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Solubility of Fine Particles of Strontium Sulfate

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The Ostwald–Freundlich equation for the solubility of fine particles was extended to crystals of any geometry with any number of different interfacial tensions. Measuring the particle sizes by electron microscopy, the solubility of $SrSO_4$ particles in the colloidal range was investigated by a tracer method at 25.0°. Results are in good agreement with the theory. The smallest particles in a given population appear to control the solubility. The solid $SrSO_4$/solution mean interfacial tension was calculated as 84 ± 8 erg. cm.$^{-2}$ at 25.0° against a much higher value given in the literature, which is considered to be in error. From precipitation experiments the size of $SrSO_4$ nuclei is estimated to be *ca.* 18 Å.

1. Introduction

The fact that finely divided solids should have a greater solubility than large crystals was pointed out as early as in 1813 by Wollaston[1] and in 1885 by Curie.[2] Gibbs[3] has treated the problem rigorously but implicitly. Although the similar problem of vapor pressure of droplets has been formulated long ago by Thomson[4] and Helmholtz,[5] the analogy appears to have been overlooked for a considerable length of time.

The first explicit equation for the excess solubility of small spheres was given by Ostwald[6] and corrected later by Freundlich.[7]

Hulett[8] made the first experimental investigation to test this relationship between supersaturation, particle size and solid/liquid interfacial tension. He measured conductometrically the supersaturation obtained by dissolving fine particles of $CaSO_4 \cdot 2\,H_2O$ and $BaSO_4$, 0.3 and 0.1 μ in diameter, respectively, measured by a microscope and calculated the corresponding interfacial tensions using Ostwald's incorrect equation.

Jones[9] who derived the correct equation by taking into account dissociation of electrolytes, recalculated these interfacial tensions and obtained 1050 and 1300 erg. cm.$^{-2}$ for $CaSO_4 \cdot 2\,H_2O$ and $BaSO_4$, respectively.

Dundon and Mack[10,11] repeated Hulett's experiments and extended them to $SrSO_4$, PbF_2, PbI_2, Ag_2CrO_4 and CaF_2. They obtained a measurable supersaturation in each case and calculated the interfacial tensions for these substances. With $SrSO_4$ particles 0.25 μ in diameter, for instance, 26% supersaturation was observed. They gave 370, 1400 and 1250 erg. cm.$^{-2}$ for the interfacial tensions of $CaSO_4 \cdot 2H_2O$, $SrSO_4$ and $BaSO_4$, respectively.

However, in the light of some theoretical considerations and because of points raised on experimental grounds, the reliability of these results was questionable. In particular, the electrical charge on dispersed particles,[12,13] the geometry of the particles, the specific effects of edges and corners of the crystals[9,14] were believed to complicate the problem. Balarev[15] has attributed the observed increase in conductivity of $BaSO_4$ solution to adsorbed $BaCl_2$ and to the mechanical effects of grinding, which appears to have been used by the early workers to reduce particles to the desired size.

Experiments carried out later by Cohen and Blekkingh[16] and Balarev[17] apparently invalidated the results of Hulett and Dundon. Using conductometric and polarographic methods Cohen and Blekkingh investigated the solubilities of various $BaSO_4$ particles whose size was determined microscopically. They did not observe any effect of the degree of dispersion on solubility. It appears from their paper, however, that the systems they investigated did not contain any particles smaller than 1 μ. Nor was Balarev able to observe any excess solubility of $BaSO_4$ particles, on washing them with water for 10–14 years (ranging 0.1–300 μ in diameter as determined by Stoke's law of sedimentation). He obtained similar negative results with $CaSO_4 \cdot 2H_2O$, $SrSO_4$, BaF_2, PbF_2, CaF_2 and heavy spar.

This puzzling controversy has been commented on in most text-books of surface and colloid chemistry. Alexander and Johnson,[18] for instance, discuss the possible effect of electrical charge and seem to believe that impurities which lower the interfacial tension by adsorption are the main cause for failure in detecting the excess solubility.

A number of theoretical and experimental difficulties in treating fine particles have been pointed out by Harbury[19] who considers the interfacial tension values obtained from solubility measurements as empirical quantities rather than fundamental.

Tourky and El Wakkad[20] measured the solubility of fine Ag_2O particles by an e.m.f. method. Although they reported a considerable increase in Ag^+ concentration by reducing the particle size (determined by sedimentation) in the manner in

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(1) W. H. Wollaston, *Phil. Trans.*, **103**, 57 (1813).

(2) P. Curie, *Bull. Soc. Min.*, **8**, 145 (1885).

(3) J. W. Gibbs, "Collected Works," Vol. I, Yale Univ. Press, 1948.

(4) W. Thomson, *Proc. Roy. Soc. Edinburgh*, 7 Feb. (1870).

(5) R. Helmholtz, *Wied. Ann.*, [3] **27**, 509 (1886).

(6) W. Ostwald, *Z. Phys. Chem.*, **34**, 495 (1900).

(7) H. Freundlich, "Colloid and Capillary Chemistry," Methuen, 1926, p. 154.

(8) G. A. Hulett, *Z. Phys. Chem.*, **37**, 385 (1901); **47**, 357 (1904).

(9) W. J. Jones, *Ann. Physik.*, **41**, 441 (1913); *Z. Phys Chem.*, **82**, 448 (1913).

(10) M. L. Dundon and E. Mack, THIS JOURNAL, **45**, 2479 (1923).

(11) M. L. Dundon, *ibid.*, **45**, 2658 (1923).

(12) W. C. Mc. C. Lewis, *Kolloid Z.*, **5**, 91 (1909).

(13) L. F. Knapp, *Trans. Faraday Soc.*, **17**, 457 (1922).

(14) J. J. P. Valeton, *Physik. Z.*, **21**, 606 (1920).

(15) D. Balarev, *Z. Anorg. Chem.*, **145**, 122 (1925); **151**, 68 (1926); **154**, 170 (1926); **163**, 213 (1927); *Kolloid-Beihefte*, **30**, 249 (1930); **32**, 205 (1931).

(16) E. Cohen and J. J. A. Blekkingh, *Z. Phys. Chem.*, **A186**, 257 (1940); *Proc. Acad. Sci. Amsterdam*, **43**, 32, 189, 334 (1940).

(17) D. Balarev, *Kolloid-Z.*, **96**, 19 (1941).

(18) A. E. Alexander and P. Johnson, "Colloid Science," Vol. I, Oxford, 1949, p. 38.

(19) L. Harbury, *J. Phys. Chem.*, **50**, 190 (1946).

(20) A. R. Tourky and S. E. S. El Wakkad, *J. Phys. and Coll. Chem.*, **53**, 1126 (1949).

which they treated the results makes it impossible to obtain internally consistent values for the interfacial tension. This inconsistency was attributed by them to adsorption of OH^- ions by Ag_2O.

Van Hook and Kilmartin[21] were also able to measure the excess solubility of small sucrose crystals by a refractometer. They calculate a value of 12 erg. cm.$^{-2}$ from their data for the interfacial tension.

More recently two interesting papers appeared almost simultaneously in which the solubility is treated in terms of specific surface instead of particle size. Alexander[22] measured the solubilities of amorphous silica of various specific surface and obtained an agreement with an Ostwald-Freundlich type equation which gives 46 erg. cm.$^{-2}$ for silica/water interfacial tension. The reported supersaturation is *ca.* 300% for 6 × 10^6 cm.^{2} g.$^{-1}$ specific surface. Van Zeggeren and Benson[23] investigated by conductometry the solubilities of NaCl specimens varying in specific surface in alcohol at 25°. Specimens were prepared by electrostatic precipitation, and their specific surfaces which cover a range of $1.2 \times 10^4 - 4.25 \times 10^5$ cm.^{2} g.$^{-1}$ were determined by B.E.T. method by N_2 adsorption. They reported a supersaturation of 6.71% for 4.25×10^5 cm.^{2} g.$^{-1}$, which corresponds to an average particle size of 650 Å., and obtained a fairly good formal agreement with the theory. Their calculated value for the interfacial tension is 171 erg. cm.$^{-2}$. The latter authors discuss the difficulties raised by Harbury[19] for this kind of treatment of fine particles and solve most of them satisfactorily. However, two important points found also in Alexander's[22] work are still open to criticism: (i) They assume that they are dealing with particles of uniform size without any experimental evidence. If the particles have a size distribution as in most real systems the system is unstable. In this case the smaller particles are expected to disappear and the larger ones to grow. It is also expected that when such a solid sample is dispersed in the solution at normal saturation the concentration of the solution should at first rise and then fall. This behavior has been observed by the previous workers[10,21] as well as these authors. At the maximum concentration which is assumed to be the equilibrium concentration the effective particle size or specific surface of the population which satisfies the solubility equation is somewhere between the minimum and maximum values. This is a fundamental difficulty in this kind of investigation. But in the absence of any knowledge of the size distribution, it is impossible even to assess the magnitude of this uncertainty. Although these authors have replaced the particle size in their equations by the specific surface, a macroscopic quantity, it is important to note that the microscopic nature of the problem is unavoidable. (ii) Apparently they have determined the specific surface of the original solid and used this in their treatment as that of the solid in equilibrium with the solution.

As emphasized by Harbury,[19] in this kind of investigation the uncertainty involved in particle size measurements, if a sample contains particles too small to be detected by an ordinary microscope, is a serious source of error. Probably the reason for the controversial results of the earlier workers[8,10,11,16,17] lies in this uncertainty. It was the purpose of the present investigation in obtaining new experimental data to test the theoretical equations to pay more attention to an accurate measurement of the particle sizes. We chose the system $SrSO_4$/water partly because it was one of the systems associated with experimental contradictions[11,17] and partly because the present investigation is part of a program of studying the behavior of fine particles of strontium compounds in connection with Sr^{90} fall-out.

2. Theoretical

Of the expressions which relate the excess solubility of a crystalline solid to the interfacial tension and the particle size, the equation derived by Moilliet and Collie[24] appears to be the most interesting one in view of rigour in derivation and generality. They treat the solubility of a parallelepiped with its three types of crystal faces having different interfacial tensions. However, it is not easy to interpret the physical meaning of the geometric mean of these interfacial tensions, which appear in their equation. Furthermore, the equation is applicable only to ideal solutions of non-electrolytes.

Although Van Zeggeren and Benson[23] treat the case of solutions of electrolytes, their equation contains only one interfacial tension whose meaning is not defined in the general case of non-isotropic crystals. Also, their thermodynamic derivation involves the unnecessary introduction of internal pressure of a solid which is not a thermodynamic quantity.

Here, we would like to present an independent derivation of a more general solubility equation.

Consider a single crystal of any geometry having any number of type of surfaces in equilibrium with the solution phase. Let s_i and γ_i be the area and interfacial tension associated with the i th type of surface, and assume that γ_i's are independent of crystal size and composition of the solution phase. At constant temperature and pressure we have

$$\mathrm{d}F = \mu_0\,\mathrm{d}n + \sum_i \gamma_i \mathrm{d}s_i \qquad (1)$$

where F is the Gibbs free energy, μ_0 is the bulk chemical potential of this crystal and n is the number of moles it contains. Dividing this expression by dn we get the over-all chemical potential μ of the crystal

$$\mu = \mu_0 + \sum_i \gamma_i\,\mathrm{d}s_i/\mathrm{d}n \qquad (2)$$

If v is the volume, ρ is the density of the crystal and M is the molecular weight, then (2) can be written as

$$\mu = \mu_0 + M/\rho \sum_i \gamma_i\,\mathrm{d}s_i/\mathrm{d}v \qquad (3)$$

According to the Gibbs boundary condition (p. 321

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(21) A. Van Hook and E. J. Kilmartin, *Z. Elektrochem.*, **56**, 302 (1952).

(22) G. B. Alexander, *J. Phys. Chem.*, **61**, 1563 (1957).

(23) F. Van Zeggeren and G. C. Benson, *Can. J. Chem.*, **35**, 1150 (1957).

(24) J. L. Moilliet and B. Collie, "Surface Activity," Van Nostrand, 1951, p. 139.

of ref. 3) a crystal which is in equilibrium with a solution phase assumes a constant geometric shape during dissolution or growth. If x is any characteristic dimension—*e.g.* length, width, depth etc.— of the crystal, if follows, that

$$s_i = k_i x^2 \tag{4}$$

for each type of surface, and

$$v = lx^3 \tag{5}$$

where k_i and l are geometric constants independent of x. k_i is characteristic for each type of surface and l is characteristic for the geometry of the whole crystal. From (4) and (5) we get

$$\mathrm{d}s_i/\mathrm{d}v = 2/3\ s_i/v \tag{6}$$

Substituting (6) into (3) we obtain

$$\mu = \mu_0 + (2M)/(3\rho v) \sum_i \gamma_i s_i \tag{7}$$

If we define a "mean interfacial tension" $\bar{\gamma}$ by

$$\bar{\gamma} = \left(\sum_i \gamma_i s_i\right) \Big/ \left(\sum_i s_i\right) \tag{8}$$

which is simply the total surface free energy divided by total surface, from (7) and (8) we get

$$\mu = \mu_0 + \left(2M \sum_i s_i\right) \Big/ (3\rho v)\ \bar{\gamma} \tag{9}$$

This equation is the general form of eq. 15 of Van Zeggeren and Benson and eq. 40 of Moilliet and Collie. Going back to eq. 4 and 5, from (9) we obtain

$$\mu = \mu_0 + (2M\alpha)/(3\rho)\ \bar{\gamma}/x \tag{10}$$

where α is a characteristic geometric factor of the crystal shape, and given by

$$\alpha = \left(\sum_i k_i\right) \Big/ l \tag{11}$$

If the substance under consideration is an electrolyte, its chemical potential μ' in the solution is given by

$$\mu' = \mu_0' + \nu RT \ln a \tag{12}$$

where μ_0' is the standard chemical potential, ν is the number of ions produced by dissociation of one mole of electrolyte, R is the gas constant, T is the absolute temperature and a is the mean activity of the electrolyte in the solution. Equating μ to μ' as required by the condition of equilibrium between the crystal and the solution, from (10) and (12) we get

$$\mu_0 + (2M\alpha)/(3\rho)\ \bar{\gamma}/x = \mu_0' + \nu RT \ln a \tag{13}$$

When x is effectively large, the second term in the left hand side of (13) vanishes and the saturation activity a assumes its normal value a_0 given by

$$\mu_0 = \mu_0' + \nu RT \ln a_0 \tag{14}$$

Finally, from (13) and (14) we obtain

$$\mathrm{Log}\ a/a_0 = (2/3 M\alpha\bar{\gamma})/(2.303\nu\ RT\ \rho x) \tag{15}$$

If the geometry of the crystal is known α can easily be calculated since, as will be seen from (4), (5) and (11), it is the ratio of the total surface area to the volume of a crystal of unit x. For instance, for a cube, if x is the length of one edge, $\alpha = 6$. In the case of a sphere of diameter x, α is also 6. In this case (15) becomes equivalent to the Ostwald-Freundlich equation. Alternatively, α can also be calculated from x and the specific surface even if the specific surface is determined with a sample of non-uniform size, provided that distribution of x is established. Indeed, it can be shown from the above definition of α that for a population of geometrically similar particles

$$\alpha = \rho\ (\sigma \Sigma x^3)/(\Sigma x^2) \tag{16}$$

where σ is the specific surface.

3. Experimental

In the present work we have determined the solubility of fine $SrSO_4$ particles of various sizes in water at 25.0°. The experimental method was so designed as to eliminate as far as possible the sources of error which might have existed in the previous investigations, as discussed in Section 1. Namely, we (a) synthesized the fine particles instead of grinding large crystals, (b) determined the solubility by a radioactive tracer technique using S^{35} as sulfate, instead of by a conductometric method to avoid possible interference of chlorides adsorbed (*cf.* section 1), and (c) measured the size of the particles in equilibrium with the solution by electron microscopy.

a. **Preparation of $SrSO_4$ Particles.**—We have investigated the precipitation of $SrSO_4$ from aqueous solutions at various reactant concentrations and the precipitates formed. We have observed, by mixing equivalent amounts of $SrCl_2$ and Li_2SO_4 solutions, that the minimum $SrSO_4$ concentration which initiates precipitation (in *ca.* 10 hr.) is 0.015 *M*. The particles formed in aqueous solutions had exactly the same spindle shape as $BaSO_4$ particles which can be seen in electron micrographs in a recent publication by Takiyama.[25] The particles so obtained were not only too large for the solubility studies but were also compound crystals with scales around them as revealed by the electron microscope at high magnifications. They were, therefore, unsuitable for the present work.

However, we were able to obtain primitive and small enough crystals of $SrSO_4$ by precipitation from alcoholic solutions as mentioned by Weiser.[26] By mixing equivalent amounts of aqueous $SrCl_2$ and Li_2SO_4 solutions together, we found that no precipitation takes place in 21 hr. in a solution which contains 0.01 *M* $SrSO_4$. If the reactant solutions contain 20% of methanol by volume, precipitation takes place in 1 minute. The crystals so formed are large and similar to those precipitated from aqueous solutions as described above. At 30% methanol concentration the same large crystals precipitate in *ca.* 30 seconds followed by formation of fine particles in *ca.* 3 minutes in small quantity. At 50% methanol concentration fine particles are formed abundantly in *ca.* 15 seconds with no formation of large crystals. At methanol concentrations higher than 50%, the higher the methanol concentration the smaller the particles formed. We have also observed that precipitation can be affected by adding a small amount of methanol after mixing the aqueous reactants of the same concentration, presumably due to local formation of relatively few particles and their subsequent growth. The particles so obtained are much larger than those formed at 50% methanol concentration.

Making use of these observations, we prepared three different samples of radioactive $SrSO_4$ particles of various size ranges using the same Li_2SO_4 stock solution which contained S^{35} as sulfate. The recipes of these batches are given in Table I.

TABLE I

Batch	A, ml.	B, ml.	C, ml.	
0.5 *N* $SrCl_2$	3	3	10	
H_2O	..	147	500	I
MeOH	300	600	..	
0.5 *N* Li_2SO_4 (S^{35})	3	3	10	
H_2O	..	147	500	II
MeOH	300	600	..	

Reactants I and II were mixed at room temperature by pouring II into I which was vigorously stirred. In the case

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(25) K. Takiyama, *Bull. Chem. Soc. Japan*, **31**, 950 (1958).

(26) H. B. Weiser, "Inorganic Colloid Chemistry," Vol. **III**, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 56.

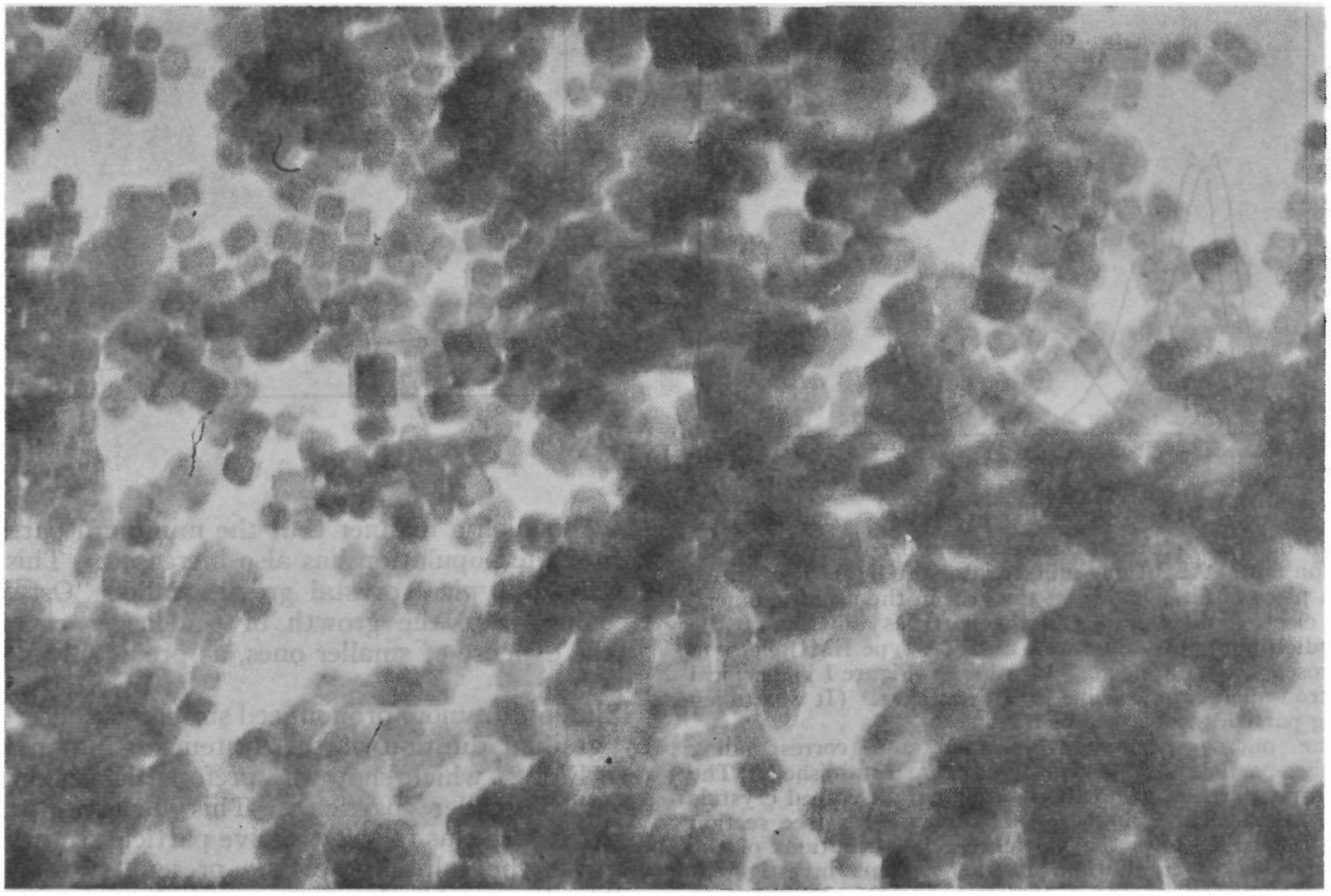

Fig. 1.

of batch C, 20 ml. methanol was added after mixing. The colloidal $SrSO_4$ so formed coagulates in a short time under these conditions. It was then allowed to settle and 24 hr. later the bulk of the supernatant was decanted off. The residue was centrifuged, decanted and washed with 6 ml. distilled water 5 times discarding the washings by centrifuging. It was observed that the first three washings eliminated effectively the bulk of chloride ion. However, further washings could not remove a persistent trace of chlorides from the solid. Similar behavior has been reported by Balarev[17] in the case of $BaSO_4$.

Large crystals of active $SrSO_4$ to be used as standard were also prepared by a method similar to that described by Lewin and Vance,[27] by using the same Li_2SO_4 solution as follows: A solution consisting of 10 ml. 0.5 N $SrCl_2$ and 40 ml. water was mixed with 10 ml. of 0.5 N Li_2SO_4 (S^{35}) + 40 ml. of water, which were preheated, kept at 100° for 1 hr. and the supernatant was decanted off. The precipitate was washed with water three times, dissolved in hot azeotropic hydrochloric acid, evaporated slowly to dryness in a beaker placed on a steam-bath and covered with a watch glass, washed with water until no chloride could be detected and dried in an oven at 175°. The crystals obtained in this manner were about 0.1 mm. in size.

b. Solubility Measurements.—Samples A, B, C and the standard sample were dispersed in 500 ml. distilled water in 1 liter volumetric flasks thermostatted at 25.0° and stirred by magnetic stirrers. With the aid of an electron microscope we have observed that all particles in these suspensions were in the form of aggregates which settled quantitatively in less than 18 hr. after stopping the stirrers and that the supernatant sampled at that moment at a depth of 1 cm. from the surface contained no particles. In this manner 1 ml. samples were drawn from the supernatants when required, weighed in counting planchettes, evaporated and their radioactivities were determined by a Geiger–Müller counter provided with an end window G. M. Tube of 1.9 mg./cm.² window thickness which was found suitable for counting soft β emissions of S^{35}.

Saturation of the solution with the standard large crystals took about 8 days of continuous stirring, as revealed by the supernatant activity, whereas the equilibrium could be established in less than 24 hr. in the case of fine particles unless the amount of solid phase was very small compared to the volume of the solution phase.

The supersaturation ratios, in terms of concentration, C/C_0 in systems A, B and C were calculated by taking the ratio of the counts of the samples drawn from these systems to the count of the standard measured at the same time and corrected for the sample weights. These were 1.50, 1.33 and 1.11, respectively, and did not change during several days of stirring.

Later, 227 ml. of suspension B was diluted dropwise with 100 ml. of water in 1 hr. (system B′) while stirring vigorously. Similarly, the system C was diluted with 325 ml. water in 1.5 hr. (system C′). C/C_0 was then determined in these diluted systems B′ and C′, after equilibration, as described above and found to be lower than those of B and C, respectively (see Table II).

We kept the suspension A stirring continuously, measured C/C_0 2 months after the first dispersion and found it to have dropped to 1.41 apparently due to particle growth (system A′). Subsequently we also diluted this system gradually with 100 ml. of water in 45 minutes (system A″) and determined C/C_0 again. All these C/C_0 values are given in Table II together with the estimated standard errors.

TABLE II

System	C/C_0 ± 0.01	Log a/a_0	$\Sigma x^2/\Sigma x$ Å.	x_{min} Å., ± 10 Å
A	1.50	0.154 ± 0.003	247	96
A′	1.41	.130 ± .003	269	130
A″	1.32	.106 ± .003	388	155
B	1.33	.109 ± .003	541	168
B′	1.18	.063 ± .004	629	252
C	1.11	.040 ± .004	1260	378
C′	1.08	.029 ± .004	1660	500

c. Partical Size Measurements.—Prior to each solubility determination, just before turning off the stirrer, 5 ml. samples were taken from the suspensions and shaken vigorously for 5 minutes after adding one drop of 0.1% fresh gelatin solution as a dispersing agent to break up the particle aggregates. In this manner colloidal dispersions were obtained. A small drop from this dispersion was then trans-

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[27] S. Z. Lewin and J. E. Vance, THIS JOURNAL, **74**, 1433 (1952).

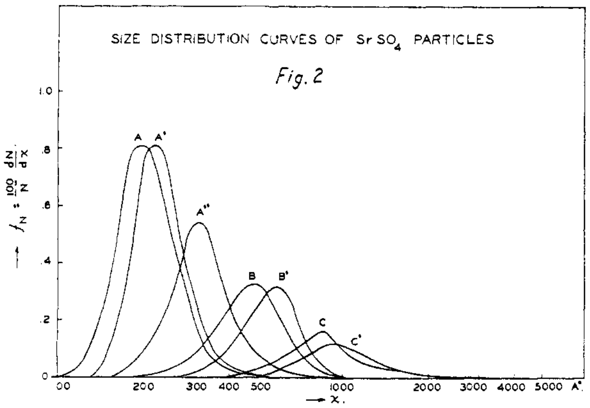

Fig. 2.

ferred on to an electron microscope grid covered with collodion film. About one minute later the liquid was drawn by a piece of filter paper off the grid in the usual manner[28] and electron micrographs of the particles adhering to the collodion film were taken with an RCA type EMU electron microscope at suitable magnifications. Figure 1 is a typical electron micrograph of fine $SrSO_4$ particles. (It was taken using particles from system B.)

The micrographs were analyzed and corresponding number-particle size distributions were established. The apparent width of the orthorhombic parallelepiped crystals were taken as the characteristic dimension *x* (see section 2). Figure 2 shows the particle size distributions of the populations in equilibrium in the systems investigated.

d. **Estimation of the Geometric Factor.**—In order to estimate the geometric factor α of the particles from eq. 16 we determined the specific surface of an inactive $SrSO_4$ sample, prepared in the same manner as Batch B but in larger quantity, by isotopic ion exchange method as described elsewhere by one of us.[29] For this purpose 1.1215 g. dry sample was dispersed in 100 ml. of 0.01 *M* Li_2SO_4 solution containing some S^{35} as sulphate and stirred at 25.0°. Activity of the supernatant was measured each time by taking 2 ml. sample, contrifuging, weighing, evaporating and counting 1 ml. of supernatant in a planchette. Figure 3 shows the activity of 1 g. of the supernatant sampled at various times but measured at the same time. The initial and extrapolated equilibrium counting rates of the solution were 3011 and 1965 c.p.m./g., respectively. From these values the specific surface σ was calculated as $3.39 \times 10^5 \pm 1.6 \times 10^4$ cm.^{2} g.$^{-1}$, taking 1.09×10^9 cm.^{2} mole^{-1} for the molar surface of $SrSO_4$.

At the end of this experiment, a sample was taken from the suspension and the size distribution of the particles was determined as described in paragraph c. The quantity $\Sigma x^3/\Sigma x^2$ calculated from these measurements was 5.2×10^{-6} cm. Using this value, the specific surface and $\rho = 3.96$ g. cm.$^{-3}$, the geometric factor α was calculated from eq. 16 as 7.0 ± 0.3.

4. Discussion

As mentioned in Section 3, b, microscopic examinations showed that, if no dispersing agent were present, all $SrSO_4$ particles in suspensions were in the form of aggregates. This indicates the absence of electrical charge on particles in the present system to interfere with the solubility as discussed by some authors.[12,13]

a. **Shifts in Size Distribution.**—Let us first consider the case of system A which exhibited a significant shift in particle size distribution to the bigger size, as shown in Fig. 2, over a period of 2 months, and a corresponding drop in solubility, as mentioned in Section 3, b. The shift has taken place in such a manner that the minimum particle size of the population has also increased. This is, clearly, a typical crystal growth called "Ostwald ripening" *i.e.*, the growth of the larger crystals at the expense of smaller ones, as predicted by the theory.

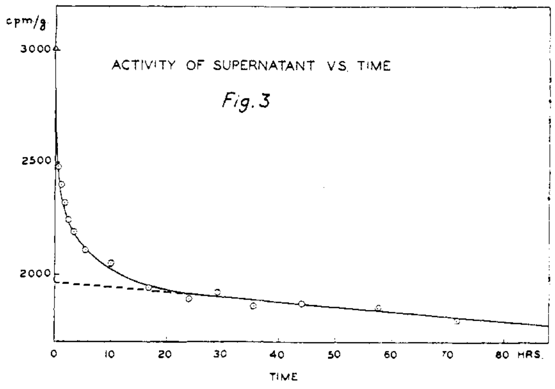

Fig. 3.

Similar but more pronounced shifts were observed by gradual dilution of the systems A′, B and C (see Fig. 2) which show the preferential solubility of the smaller particles. This behavior also gives us a clue as to the effective particle size which controls the solubility of the present system, as will be discussed in the next paragraph.

b. **Solubility and Particle Size.**—To take into account the deviation of the solution from the ideal, we converted the concentration ratios C/C_0 to activity ratios a/a_0 by using the activity coefficients of $SrSO_4$ calculated from the Debye-Hückel equation. Log a/a_0 values so obtained are given in the third column of Table II with the corresponding standard errors.

In order to test the theoretical equation 15 a plot of Log a/a_0 must be made against the reciprocal of particle size. However, as mentioned in Section 1, we were confronted with the difficulty of which particle size to use since the particles were far from being uniform in size (Fig. 2). The first attempt to use as the effective size various average sizes such as the number average, the surface average and the volume average. The peak values of the number, width, surface and volume distribution curves was also used. The ratio $\Sigma x^2/\Sigma x$ was also considered and this ratio can be shown to be the effective size if the amount of solid to be dissolved reversibly per unit surface area is irrespective of the particle size. Finally, the ratio $\Sigma x^3/\Sigma x^2$, equal to the average size calculated from the specific surface, (*cf.* eq. 16) was calculated. This is the ratio used in the treatment of Van Hook and Kilmartin,[21] and that of Alexander[22] and is virtually that used by Van Zeggeren and Benson.[23] In all cases, as predicted by eq. 15, a reasonable straight line relationship was obtained for all points except those of system B. On the basis of the plot, no preference could be made between these various variables characterizing the particle size. The numerical values of these variables, one must observe, are very close to each other. One of these plots, *i.e.* using $\Sigma x^2/\Sigma x$ as variable, is shown in Fig. 4. The values of $\Sigma x^2/\Sigma x$ are given in the fourth column of Table II.

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(28) C. E. Hall, "Introduction to Electron Microscopy," McGraw-Hill Book Co., New York, N. Y., 1953, p. 319.

(29) B. V. Enüstün, *Comm. Fac. Sci. Univ. Ankara*, *B* (in press).

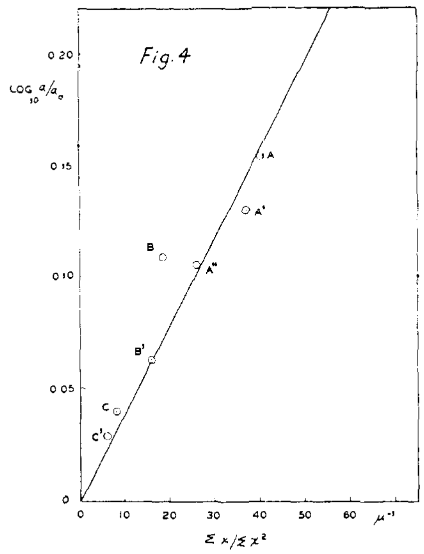

Fig. 4.

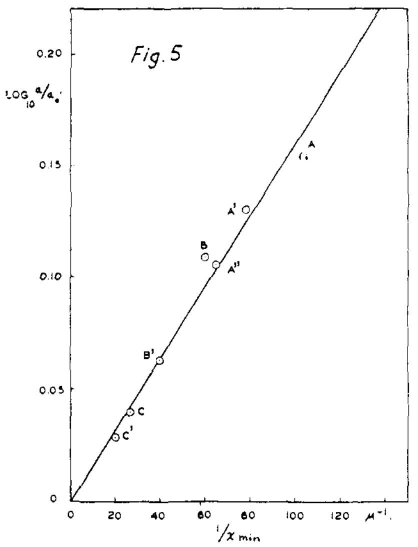

Fig. 5.

At this stage our attention was drawn to the behavior of systems A″ and B. It will be seen from Fig. 2 and Table II that, despite the considerable difference between the particle size distributions in these systems, the solubilities are practically the same. But, it is interesting to note that these systems have another common feature, *i.e.* their minimum particle sizes are also practically the same. This observation coupled with the disappearance of the smallest particles on dilution, as mentioned in the preceeding paragraph, suggested that the solution was in equilibrium with the smallest particles rather than any larger ones, or in other words, the *effective size was the minimum particle size.*

This suggestion became a conviction when we made the following experiments: A solution which was equilibrated with fine particles showed no change in concentration when stirred with large crystals 0.1 mm. in size for 24 hr. The concentration of a solution which was equilibrated with large crystals, however, increased substantially when stirred with fine particles for the same period of time. This meant that the larger particles in the population of graded sizes were not in thermodynamic equilibrium with the solution and, therefore, had no influence on the solubility. In other words, the solution was in equilibrium with the smallest particles, and in a supersaturated state with respect to any larger particles. This is, undoubtedly, because of low rate of crystallization, as indicated by very slow Ostwald ripening (paragraph a) and a constant supersaturation for a considerable time (section 3, b) as also reported by Dundon,[11] compared to the rate of solution. This result is, of course, neither new, nor surprising. It is a well known fact that the persistence of supersaturation is observed far more often than undersaturation. But it brings out once more the fundamental difference between the mechanism of dissolution and crystallization phenomena. In the case of fine particles the manifestation of this difference is more striking since the smaller particles have not only greater solubility but also greater rate of solution per unit surface area as shown by Roller.[30]

The state of affairs in the case of $CaSO_4 \cdot 2\ H_2O$ appears to be somewhat different. Dundon and Mack[10] report that the solubility first increases on dispersing fine gypsum particles, then falls to its normal value indicating a rapid crystal growth in contrast to $SrSO_4$ and $BaSO_4$.[11] This difference in the rate of crystallization can perhaps be attributed to the fact that $CaSO_4$ crystallizes with 2 H_2O whereas $SrSO_4$ and $BaSO_4$ crystals have no crystal water. Probably, the hydrated ions in solution in the latter cases require a high activation energy to be freed from all hydrating H_2O molecules before they can be accommodated in the crystal lattice, thus reduce the rate of crystallization.

In the light of foregoing discussion we can conclude that the effective particle size which satisfies eq. 15 is the minimum size of the population for the present system. Accordingly, we plot Log a/a_0 in Fig. 5 against the reciprocal of minimum size which is given in the fifth column of Table II for each system. Comparing Fig. 5 with Fig. 4, it will be seen that a better agreement with eq. 15 is obtained this way, which is as good as can be expected. The equation of the best straight line drawn from the origin through the points in Fig. 5 is

$$\log a/a_0 = 16/x \qquad (17)$$

which represents the solubility of $SrSO_4$ particles at 25.0° within ±8.4% standard deviation in Log a/a_0 where x is the width of the smallest crystals measured in Å.

Having established the relationship between the solubility of $SrSO_4$ and its particle size, it is appropriate here to compare the present data with the results reported in the literature and to discuss and give reasons for the controversial results of the earlier workers mentioned in section 1. Since the size of the smallest particles controls the solubility, we can safely attribute these contradictions to the failure in detection of these small particles rather than to any experimental error involved in solubility measurements. 26% supersaturation reported by Dundon[11] for 0.25 μ particles appears

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(30) P. S. Roller, *J. Phys. Chem.*, **35**, 1133 (1931).

to be too high when compared with the present data given in Table II. It is reasonable to believe that Dundon had much smaller particles in his $SrSO_4$ sample which could not be detected by ordinary microscope and that the particles investigated by Balarev[17] were not small enough to produce measurable supersaturation.

Probably the same argument applies to the case of other substances studied by the earlier workers.[8,10,11,16,17] For instance, it is very likely that Balarev's prolonged washing has eliminated (*cf.* paragraph a) the particles of $BaSO_4$ smaller than 0.1 μ which were present but not detected in the suspensions used by Hulett[8] and Dundon. The particles of $BaSO_4$ investigated by Cohen and Blekkingh were definitely too coarse (see section 1) to produce supersaturation.[16]

c. Interfacial Tension.—Substituting $\nu = 2$, $\alpha = 7.0$ (section 3,d) for $SrSO_4$ and the values of the other constants in eq. 15, from (15) and (17) we obtain $\bar{\gamma} = 84 \pm 8$ erg. cm.$^{-2}$ for solid $SrSO_4$/solution mean interfacial tension at 25.0°. The value 1400 erg. cm.$^{-2}$ calculated by Dundon from his results appears to be much too high. This is merely because of the fact that his estimated particle size must have been much larger than the size of the smallest particles which were actually present in the system investigated (paragraph b). Although Dundon's calculation was based on the Ostwald–Freundlich equation which is applicable to spherical particles, this is not expected to make an appreciable difference in $\bar{\gamma}$ calculated since, as pointed out in section 2, the Ostwald–Freundlich equation corresponds to the use of a geometric factor 6 in our treatment instead of 7 (or may be even 6.24 as will be discussed in paragraph d) for $SrSO_4$ crystals.

It is interesting to note that the order of magnitude of the solid/liquid interfacial tension values given by the early workers[8,10,11] who have used ordinary microscope for particle size measurements is significantly bigger than that of values obtained by the recent workers[21,22,23] who actually or virtually have calculated the particle size from the specific surface determined by surface phenomena. This is because of the fact that the particle size determination by the latter method takes care of the submicroscopic particles. Although the specific surface method gives a more realistic estimate of particle size and, therefore, interfacial tension, the particle size so obtained is an average value, and the question of how close this average is to the effective size (section 1) is still open. However, the interfacial tension values obtained by a specific surface method is expected to be at least of the right order of magnitude. Indeed, the values 46 erg. cm.$^{-2}$ for silica/water, 171 erg. cm.$^{-2}$ for NaCl/alcohol obtained by Alexander[22] and Van Zeggeren and Benson,[23] respectively, appear to be reasonable estimates when compared with 84 erg. cm.$^{-2}$ for the present system. The value 12 erg. cm.$^{-2}$ given for sucrose/solution by Van Hook[21] is also a reasonable figure for the surface tension of a molecular lattice measured against a concentrated solution.

Moilliet and Collie[24] derive relationships between the three interfacial tensions of a parallelepiped, from the Gibbs boundary condition, which in the case of rectangular parallelepiped crystals of $SrSO_4$ reduce to

$$\gamma_1 bc = \gamma_2 ac = \gamma_3 ab \qquad (18)$$

where a, b, c are the dimensions of such a crystal and γ_1, γ_2, γ_3 are the interfacial tensions associated with 100, 010, 001 faces, respectively. We also have from eq. 8, by definition

$$\bar{\gamma}(ab + bc + ac) = \gamma_1 bc + \gamma_2 ac + \gamma_3 ab \qquad (19)$$

From (18) and (19) we get

$$\begin{aligned} \gamma_1 &= 1/3\ \bar{\gamma}(1 + a/b + a/c) \\ \gamma_2 &= 1/3\ \bar{\gamma}(1 + b/a + b/c) \qquad (20) \\ \gamma_3 &= 1/3\ \bar{\gamma}(1 + c/a + c/b) \end{aligned}$$

Electron micrographs suggest that the dimensions of the primitive orthorhombic crystals of $SrSO_4$ are in the same proportions as the unit cell dimensions 8.36, 5.36, 6.84 Å.[31] This can be seen from Fig. 1 showing such $SrSO_4$ crystals which expose their 010 faces. Therefore, assuming a, b, c to be in the same proportion as the unit cell dimensions and substituting $\bar{\gamma} = 84$ erg. cm.$^{-2}$ in eq. 20, we obtain $\gamma_1 = 106$, $\gamma_2 = 68$ and $\gamma_3 = 87$ erg. cm.$^{-2}$.

d. Geometric Factor.—If we calculate the geometric factor α, by assuming that $SrSO_4$ crystals have the same geometry as the unit cell and taking the dimension c as the characteristic dimension x (see section 2), we find $\alpha = 6.24$. The experimental value 7.0 appears, therefore, a little too big. We believe, this is due to the fact that some crystals in the specimens mounted for electron micrography were slightly tilted with respect to the electron beam, because of surface irregularities of the collodion substrate, in such a way that the measured width x of the image so obtained was on the average bigger than actual c by a factor of 7.0/6.24. Thus, α calculated from (16) was also overestimated by the same factor. However, in spite of this we used 7.0 for α in calculating $\bar{\gamma}$ since errors in α and x originating from this source eventually cancel in eq. 15.

e. Size of Nuclei.—As mentioned in section 3a, our estimate of the minimum $SrSO_4$ concentration which initiates precipitation on mixing equivalent amounts of $SrCl_2$ and Li_2SO_4 solutions is 0.015 *M*. Taking 114 mg. l.$^{-1}$. (This figure is given in "handbook of Chemistry of Physics" (1956–1957) for 30° which agrees with our estimate of solubility of $SrSO_4$ crystals 0.1 mm. in size, using a tracer method.) For the normal solubility of $SrSO_4$, this corresponds to a supersaturation ratio of 24.2 against 13–26 reported by Figurovskii and Komarova.[32] Lucchesi[33] claims, however, that he was able to get precipitate at a concentration of 0.001 *M*. La Mer and Dinegar,[34] on the other hand, has reported a value of 2.95 for the limiting supersaturation ratio in terms of activities. If we convert our and Lucchesi's figures to activity ratios, using the Debye–Hückel equation for the activity coefficients, we find 7.53 and 1.41, respectively. Therefore, both Lucchesi's and LaMer's, figures

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(31) R. W. G. Wyckoff, "Crystal Structure," Vol. II, Interscience Publishing Co., New York, N. Y., 1951, Chapter VIII, Table p. 21.

(32) N. A. Figurovskii and A. Komarova, *Zhur. Neorg. Khim.*, 1, 2820 (1956).

(33) P. J. Lucchesi, *J. Coll. Sci.*, **11**, 113 (1956).

(34) V. K. La Mer and R. H. Dinegar, THIS JOURNAL, **73**, 380 (1951).

appear to be too low compared to ours, which is in agreement with Figurovskii's result.

Substituting $a/a_0 = 7.53$ in eq. 17 we find x = 18 Å. which can be considered as the width (*i.e.*, c dimension) of $SrSO_4$ nuclei. This is about 3 times the c dimension of the unit cell 6.84 Å. (paragraph c). It can be concluded, therefore, that a nucleus consists of $3^3 = 27$ unit cells.

By similar calculations La Mer arrives at a value of 100 Å. for the size of $BaSO_4$ nuclei from their experimental results. Nevertheless, in their calculation they use Hulett's value (1500 erg. cm.$^{-2}$) for the interfacial tension of $BaSO_4$ which we consider too high (*cf.* paragraph c and section 1). If we can assume that the c dimension of a $BaSO_4$ nucleus is also 3 times that of a unit cell, *i.e.*, 7.14 Å.,[31] using LaMer's value of 21.5 for the critical a/a_0 and α calculated from the unit cell dimensions,[34] we obtain from eq. 15 $\bar{\gamma} = 150$ erg. cm.$^{-2}$ for $BaSO_4$/solution mean interfacial tension.

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Structure of the Double Layer and Electrode Processes. II. Effect of the Nature of the Electrode and Application of the Thallium-Amalgam Electrode

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The influence of the nature of the electrode in electrochemical kinetics in the absence of specific electrode effects is interpreted on the basis of a change in the double layer structure. This double layer effect, which can be quite significant, should also be considered in kinetic correlations for processes with specific electrode effects. Application is made of the dropping thallium-amalgam electrode (up to 31% Tl) for which the point of zero charge can be shifted continuously by as much as −0.4 volt with respect to this point for mercury. The following reductions are studied: bromate and iodate in alkaline solution, hexacyanochromate(III) in cyanide medium, chromate in alkaline solution and tetracyano cadmium(II) in cyanide medium. Shifts of the Tafel line for bromate and variations of the exchange current density for hexacyanochromate(III) are interpreted quantitatively. Chromate waves for the dropping thallium amalgam electrode in supporting electrolyte of low concentration exhibit a pronounced minimum which is quantitatively discussed. The maximum in the tetracyano cadmium(II) waves is abscribed to a double layer effect in agreement with other investigators, and a quantitative study is attempted for the results obtained with the dropping mercury electrode.

Introduction

The structure of the double layer at an electrode–electrolyte interface affects the kinetics of electrochemical reactions occurring on this electrode for two reasons: (a) the concentrations of ionic reactants are not the same at the reaction site as in the bulk of the solution and (b) the effective difference of potential must be corrected for the difference of potential across the diffuse double layer. These two fundamental effects were suggested by Frumkin and investigated principally by him and his school.[2] Much interest has been shown recently in such studies by other investigators.[3-7] (For recent reviews of double layer effects in polarography see ref. 8 and 9; also ref. 3.) In general, interest has been focused on factors governed by solution composition rather than on the effect of the electrode nature. Frumkin and co-workers did study the minimum in certain current-potential curves with electrodes of different metals[10] but this is one of the rare systematic studies of the influence of electrode material on double layer effects in correlation with kinetics.

We began a study of the electrode effect by comparison of mercury and gallium electrodes but soon adopted the more versatile thallium amalgam electrode of varying composition. The point of zero charge of the latter electrode can be shifted by as much as −0.4 volt in comparison with a mercury electrode as was shown by Frumkin and Gorodetzkaya.[11] This shift of the point of zero charge may result in a significant change in the difference of potential across the diffuse double layer (Fig. 1) and a concomitant change in the kinetics of an electrode reaction occurring on the amalgam. The thallium amalgam electrode has two advantages over the use of solid electrodes of different nature in such studies: (a) the point of zero charge can be changed continuously, and (b) spurious effects observed with solid electrodes (contamination, roughness, etc.) are minimized or eliminated by the use of a dropping amalgam electrode with a continuously renewed surface.

The following reactions were studied: (a) reduction of bromate and iodate in alkaline solution as examples of slow electrode processes without chemical complication; (b) the reduction of hexacyanochromate(III) as an example of fast reaction; (c) the reduction of chromate ion in alkaline medium as an example of a process yielding current–potential curves with a minimum when amalgam electrodes of proper concentration are

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(1) Predoctoral fellow, 1957–1959.

(2) For an extensive review, see for instance A. N. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955).

(3) M. Breiter, M. Kleinerman and P. Delahay, THIS JOURNAL, **80**, 5111 (1958). A detailed bibliography is given.

(4) L. Gierst, "Cinétique d'approche et réactions d'électrodes irréversibles," thèse d'agrégation, University of Brussels, 1958.

(5) L. Gierst, article in "Transactions of the Symposium on Electrode Processes, Philadelphia, May 1959," E. Yeager, editor, John Wiley and Sons, Inc., New York, N. Y., in course of publication.

(6) R. Parsons, *ibid.*, in course of publication.

(7) W. H. Reinmuth, L. B. Rogers and L. E. I. Hummelstedt, THIS JOURNAL, **81**, 2947 (1959).

(8) P. Delahay, article in "Advances in Polarography," P. Zuman, editor, Interscience Publishing Co., New York, N. Y., in course of publication.

(9) P. Delahay, article in "Proceedings of the Second International Congress of Polarography," Pergamon, London, in course of publication.

(10) A. N. Frumkin, article in ref. 5; see also ref. 2.

(11) A. N. Frumkin and A. W. Gorodetzkaya, *Z. physik. Chem.*, **136A**, 451 (1928). We are indebted to Dr. L. Gierst for calling this investigation to our attention.