without effect on the growth.

It was thought that the initial growth surge observed with barium sulphate[47] may have been caused by a pitted surface such as that observed by Dawson and McGaffney[104] in colloidal barium sulphate, but results of experiments with modified seed suspensions did not support this view. Further results pointed to surface nucleation as being the cause and, as required by this theory, the duration of the initial fast period decreased with decreasing degree of supersaturation, and increasing number of growth sites available initially. For a given supersaturation, a sufficient number of growth sites had to be provided for second order growth. Nielsen[105] also postulated a controlling surface nucleation process in the spontaneous crystallisation of barium sulphate from solutions in which the initial concentration was less than 4×10^{-4}M. The crystal growth of lead sulphate from equivalent ionic concentrations has been shown[48] to exhibit the same characteristics as barium sulphate.

In the present work the crystallisation of strontium sulphate on seed crystals followed the above pattern also, but it was very sensitive to the presence of any impurity, extremely small amounts of which almost completely inhibited growth.

Experimental

Preparation of Cell Solutions

In the early experiments on the crystallisation of strontium sulphate, unusual and surprising results were obtained, and a variety of methods of preparing the cell solution was used. Cell solutions were prepared by the same technique as the silver chloride solutions (p43), analar strontium chloride and sodium sulphate being added to conductivity water prepared on a mixed bed ion exchange resin column. In a few cases the strontium chloride was replaced by strontium nitrate.

In some experiments the cell solution was prepared by the addition of sulphuric acid and strontium hydroxide to deionised conductivity water in the cell. A sulphuric acid solution of concentration approximately 0.6 molar, standardised by titration against standard sodium hydroxide[106], was diluted to give a sulphate ion concentration in the cell of 7.500×10^{-4} gm.ions.litre^{-1}. A solution of strontium hydroxide in carbon dioxide free conductivity water was prepared[107] in a nitrogen atmosphere in a Winchester, connected to an automatic burette, from which the solution could be added from a point immediately above the surface of the cell solution. The concentration of the solution, approximately 0.025M., was such that the addition of about 10ml. to the cell was sufficient to neutralise exactly the sulphuric acid already present, the equivalence point being accurately determined by a conductimetric titration in situ. The pH of the strontium sulphate solution, obtained by glass electrode potentiometric measurements at the end of the crystallisation, was 6.05 units.

The conductivity water used in the later experiments was prepared in an all glass, nitrogen-flushed Bourdillon-type still. The cell was washed after each experiment with 3% hydrochloric acid and distilled water.

Preparation of Seed Crystals

Seed crystals of strontium sulphate could not be prepared by recrystallisation on a large scale, since there is a very small change in solubility with temperature. Equimolar proportions of a strontium salt and a sulphate were added to hot distilled water and the precipitate was digested for several hours, and allowed to cool slowly overnight. The seed crystals were then thoroughly washed by decantation with distilled and conductivity water, and transferred to pyrex stock flasks. They were allowed to age in a water thermostat at 25°.

Suspensions A,B: prepared by the addition of 250 ml. portions of 0.25M. strontium chloride and sulphuric acid to 1.5 litres of distilled water, the seed crystals were aged in deionised conductivity water. The suspensions were composed of extremely fine and regular rhombs, although some very small particles were also present. The average crystal size was 12-15μ, and the rhombs had an angle of 76° ± 1°, or in a few cases 90°.

Suspensions C,D,E: 0.5 litre portions of 0.1M. strontium hydroxide and sulphuric acid were added to 1 litre of distilled water, and the precipitates were again aged in deionised conductivity water. Examination of suspension c one month after its preparation , showed that it consisted of extremely small crystals in irregular aggregates. Examined a year later, the aggregates had almost completely dispersed and the crystals were all rhombic, 15μ in size, with an angle again of 77°. On both inspections, a few crystals were observed which were much larger than the average, and these measured at the smallest 50μ.

Suspensions F,G: 1 litre portions of 0.05M. strontium hydroxide and sulphuric acid were mixed, and the precipitate was washed and aged in distilled conductivity water. The crystals, a few days later, were small, and of poor shape and existed as large aggregates.

The amounts of seed crystals used in each experiment, given in Tables 15 and 22, were determined directly by filtering the final solutions through a sintered glass filter stick, and drying the solid to constant weight.

Solubility Value

Literature values for the solubility of strontium sulphate vary considerably and results obtained by conductimetric measurements range from about $5.3\text{x}10^{-4}$ mole.litre^{-1} to $7.5\text{x}10^{-4}$ mole.litre^{-1}, with other values considerably higher. Kohlrausch[108] and Enustun and Turkevitch[100] obtained a value of $6.22\text{x}10^{-4}$ mole.litre^{-1}, and several results about 7% greater have been reported[4,109,110]. It has been found[100] that the solubility depends on the minimum crystal size, and the discrepancies in the values quoted above can therefore be attributed to different conditions of preparation of the strontium sulphate crystals.

The solubility was determined by allowing growth and dissolution experiments to proceed to equilibrium, and small differences were found, depending on the conditions of preparation of the seed crystals and their resulting size. The value employed for seed *g*, for example, was $6.020\text{x}10^{-4}$ mole.litre^{-1}, corresponding to a thermodynamic solubility product

$$K_{Th} = [Sr^{2+}][SO_4^{\ 2-}].f_2^{\ 2}$$

$$= 2.327\text{x}10^{-7}\ \text{mole}^2.\text{litre}^{-2}.$$

The activity coefficient f_2 was evaluated using the Davies' equation, (equation 9). The solubility value was calculated at the ionic strength of each experiment and was assumed constant throughout the experiment.

Equivalent Conductivity and Equations

The limiting ionic conductivities of the strontium and sulphate ions are 59.46[111] and 80.02[112] respectively, and the equivalent conductivity is given by the equation

$$\Lambda_{SrSO_4} = 139.48 - 496.23m^{\frac{1}{2}}.$$

where m is the ionic concentration in moles.litre^{-1}. Since the change in Ionic Strength during an experiment was small, Λ_{SrSO_4} was considered constant, and equal to 125.89 at a concentration of 7.50×10^{-4} mole.litre^{-1}.

The results of the experiments were interpreted in the same way as the silver chloride results. The effective surface area of seed crystals participating in a crystallisation experiment will increase with time, but since the reactions proceeded so slowly, comparatively large amounts of seed were used, and the resulting change in weight amounted to less than 0.1% of the total in most cases. The correction was therefore neglected.

Results

In the initial experiments, the supersaturated solutions of strontium sulphate were prepared from conductivity water obtained from a mixed bed ion exchange resin column. The seed suspensions a and b were also prepared, washed and aged in deionised conductivity water. The results of some of the experiments using these seed suspensions are summarised in Table 13, in which m_∞ is the solution concentration when the rate of crystallisation had become negligible. Graphs of conductivity vs. time are shown in Figures 19 and 20. The rate curves showed that after a comparatively fast start, the rate of crystallisation was very slow, and after 36 hours, crystal growth had almost ceased with less than 25% of the reaction completed. Examination of the kinetics of the fast initial period gave values of n as high as 12, as in experiment 4. The equilibrium conductivities in many of the experiments corresponded to solubility values for strontium sulphate which were considerably greater than the results of earlier workers, these final values depending on the initial strontium sulphate concentration. The rate plots in many of the experiments showed irregularities, when crystallisation partly or completely stopped for a period, the occurrance and duration of which appeared to follow no set pattern.

Several dissolution experiments, in which seed crystals were added to conductivity water or subsaturated solutions, were made to determine the solubilities of the individual seed suspensions. In these cases also, the reactions did not proceed to a small equilibrium value, but the final concentrations were greater, the smaller the initial subsaturation.

These results indicated that adsorption was occurring on the surface of the seed crystals, and both the crystal growth and dissolution processes were being inhibited. In experiment 18, 5ml.

of seed suspension b were added to the cell solution, and crystallisation was allowed to reach equilibrium, where it remained steady for 25 hours. On the addition of a further 5 ml. of seed, the crystal growth recommenced. A much greater initial supersaturation was used in experiment 19, and two additions of seed crystals resulted in amounts of crystallisation proportional to the 2 ml. and 5 ml. of suspension respectively used. After both periods of growth the conductivity of the solution remained steady for at least 30 hours. The conductivity vs. time plots are shown in Figure 20. This supported the theory that the growth sites on the strontium sulphate seed crystals were being blocked during the course of an experiment.

It has been shown[104,113] that barium sulphate crystals occluded other ions, and in particular chloride ions, from a supernatant solution, and to investigate this effect with strontium sulphate crystals, the strontium chloride used in the preparation of the cell solutions was replaced by strontium nitrate. This was used in experiment 20 and again the same behaviour was observed.

Since chloride ions had been present in the preparation of the seed crystals also, new suspensions c, d and e were prepared from strontium hydroxide and sulphuric acid solutions. Crystal growth proceeded to much nearer solubility in experiments using seed suspension c, which provided a much greater surface area, owing to the smaller crystal size and greater seed concentration, of the order of 200 mgms. per ml. The small irregularities observed near

TABLE 13

Crystallisation of Strontium Sulphate

Experiments in Deionised Water.

Experiment No.	$m_i \times 10^4$ mole/l	$-\Delta m \times 10^4$ mole/l	$m_\infty \times 10^4$ mole/l	Seed Suspension
4	9.990	0.530	9.460	a
9	9.003	0.280	8.723	a
13	6.570	0.047	6.523	b
15	6.352	0.021	6.331	b
18(a)	6.600	0.072	6.528	b
(b)	6.523	0.043	6.480	b
19(a)	7.500	0.191	7.309	b
(b)	7.294	0.272	7.022	b
20(a)	6.600	0.062	6.538	b
(b)	6.533	0.053	6.480	a
23	7.501	---	---	c
25	7.503	---	---	c
26	7.500	---	---	c
30	7.509	---	---	d

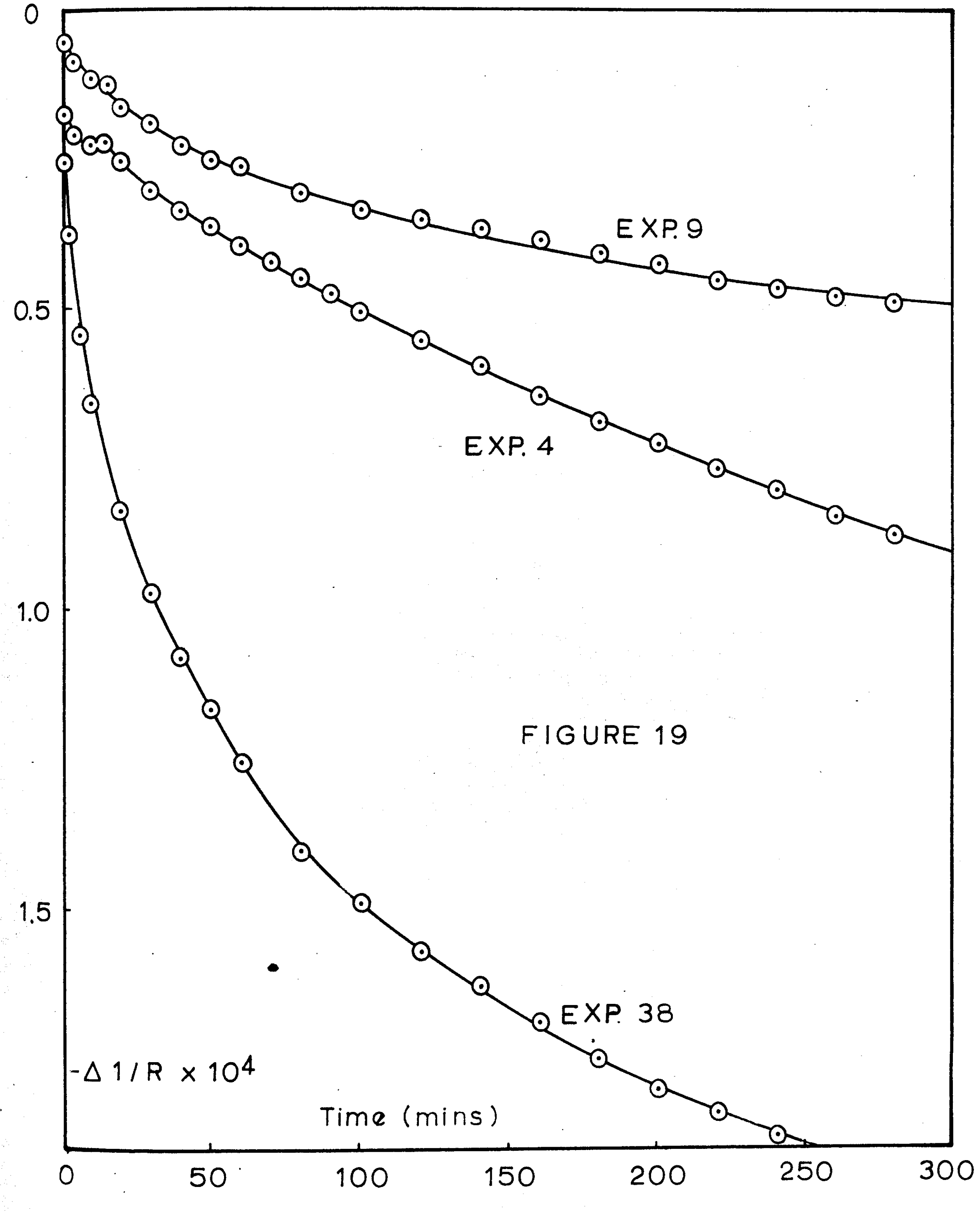

0
0.5
1.0
1.5
EXP. 9
EXP. 4
EXP. 38
-Δ 1/R x 10^4
Time (mins)
0
50
100
150
200
250
300

FIGURE 19

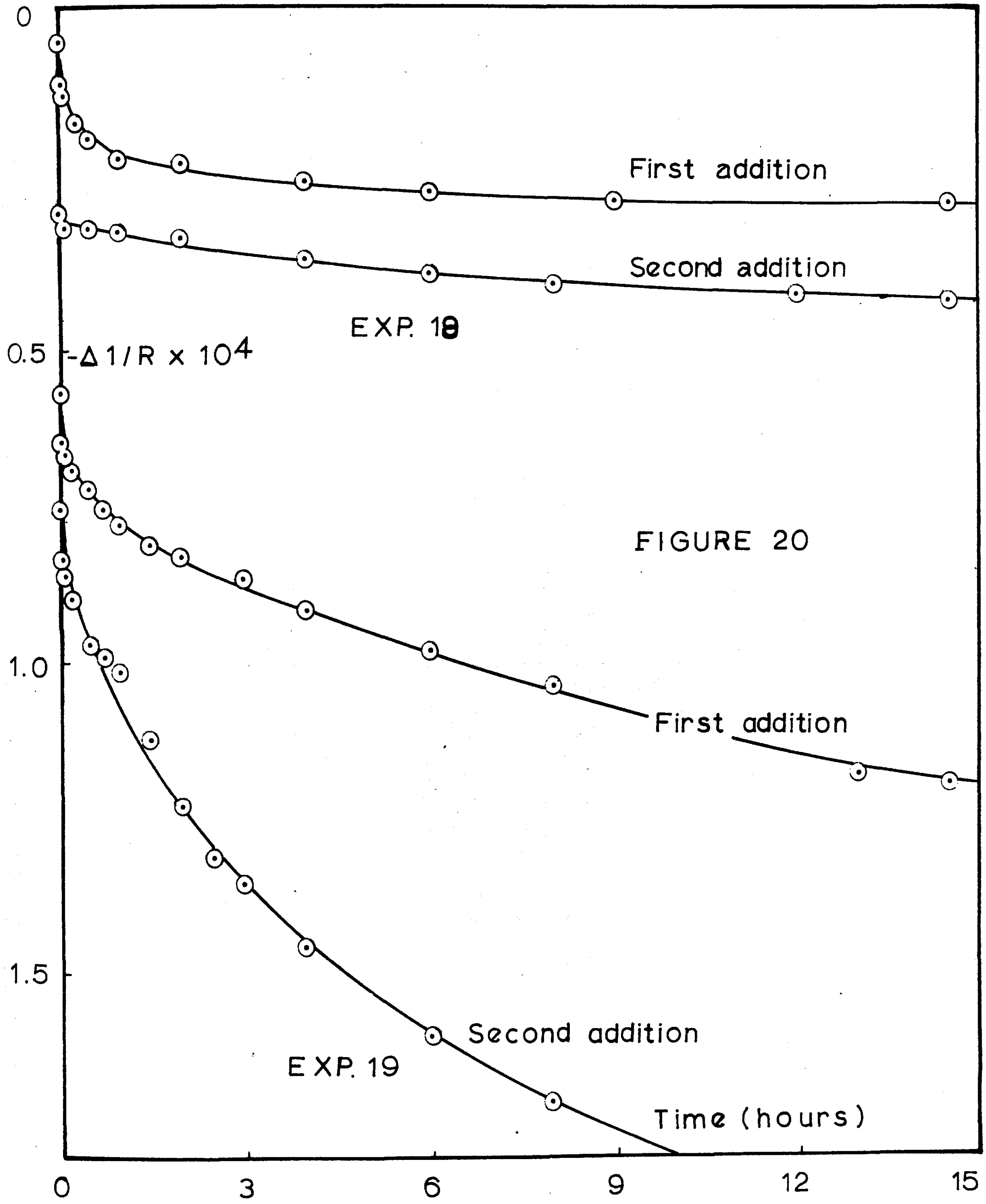

First addition
Second addition
EXP. 18
-Δ 1/R x 10⁴
First addition
Second addition
EXP. 19
Time (hours)
0
0.5
1.0
1.5
0
3
6
9
12
15

FIGURE 20

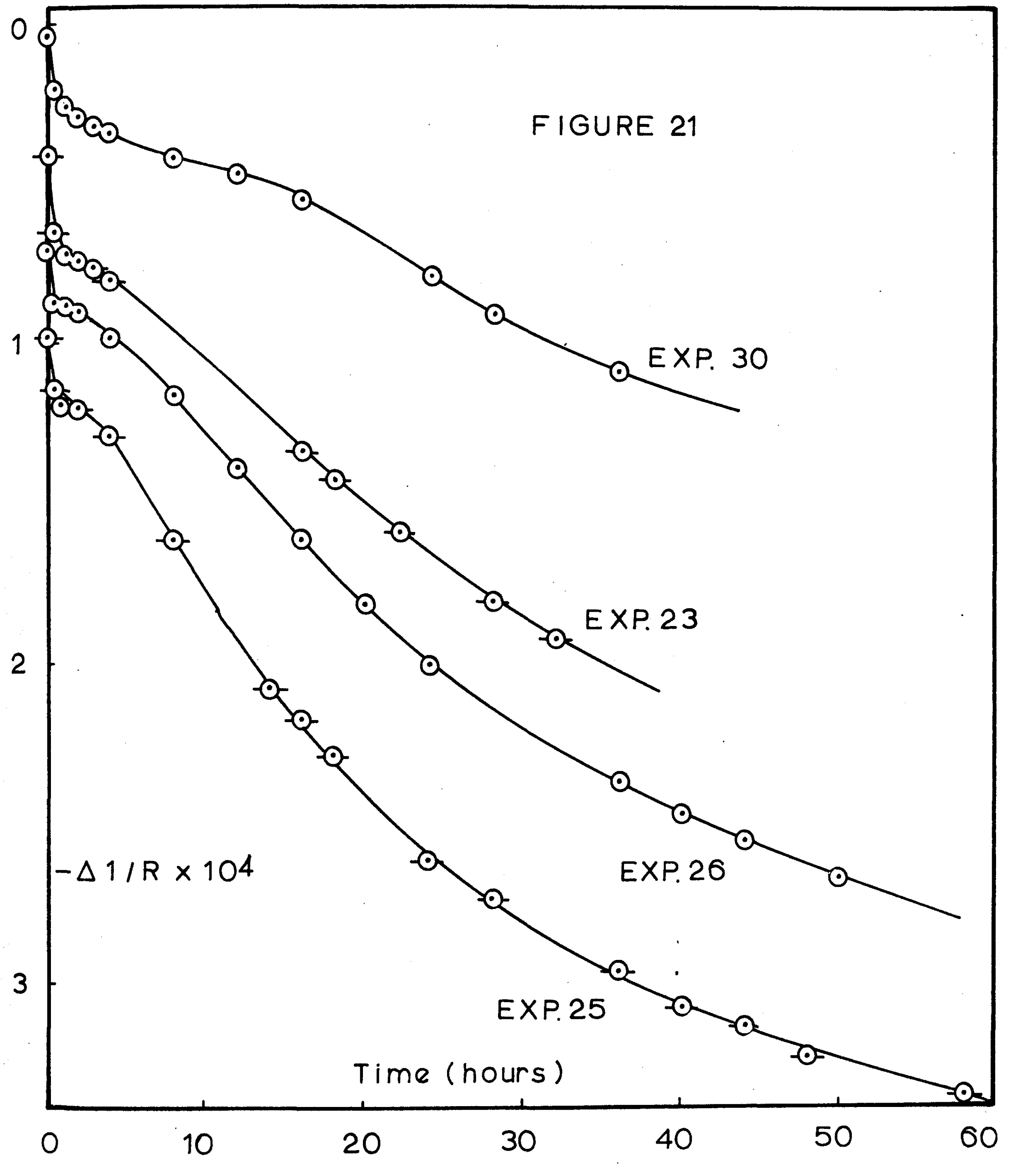


FIGURE 21
EXP. 30
EXP. 23
EXP. 26
EXP. 25
$-\Delta 1/R \times 10^4$
Time (hours)
0
1
2
3
0
10
20
30
40
50
60

TABLE 14

Crystallisation of Strontium Sulphate

$1/R$ x 10^3 ohm^{-1}	$-\Delta m$ x 10^4 mole/l	m_t x 10^4 mole/l	(m_t-m_e) x 10^4 mole/l	$(m_t-m_e)^2$ x 10^8 mole^2/l^2	$-\Delta\frac{1}{R}/\Delta t$ x 10^7 m/l/min	$-dm/dt$ x k0^8 m/l/min
Experiment 25.						
5.441	0.000	7.503	1.063	--	--	--
5.400	0.114	7.389	0.949	0.901	1.55	4.31
5.370	0.197	7.306	0.866	0.750	1.36	3.78
5.340	0.281	7.222	0.782	0.611	1.14	3.17
5.310	0.365	7.138	0.698	0.495	0.90	2.50
5.280	0.448	7.055	0.615	0.378	0.68	1.89
5.250	0.532	6.971	0.531	0.282	0.50	1.39
5.220	0.615	6.888	0.448	0.201	0.34	0.95
Experiment 26.						
5.418	0.000	7.500	1.060	--	--	--
5.370	0.134	7.366	0.926	0.857	1.08	3.00
5.340	0.217	7.283	0.843	0.710	0.88	2.45
5.310	0.300	7.200	0.760	0.577	0.80	2.22
5.280	0.384	7.116	0.676	0.457	0.61	1.70
5.250	0.467	7.033	0.593	0.352	0.42	1.17
5.223	0.542	6.958	0.518	0.268	0.30	0.84

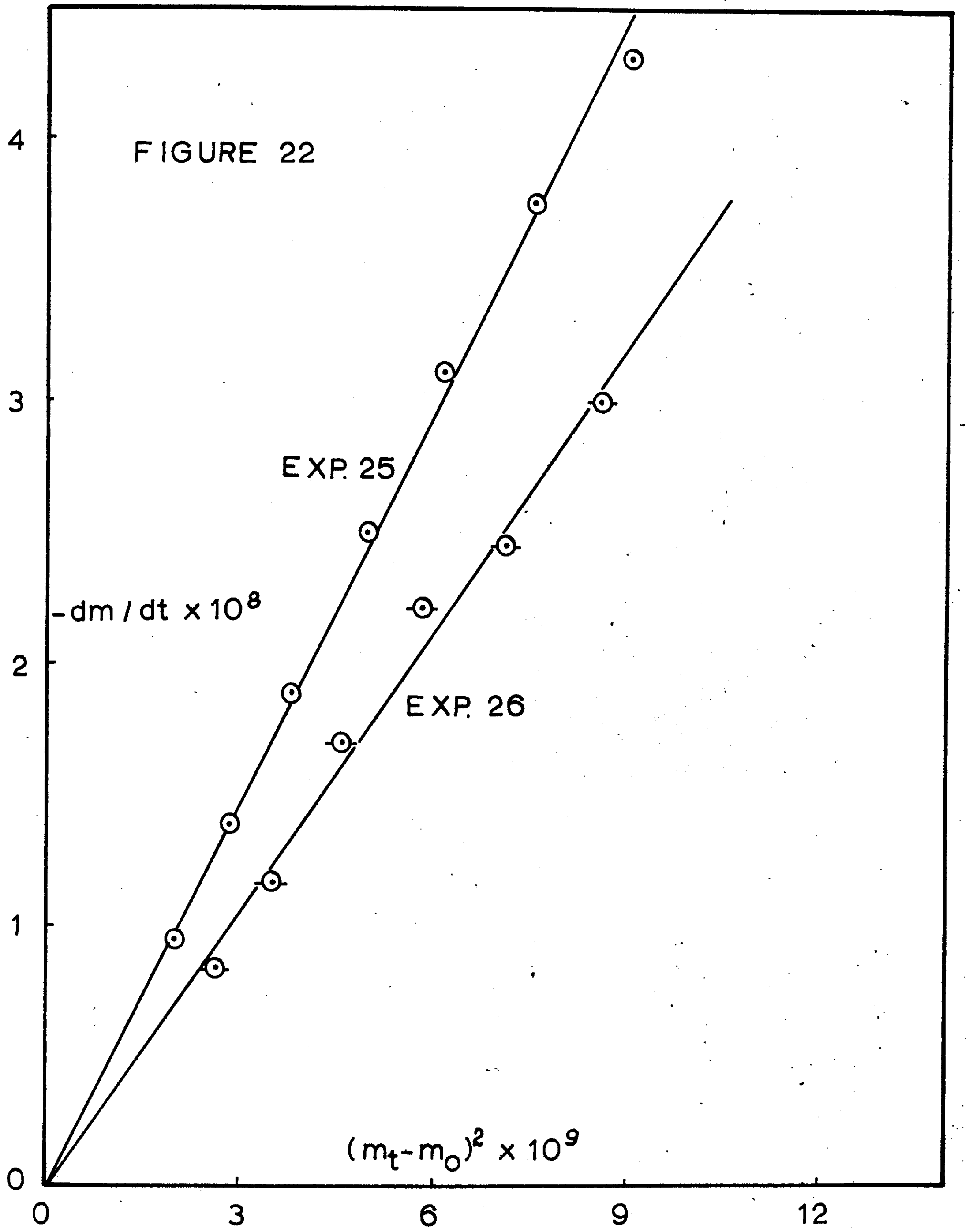


FIGURE 22

the start of the earlier experiments were considerably more pronounced with new seed, as can be seen in Figure 21. After this period of restricted growth, which corresponded to 10-12% of the total, second order kinetics were obeyed, as is shown in Figure 22 for experiments 25 and 26. The rate of crystallisation was slow, and the last points shown on this graph, corresponding to 38% and 52% of the growth respectively, were reached only after 60 hours. The rate constants were respectively 4.93 and 3.60 litre. mole^{-1}.min^{-1}.

The cell solution was also prepared from strontium hydroxide and sulphuric acid solutions to exclude all ions other than strontium and sulphate. Seed suspension d, a much more dilute suspension than c, was used in experiment 30, and crystallisation again stopped whilst the solution was substantially supersaturated.

Experiments were also carried out with seed crystals prepared on the same day, or with aged crystals which had been boiled in conductivity water on the day of the experiment, but again no significant difference in the crystal growth characteristics was observed.

The deionised conductivity water was replaced by conductivity water prepared in a Bourdillon Still, and this was used in the preparation of the cell solutions and the seed suspensions f and g. Crystallisation experiments at equivalent and non-equivalent initial ionic concentrations are summarised in Table 15, and graphs of conductivity vs. time are shown in Figures 23, 25, 28 and 31.

In experiments 33 and 35, seed suspension <u>c</u> was used, and plots of the rate of crystallisation, $\Delta m/\Delta t$, against $(m_t - m_o)^2$ are shown in Figure 24. After initial fast portions equivalent to almost 20% of the crystal growth, the reactions followed second order kinetics. The last points shown on the straight lines correspond to 52% and 40% of the total crystallisation respectively. The rate constants for the experiments of 3.73 and 3.33 litre.mole^{-1}.min^{-1}. per gm. of seed crystals agree well with the <u>ks</u> values obtained in experiments 25 and 26. The much more dilute seed suspension <u>e</u> was used in experiment 36 and, as Figure 26 shows, second order kinetics after a fast start were again obtained. The seed crystals had not aged for long however, and the <u>ks</u> value of 10.0 litre.mole^{-1}.min^{-1}. per gm. of seed crystals was considerably higher than for seed <u>c</u>.

Seed suspensions <u>f</u> and <u>g</u> were used in the later experiments, and conductivity vs. time plots for experiments 37 and 38 are shown in Figures 25 and 28 respectively. Figure 19 allows the different effects of deionised and distilled water on the crystallisation rate plots to be compared. Plots of $\Delta m/\Delta t$ vs. $(m_t - m_o)^2$ in Figures 27 and 29 show that second order kinetics are again obeyed after the characteristic initial fast portion for 20% of the crystal growth. The experiments were followed for 87% and 75% of the reaction respectively, and their rate constants of 63.5 and 44.2 litre.mole^{-1}. min^{-1}. per gm. of seed crystals were very much greater than in the earlier experiments. Experiment 48 was carried out at a later date when the seed crystals had aged for 5 months, in order to provide a

TABLE 15

Crystallisation of Strontium Sulphate

Experiments in Distilled Water.

Expt No.	$[Sr^{++}]_i$ x 10^4 mole/l	$[SO_4^{=}]_i$ x 10^4 mole/l	Seed Suspn	Amt.of Seed gms	ks $l.m^{-1}.min^{-1}.$	Initial Period
33	7.500	7.500	c	1.140	4.25	330 min
35	7.700	7.700	c	0.945	3.15	390 min
36	7.500	7.500	e	0.145	1.45	12-14 hrs
37	7.500	7.500	f	0.700	44.5	15-20 min
38	10.000	10.000	f	0.076*	3.35	200 min
41	5.382	10.685	g	0.220	16.3	12 min
42	10.606	5.302	g	0.120	7.3	25 min
43	10.606	5.303	g	0.440	29.1	8-10 min
48	7.500	7.500	g	0.455	17.5	12 min

* 1ml. seed

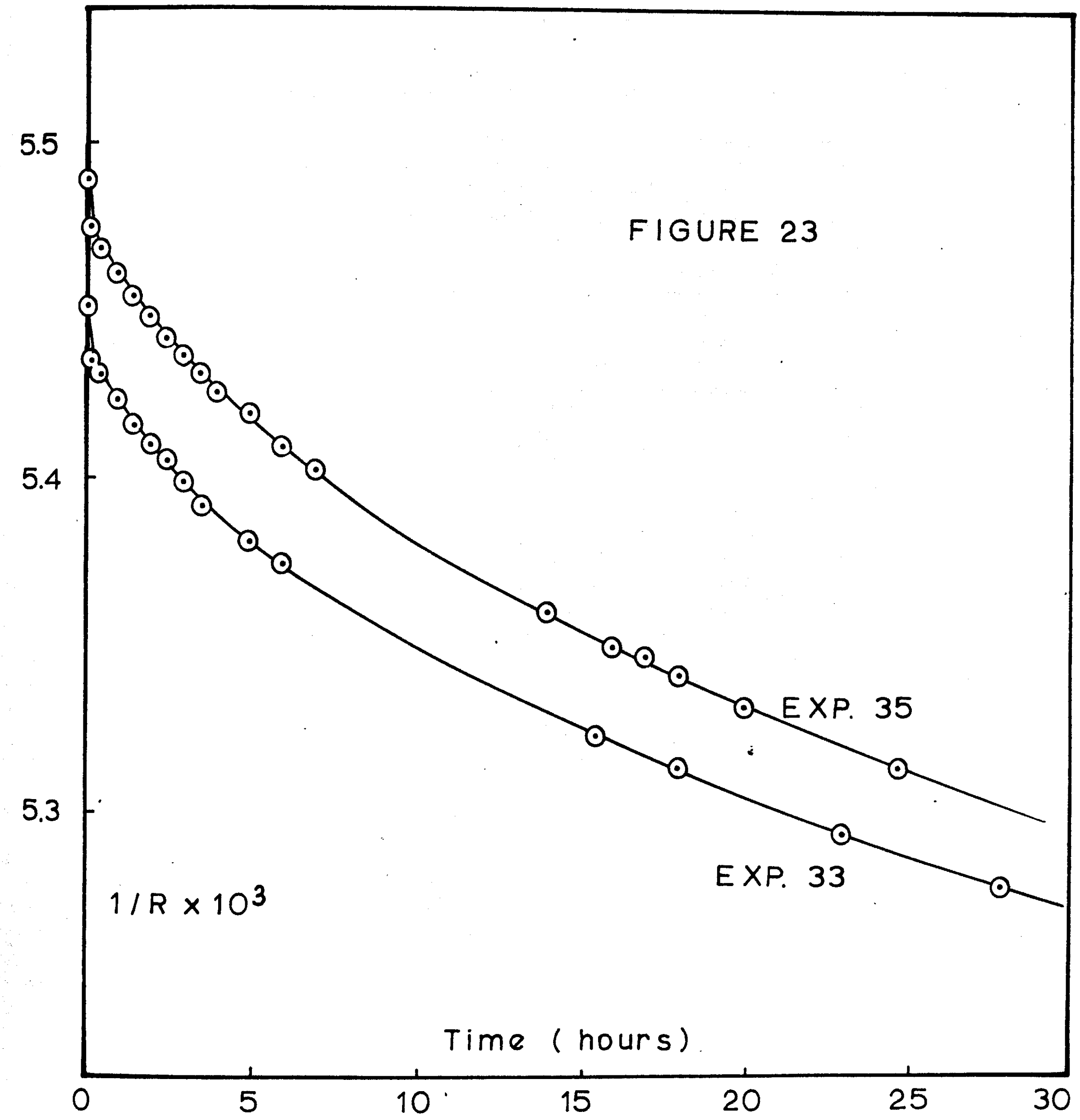


FIGURE 23

TABLE 16

Crystallisation of Strontium Sulphate

$1/R$ x 10^3 ohm^{-1}	$-\Delta m$ x 10^4 mole/l	m_t x 10^4 mole/l	(m_t-m_0) x 10^4 mole/l	$(m_t-m_0)^2$ x 10^8 $mole^2/l^2$	$-\Delta\frac{1}{R}/\Delta t$ x 10^7 m/l/min	$-dm/dt$ x 10^8 m/l/min
Experiment 33.						
5.455	0.000	7.500	1.060	--	--	--
5.395	0.167	7.333	0.893	0.798	1.52	4.23
5.380	0.208	7.292	0.852	0.726	1.22	3.39
5.365	0.250	7.250	0.810	0.656	1.01	2.81
5.350	0.292	7.208	0.768	0.590	0.92	2.56
5.335	0.334	7.166	0.726	0.527	0.82	2.28
5.320	0.375	7.125	0.685	0.469	0.70	1.94
5.305	0.417	7.083	0.643	0.413	0.64	1.78
5.290	0.459	7.041	0.601	0.361	0.55	1.53
5.275	0.501	6.999	0.559	0.312	0.50	1.39
5.260	0.543	6.957	0.517	0.267	0.42	1.17

TABLE 16 cont.

Crystallisation of Strontium Sulphate

$1/R$ x 10^3 ohm^{-1}	$-\Delta m$ x 10^4 mole/l	m_t x 10^4 mole/l	(m_t-m_e) x 10^4 mole/l	$(m_t-m_e)^2$ x 10^8 mole^2/l^2	$-\Delta\frac{1}{R}/\Delta t$ x 10^7 m/l/min	$-dm/dt$ x 10^8 m/l/min
Experiment 35.						
5.495	0.000	7.700	1.260	--	--	--
5.465	0.083	7.617	1.177	1.386	2.64	7.33
5.450	0.125	7.575	1.135	1.289	2.13	5.92
5.435	0.167	7.533	1.093	1.195	1.71	4.75
5.420	0.208	7.492	1.052	1.107	1.38	3.83
5.405	0.250	7.450	1.010	1.020	1.18	3.28
5.390	0.292	7.408	0.968	0.937	1.08	3.00
5.375	0.334	7.366	0.926	0.857	0.99	2.75
5.360	0.375	7.325	0.885	0.783	0.88	2.44
5.345	0.417	7.283	0.843	0.710	0.81	2.25
5.330	0.459	7.241	0.801	0.641	0.73	2.03
5.315	0.500	7.200	0.760	0.577	0.67	1.86

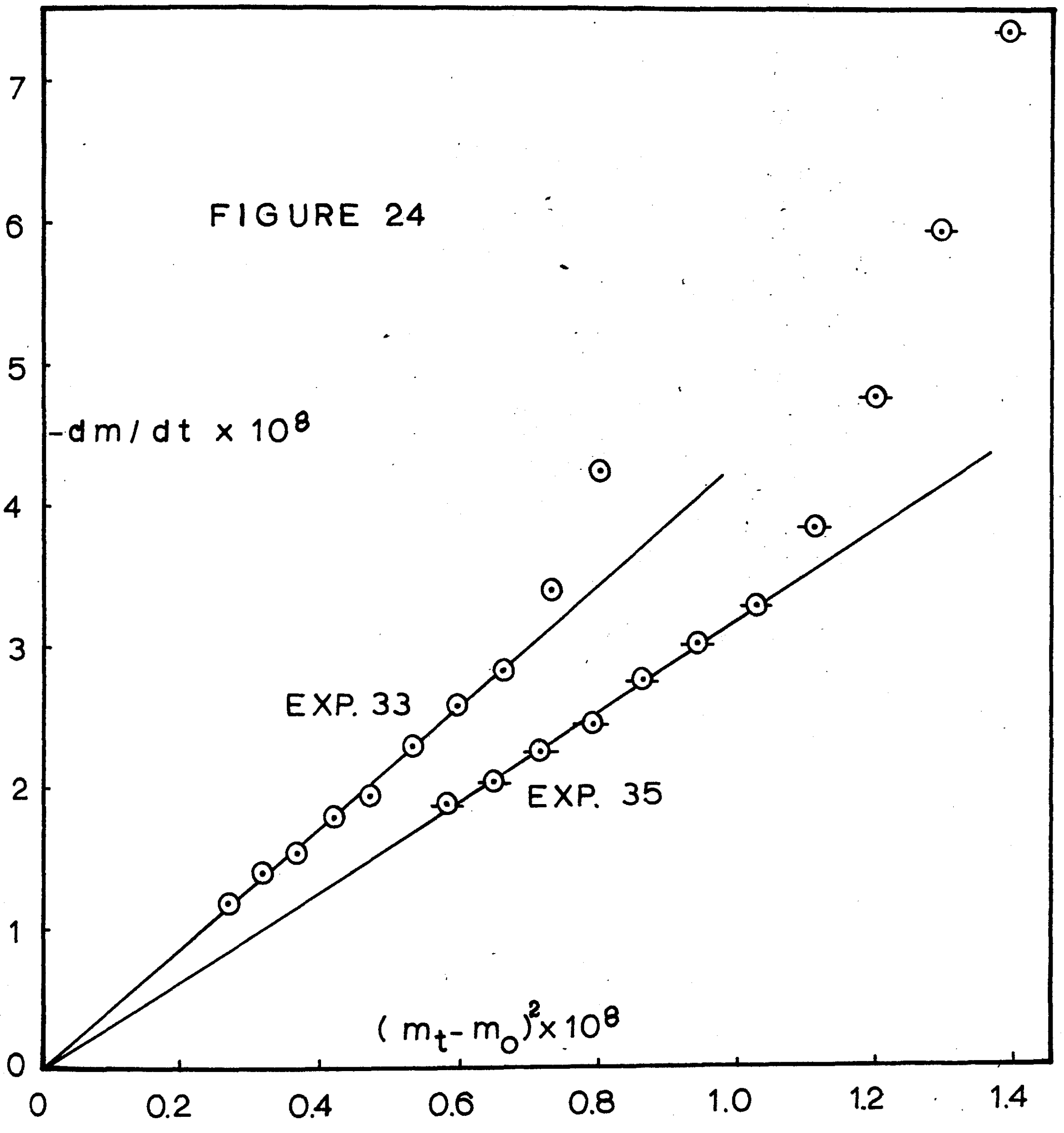


FIGURE 24

-dm/dt x 10^8
(m_t - m_o)^2 x 10^8
EXP. 33
EXP. 35
0
1
2
3
4
5
6
7
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

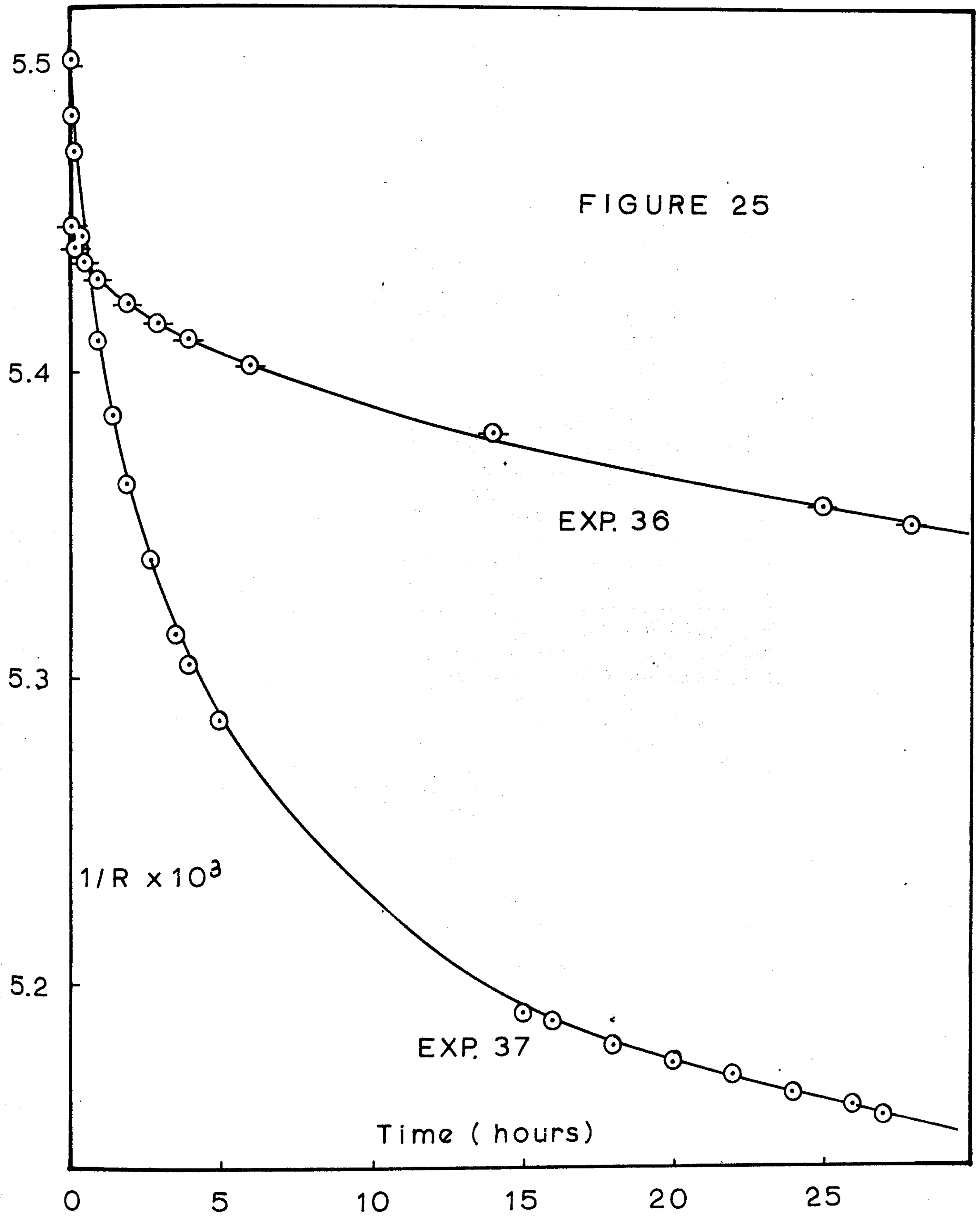


FIGURE 25
5.5
5.4
5.3
5.2
1/R x 10^3
EXP. 36
EXP. 37
Time (hours)
0
5
10
15
20
25

TABLE 17

Crystallisation of Strontium Sulphate

$1/R$ x 10^3 ohm^{-1}	$-\Delta m$ x 10^4 mole/l	m_t x 10^4 mole/l	(m_t-m_o) x 10^4 mole/l	$(m_t-m_o)^2$ x 10^8 $mole^2/l^2$	$-\Delta\frac{1}{R}/\Delta t$ x 10^7 m/l/min	$-dm/dt$ x 10^8 m/l/min
Experiment 36.						
5.449	0.000	7.500	1.060	--	--	--
5.429	0.056	7.444	1.004	1.008	1.50	4.17
5.409	0.111	7.389	0.949	0.900	0.73	2.03
5.389	0.167	7.333	0.893	0.798	0.46	1.28
5.379	0.195	7.305	0.865	0.749	0.39	1.09
5.369	0.222	7.278	0.838	0.701	0.37	1.03
5.349	0.278	7.222	0.782	0.611	0.31	0.87
5.329	0.334	7.166	0.726	0.527	0.27	0.75

TABLE 18

Crystallisation of Strontium Sulphate

$1/R$ x 10^3 ohm^{-1}	$-\Delta m$ x 10^4 mole/l	m_t x 10^4 mole/l	(m_t-m_o) x 10^4 mole/l	$(m_t-m_o)^2$ x 10^8 mole^2/l^2	$-\Delta\frac{1}{R}/\Delta t$ x 10^7 m/l/min	$-dm/dt$ x 10^7 m/l/min
Experiment 37.						
5.510	0.000	7.500	1.060	--	--	--
5.480	0.083	7.417	0.977	0.954	19.9	5.43
5.450	0.167	7.333	0.893	0.797	12.9	3.58
5.420	0.250	7.250	0.810	0.656	10.65	2.96
5.390	0.334	7.166	0.726	0.527	8.53	2.37
5.360	0.417	7.083	0.643	0.413	6.61	1.83
5.330	0.500	7.000	0.560	0.314	4.86	1.35
5.300	0.584	6.916	0.476	0.227	3.49	0.97
5.270	0.667	6.833	0.393	0.154	2.46	0.68
5.240	0.751	6.749	0.309	0.095	1.78	0.49
5.210	0.834	6.666	0.226	0.051	1.06	0.29
5.180	0.917	6.583	0.143	0.020	0.46	0.13

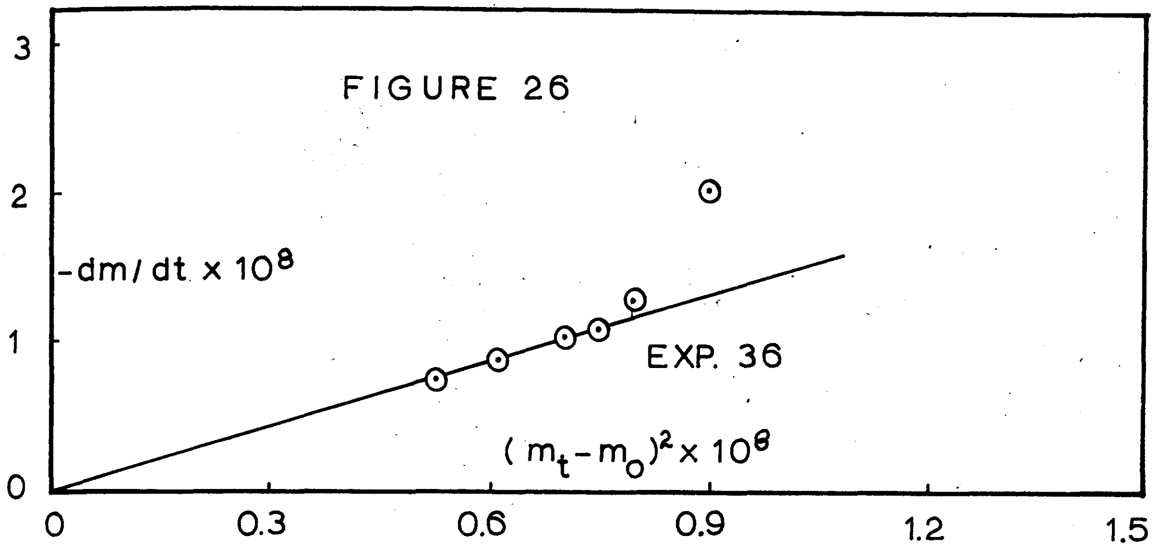


FIGURE 26

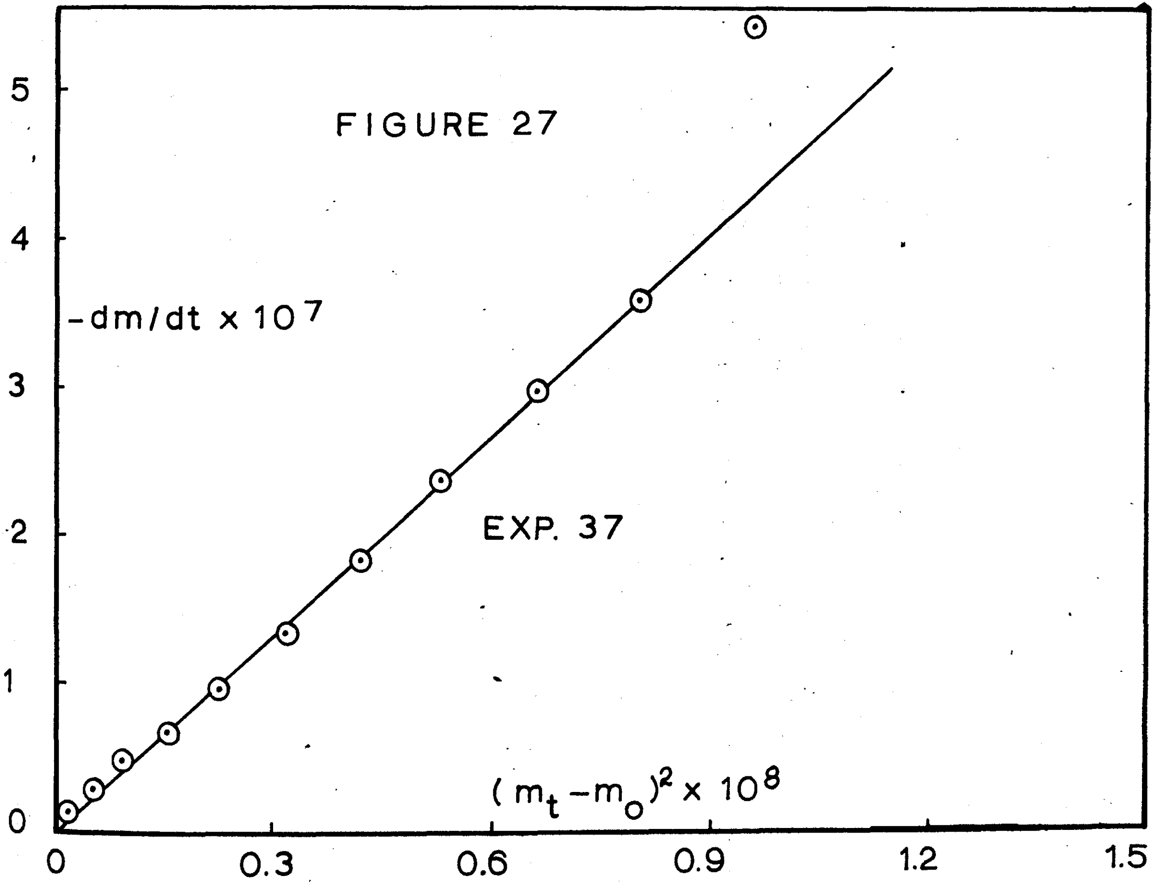


FIGURE 27

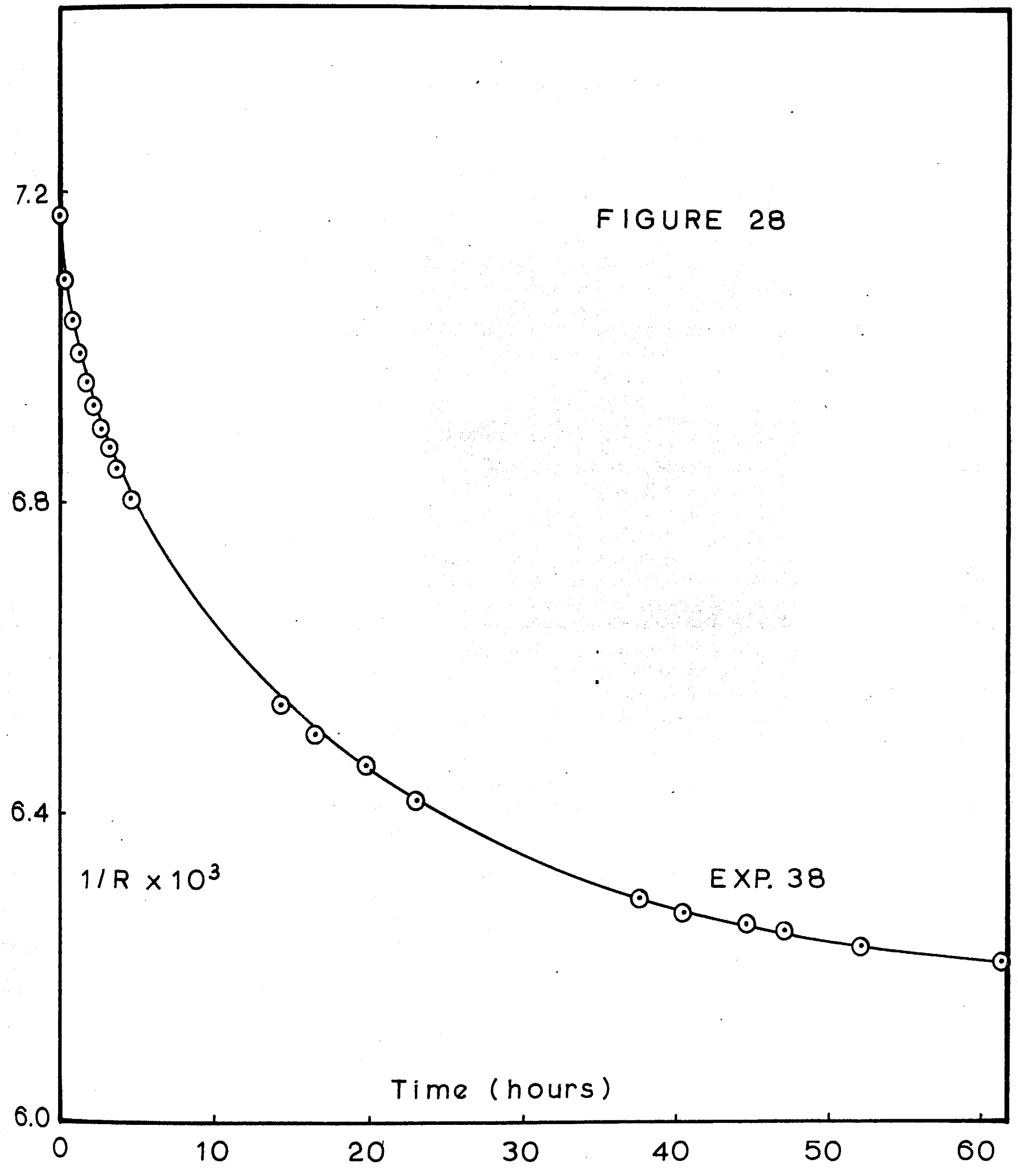


FIGURE 28
EXP. 38
1/R x 10^3
Time (hours)
7.2
6.8
6.4
6.0
0
10
20
30
40
50
60

TABLE 19

Crystallisation of Strontium Sulphate

$1/R$ $\times 10^3$ ohm^{-1}	$-\Delta m$ $\times 10^4$ mole/l	m_t $\times 10^4$ mole/l	(m_t-m_0) $\times 10^4$ mole/l	$(m_t-m_0)^2$ $\times 10^8$ $mole^2/l^2$	$-\Delta\frac{1}{R}/\Delta t$ $\times 10^7$ m/l/min	$-dm/dt$ $\times 10^7$ m/l/min
Experiment 38.						
7.130	0.000	10.000	3.423	--	--	--
7.030	0.283	9.717	3.140	9.859	17.2	4.86
6.930	0.565	9.435	2.858	8.168	11.75	3.32
6.830	0.848	9.152	2.575	6.631	8.45	2.39
6.780	0.990	9.010	2.433	5.919	6.98	1.97
6.730	1.131	8.869	2.292	5.253	6.25	1.76
6.630	1.414	8.586	2.009	4.036	4.76	1.34
6.530	1.697	8.303	1.726	2.979	3.51	0.99
6.430	1.980	8.020	1.443	2.082	2.51	0.71
6.330	2.262	7.738	1.161	1.348	1.58	0.44
6.230	2.545	7.455	0.878	0.772	0.84	0.24

TABLE 20

Crystallisation of Strontium Sulphate

t mins	$1/R$ $\times 10^3$ ohm^{-1}	$-\Delta m$ $\times 10^4$ mole/l	m_t $\times 10^4$ mole/l	(m_t-m_o) $\times 10^4$ mole/l	I* $\times 10^{-4}$ $(\text{mole/l})^{-1}$
Experiment 48.					
0	5.392	0 000	7.500	1.060	0.000
11	5.361	0.085	7.415	0.975	0.083
20	5.356	0.099	7.401	0.961	0.098
40	5.345	0.131	7.369	0.929	0.134
63	5.333	0.165	7.335	0.895	0.174
100	5.315	0.214	7.286	0.846	0.239
140	5.298	0.262	7.238	0.798	0.310
180	5.282	0.305	7.195	0.755	0.382
240	5.263	0.358	7.142	0.702	0.480
750	5.167	0.626	6.874	0.434	1.362
870	5.153	0.665	6.835	0.395	1.592

$$* \; I = (m_t - m_o)^{-1} - (m_i - m_o)^{-1}$$

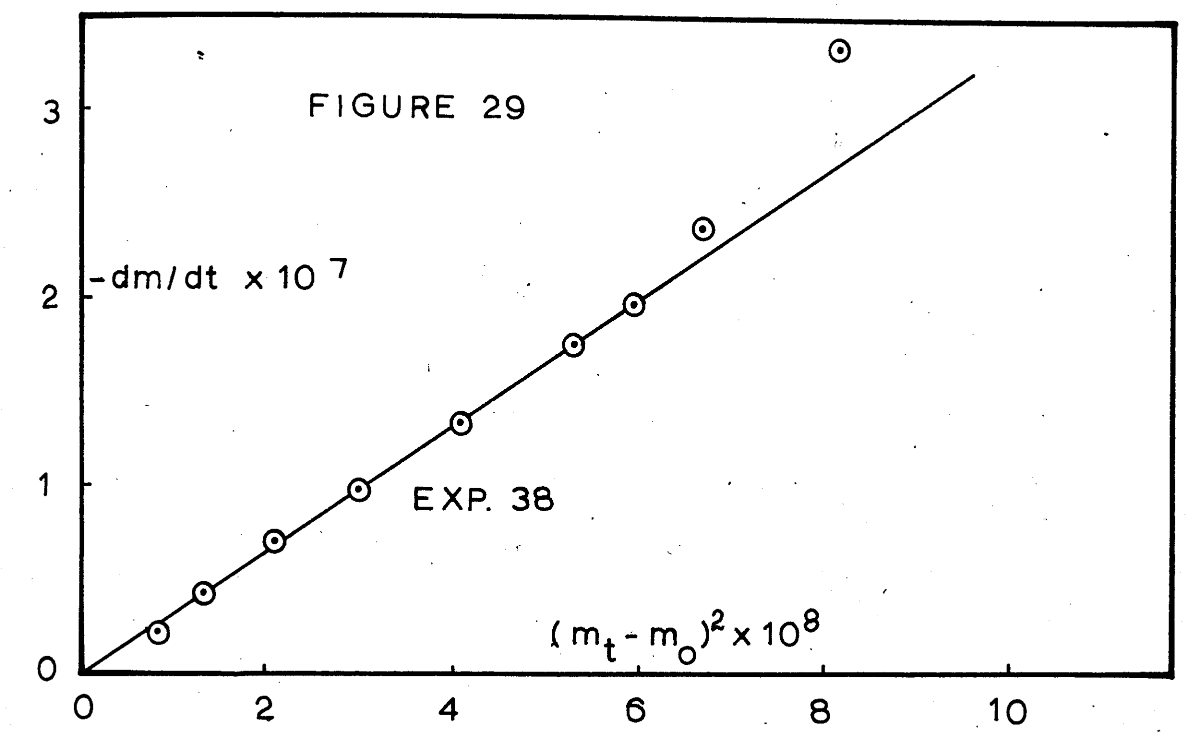


FIGURE 29

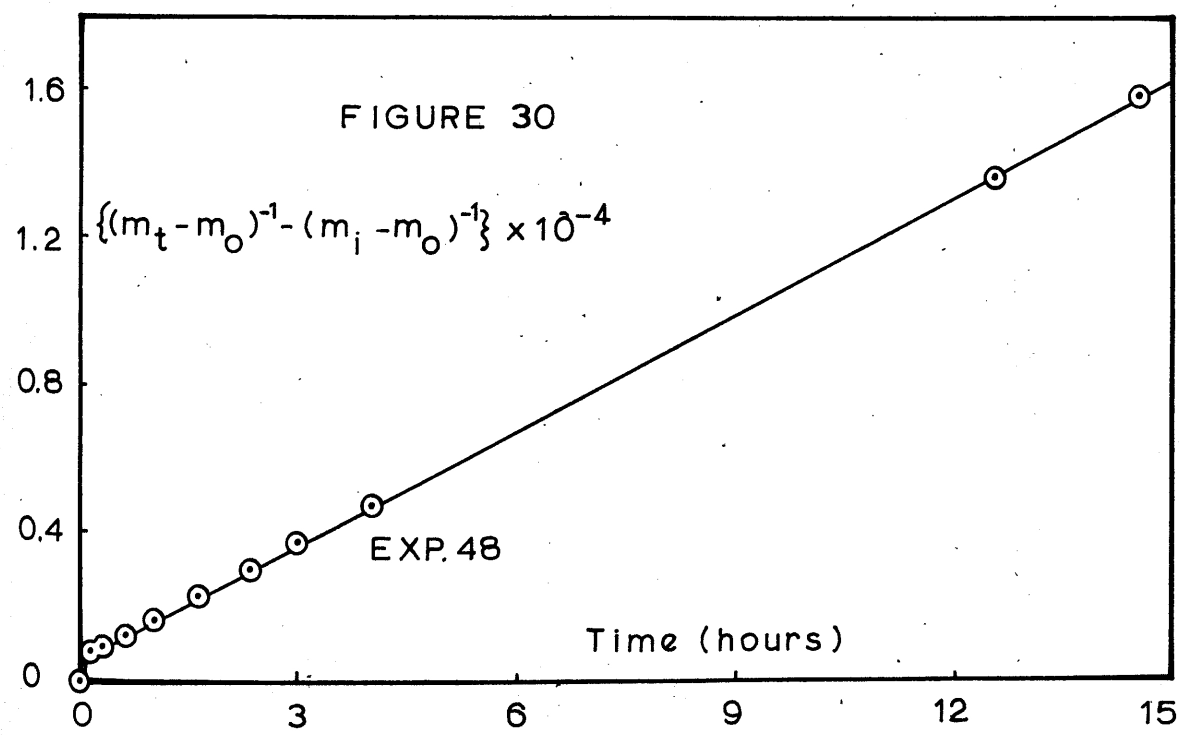


FIGURE 30

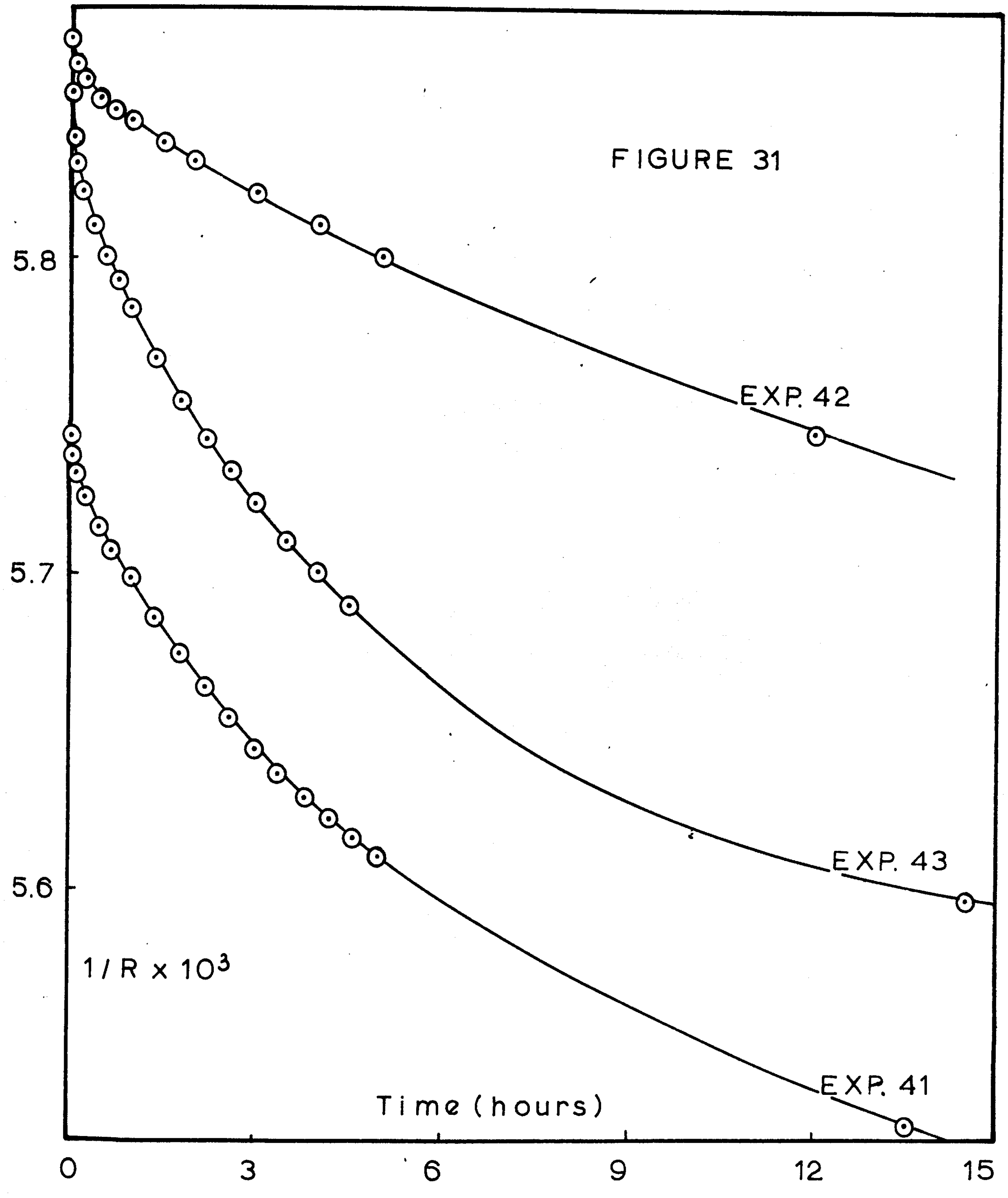


FIGURE 31
EXP. 42
EXP. 43
EXP. 41
5.8
5.7
5.6
1/R x 10³
Time (hours)
0
3
6
9
12
15

TABLE 21

Crystallisation of Strontium Sulphate

t mins	$1/R$ x 10^3 ohm^{-1}	$-\delta(\Delta)$ x 10^4 mole/l	$[Sr^{++}]$ x 10^4 mole/l	$[SO_4^{=}]$ x 10^4 mole/l	Δ x 10^4 mole/l	I^* x 10^{-4} $(m/l)^{-1}$
Experiment 41.						
0	5.747	0.000	5.382	10.686	1.060	0.000
6	5.732	0.041	5.341	10.645	1.019	0.038
18	5.722	0.069	5.313	10.617	0.991	0.066
42	5.708	0.110	5.272	10.576	0.950	0.110
84	5.686	0.169	5.213	10.517	0.891	0.179
144	5.659	0.244	5.138	10.442	0.816	0.282
216	5.633	0.317	5.065	10.369	0.743	0.403
252	5.622	0.347	5.035	10.339	0.713	0.460
300	5.610	0.379	5.003	10.307	0.681	0.525
960	5.507	0.668	4.714	10.018	0.392	1.608
Experiment 42.						
0	5.873	0.000	10.606	5.302	1.009	0.000
10	5.860	0.037	10.569	5.265	0.972	0.038
20	5.855	0.051	10.555	5.251	0.958	0.052
30	5.851	0.061	10.545	5.241	0.948	0.064
60	5.843	0.082	10.524	5.220	0.927	0.088
90	5.837	0.100	10.506	5.202	0.909	0.109
120	5.831	0.117	10.489	5.185	0.892	0.130
180	5.820	0.146	10.460	5.156	0.862	0.168
240	5.811	0.173	10.433	5.129	0.836	0.205
300	5.801	0.201	10.405	5.101	0.808	0.247
720	5.746	0.355	10.251	4.947	0.654	0.538

TABLE 21 cont.

t mins	$1/R$ $\times 10^3$ ohm^{-1}	$-\delta(\Delta)$ $\times 10^4$ mole/l	$[Sr^{++}]$ $\times 10^4$ mole/l	$[SO_4^{=}]$ $\times 10^4$ mole/l	Δ $\times 10^4$ mole/l	I* $\times 10^{-4}$ $(m/l)^{-1}$
Experiment 43.						
0	5.870	0.000	10.606	5.303	1.010	0.000
3	5.849	0.059	10.547	5.244	0.951	0.062
12	5.831	0.108	10.498	5.195	0.902	0.119
30	5.815	0.152	10.454	5.151	0.858	0.175
60	5.794	0.210	10.396	5.093	0.800	0.260
96	5.772	0.273	10.333	5.030	0.737	0.368
148	5.746	0.345	10.261	4.958	0.665	0.515
210	5.720	0.417	10.189	4.886	0.593	0.696
270	5.700	0.472	10.134	4.831	0.538	0.871
870	5.607	0.732	9.874	4.571	0.278	2.616

$* \; I = (\Delta^{-1} - \Delta_i^{-1})$

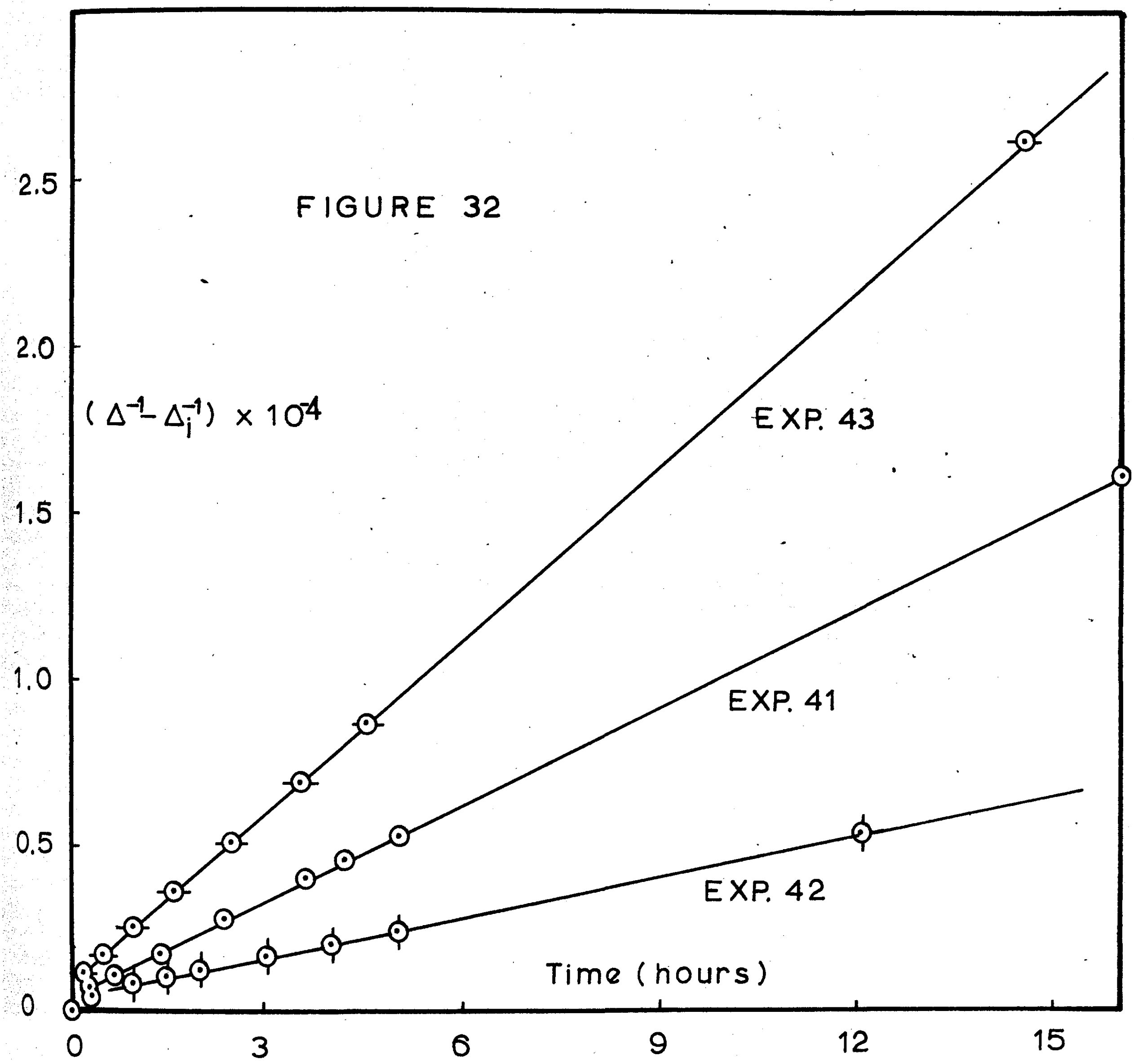


FIGURE 32

$(\Delta^{-1} - \Delta_i^{-1}) \times 10^{-4}$
EXP. 43
EXP. 41
EXP. 42
Time (hours)
0
0.5
1.0
1.5
2.0
2.5
0
3
6
9
12
15

close comparison with experiments on crystallisation from solutions containing adsorbates. The straight line obtained in the plot of $\{(m_t - m_o)^{-1} - (m_i - m_o)^{-1}\}$ vs. t, the integrated form of equation (11), is shown in Figure 30. Crystal growth was followed for 63% of the reaction, less than 10% of which occurred in the short initial fast portion.

Crystallisation into solutions containing non-equivalent initial concentrations of strontium and sulphate ions was also examined, and the conductivity vs. time plots for the experiments are shown in Figure 31. Graphs of $(\Delta^{-1} - \Delta_i^{-1})$ vs. t are shown in Figure 32, and the equation

$$-\frac{dm}{dt} = ks\ (\Delta)^2$$

is followed in each case. Fast initial portions are present, as in the equivalent concentration experiments, but they are shorter and account for only 5-8% of the total crystal growth. Experiments 41, 42 and 43 were followed for 63%, 36% and 73% of the reaction respectively. The rate constants of 74.2, 61.2 and 55.7 litre.mole^{-1}. min^{-1}. per gm. of seed crystals are in good agreement with the corresponding values for experiments 37 and 38.

Since experiments done using deionised conductivity water showed that the effect of impurities on the crystal growth of strontium sulphate was very pronounced, the effect of the addition of dilute solutions of adsorbates to supersaturated solutions of strontium sulphate was examined. Initial concentrations of strontium sulphate and the adsorbates, sodium pyrophosphate and sodium trimetaphosphate, and the amounts of seed crystals used are given in Table 22. Graphs of conductivity vs. time for the experiments are compared in Figure 33 with the rate plot for experiment 48. The amount of growth in the experiments where adsorbates was present was much too small to permit analysis of the kinetics. The greatest amount of growth occurred in experiment 43, where almost 10% of the total reaction was completed in in the first five hours, at which stage the rate of crystallisation was negligible.

Discussion

Apart from an abnormally fast initial portion, the growth of strontium sulphate seed crystals from supersaturated solutions containing equivalent or non-equivalent initial concentrations of strontium and sulphate ions follows a second order rate equation, similar to that proposed by Davies and Jones. The crystallisation was followed for almost 90% of the total reaction without any divergence from second order kinetics being observed. This result agrees with that observed with barium sulphate[47], but in the crystal growth of lead sulphate from non-equivalent ionic concentrations, Little[48] obtained n values greater than two. For lead to sulphate ionic ratios of 4:1 and 1:4, for example, values of n as high as ten were found.

The characteristics of the initial growth surge support the

TABLE 22
Crystallisation of Strontium Sulphate in the presence of Adsorbates.

Expt No.	$m_i \times 10^4$ mole/l	Concn. of Adsorbate*	Seed Suspn.	Seed Concn. mgm/ml
45	7.500	3.30×10^{-6} A	g	202
46	7.500	4.30×10^{-7} A	g	200
47	7.500	4.91×10^{-8} B	g	178
48	7.500	0.00	g	91
49	7.500	1.00×10^{-9} B	g	248

* A - Sodium Pyrophosphate
B - Sodium Trimetaphosphate

TABLE 23
Dissolution of Strontium Sulphate

Expt No.	$m_i \times 10^4$ mole/l	Seed Suspension	Wt. of Seed mgms	Conductivity Water used
6	5.000	a	-	Deionised
39	5.000	g	420	Distilled
40	5.600	g	55	Distilled

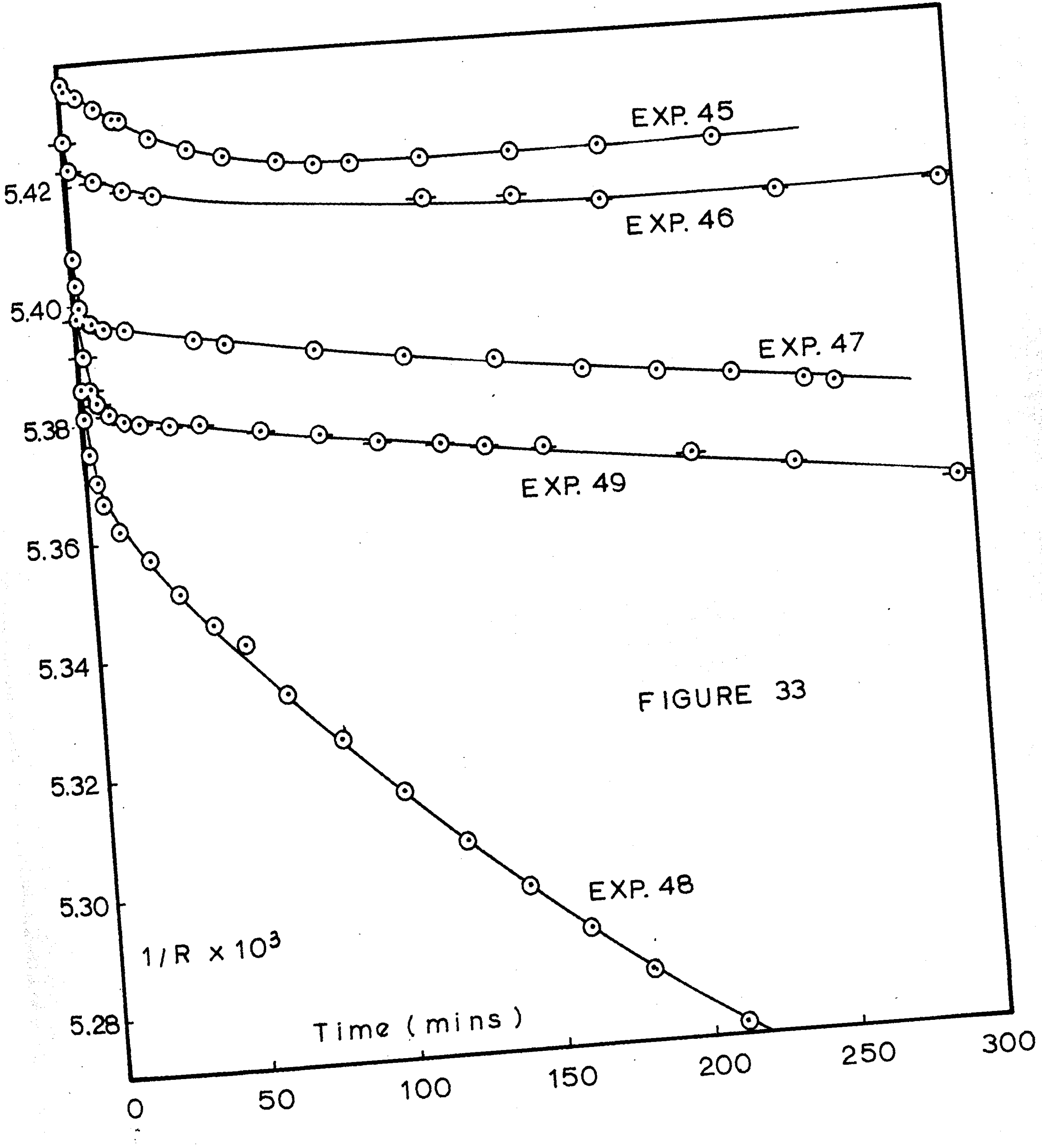

EXP. 45
EXP. 46
EXP. 47
EXP. 49
EXP. 48
5.42
5.40
5.38
5.36
5.34
5.32
5.30
5.28
1/R x 10³
Time (mins)
0
50
100
150
200
250
300

FIGURE 33

suggestion of two-dimensional surface nucleation[47], used to explain a similar effect with barium sulphate. The amount of seed crystals used to inoculate the supersaturated solution appears to provide insufficient growth sites for pure second order growth to occur throughout, and the cell concentration is too low to allow the spontaneous bulk nucleation observed in the crystallisation of magnesium oxalate[46]. On the addition of seed crystals to the cell solution, it seems that the normal crystal growth is accompanied by simultaneous nucleation on the surface of the crystals, which eventually provides enough growth sites for all further crystallisation to take place by the growth mechanism.

The theory of surface nucleation is supported by the observations that an increase in the initial supersaturation and the use of smaller amounts of seed crystals increase the duration of the initial surge. Table 15 shows that with the similarly prepared seed suspensions <u>c</u> and <u>e</u>, the use of a relatively small amount of seed in experiment 36 resulted in a much longer initial fast period. An increase in the initial supersaturation and the use of a very small amount of seed crystals in experiment 38, compared to experiment 37, increased the duration of the initial period by a factor of 10. In the non-equivalent experiments, the same initial supersaturation was used, and, as is seen in Table 15, the duration of the growth surge increased with decreasing amount of seed. Since, at the start of an experiment, growth and nucleation occur simultaneously, the experiments will not be exactly reproducible, and this is borne out by a poor agreement between the rate constants. For seed suspensions prepared and aged in distilled water, the rate constant was 60±15 litre.mole^{-1}.min^{-1}. per gm. of seed crystals. No significant difference in rate constants was observed between experiments with equivalent and non-equivalent concentrations. In this respect, the crystal growth of strontium sulphate differs from that of barium sulphate and lead sulphate, both of which show a decrease in rate with non-equivalent concentrations. In the former case the decrease is greater with the anion in excess, and in the latter with the cation in excess.

One of the notable features of this work was the difference in the results obtained when distilled and deionised conductivity waters were used. Experiments carried out in the presence of small amounts of adsorbate have shown that the crystallisation of strontium sulphate is profoundly affected by traces of impurity. Miura, Otani, Kodama and Shinagawa found[103] that the presence of 1×10^{-5}M. sodium pyrophosphate completely inhibited spontaneous crystallisation, and the effect with sodium trimetaphosphate became significant at 1×10^{-4}M. In the present work, a concentration of 1×10^{-9}M. of the relatively ineffective adsorbate, sodium trimetaphosphate, was sufficient to stop the crystallisation almost entirely after a few minutes. Almost all the growth took place in this initial period, the duration of which increased as the adsorbate concentration decreased.

In contrast to the effect of small amounts of adsorbate on the crystallisation of strontium sulphate, the kinetic order of the crystal growths of magnesium oxalate[46] and silver chloride[89] has been shown to be unaffected by the presence of impurities, although the rate constants are reduced. Little has studied the effect of the condensed phosphates on the crystallisation of lead sulphate[48], and found that the rate of growth decreased with increasing concentration of additive, until a concentration was reached at which growth was completely inhibited. When log $\frac{dm}{dt}$ was plotted against log $(m_t - m_o)$, two intersecting straight lines were obtained of gradients n_1 and n_2, representing, respectively, the initial growth surge and the main part of the growth. When distilled water was used, $n_2 = 2$ in solutions containing relatively high concentrations of anionic adsorbate (at least 10^{-5}M. for sodium pyrophosphate), but with deionised water, low concentrations of impurity led to values of n_2 greater than 2 and increasing as the amount of impurity increased. In the presence of the cationic additive cetyl trimethyl ammonium bromide in distilled water, an initial growth surge was again obtained, but n_2 remained 2 up to a concentration of 10^{-4}M. of adsorbate.

Sears has suggested[70] that the adsorption of impurity reduces the critical free energy for two-dimensional nucleation, causing an increase in surface nucleation. Thus, as the concentration of additive in the lead sulphate experiments increased, the duration of the initial surge, which has been attributed to two-dimensional nucleation, and the value of $\underline{n}$, increased. The kinetic order of the major part of the growth also increased as more adsorbate was added, and it appeared probable that as new growth sites were created, some were immediately occupied by impurity molecules. Further, less extensive nucleation would then be necessary and this may never have stopped completely.

The present results show that the crystal growth of strontium sulphate is affected by the presence of additives to a much greater extent than lead sulphate, and even with the small concentrations used, so little growth took place that it was impossible to determine the kinetics of the reaction. Any growth sites originally present on the seed crystals or subsequently formed by surface nucleation, must have been almost immediately blocked by the adsorbate until, a few minutes after the start of the experiments, the crystal surfaces were completely covered and no further nucleation or growth was observed. The effect of minute amounts of impurity can however be seen in the experiments in which the solutions were prepared with deionised water, which has been found to contain small amounts of organic matter from the ion-exchange resin[35,14]. When the dilute seed suspensions a and b were used, the initial growth surge was lengthy and the value of n_1 was high, in which respects it paralleled the behaviour of lead sulphate with adsorbates. With strontium sulphate however, the impurity molecules were eventually able to arrest the growth almost completely, with only about a quarter of the total reaction completed. Only in experiments 25 and 26, in which very large quantities of seed crystals were used, did the crystallisation proceed to the expected solubility value. In both cases the major part of the growth followed a second order kinetic equation, but the rate constants were less than a tenth of the values obtained in the experiments in which the solutions and seed suspensions were prepared from distilled water. The initial growth surge was followed by a period when crystallisation ceased almost entirely, and this can be attributed to adsorbate molecules occupying the growth sites as they were formed. A reduction in the critical free energy for nucleation, due to the presence of adsorbate on the crystal surface, would ensure that considerable surface nucleation still occurred, and when there was no longer sufficient impurity in the solution to block new growth sites, enough of these would be formed to permit normal second order growth to proceed by a dislocation mechanism. When seed crystals with adsorbed impurity, from being aged in deionised water, were used to inoculate solutions prepared with distilled water, as in experiments 33 and 35, the crystallisation rate curves each showed a long growth surge, as expected on the above hypothesis.

Appendix

The Dissolution of Strontium Sulphate Crystals

Results

Some experiments were done on the dissolution of strontium sulphate seed crystals. Crystals were allowed to dissolve in subsaturated solutions containing equivalent concentrations of strontium and sulphate ions, and from the readings of the change in conductivity with time, the kinetics of dissolution have been examined at 25°.

In the first series of experiments, the seed suspensions and the cell solutions were prepared using deionised conductivity water and in every case, the dissolution was severely retarded by the presence of impurity. When the seed crystals were added to 35% subsaturated solutions, only 15% of the total reaction occurred in the 3-4 hours before the dissolution stopped completely. A typical curve obtained by plotting the reciprocal of resistance against time for experiment 6 is shown in Figure 34, and some experimental details are included in Table 23. When crystals were added to deionised conductivity water, the equilibrium concentration value, reached after about 50 hours was as small as 5.0×10^{-4} mole.litre^{-1}.

Dissolution experiments using crystals and subsaturated solutions prepared with distilled conductivity water, are summarised in Table 23. Curves of conductivity against time are given in Figure 34, and these show how much greater the amount of dissolution was than in the experiment which used deionised water.

The solubility of strontium sulphate, determined in these dissolution experiments, agreed very well with the value obtained in the crystallisation series. The thermodynamic solubility product was

$$K_{Th} = 2.327\text{x}10^{-7} \text{ mole}^{2}.\text{litre}^{-2}.$$

and the solubility value used in the experiments was corrected for ionic strength effects, using activity coefficients calculated from the Davies' equation (equation 9).

The dissolution followed the equation

$$\frac{dm}{dt} = k_{d}.s(m_{\varrho}-m_{t})^{2} \quad . \quad . \quad . \quad . \qquad (12)$$

after an initial fast portion. The straight lines obtained by plotting $\left\{(m_{\varrho}-m_{t})^{-1} - (m_{\varrho}-m_{i})^{-1}\right\}$ vs. time are shown in Figure 35, the experimental data for which is given in Table 24.

In experiment 39, in which a greater subsaturation and amount of crystals was used than in experiment 40, the initial surge accounted for almost 50% of the total dissolved. Only 15-20% of the dissolution occurred in the fast portion in experiment 40.

In equation 12, s is some function of the surface area of the seed crystals, which decreases as dissolution proceeds. A correction factor should therefore be included in the equation, but since relatively large amounts of seed crystals were used, the decrease in weight was less than 1% and the correction was therefore neglected.

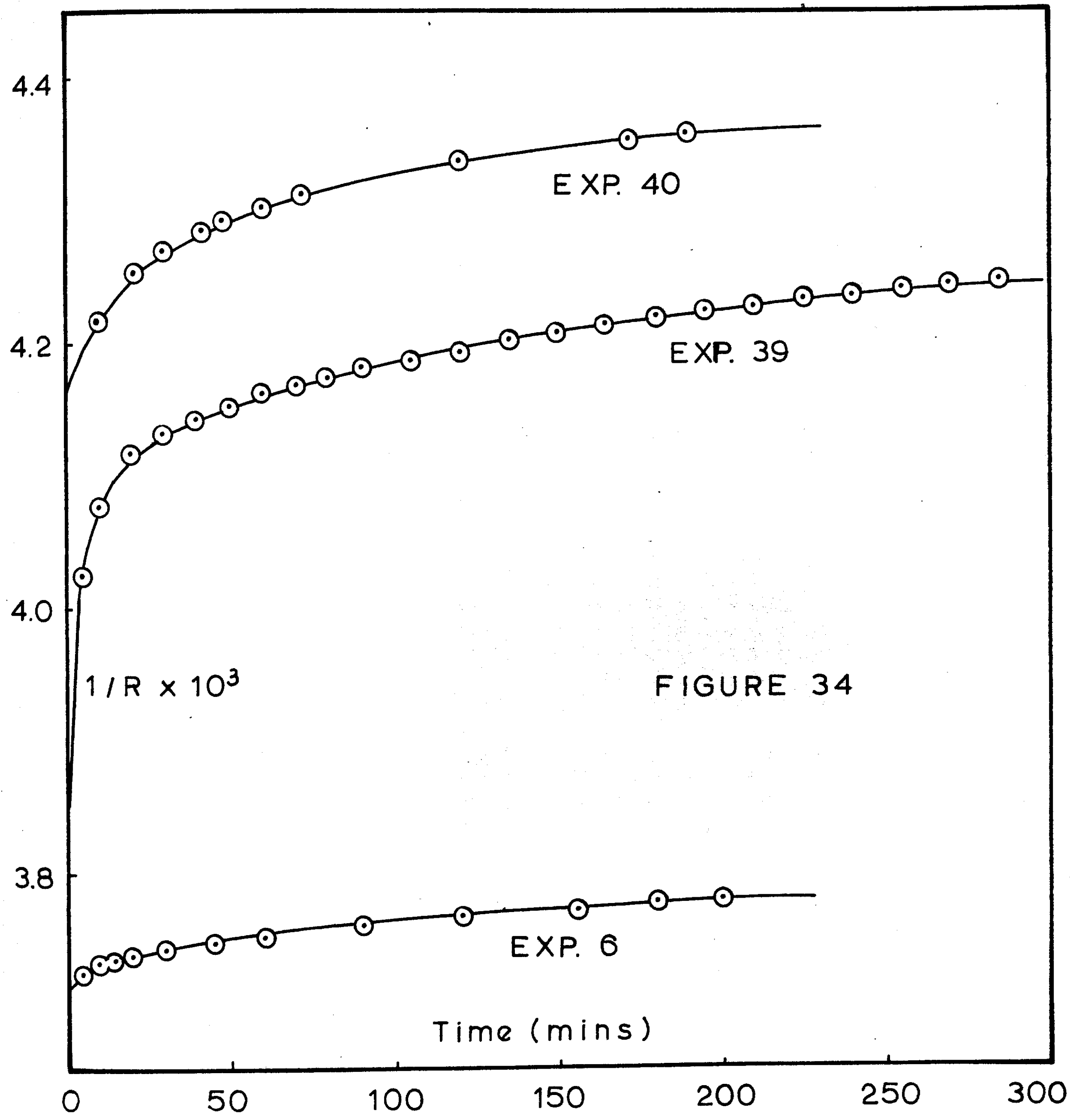

4.4
4.2
4.0
3.8
1/R x 10^3
EXP. 40
EXP. 39
EXP. 6
Time (mins)
0
50
100
150
200
250
300

FIGURE 34

TABLE 24

Dissolution of Strontium Sulphate

t mins	$1/R$ $\times 10^3$ ohm^{-1}	m_t $\times 10^4$ mole/l	Δm $\times 10^4$ mole/l	(m_o-m_t) $\times 10^4$ mole/l	I* $\times 10^{-4}$ $(mole/l)^{-1}$
Experiment 39.					
0	3.8500	5.000	0.0000	1.2480	0.00
5	4.0254	5.480	0.4805	0.7675	0.50
20	4.1165	5.730	0.7302	0.5178	1.13
40	4.1430	5.803	0.8028	0.4452	1.43
60	4.1626	5.856	0.8565	0.3915	1.75
90	4.1806	5.906	0.9058	0.3422	2.12
120	4.1941	5.943	0.9428	0.3052	2.49
180	4.2208	6.016	1.0160	0.2320	3.51
240	4.2351	6.055	1.0552	0.1928	4.39
285	4.2464	6.086	1.0861	0.1619	5.37
Experiment 40.					
0	4.1600	5.600	0.0000	0.6700	0.00
10	4.2174	5.757	0.1573	0.5127	0.46
21	4.2536	5.856	0.2565	0.4135	0.93
30	4.2695	5.900	0.2997	0.3703	1.21
42	4.2854	5.943	0.3432	0.3268	1.57
48	4.2926	5.963	0.3633	0.3067	1.77
60	4.3033	5.993	0.3927	0.2773	2.11
72	4.3112	6.014	0.4143	0.2557	2.41
120	4.3365	6.084	0.4838	0.1862	3.88
172	4.3519	6.126	0.5258	0.1442	5.43
189	4.3568	6.139	0.5393	0.1307	6.12

$* \; I = (m_o-m_t)^{-1} - (m_o-m_i)^{-1}$

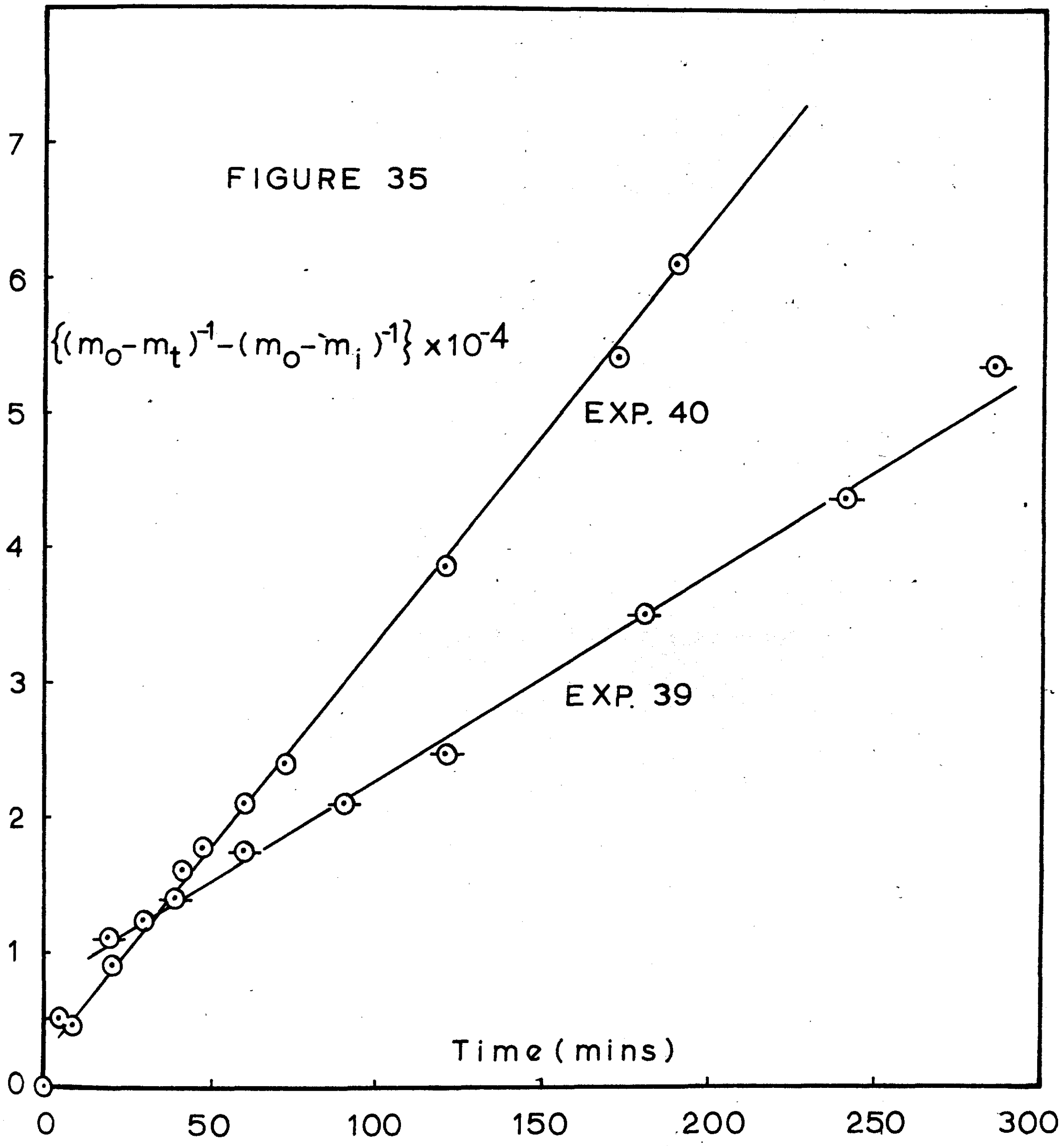


FIGURE 35
$\{(m_o-m_t)^{-1}-(m_o-m_i)^{-1}\}\times10^{-4}$
EXP. 40
EXP. 39
Time (mins)
0
1
2
3
4
5
6
7
0
50
100
150
200
250
300

Discussion

The dissolution of strontium sulphate into subsaturated solutions at 25° follows a second order rate law (equation 12), after an initial fast portion. Under similar conditions, the dissolution of silver chloride and silver chromate crystals into subsaturated solutions have been shown to be first order reactions[93]. Jones, however, found that the dissolution of strontium and lead sulphates followed a second order law[94], and this has been observed by Little for lead and barium sulphates also[48]. The solution of some 2:2 electrolytes does not appear therefore to be a straightforward diffusion controlled process, and another step, probably taking place at the crystal surface, is rate determining.

If the steps occurring at the crystal surface are sufficiently rapid, the rate controlling mechanism will be the diffusion of ions away from the surface, and the reaction will be first order. A kinetic order greater than unity could be expected however, if the slow step involved the removal of a pair of positive and negative ions from the crystal lattice, then separation against mutual attraction, and subsequent hydration. The electrostatic forces of attraction between the ions in the crystal lattice, and between the ions in solution, are much stronger for 2:2 electrolytes than for 1:1 electrolytes, and the work required to separate the ions will therefore be greater for the former. This is seen in their respective lattice energies of approximately 540 Kcals. for barium sulphate and 207 Kcals. for silver chloride.

Less energy is required therefore to remove the ions from the crystal with a 1:1 electrolyte, and the subsequent diffusion of hydrated ions away from the surface is slower than the separation of ions from the crystal lattice, as is shown by the first order kinetics usually observed. For 2:2 electrolytes the reaction at the surface may be slower than the rate of diffusion, resulting in a second order reaction.

Little found an initial fast portion in the dissolution of lead sulphate and barium sulphate[48] with $\underline{n} > 2$. This has also been observed in the present work for the solution of strontium sulphate, and the fast part appears to become longer as the supersaturation and amount of seed crystals increase. Because of the different extents of this fast portion, it is not useful to express the subsequent rate constants in these experiments.

The initial dissolution surge may be attributed to rapid dissolution at sites of high localised energy, such as the centres of dislocations which, for a divalent salt, will carry a relatively high charge. Rapid solution will occur at inner regions of the crystal, rather than uniform dissolution over the surface, and it will cease when the energy at the centre of the dislocation becomes equal to that at the surface. Dissolution will then proceed by the second order mechanism, the rate determining step being the removal of ions from the lattice. The seed crystals of strontium sulphate were prepared by precipitation, and this would favour the formation of dislocations much more than the slow recrystallisation method used for silver chloride crystals.

The dissolution of strontium sulphate was affected by the use of deionised conductivity water, which has been shown to contain traces of impurity, to such an extent that the kinetics of the reaction could not be studied. The rate of solution was very slow throughout and became negligible after about 4 hours, or 15% of the reaction. Little found[48] that the presence of small amounts of tetrametaphosphate ions reduced the rate of solution of lead sulphate, but the reaction was still second order for the main part. This retardation was greater in deionised water than in distilled water.

The dissolution of a perfect crystal is thought to commence by the creation of unit pits, one molecule deep, which grow by steps retreating across the crystal surface. Since such pits are most likely to form at dislocations, it can be assumed that dissolution proceeds from these sites of local high energy on the crystal faces. The energy of the dislocation will be lowered by the presence of impurity molecules which will adsorb at the active sites, and the rate of formation of unit pits will therefore also be reduced. Impurities also retard the movement of the monomolecular steps so that the dissolution tends to proceed more rapidly into the crystal than over its surface. In the present series of experiments using deionised, water, the amount of impurity adsorbed appears to be sufficient to make the initiation of unit pits energetically unfavourable. Further solution by the retreat of the monomolecular steps is also inhibited almost completely after a relatively short time.

PART 3

Crystallisation of Silver Iodate in Aqueous Solution

Introduction

The crystal growth of silver iodate from supersaturated solutions at 25° has been examined conductimetrically by allowing growth to take place on inoculating seed crystals. Although silver iodate has been much used in studies of the stability constants of silver ion complexes, no work appears to have been done on its crystal growth. Kolthoff and Lingane[115], in their determination of the solubility of silver iodate by conductimetric methods, observed that when crystals were added to the cell solution, the resistance dropped to within 2% of the final value after 30 minutes, and solubility equilibrium was reached within one hour.

The crystal growth was studied from solutions of equivalent and non-equivalent concentrations of silver and iodate ions and appears to follow the theory of crystallisation for a 1:1 electrolyte. In the presence of traces of impurity in the solution, there is evidence for additional surface nucleation. The spontaneous crystallisation of slightly supercritical solutions was also followed, and the results were in agreement with the view that a definable boundary exists between the metastable and labile regions of supersaturation.

Experimental

Preparation of Solutions

The supersaturated solutions of silver iodate were prepared from Analar silver nitrate and potassium iodate by the method described on p43. Deionised conductivity water was used in the early experiments, but this was replaced in later work by conductivity water prepared in a Bourdillon Still.

Preparation of Seed Suspensions

Silver iodate was prepared by the slow addition of hot 0.2M. solutions of silver nitrate and potassium iodate to hot distilled water. The thick white precipitate was stirred for a few hours and then washed repeatedly with distilled water. The crystals were redissolved in hot distilled water, filtered rapidly into a lagged flask and left to cool slowly in the dark. The seed crystals, in the form of thin needles, were washed and aged in conductivity water in a blackened pyrex bottle.

Seed suspensions a, b, c and d were washed and aged in deionised conductivity water, and their average seed concentration and crystal size are given in Table 25.

Suspensions e, f and g were prepared, washed and aged using distilled conductivity water throughout. The average crystal size was again $150\mu \times 12\mu$, and the amount of seed used in each experiment is given in Table 30.

Solubility of Silver Iodate

The solubility of silver iodate has been investigated by many workers in recent years and the results lie within narrow limits. Kolthoff and Lingane[115] and Li and Lo[115], who determined the silver and iodate ionic concentrations independently by potentiometric and iodometric titrations, obtained values of the solubility, corrected to zero ionic strength, S_o, of 1.744×10^{-4} mole.litre^{-1} and 1.748×10^{-4} mole.litre^{-1}. A slightly higher value, 1.767×10^{-4} mole.litre^{-1}, was obtained by Keefer and Reiber[117], and Monk[118], who used relatively large granular crystals, found $S_o = 1.760 \times 10^{-4}$ mole.litre^{-1}. Ricci and Amron[119] removed the very fine silver iodate particles from their solutions, since they observed that samples showing appreciable Tyndall effects gave high results, and they obtained $S_o = 1.769 \times 10^{-4}$ mole.litre^{-1}.

The solubility of seed crystals used in the present work was determined from crystallisation and dissolution experiments, the results of which agreed well for the different seed suspensions. The thermodynamic solubility product

$$K = [Ag^+][IO_3^-].\ f_1^{\,2}$$

was found to be 3.129×10^{-8} (mole.litre^{-1})^2, corresponding to an S_o value of 1.769×10^{-4} mole. litre^{-1}. Equation 9 was used to evaluate $\underline{f_1}$.

Conductivity Values

The limiting ionic conductances of the silver and iodate ions are respectively 61.92[84] and 40.75[120], and the equivalent conductivity of silver iodate in water was obtained from the Onsager equation

$$\Lambda_{AgIO_3} = 102.67 - 83.71m^{\frac{1}{2}}.$$

Since the changes in concentration during a crystallisation experiment were very small, the equivalent conductivity was taken as constant, and equal to the value 101.48 at a concentration of 2.00×10^{-4} mole.litre^{-1}.

The changes in concentration of the silver iodate solutions were calculated from the observed conductances and since the amount of silver iodate deposited amounted to only about 0.01% of the weight of seed crystals added, the surface area of the crystals did not change appreciably during the course of an experiment.

Results

Preliminary experiments were done to determine the maximum concentration at which silver iodate solutions could be prepared without crystallising spontaneously, and this critical supersaturation was estimated by the method of Davies and Jones[3]. The supersaturated solutions were prepared in a similar manner as in the crystal growth experiments, except that while the first dilute solution was being added to conductivity water in the cell and being allowed to come to temperature and carbon dioxide equilibrium, the other dilute solution was being equilibrated under a stream of nitrogen in the thermostat. A measured sample of the latter was added to the cell relatively quickly, and it was found that the conductance of the silver iodate solution settled almost instantaneously and, with subcritical concentrations, would remain steady for at least thirty hours.

When the cell concentration was supercritical, plots of conductivity vs. time showed a very slow initial fall, which was

TABLE 25

Silver Iodate Seed Suspensions

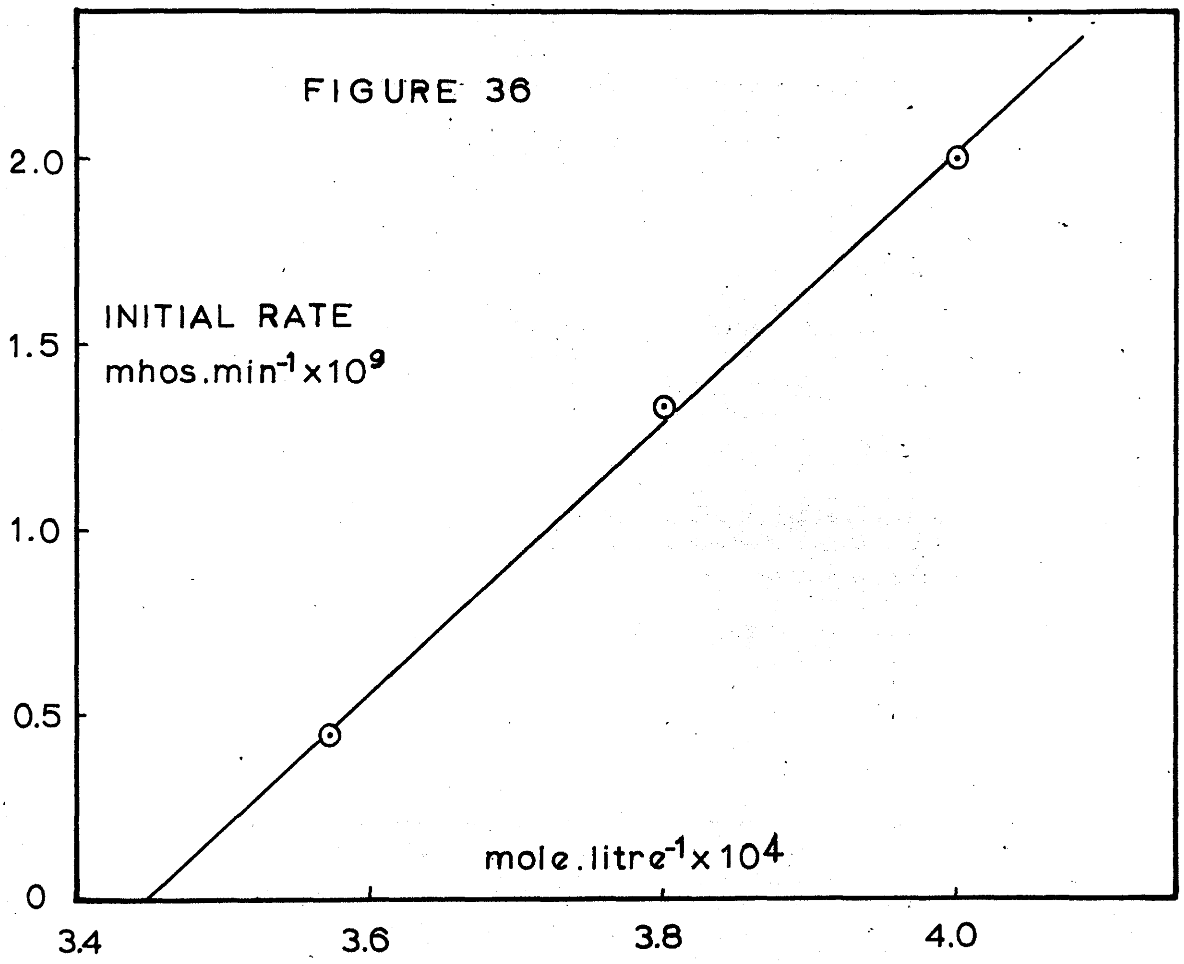
Seed Suspension	Average Seed Concentration mg/ml of suspn.	Average Crystal Size microns
a	40	100 x 8
b	10	150 x 12
c	10	150 x 12
d	25	150 x 12

TABLE 26

Critical Concentration of Silver Iodate

Experiment No.	Initial Concentration mole/l x 10^4	Rate of Change of Conductivity mho.min^{-1} x 10^9
12	4.000	2.00
13	3.572	0.45
14	3.800	1.33

FIGURE 36


2.0
1.5
1.0
0.5
0
INITIAL RATE
mhos.min^{-1} x10^{9}
mole.litre^{-1} x 10^{4}
3.4
3.6
3.8
4.0

attributed to the spontaneous formation of nuclei, and when sufficient sites were present for subsequent growth to commence, the conductance values began to fall off markedly. The gradient of the initial slow portion was a measure of the rate of increase in the number of nuclei in the solution, and values of the rate of change in conductance and initial concentrations are given in Table 26. At the critical supersaturation, there should be no increase in the number of nuclei, since their rates of formation and redissolution should be equal. A graph of, rate of change of conductivity vs. initial concentration is shown in Figure 36 and the critical concentration, obtained by extrapolating the straight line to zero rate of change, is 3.45×10^{-4} mole.litre^{-1}. This corresponds to approximately 250% supersaturation.

In the study of the crystal growth of silver iodate, the experimental techniques and the method of calculation of results were the same as for the silver chloride work. In the early experiments the crystallisation was affected by traces of impurity, derived from the ion exchange resin columns in a similar manner to the growth of strontium sulphate. Some of these experiments are summarised in Table 27, and their conductivity vs. time plots (Figures 37, 38 and 39) illustrate the variety of results obtained with different seed suspensions. The rate of crystallisation with the dilute suspensions b and c was relatively very slow, only 14-17% of the total growth being completed in the first 3 hours and less than 25% in the first day. These experiments did not proceed far enough for an analysis of their kinetics to be of value, but each of them showed an initial growth surge of a kinetic order much greater than 2. The irregular portion present in the strontium sulphate rate plots, when growth ceased almost completely for a few minutes immediately after the initial surge, was also exhibited to varying degrees in some silver iodate experiments.

A concentrated seed suspension and a high initial cell concentration were used in Experiment 10, and although again less than 20% of the reaction was completed in 3 hours, the rate plot exhibits no growth surge or irregularities. The plot of the integrated form of the equation

$$-\frac{dm}{dt} = ks(m_t - m_o)^2$$

in Figure 41 shows that the kinetics are second order for the 65% of the reaction followed.

The seed crystals used in the above experiments had aged for 2-3 months, and when suspension d which had aged for only 10 days was used, as in Experiments 27 and 28, the rate of crystallisation was considerably greater. As Figure 40 shows, the crystal growth commenced with a very pronounced growth surge which lasted for 20-25 minutes and accounted for approximately half of the total growth. After this portion, which had an apparent kinetic order of 7-8, the crystallisation was followed for 80% of the total and no further deviation from second order kinetics was observed. The use of seed a resulted in a k of 90 litre.mole^{-1}. min^{-1}. per gm. of seed crystals, whereas seed d, aged for a much shorter period, gave a second order rate constant of 4.1×10^3 litre. mole^{-1}.min^{-1}. per gm. of seed.

TABLE 27

Crystallisation of Silver Iodate

Experiments in Deionised Water.

Experiment No.	Initial Concentration mole/l x 10^4	Seed Suspension	ks x 10^2 $l.mole^{-1}.min^{-1}$
8	2.1874	b	-
10	2.5498	a	0.18
16	2.1391	b	-
21	2.2000	c	-
27	2.0100	d	5.1
28	2.0100	d	4.8

$S_o = 1.769 \times 10^{-4}$ mole.litre^{-1}

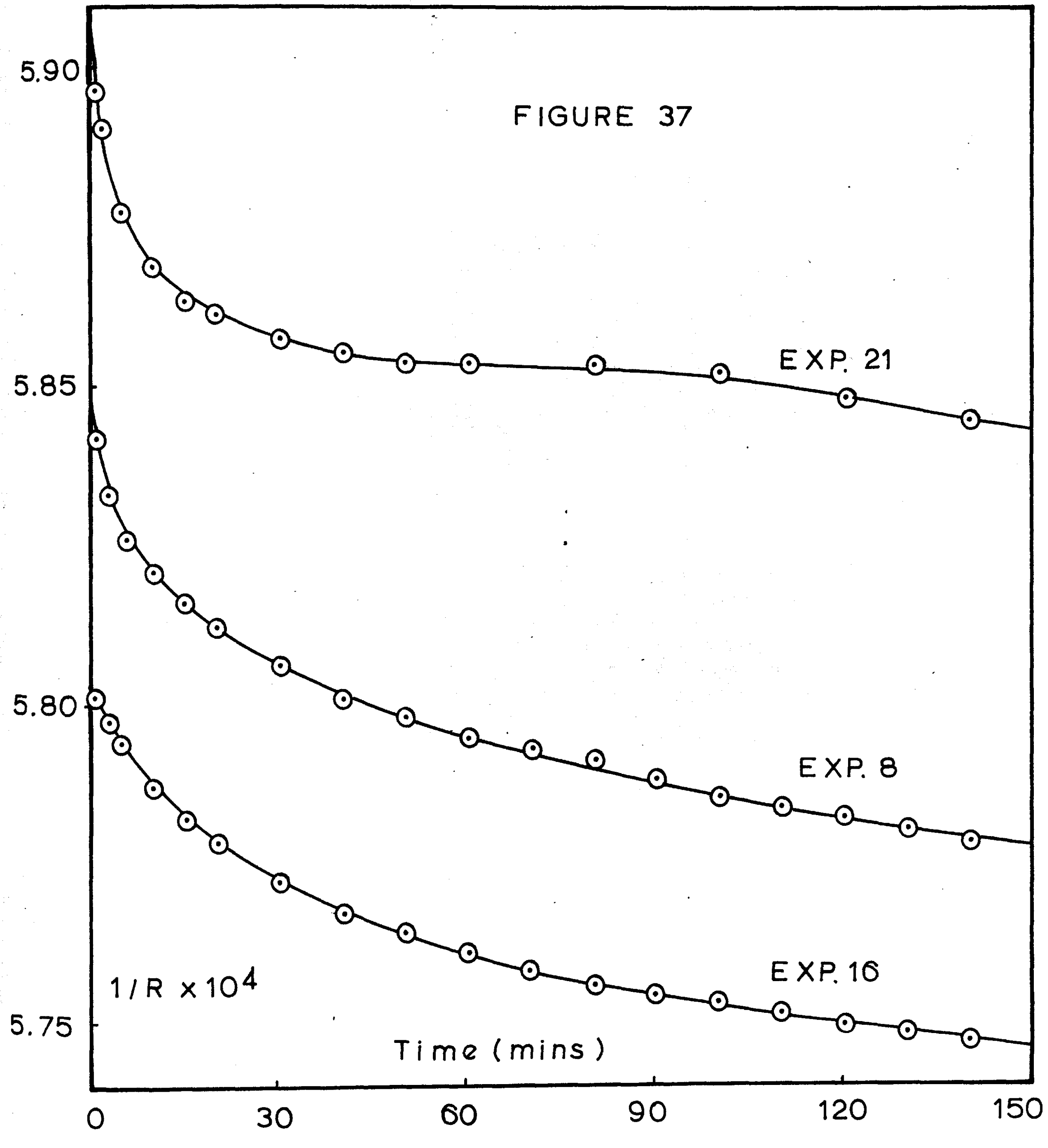
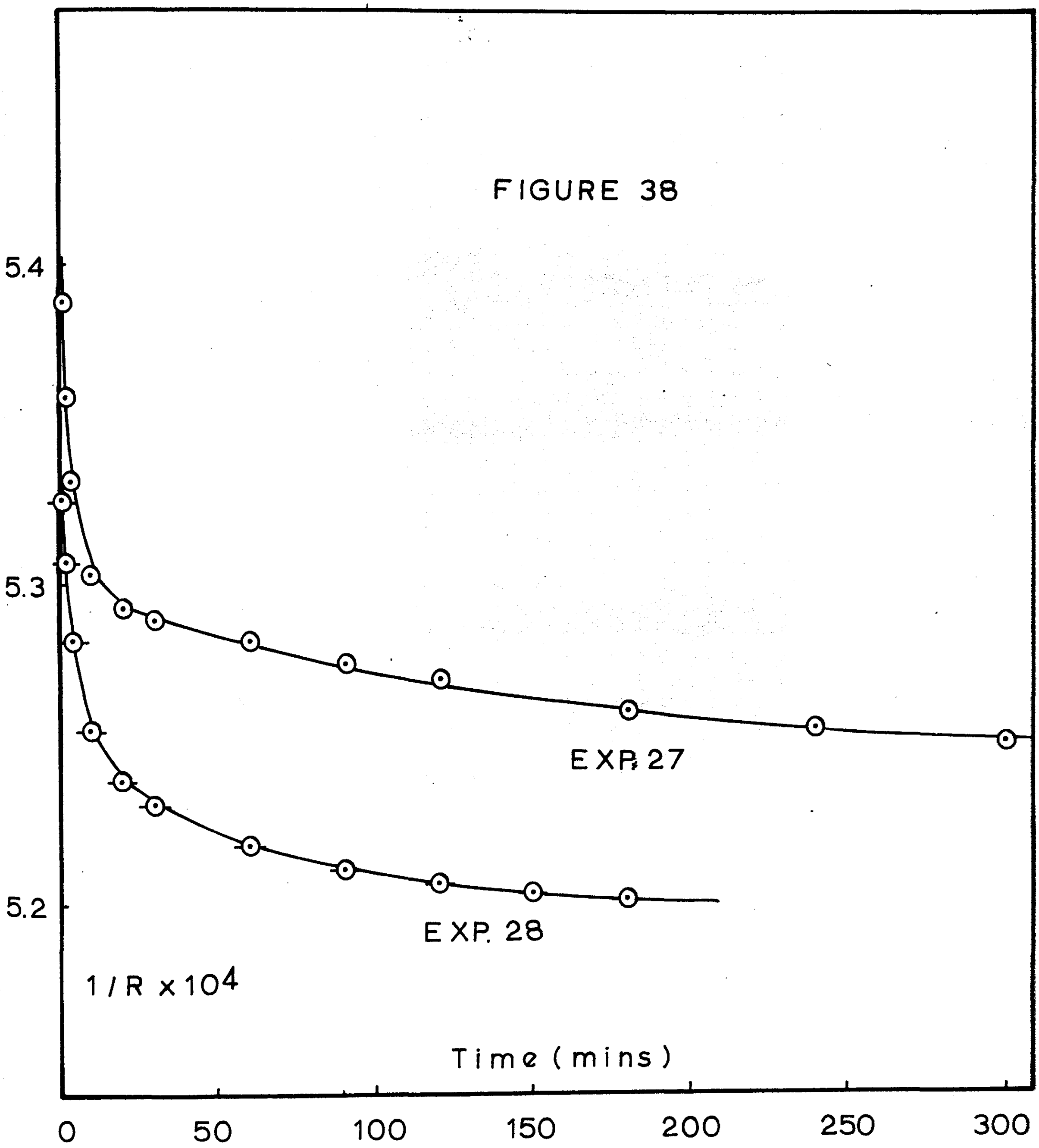


FIGURE 37
EXP. 21
EXP. 8
EXP. 16
1/R x 10^4
Time (mins)
5.90
5.85
5.80
5.75
0
30
60
90
120
150

FIGURE 38



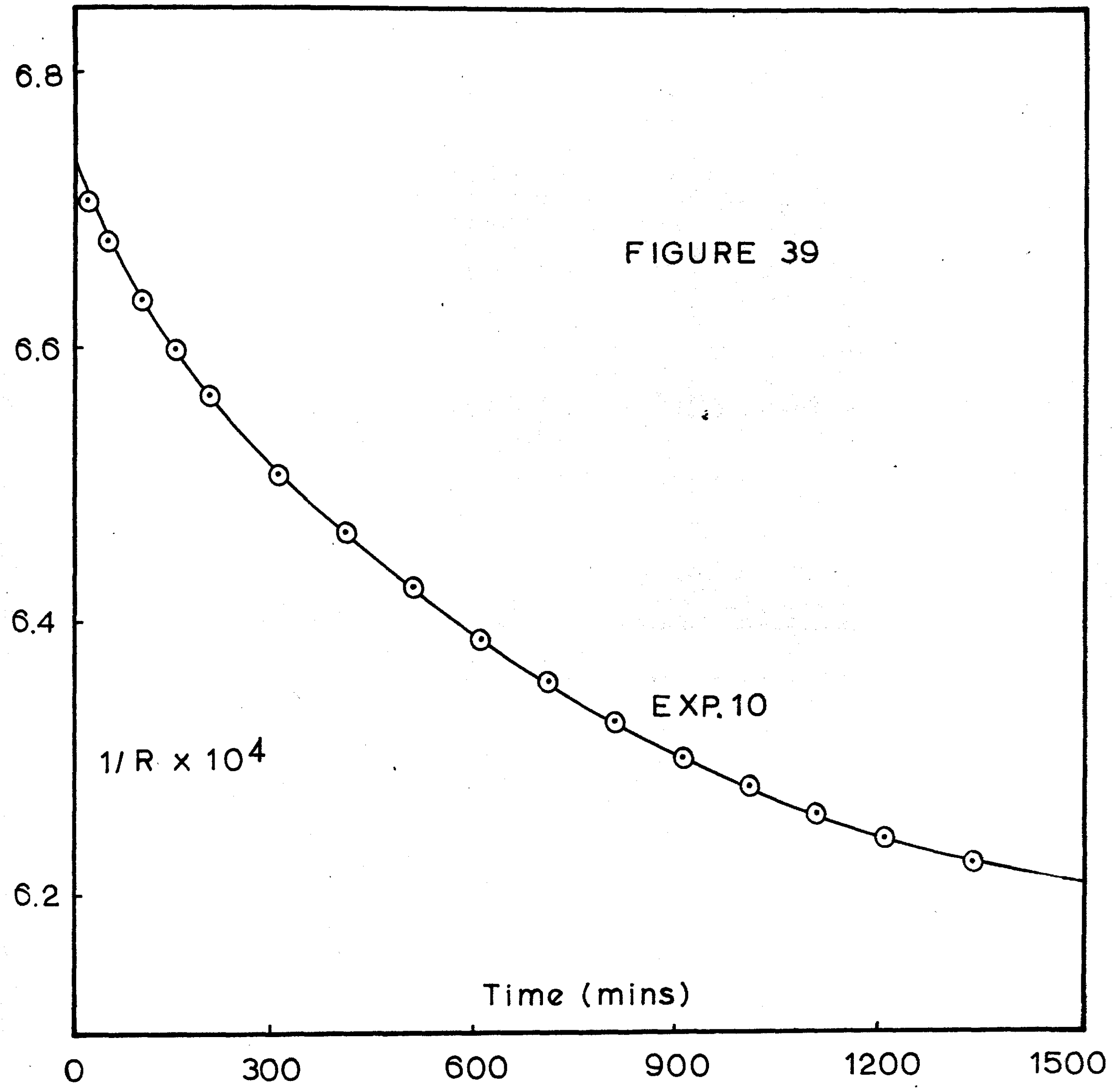


FIGURE 39
EXP. 10
1/R x 10^4
6.8
6.6
6.4
6.2
Time (mins)
0
300
600
900
1200
1500

TABLE 28

Crystallisation of Silver Iodate

t mins	$1/R$ $\times 10^4$ ohm^{-1}	m_t $\times 10^4$ mole/l	$-\Delta m$ $\times 10^4$ mole/l	$(m_t - m_o)$ $\times 10^4$ mole/l	I* $\times 10^{-5}$ $(\text{mole/l})^{-1}$
Experiment 27.					
0	5.4200	2.0100	0.0000	0.1930	0.00
4	5.3322	1.9290	0.0810	0.1120	0.37
10	5.3039	1.9028	0.1072	0.0858	0.64
20	5.2935	1.8932	0.1168	0.0762	0.79
30	5.2897	1.8897	0.1203	0.0727	0.85
60	5.2825	1.8830	0.1270	0.0660	0.99
90	5.2755	1.8765	0.1335	0.0595	1.16
120	5.2702	1.8716	0.1384	0.0546	1.31
180	5.2609	1.8630	0.1470	0.0460	1.65
240	5.2555	1.8580	0.1520	0.0410	1.92
300	5.2509	1.8536	0.1564	0.0366	2.21
Experiment 28.					
0	5.3500	2.0100	0.0000	0.1930	0.00
4	5.2834	1.9483	0.0617	0.1313	0.24
10	5.2549	1.9220	0.0880	0.1050	0.43
20	5.2395	1.9077	0.1023	0.0907	0.58
30	5.2320	1.9008	0.1092	0.0838	0.67
60	5.2185	1.8883	0.1217	0.0713	0.84
90	5.2115	1.8818	0.1282	0.0648	0.98
120	5.2074	1.8781	0.1319	0.0611	1.13
150	5.2040	1.8749	0.1351	0.0579	1.27
180	5.2020	1.8731	0.1369	0.0561	1.41

$* \; I = (m_t - m_o)^{-1} - (m_i - m_o)^{-1}$

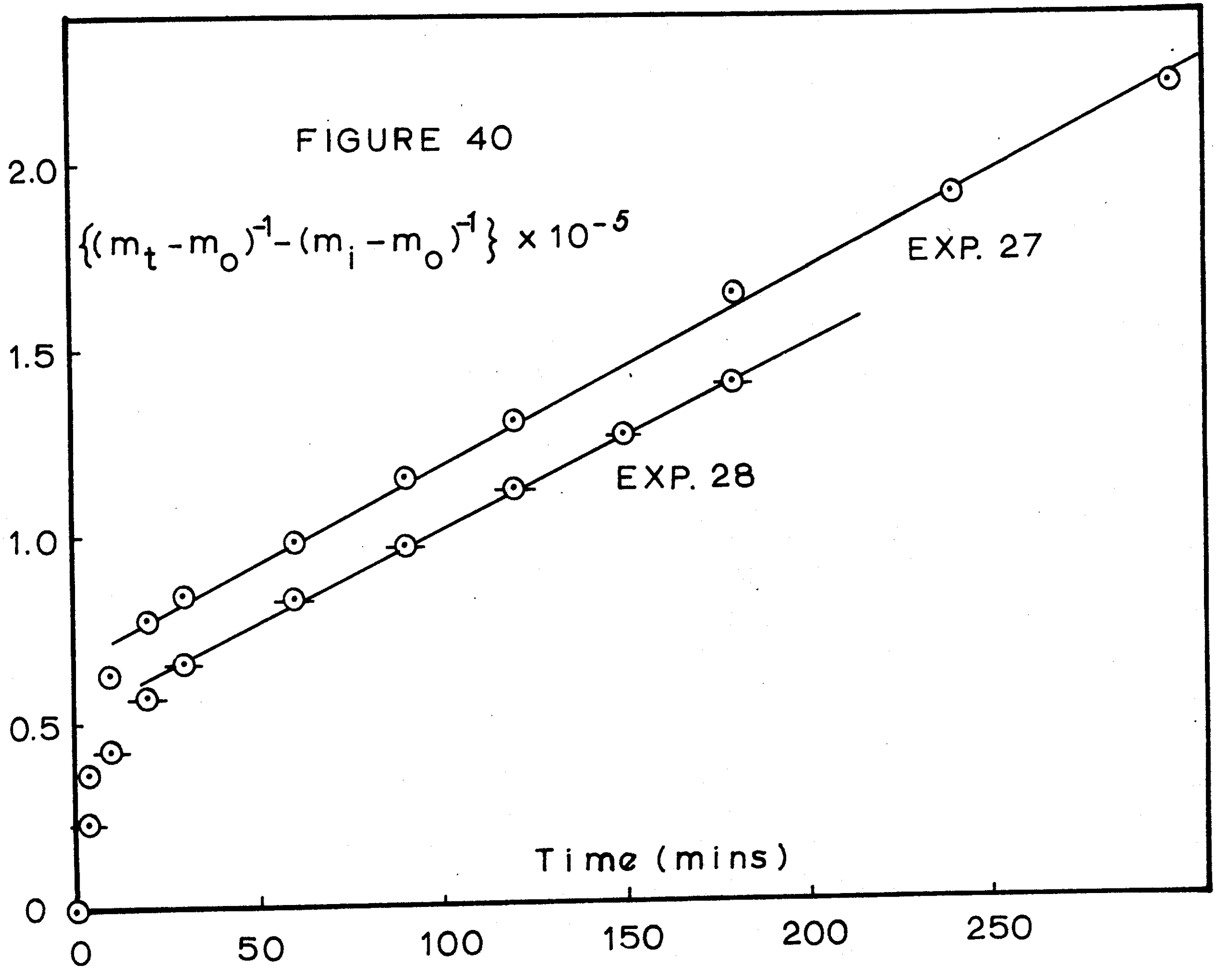


FIGURE 40

$\{(m_t - m_o)^{-1} - (m_i - m_o)^{-1}\} \times 10^{-5}$
2.0
1.5
1.0
0.5
0
EXP. 27
EXP. 28
Time (mins)
0
50
100
150
200
250

TABLE 29

Crystallisation of Silver Iodate

t mins	$1/R$ x 10^4 ohm^{-1}	m_t x 10^4 mole/l	$-\Delta m$ x 10^4 mole/l	(m_t-m_o) x 10^4 mole/l	I* x 10^{-4} $(mole/l)^{-1}$
Experiment 10.					
0	6.7380	2.5498	0.0000	0.7328	0.00
5	6.7233	2.5363	0.0135	0.7193	0.02
25	6.7003	2.5151	0.0347	0.6981	0.06
48	6.6787	2.4952	0.0546	0.6782	0.11
84	6.6504	2.4691	0.0807	0.6521	0.17
112	6.6274	2.4479	0.1019	0.6309	0.22
172	6.5839	2.4078	0.1420	0.5908	0.33
242	6.5425	2.3696	0.1802	0.5526	0.44
587	6.3958	2.2344	0.3154	0.4174	1.03
1280	6.2326	2.0840	0.4658	0.2670	2.38

$$* \; I = (m_t-m_o)^{-1} - (m_i-m_o)^{-1}$$

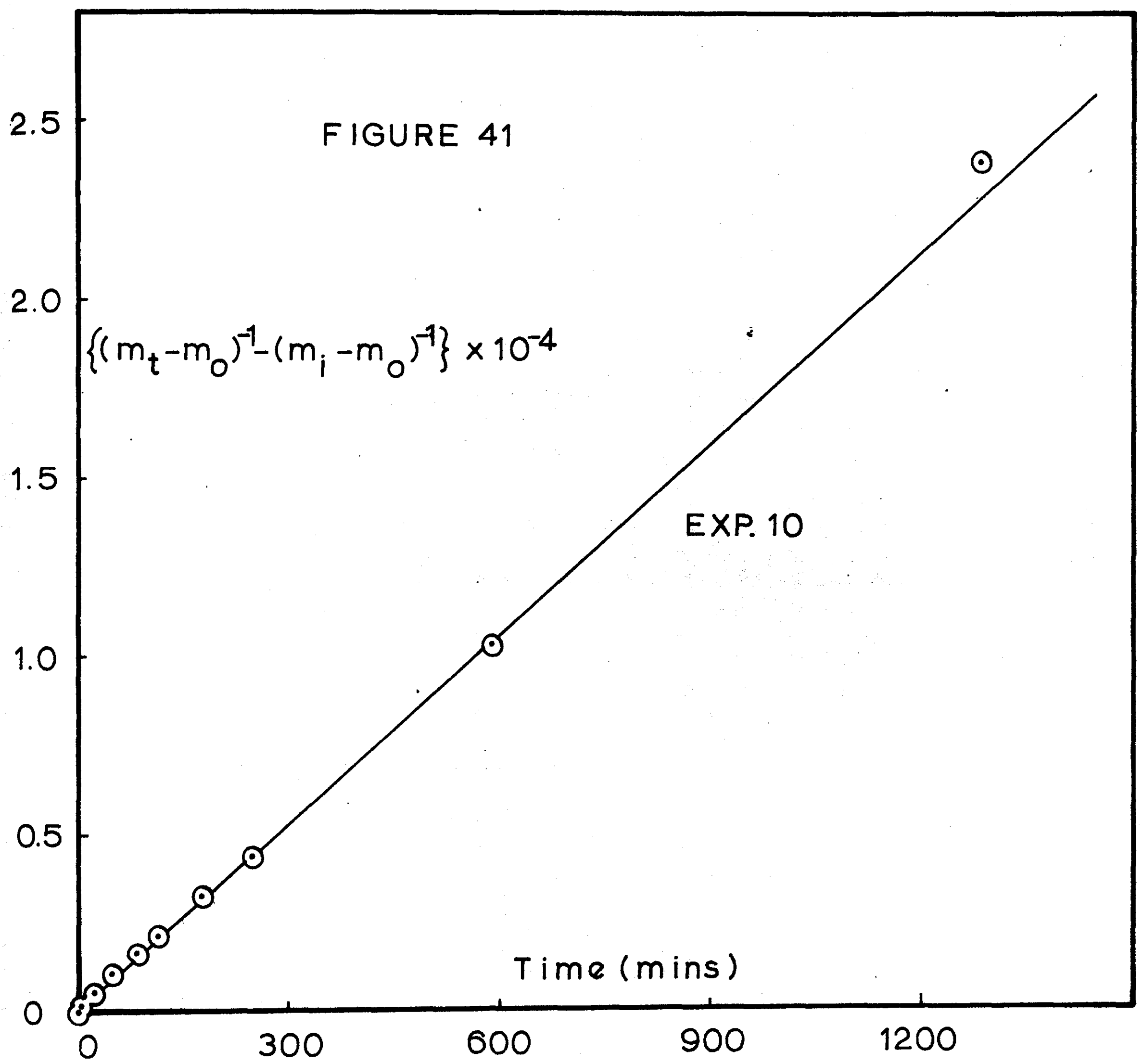


FIGURE 41
$\{(m_t-m_o)^{-1}-(m_i-m_o)^{-1}\}\times10^{-4}$
EXP. 10
Time (mins)
2.5
2.0
1.5
1.0
0.5
0
0
300
600
900
1200

A further crystal growth series was done using distilled conductivity water and some of the experiments are summarised in Table 30. In Figure 42, graphs of conductivity vs. time are given for the experiments in which the initial concentrations of silver and iodate ions were equal. The crystallisation was followed for 90-94% of the total growth, and the straight lines obtained with plots of the integrated form of the second order rate equation are shown in Figure 43.

If we assume the surface area function s to be constant for the seed crystals used in each experiment, and incorporate it in the rate constant ks, we obtain the values shown in Table 30. The mean value of 5.1×10^4 litre.mole^{-1}.min^{-1}. per gm. of seed crystals is very much greater than those obtained in experiments using deionised conductivity water.

Crystal growth from solutions containing non-equivalent initial concentrations of silver and iodate ions was also examined, and graphs of conductivity vs. time for experiments in which the initial ionic ratios were 2:1 and 4:1 are shown in Figures 44 and 46 respectively. The crystallisation was followed for over 80% of the total reaction with silver ion in excess (Experiments 31 and 34) and over 90% with iodate ion in excess (Experiments 30, 40, 32 and 42), and the straight lines obtained when $\{\Delta^{-1}-\Delta_i^{-1}\}$ was plotted against time are shown in Figures 45 and 47.

The rate constants were independent of the ion in excess and the ionic ratio, and the mean <u>ks</u> value of $(5.15 \pm 0.4) \times 10^4$ litre.mole^{-1}. min^{-1}. per gm. of seed crystals agreed very well with the results obtained in experiments with equivalent silver and iodate ion concentrations.

Discussion

The growth of silver iodate seed crystals from supersaturated solutions containing equivalent or non-equivalent initial concentrations of silver and iodate ions follows the theory of crystallisation proposed by Davies and Jones[44]. The crystallisation was studied for over 80% of the reaction in all experiments with no deviation from a second order kinetic law. The initial growth surge observed in the crystallisation of barium and strontium sulphates[47], and the induction period with magnesium oxalate[46] are absent, indicating that the inoculating seed crystals provide sufficient growth sites to accomodate pure second order growth without additional nucleation.

The rate constants agree well for the different seed suspensions prepared and aged using distilled water, and the values do not decrease when the ionic ratio in the solution differs from unity. This result also supports the theory of crystal growth, and is similar to that found with strontium sulphate and silver chloride[44] seed crystals. It is not general however, since in experiments on the growth of barium sulphate, magnesium oxalate and silver chromate[45], the rate constants were lowered when one of the ions was in excess.

When the experiments are done using solutions prepared with

TABLE 30

Crystallisation of Silver Iodate

Experiments in Distilled Water.

Expt No.	$[Ag^+]_i \times 10^4$ mole/l	$[IO_3^-]_i \times 10^4$ mole/l	$[Ag^+][IO_3^-] \times 10^8$ $(mole/l)^2$	Seed Suspn	Amt. of Seed gms	ks $\times 10^3$ $l.m^{-1}.min^{-1}$.
29	2.0100	2.0100	4.040	e	0.095	4.55
38	1.9800	1.9800	3.920	f	0.135	7.42
41	2.0100	2.0100	4.040	g	0.047	2.36
30	1.4273	2.8485	4.066	e	0.122	5.77
31	2.8424	1.4212	4.040	e	0.085	4.00
40	1.4212	2.8340	4.028	g	0.062	3.10
32	1.1224	4.4896	5.040	e	0.229	13.2
34	4.3060	1.0062	4.333	e	0.105	5.15
42	1.0250	4.1000	4.203	g	0.055	3.08

$K_{Th} = 3.129 \times 10^{-8}$ $(mole.litre^{-1})^2$

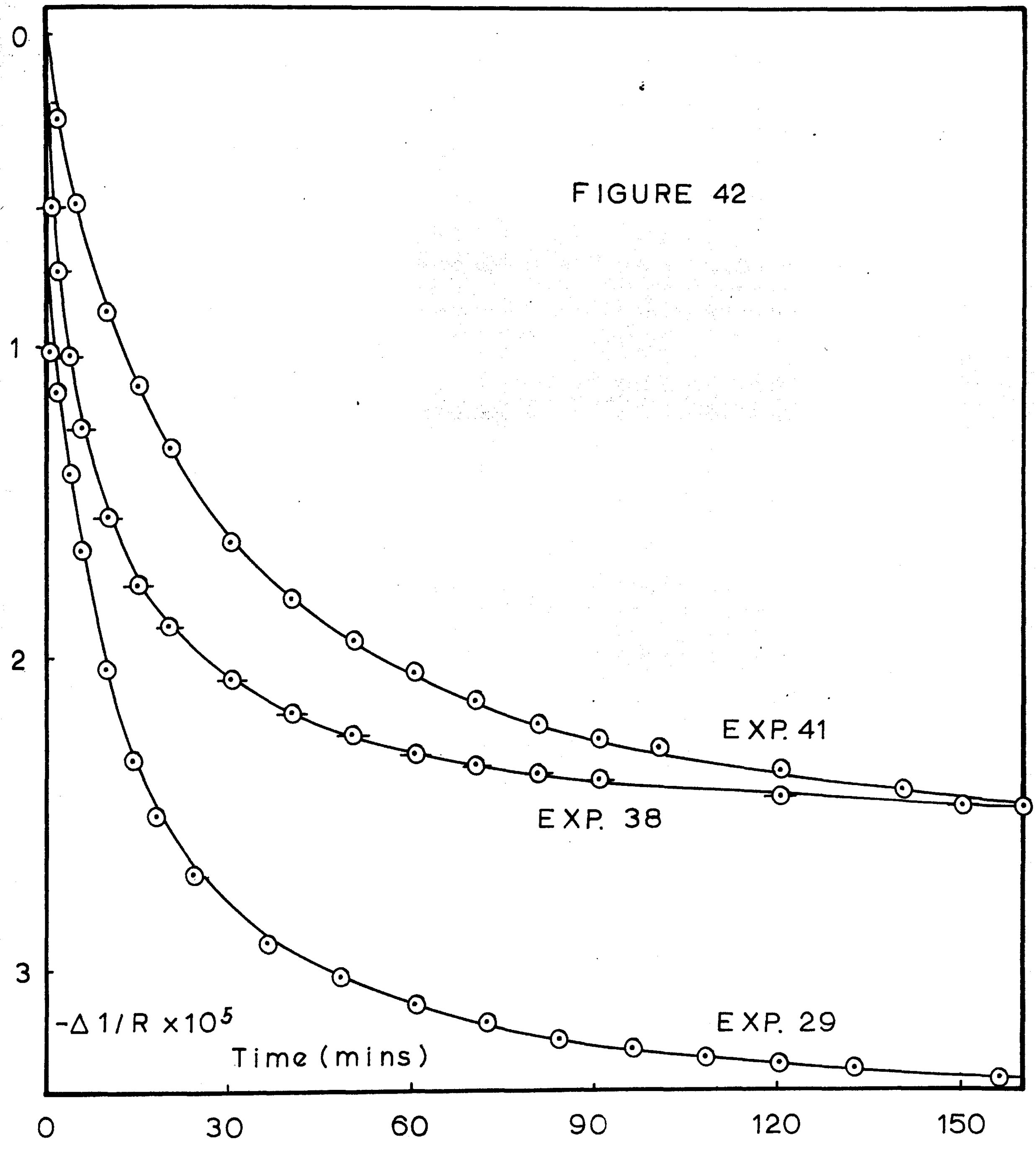


FIGURE 42
EXP. 41
EXP. 38
EXP. 29
0
1
2
3
-Δ 1/R x10^5
Time (mins)
0
30
60
90
120
150

TABLE 31

Crystallisation of Silver Iodate

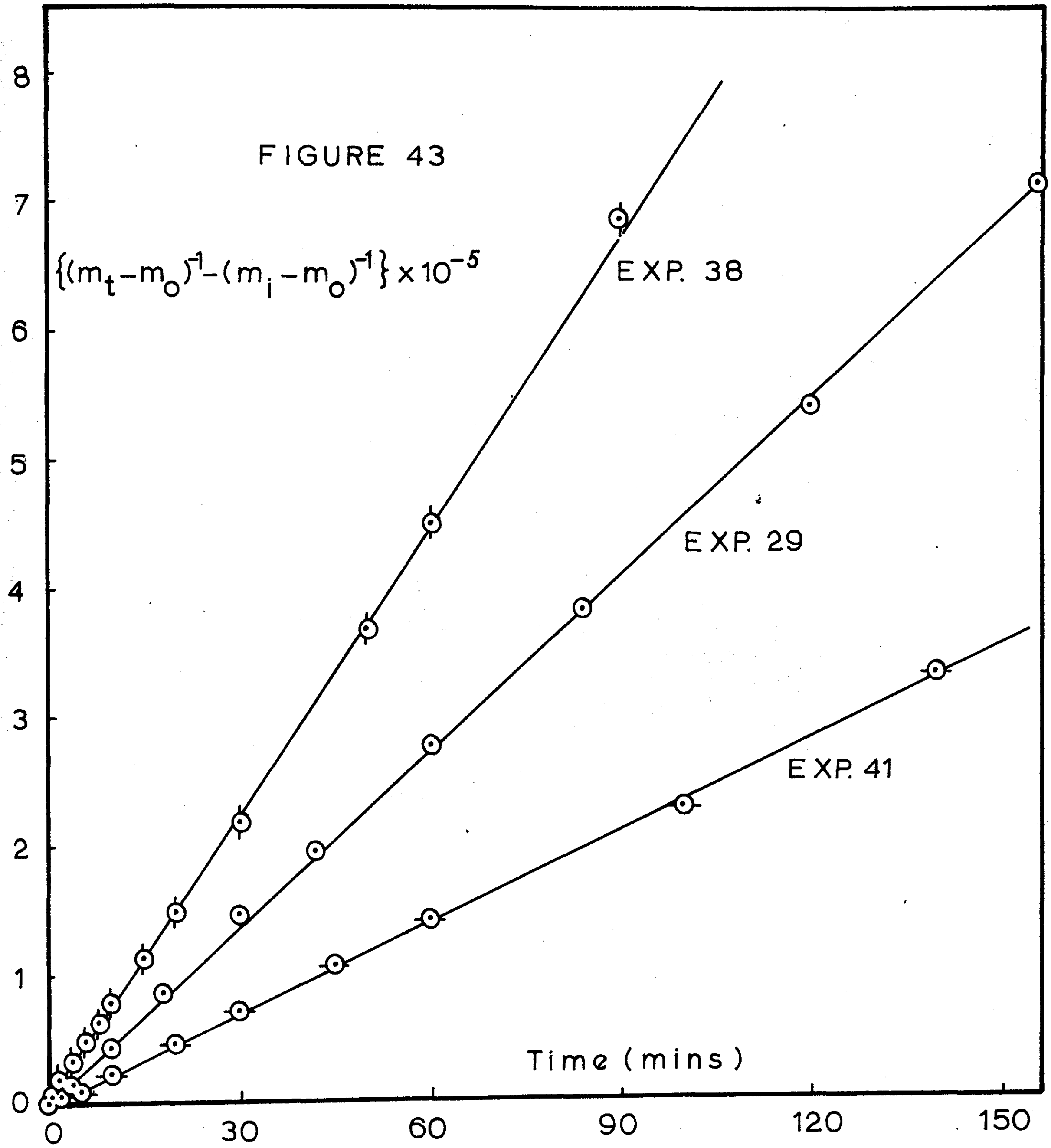
t mins	1/R x 10^4 ohm^{-1}	m_t x 10^4 mole/l	$-\Delta m$ x 10^4 mole/l	(m_t-m_o) x 10^4 mole/l	I* x 10^{-5} $(mole/l)^{-1}$
Experiment 29					
0	7.3843	2.0100	0.0000	0.1930	0.00
1	7.3597	1.9930	0.0170	0.1760	0.05
4	7.3198	1.9654	0.0446	0.1484	0.15
10	7.2567	1.9218	0.0882	0.1048	0.43
18	7.2097	1.8894	0.1206	0.0724	0.86
30	7.1781	1.8675	0.1425	0.0505	1.46
42	7.1636	1.8575	0.1525	0.0405	1.95
60	7.1491	1.8475	0.1625	0.0305	2.76
84	7.1385	1.8402	0.1698	0.0232	3.81
120	7.1295	1.8339	0.1761	0.0169	5.40
156	7.1240	1.8301	0.1799	0.0131	7.11
180	7.1217	1.8285	0.1815	0.0115	8.18
Experiment 41					
0	7.3400	2.0100	0.0000	0.1930	0.00
2	7.3139	1.9920	0.0180	0.1750	0.05
5	7.2870	1.9734	0.0366	0.1564	0.10
10	7.2516	1.9489	0.0611	0.1319	0.23
20	7.2078	1.9186	0.0914	0.1016	0.46
30	7.1782	1.8982	0.1118	0.0812	0.71
45	7.1520	1.8801	0.1299	0.0631	1.06
60	7.1360	1.8690	0.1410	0.0520	1.41
100	7.1124	1.8527	0.1573	0.0357	2.29
140	7.0986	1.8432	0.1668	0.0262	3.31
180	7.0884	1.8361	0.1739	0.0191	4.71

TABLE 31 cont.

t mins	$1/R$ $\times 10^4$ ohm^{-1}	m_t $\times 10^4$ mole/l	$-\Delta m$ $\times 10^4$ mole/l	$(m_t - m_o)$ $\times 10^4$ mole/l	I* $\times 10^{-5}$ $(mole/l)^{-1}$
Experiment 38.					
0	7.4580	1.9800	0.0000	0.1630	0.00
2	7.4055	1.9437	0.0363	0.1267	0.18
4	7.3777	1.9245	0.0555	0.1075	0.32
6	7.3547	1.9086	0.0714	0.0916	0.48
8	7.3388	1.8976	0.0824	0.0806	0.63
10	7.3262	1.8889	0.0911	0.0719	0.78
15	7.3049	1.8742	0.1058	0.0572	1.14
20	7.2910	1.8646	0.1154	0.0476	1.49
30	7.2738	1.8527	0.1273	0.0357	2.19
50	7.2559	1.8403	0.1397	0.0233	3.68
60	7.2505	1.8366	0.1434	0.0196	4.49
90	7.2416	1.8304	0.1496	0.0134	6.85

$$* \; I = (m_t - m_o)^{-1} - (m_i - m_o)^{-1}$$

FIGURE 43


$\{(m_t-m_o)^{-1}-(m_i-m_o)^{-1}\}\times10^{-5}$
EXP. 38
EXP. 29
EXP. 41
Time (mins)
0
1
2
3
4
5
6
7
8
0
30
60
90
120
150

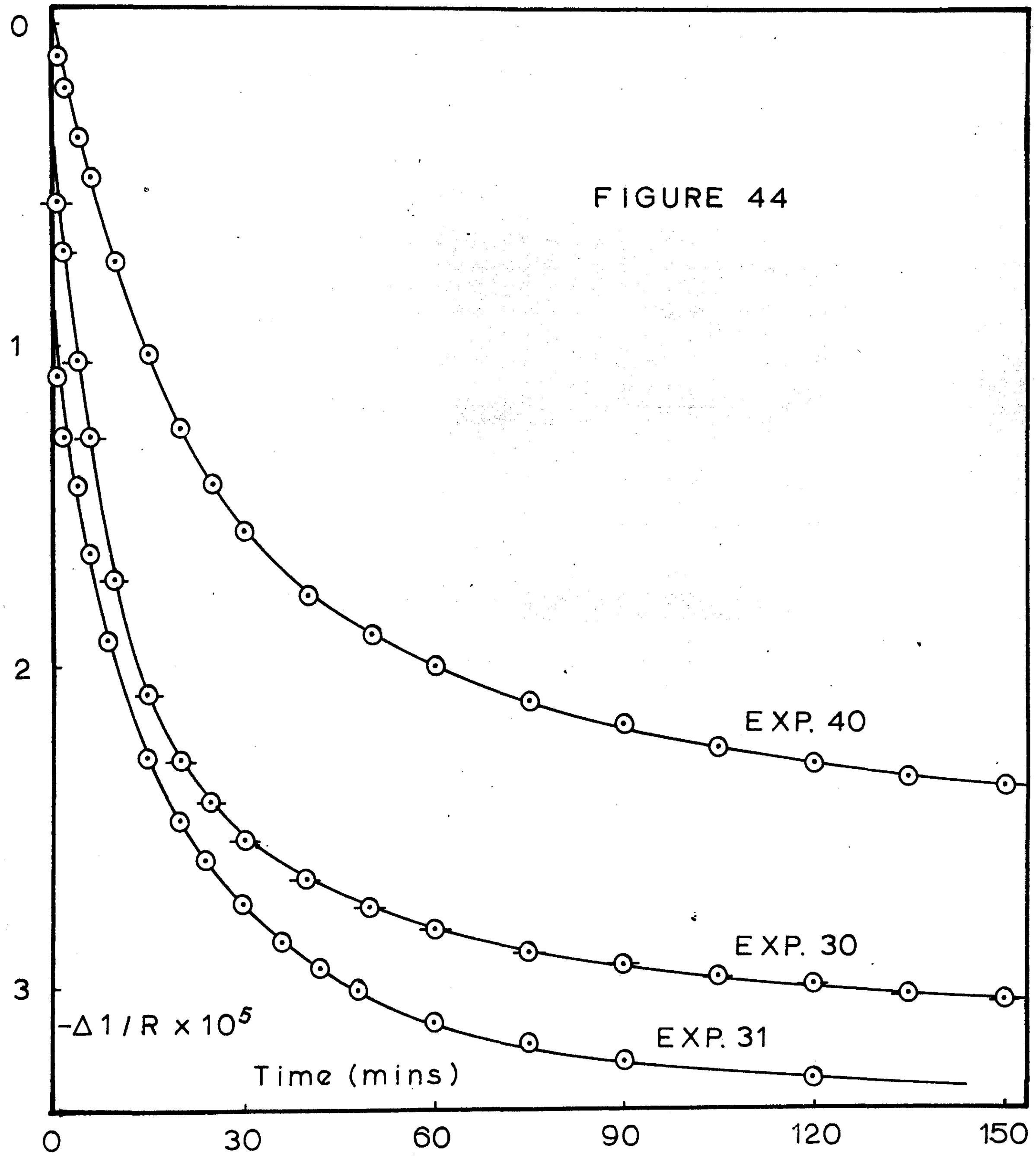


FIGURE 44
EXP. 40
EXP. 30
EXP. 31
$-\Delta 1/R \times 10^5$
Time (mins)
0
1
2
3
0
30
60
90
120
150

TABLE 32

Crystallisation of Silver Iodate

t mins	1/R x 10^4 ohm^{-1}	$[Ag^+]$ x 10^4 mole/l	$[IO_3^-]$ x 10^4 mole/l	$-\delta(\Delta)$ x 10^4 mole/l	Δ x 10^4 mole/l	I* x 10^{-5} $(m/l)^{-1}$
Experiment 30.						
0	7.6600	1.4273	2.8485	0.0000	0.1929	0.00
4	7.5984	1.3849	2.8061	0.0424	0.1505	0.15
9	7.5360	1.3419	2.7631	0.0854	0.1075	0.42
15	7.4906	1.3106	2.7318	0.1167	0.0762	0.80
24	7.4576	1.2879	2.7091	0.1394	0.0535	1.35
36	7.4368	1.2735	2.6947	0.1538	0.0391	2.04
49	7.4240	1.2647	2.6859	0.1626	0.0303	2.78
60	7.4171	1.2599	2.6811	0.1674	0.0255	3.40
84	7.4072	1.2531	2.6743	0.1742	0.0187	4.83
114	7.4009	1.2488	2.6700	0.1785	0.0144	6.43
156	7.3950	1.2447	2.6659	0.1826	0.0103	9.19
Experiment 31.						
0	8.3500	2.8424	1.4212	0.0000	0.1866	0.00
4	8.2955	2.8048	1.3836	0.0376	0.1490	0.14
9	8.2478	2.7718	1.3506	0.0706	0.1160	0.33
15	8.2113	2.7466	1.3254	0.0958	0.0908	0.57
24	8.1798	2.7248	1.3036	0.1176	0.0690	0.92
36	8.1533	2.7065	1.2853	0.1359	0.0507	1.43
48	8.1385	2.6963	1.2751	0.1461	0.0405	1.93
60	8.1285	2.6893	1.2681	0.1531	0.0335	2.45
75	8.1209	2.6841	1.2629	0.1583	0.0283	3.00

* $I = (\Delta^{-1} - \Delta_i^{-1})$

TABLE 32 cont.

t mins	$1/R$ x 10^4 ohm^{-1}	$[Ag^+]$ x 10^4 mole/l	$[IO_3^-]$ x 10^4 mole/l	$-\delta(\Delta)$ x 10^4 mole/l	Δ x 10^4 mole/l	I* x 10^{-5} $(m/l)^{-1}$
Experiment 40.						
0	7.5800	1.4212	2.8340	0.0000	0.1838	0.00
2	7.5591	1.4067	2.8195	0.0145	0.1693	0.05
5	7.5373	1.3917	2.8045	0.0295	0.1543	0.11
10	7.5051	1.3694	2.7822	0.0518	0.1320	0.22
20	7.4532	1.3335	2.7463	0.0877	0.0961	0.50
30	7.4212	1.3114	2.7242	0.1098	0.0740	0.81
40	7.4010	1.2975	2.7103	0.1237	0.0601	1.12
60	7.3788	1.2822	2.6950	0.1390	0.0448	1.69
90	7.3602	1.2687	2.6815	0.1525	0.0313	2.65
120	7.3490	1.2615	2.6743	0.1597	0.0241	3.59
150	7.3426	1.2571	2.6699	0.1641	0.0197	4.52
180	7.3391	1.2547	2.6675	0.1665	0.0173	5.25

* $I = (\Delta^{-1} - \Delta_i^{-1})$

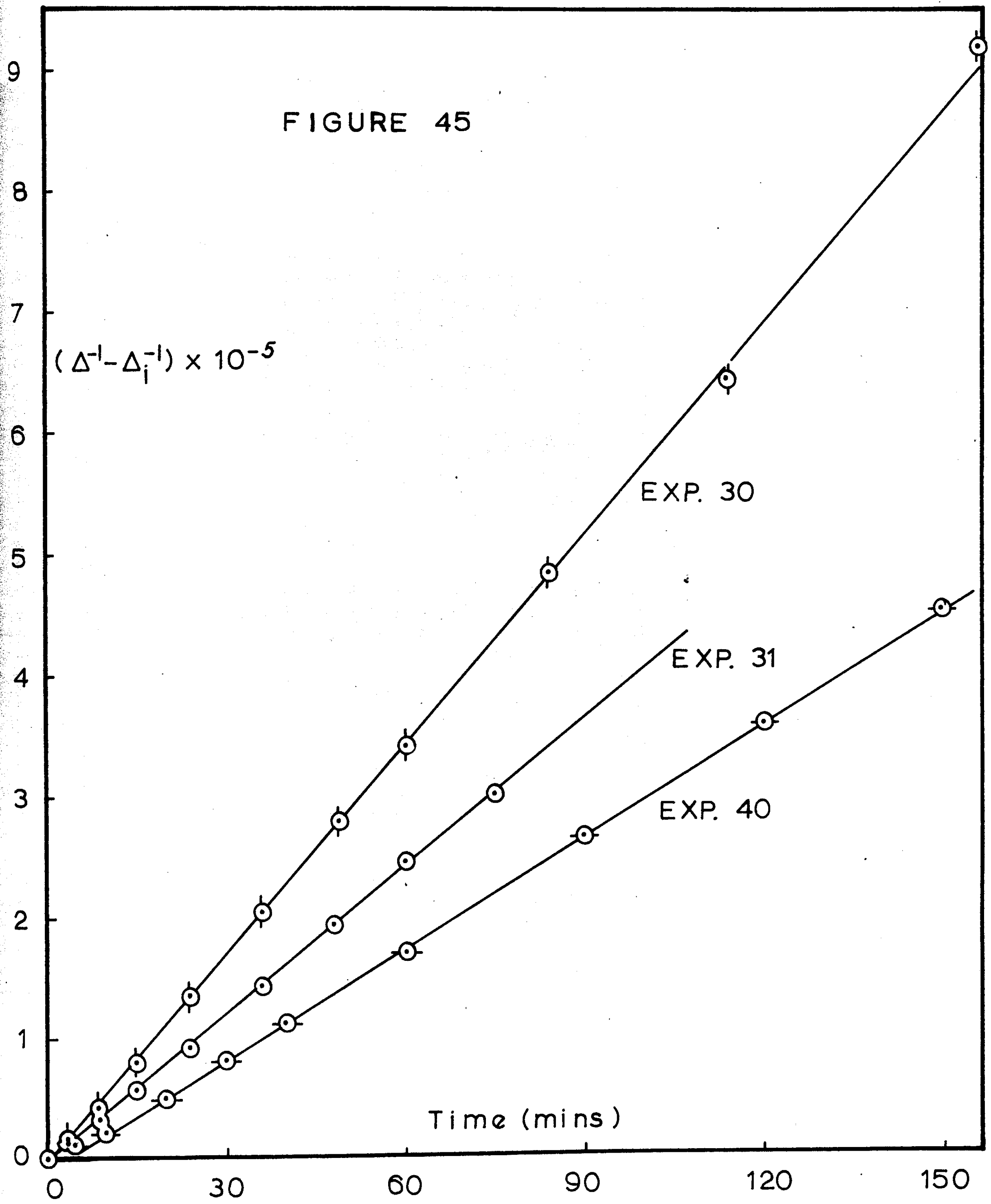


FIGURE 45
$(\Delta^{-1}-\Delta_i^{-1}) \times 10^{-5}$
EXP. 30
EXP. 31
EXP. 40
Time (mins)
0
1
2
3
4
5
6
7
8
9
0
30
60
90
120
150

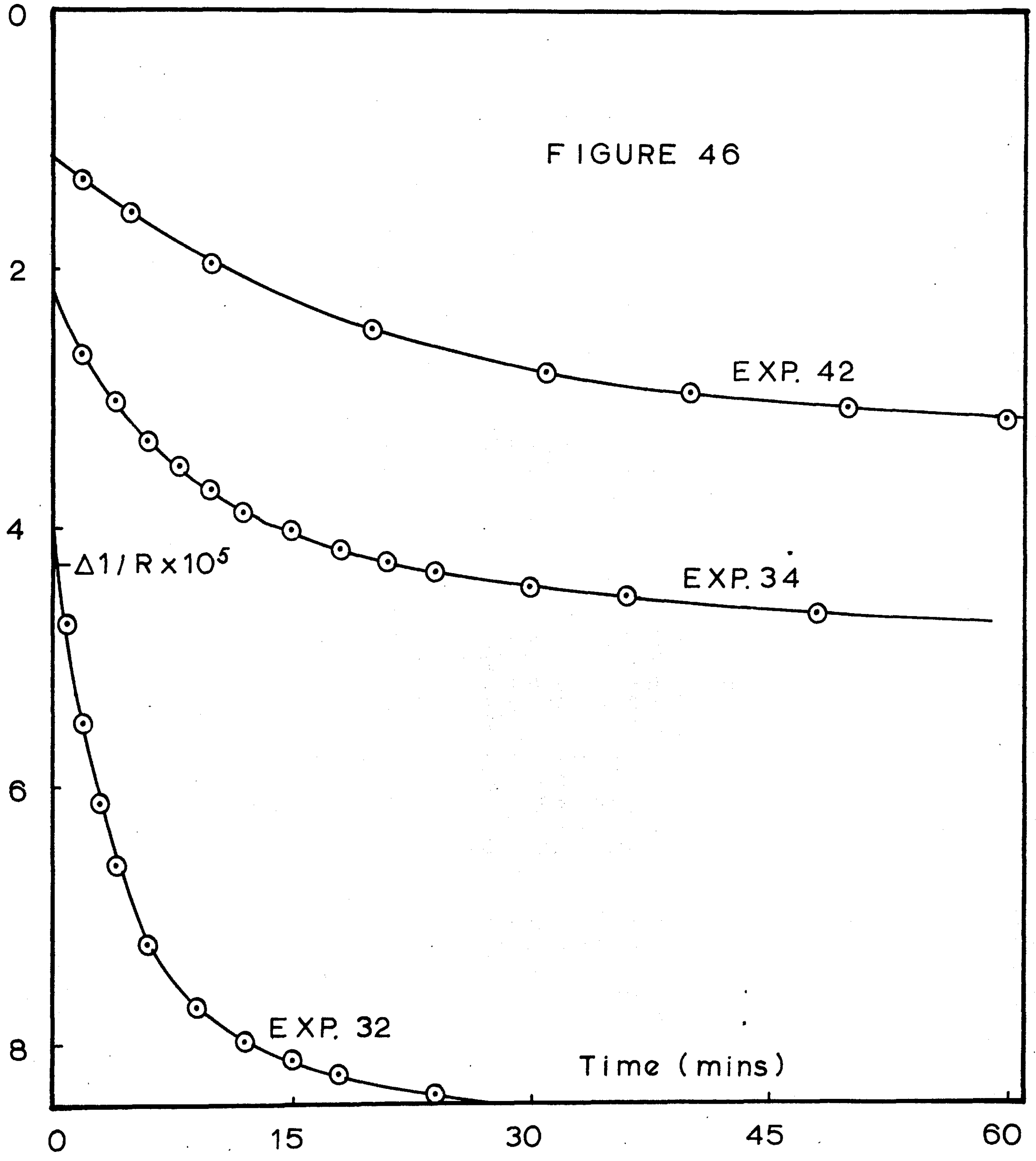


FIGURE 46
EXP. 42
EXP. 34
EXP. 32
-Δ1/R x 10^5
Time (mins)
0
2
4
6
8
0
15
30
45
60

TABLE 33

Crystallisation of Silver Iodate

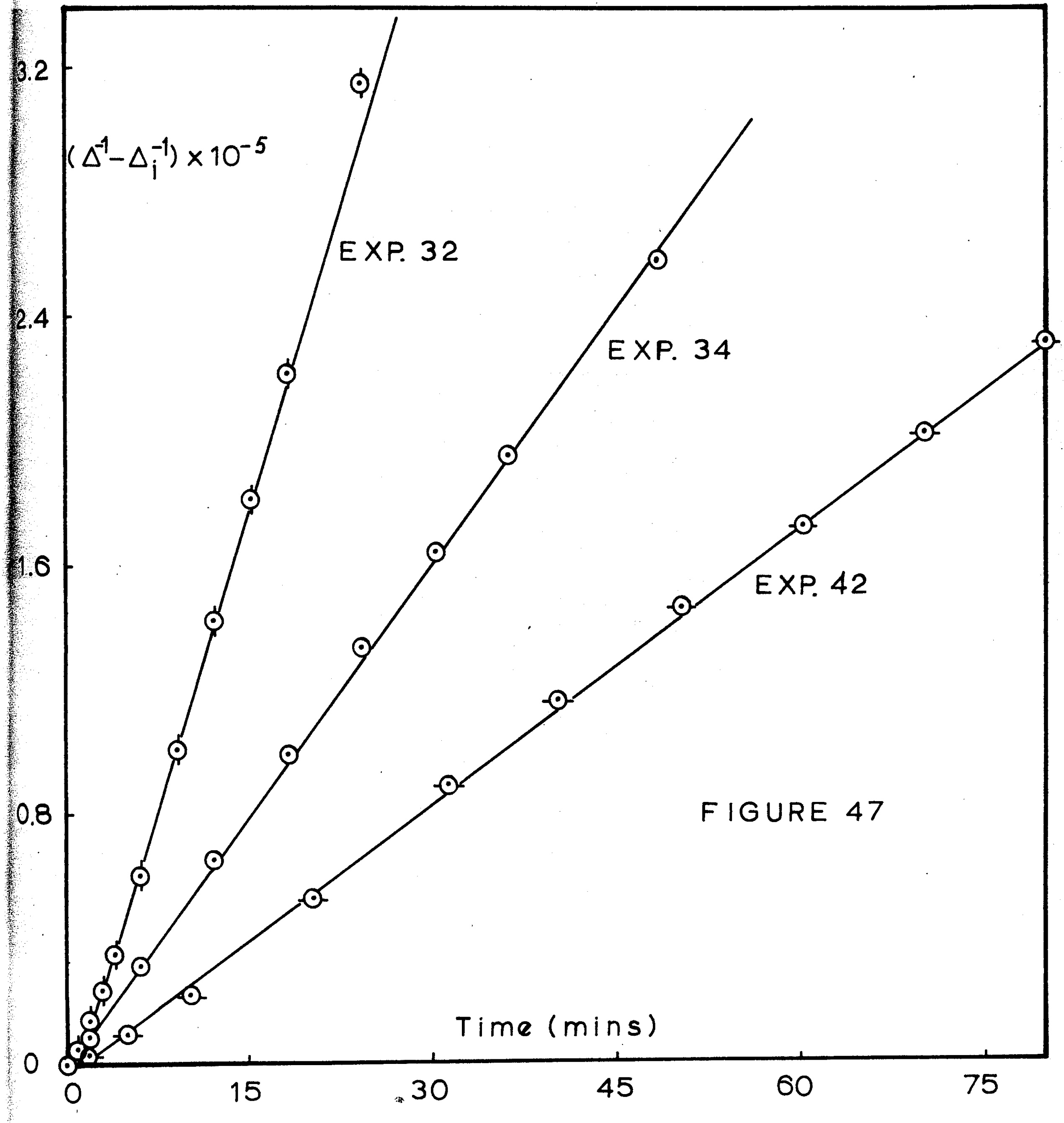
t mins	$1/R$ $\times 10^4$ ohm^{-1}	$[Ag^+]$ $\times 10^4$ mole/l	$[IO_3^-]$ $\times 10^4$ mole/l	$-\delta(\Delta)$ $\times 10^4$ mole/l	Δ $\times 10^4$ mole/l	I* $\times 10^{-5}$ $(m/l)^{-1}$
Experiment 32.						
0	9.6950	1.1224	4.4896	0.0000	0.3292	0.00
1	9.6250	1.0742	4.4414	0.0482	0.2810	0.05
2	9.5484	1.0214	4.3886	0.1010	0.2282	0.14
3	9.4856	0.9781	4.3453	0.1443	0.1849	0.24
4	9.4370	0.9446	4.3118	0.1778	0.1514	0.36
6	9.3760	0.9026	4.2698	0.2198	0.1094	0.61
9	9.3266	0.8686	4.2358	0.2538	0.0754	1.02
12	9.3008	0.8508	4.2180	0.2716	0.0576	1.43
15	9.2857	0.8404	4.2076	0.2820	0.0472	1.82
18	9.2747	0.8328	4.2000	0.2896	0.0396	2.22
24	9.2592	0.8221	4.1893	0.3003	0.0289	3.15
Experiment 34.						
0	10.3800	4.3060	1.0062	0.0000	0.2026	0.00
2	10.3338	4.2741	0.9743	0.0319	0.1707	0.09
6	10.2657	4.2270	0.9272	0.0790	0.1236	0.32
12	10.2102	4.1886	0.8888	0.1174	0.0852	0.66
18	10.1828	4.1697	0.8699	0.1363	0.0663	1.00
24	10.1649	4.1573	0.8575	0.1487	0.0539	1.34
30	10.1543	4.1500	0.8502	0.1560	0.0466	1.65
36	10.1458	4.1441	0.8443	0.1619	0.0407	1.96
48	10.1342	4.1361	0.8363	0.1699	0.0327	2.58

* $I = (\Delta^{-1} - \Delta_i^{-1})$

TABLE 33 cont.

t mins	$1/R$ $\times 10^4$ ohm^{-1}	$[Ag^+]$ $\times 10^4$ mole/l	$[IO_3^-]$ $\times 10^4$ mole/l	$-\delta(\Delta)$ $\times 10^4$ mole/l	Δ $\times 10^4$ mole/l	I* $\times 10^{-5}$ $(m/l)^{-1}$
Experiment 42.						
0	8.8850	1.0250	4.1000	0.0000	0.1831	0.00
2	8.8690	1.0139	4.0889	0.0111	0.1720	0.03
5	8.8416	0.9950	4.0700	0.0300	0.1531	0.10
10	8.8040	0.9690	4.0440	0.0560	0.1271	0.23
20	8.7518	0.9329	4.0079	0.0921	0.0910	0.54
31	8.7199	0.9109	3.9859	0.1141	0.0690	0.90
40	8.7041	0.9000	3.9750	0.1250	0.0581	1.17
50	8.6915	0.8913	3.9663	0.1337	0.0494	1.47
60	8.6835	0.8857	3.9607	0.1393	0.0438	1.73
70	8.6762	0.8807	3.9957	0.1443	0.0388	2.03
80	8.6706	0.8768	3.9518	0.1482	0.0349	2.32

$* \; I = (\Delta^{-1} - \Delta_i^{-1})$



$(\Delta^{-1}-\Delta_i^{-1})\times 10^{-5}$
3.2
2.4
1.6
0.8
0
EXP. 32
EXP. 34
EXP. 42
Time (mins)
0
15
30
45
60
75

FIGURE 47

deionised conductivity water however, the growth characteristics are altered by the slight traces of impurity present. On inoculating the solution with seed crystals, crystallisation commences with a fast portion in which almost half the total growth occurs, after which the kinetics follow equation (2), where $\underline{n} = 2$. In some cases the kinetics of the fast initial portion can also be represented by equation (2), but the value of $\underline{n}$ is high, of the order of 7 or 8.

A fast initial stage in the crystal growth of the sulphates of barium, strontium and lead was attributed to two-dimensional surface nucleation, caused by insufficient growth sites being present initially on the added seed crystals. The nucleation took place at active sites on the crystals and continued until the supersaturation at the crystal surface was low enough for the growth to be accomodated at the available sites. Moreover, in the crystallisation of lead sulphate[48], the adsorption of impurity from the cell solution increased the duration and rate of the initial surge, by reducing the free energy required for surface nucleation. The silver iodate seed crystals were aged in deionised water, and again the presence of impurity greatly reduces the number of growth sites and encourages surface nucleation.

When dilute seed suspensions are used, a much shorter initial surge is observed, and the subsequent growth is in all cases very slow, partly or completely stopping for a short time in some experiments. This was observed also in strontium sulphate experiments in deionised water, and it was attributed to molecules of impurity blocking the growth sites as they were formed, until no more impurity remained to do so. As is seen from the difference in duration of the fast and slow periods, it is difficult to obtain good reproducibility in these experiments, mainly due to variations in the amount of seed crystals added and the concentration of impurity, neither of which can be effectively controlled.

Second order growth throughout is observed with seed suspension a, which has a very large surface area due to its much higher concentration and smaller crystal size. No initial growth surge is present, which indicates that no surface nucleation is occurring, although the slow rate of growth suggests that the number of active sites is not great. The absence of the fast portion is more surprising, since the initial supersaturation is relatively very high, and the results of the work on strontium and lead sulphates have shown that this increases the duration and order of the surge. It appears that sufficient growth sites are present for pure second order crystal growth, but that this amount is still very much less than that present in the distilled water experiments.

The rate of crystallisation in the distilled water experiments is very fast and the amount of seed crystals used, and consequently the number of growth sites, must be much greater than the minimum required for uncomplicated second order kinetics. In some deionised water experiments a large amount of two-dimensional nucleation occurs, and even after this, the rate of the second order growth is less than a tenth of the rate in distilled water. When in these cases, no additional nucleation takes place, the ks value is very small, as little as 0.2% of the value obtained in a comparable experiment using pure solutions.

The work on the determination of the critical concentration of silver iodate gives results very similar to those obtained by Davies and Jones with silver chloride[3]. Ostwald's view that there were two regions of supersaturation, the metastable and the labile regions, which were separated by a sharply definable boundary, has been modified, and the critical supersaturation is now identified with a limited range of concentrations. The closeness of the experimental points to a straight line in the present work is in agreement with this concept of a narrow critical concentration range.

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