at 22 Å. It is evident that there is no serious disagreement between the two methods when applied to finely porous substances.

It is recognized that the concept of a meniscus in equilibrium with a vapor ceases to have precise meaning as the capillary radius approaches the diameter of the adsorbate molecules. Consequently extension of the use of the Kelvin equation to pores of very small radius constitutes a sort of extrapolation which cannot be rigorously justified. However, it will be noted that, in general, only a small fraction of the total volume is contained in pores of such small radius as to cast doubt on the applicability of the Kelvin relationship. For example, it seems gratuitous to assume the likelihood of a sudden break in a smooth curve such as that of Fig. 6, occurring due to a sudden failure of the Kelvin equation to apply, at 15 or 10 Å. radius.

Further confirmation of the accuracy of both this method and that of Oulton is given by the high pressure mercury porosimeter work of Drake[11] in which he finds by a more direct approach that a silica–alumina gel of the cracking catalyst type has a sharp pore volume maximum in the neighborhood of 20 Å. radius. An exact comparison between the results of Drake, Oulton and this paper is, of course, impossible since there is no certainty that the same kind of catalyst was used in each case. However, the catalysts were of the same general type and the similarity of the results are to that extent confirmatory. High pressure mercury porosimeter measurements are being made on a selection of the adsorbents discussed in this paper so as to obtain such a direct comparison. These data will be published in the second paper of this series.

Acknowledgment.—The authors wish to acknowledge their indebtedness to Dr. A. Wheeler for his helpful suggestions on the theoretical aspects of the work. They are grateful to Baugh and Sons Company for permission to publish this paper.

Summary

An analysis of the nitrogen desorption isotherms based upon the Wheeler theory of combined physical adsorption and capillary condensation has been developed.

A method for computing the pore volume and area distribution directly from the desorption isotherm of porous substances is presented. The method has been successfully applied to adsorbents covering a wide range of pore volume maxima.

PITTSBURGH, PA. RECEIVED MAY 1, 1950

(11) L. C. Drake, *Ind. Eng. Chem.*, **41**, 780 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Limiting Degrees of Supersaturation of the Sparingly Soluble Sulfates

BY VICTOR K. LA MER AND ROBERT H. DINEGAR

Introduction

Von Weimarn[1] observed that the form of the precipitate of $BaSO_4$ produced by mixing solutions of $Ba(CNS)_2$ and $MnSO_4$[2,3] depended on whether the initial concentrations of reagents were relatively low (crystals) or relatively high (jellies). He formulated these results in terms of a set of Precipitation laws, and concluded that the velocity of precipitation was a direct function of supersaturation; also that the higher the velocity of precipitation the larger the number of particles formed. He concluded that not only was the degree of supersaturation important in determining the form of the precipitate, but, in addition, so was the absolute magnitude of this concentration; for example, whether it arose from a large total concentration or from a small solubility. In the first case, a large amount of the dispersed phase will be produced and in the second very little.

Von Weimarn's results, however, are not precise since his technique may have produced local supersaturations. In any case, his interpretation neglected the important role of the ionic environment on ionic equilibria. Thus his data for the supersaturation ratio needed for the spontaneous formation of crystalline $BaSO_4$ particles may be interpreted as lying anywhere between the limits of 8 and 48.

On the other hand, A. M. Belousov and A. B. Terenteeva[4] report that by direct mixing of soluble barium and sulfate compounds, the equilibrium value for the solubility of $BaSO_4$ could be exceeded approximately 100-fold before a precipitate appeared. Their measurements, however, were very rough.

Recent advances[5] in the theory of phase transitions invite a reinvestigation of Von Weimarn's methods and conclusions from new points of view and their extension to other systems. To obtain reproducible values of the maximum concentrations of metal ion and $SO_4^=$ that can coexist in solution before the rapid spontaneous formation of particles takes place, we have substituted the production of sulfate ion by a slow chemical process for the usual techniques of direct mixing of reagents.

Although methods for producing colloidal lead and strontium sulfates have been reported, no quantitative data are available on the critical degree of supersaturation tolerated by solutions of these salts.

Theoretical Discussion

Dilute solutions of sodium persulfate in the presence of sodium thiosulfate decompose slowly

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(1) P. P. Von Weimarn, *Chem. Revs.*, **2**, 217 (1926).

(2) H. B. Weiser, "Colloid Chemistry," Chapter IX, John Wiley and Sons, Inc., New York, N. Y., 1939.

(3) H. B. Weiser, *Inorg. Colloid Chem.*, **11**, 11 (1938).

(4) A. M. Belousov and A. B. Terenteeva, *J. Applied Chem.* (*U. S. S. R.*), **13**, 463 (1940).

(5) V. K. La Mer and R. H. Dinegar, THIS JOURNAL, **72**, 4847 (1950).

to form sulfate and tetrathionate ions[6] according to the stoichiometric equation

$$S_2O_8^= + 2S_2O_3^= \longrightarrow 2SO_4^= + S_4O_6^=$$

In the presence of a soluble barium or strontium salt, and at a well-defined time depending on the initial concentrations of reactants and the concentration of M^{++}, a precipitate of MSO_4 becomes visible. The appearance of this precipitate corresponds to the limiting degree of supersaturation needed for the rapid spontaneous formation of discrete MSO_4 particles in the particular ionic environment.

The phase transition resembles that discussed previously[5] for the production of colloidal sulfur by the acid decomposition of sodium thiosulfate except that MSO_4 now replaces sulfur as the condensing species.

Two mechanisms may be involved. Fluctuations in local concentration initiate association reactions of the type $x\text{MSO}_4 \rightleftarrows (\text{MSO}_4)_x$. The formation of $(MSO_4)_x$ may also result from the alternate additions of M^{++} and $SO_4^=$ to MSO_4 in successive steps. Both mechanisms lead to the same result and only the end result, namely, the formation of complexes of $(MSO_4)_x$ of various sizes in statistical equilibrium with M^{++} and $SO_4^=$ require consideration.

Following Frenkel,[7] we shall designate a complex of the type $(MSO_4)_x$ as an embryo. At first, when the ion product $(M^{++})(SO_4^=)$ is below the saturation value for the stable macro solid phase, all embryos obviously dissociate and regenerate M^{++} and $SO_4^=$. As the concentration of sulfate ion generated by the chemical process increases, the average value of x and particularly the number of embryos corresponding to a given x value increases very rapidly.

Even though the value for the ion product may have exceeded the saturation value for the macro phase, the overwhelming majority of the embryos are still unstable in respect to M^{++} and $SO_4^=$ and consequently redissolve.

It is only when the ion product exceeds the equilibrium value by a certain critical amount that the formation of the stable macro phase proceeds at a measurable rate. These critical embryos where x is now large, corresponding to a particle radius of the order of 10^{-7} cm., will be designated as nuclei.

A nucleus is unstable with respect to both M^{++} and $SO_4^=$ and the stable macro phase, and corresponds to a complex of maximum (Gibbs) free energy in respect to size of particle. A nucleus therefore differs from an ordinary embryo in that the further addition of MSO_4 produces a decrease in free energy. Hence, the process of further growth is spontaneous.

Experimental

A known concentration of $Ba(NO_3)_2$ or $Sr(NO_3)_2$ solution was added to a reaction flask containing a potassium persulfate solution of known composition. Sodium thiosulfate solution was then added and the reacting solutions mixed immediately and thoroughly, all being thermostated at 25 ± 0.02°. At frequent intervals the flask was examined with a beam of white light for the appearance of a scintillating Tyndall beam using unreacted solutions of the salts for comparison. The time of appearance of MSO_4 particles could be determined to within 5 minutes. The turbidity at the condensation point increased rapidly and was quickly replaced by the appearance of large crystals which settled to the bottom of the flask.

The sudden increase in optical density $D = \log I_0/I$ with time was followed in a Beckman spectrophotometer in a few experiments. Unfortunately, the $BaSO_4$ which precipitated on the walls of the cuvette could not be removed without injuring the optical properties of the glass windows and the procedure had to be abandoned. The rapid increase in optical density from a zero value indicated that the precision in timing would not have been much improved by the use of the spectrophotometer.

The concentration of sulfate ion present at any given time was determined by titration. At various times during the course of the reaction, 25-cc. samples of the reaction mixture were titrated rapidly for the decrease in the thiosulfate (giving the increase in sulfate directly) using standard I_2 in KI, whose molarity was approximately one-half that of the sodium thiosulfate solution used. The indicator was 1 cc. of a 1% starch solution. The results of the titration curves were then plotted as a function of time and correlated with the corresponding time of appearance of turbidity in the reaction flask. Knowing the Ba^{++} (or Sr^{++}) concentration, the ion product of supersaturation could be calculated.

The solubility products of $BaSO_4$ at saturation and at supersaturation were corrected for the mean activity coefficient γ at the ionic strength of the solution according to the relationship

$$[K^0_{SP}]_{\gamma=1} = (\gamma)^2(K_{SP})$$

The critical supersaturation ratio is defined as the square root of the ratio of the ion activity products in the supersaturated to the saturated state. The mean activity coefficient γ_{BaSO_4} for the ionic strength (μ) used was calculated from the extended form of the Debye–Hückel equation as given by Gronwall, La Mer and Sandved for 2–2 electrolytes, for a = 3.6 Å. These values are in agreement with the experimental values found for cadmium and zinc sulfates.[8] For $BaSO_4$ K^0_{SP} is 1.2×10^{-10}.[9] Using the conductance data for $SrSO_4$ from "Int. Crit. Tables," Vol. VI, p. 257, and $\alpha = \Lambda/\Lambda_0 = 0.92$ for the saturated solution, we compute $K^0_{SP} = 3.2 \times 10^{-7}$ at 25°. Yost and Russel (ref.6, p. 342) give the solubility at 25° as 0.134 g./l. Assuming $\gamma = 0.75$ for the saturated solution (7.3×10^{-4} m./l.), $K^0_{SP} = 3 \times 10^{-7}$ for $SrSO_4$.

Discussion of Results

The results of three titrations are plotted in Fig. 1. The decrease in sodium thiosulfate concentrations (increase of sulfate) is a linear function of time over the extent of the reaction studied (~10%). Other experiments (Fig. 2 in the presence of Sr^{++} instead of Ba^{++}) show this linear relationship to hold as far as 50% decomposition and at a much higher (*ca.* 0.1) ionic strength. The reaction is independent of the thiosulfate ion concentration and first order with respect to persulfate ion.[10] The slopes of the titration curves denoted by k' along with the specific rate constant $k^\circ = k'/S_2O_8$ are presented at the bottom of Table I. Just as reported by previous investigators,[10] for the uncatalyzed reaction the rate is not particularly reproducible in ordinary distilled water, and for that reason the sulfate concentration was determined as a function of time in every run.

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[6] D. M. Yost and H. Russell, "Systematic Inorganic Chem. of the 5th and 6th Group Non-metallic Elements," Prentice-Hall, New York, 1946.

[7] J. Frenkel, "Kinetic Theory of Liquids," Chapter 7, Oxford Univ. Press, London, 1946.

[8] V. K. La Mer and W. G. Parks, THIS JOURNAL, **53**, 2040 (1931); V. K. La Mer and I. A. Cowperthwaite, *ibid.*, **53**, 4243 (1931).

[9] "International Critical Tables," Vol. VI, p. 256.

[10] King and Steinbeck, THIS JOURNAL, **52**, 4779 (1930).

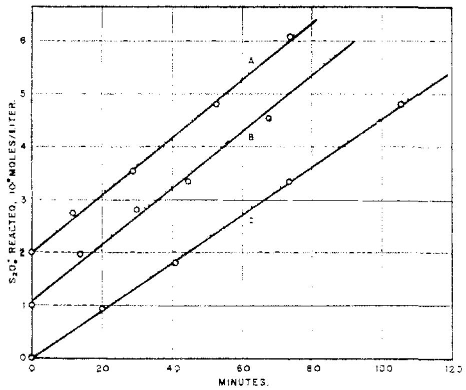

Fig. 1.—Sulfate ion concentration as a function of time for the reaction persulfate plus thiosulfate; both $K_2S_2O_8$ and $Na_2S_2O_3$ are 5 × 10^{-3} m./l.

Curve	10^3 $Ba(NO_3)_2$, m./l.	Plotting increment in ordinate
A	1.5	2
B	1.0	1
C	0.5	0

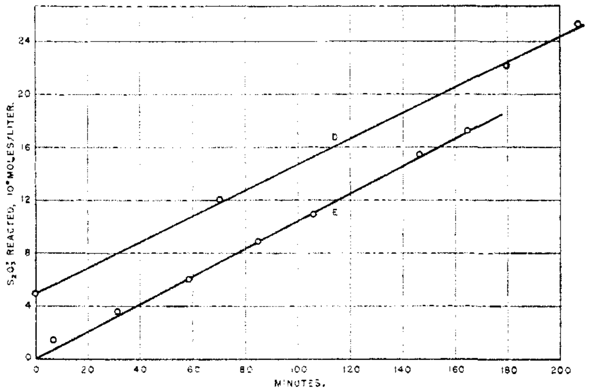

Fig. 2.—Sulfate ion concentration as a function of time for the reaction persulfate plus thiosulfate; both $K_2S_2O_8$ and $Na_2S_2O_3$ are 5 × 10^{-3} m./l.

Curve	10^3 $Sr(NO_3)_2$, m./l.	Plotting increment in ordinate
D	20.0	5
E	50.0	0

TABLE I

SUPERSATURATION OF $BaSO_4$ AT 25.0°

Run no.	10^4 m./l. $Ba(NO_3)_2$	Elapsed time after mixing, min.	10^4 m./l. $SO_4^=$	10^7 ion product	$10^3\mu$	γ	$\sqrt{K^0_{ss}/K^0_{sp}}$
1	0.01	24 hr.	50	0.05	30.0	0.44	2.8 no ppt.
2	0.5	7	25	1.25	30.0	.44	14 no ppt.
3	5	89	5.6	2.8	31.5	.43	21
4	5	80	5.8	2.9	31.5	.43	21
5	5	94	5.5	2.8	31.5	.43	21
6	5	105	5.5	2.8	31.5	.43	21
7	5	95	5.0	2.5	31.5	.43	20
8	5	108	4.8	2.4	31.5	.43	19 av.
9	5	120	5.0	2.5	31.5	.43	20 21.5
10	10	50	3.4	3.4	33.0	.42	22
11	10	54	3.3	3.3	33.0	.42	22
12	15	38	2.6	3.9	34.5	.42	24
13	20	22	1.8	3.6	36.0	.41	22
14	20	25	1.8	3.6	36.0	.41	22
15	20	27	1.9	3.8	36.5	.41	23
16	20	26	1.7	3.4	36.5	.41	22
17	20	140	2.5	5.0	36.5	.41	32 (13°C.)

Run no.	10^6 k', mole/l./min.	10^3 k,⁰ min.$^{-1}$	10^3 ionic strength
..	5.7	1.14	31.5
3	5.7	1.14	31.5
4	6.6	1.32	31.5
5	5.3	1.06	31.5
6	5.0	1.00	31.5
7	4.6	0.92	31.5
8	3.9	.78	31.5
9	3.7	.74	31.5
10	5.8	1.18	33.0
11	5.2	1.04	33.0
12	5.5	1.10	34.5
13	5.6	1.16	36.0
14	5.4	1.08	36.0
15	5.1	1.02	36.5
16	4.6	0.93	36.5

TABLE II

SALT EFFECT ON SUPERSATURATION OF $BaSO_4$ AT 25°

Elapsed time after mixing, min.	$10^4SO_4^=$, (m./l.)	10^8 ion product	$10^3\mu$	γ $ZnSO_4$	$\sqrt{K^0_{ss}/K^0_{SP}}$
110	4.9	24.5	31.5	0.43	19
120	5.0	25.0	31.5	.43	20
128	5.9	29.5	38.5	.40	20
120	5.6	28.0	38.5	.40	19
127	5.5	27.5	60	.33	16
135	5.5	27.5	60	.33	16
120	7.5	37.5	100	.28	15
120	7.5	37.5	100	.28	15
85	6.6	33.0	100[a]	.28	14
86	6.6	33.0	100[a]	.28	14

[a] $Sr(NO_3)_2$ used to obtain ionic strength; all others, $Mg(NO_3)_2$, $Ba(NO_3)_2$ = 5 × 10^{-4} m./l.

The concentration of $SO_4^=$ present at the time of appearance of discrete $BaSO_4$ particles was measured over a range of concentration of Ba^{++} from 10^{-6} m./l. to $2 \cdot 10^{-3}$ m./l. as shown in column 1 in Table I. At Ba^{++} concentrations of 10^{-6} m./l. and $5 \cdot 10^{-5}$ m./l., no precipitate of $BaSO_4$ was observed even after periods of 24 and 7 hours. Excess $Ba(NO_3)_2$, when added to an aliquot, produced $BaSO_4$ showing that $SO_4^=$ had been formed but not in a quantity sufficient for visual detection.

The value of the supersaturation ratio, $\sqrt{K^0_{ss}/K^0_{sp}}$, is constant (average value 21.5 ± 0.4) over a range of (Ba^{++}) = 5 to 20 (10^{-4}) m./l. for fourteen experiments at 25°. Two experiments at 13° gave an average value of 32 for the ratio.

In Table II, the ionic environment was varied by the addition of the salts $Mg(NO_3)_2$ and $Sr(NO_3)_2$. Assuming that the activity coefficient employed, namely, that for $ZnSO_4$ at the given ionic strength is appropriate for $BaSO_4$ in these specific media, the corrected supersaturation ratio still shows a perceptible decrease with increasing ionic strength. However, until the activity coefficient of $BaSO_4$ is actually measured in these specific environments we do not feel that this small decrease should be stressed.

Table III gives comparable data for the supersaturation of $SrSO_4$. The average value of the corrected ratio is 2.95 ± 0.04 for the eight experiments in the absence of foreign salts. The addition of KNO_3 and $Mg(NO_3)_2$ lowers the ratio to 2.4, again assuming that γ can be correctly calculated from the ionic strength relation.

The supersaturation of the sparingly soluble lead sulfate could not be measured by the method employed for barium and strontium, because lead

TABLE III

SUPERSATURATION OF $SrSO_4$ AT 25° K^0_{SP} 3.1×10^{-7} ($\gamma = 1$)

$Sr(NO_3)_2$, 10^3 m./l.	Elapsed time after mixing, min.	$10^3SO_4^{=}$, (m./l.)	10^6 ion product	$10^2\mu$	γ $ZnSO_4$	$\sqrt{K^0_{ss}/K^0_{SP}}$ [c]
2	219	1.60	3.20	9	0.29	2.9
2	202	1.50	3.00	9	.29	2.9
2[a]	235	1.90	3.80	18	.21	(2.3)
2[b]	174	2.05	4.10	18	.21	(2.4)
2[b]	204	2.00	4.00	18	.21	(2.4)
5	130	1.35	6.75	18	.21	3.1
5	150	1.30	6.50	18	.21	3.1
5	140	1.20	6.00	18	.21	3.0
7	113	1.12	7.84	24	.19	3.0
7	113	0.99	6.93	24	.19	2.8
7	113	.99	6.93	24	.19	2.8

[a] KNO_3 added. [b] $Mg(NO_3)_2$ added. [c] Av. value 2.95 ± 0.04 in absence of foreign salts.

forms complex ions with thiosulfate. Mr. Jean Turgeon, to whom we are indebted for assistance in the present investigation, is studying $PbSO_4$ by generating sulfate by the silver ion catalyzed oxidation of Cr^{+++} by $S_2O_8^{=}$. His preliminary results indicate a much lower limiting supersaturation for $PbSO_4$ as compared to $BaSO_4$ and $SrSO_4$.

General Considerations

The critical concentration is actually a very narrow region in which the number of nuclei increases tremendously with increasing concentration.[5,7] At all concentrations above the thermodynamic solubility value there is a finite probability that some nuclei will be produced. If the number of nuclei present is small, the system remains as a homogeneous single phase for long periods of time since the formation of a second phase takes place only by the growth of nuclei. Perceptible growth cannot be detected unless a large concentration of nuclei is present; otherwise, the formation of a second phase will not occur.[11]

The concentration of nuclei present at any particular time is determined not only by the concentration of dissolved material, but possibly also by the length of time the concentration has exceeded the saturation value. For low values of supersaturation longer times will be necessary to produce a sufficient number of nuclei since the number formed is proportional to the time. The concentration of dissolved material affects the number of nuclei in a much more drastic way.

Consider the over-all equation

$$nx \rightleftharpoons x_n$$

for any two concentrations of ion pairs, (x) and (x'), the law of mass action requires

$$x_n = x'_n(x/x')^n$$

Thus for any large value of n, which is usually of the order of 100, the concentration of nuclei (x_n) changes extremely rapidly with increase in concentration of dissolved material (x). Thus, if one increases continually the concentration of dissolved material, the system should always become heterogeneous at about the same value of the concentration and be practically independent of the length of the time the supersaturated condition has existed. Our data indicate that this is true to a first approximation. These values then may be considered to be the upper limit of the supersaturation ratios needed for rapid spontaneous particle formation. In the limit of zero time, it is not expected that the supersaturation ratio would increase appreciably since the rate of change with time is small. Statistical theory suggests that in the limit of infinite time, an extremely small supersaturation concentration would be needed. In fact, these limits were investigated many years ago by Von Weimarn by the direct mixing of the reagents.[1] His values given in ref. (2, 3) are shown in Table IV. The region designated by Von Weimarn as bounded by the supersaturation ratios needed for slow and instantaneous precipitation has now been more completely investigated.

TABLE IV

RECALCULATION OF VON WEIMARN'S DATA DIRECT ADDITION OF $Ba(CNS)_2$ TO $MnSO_4$

10^5 m./l. both reagents	$10^4\mu$	γ	Supersatn. ratio	Nature of ppt.
3.5	2.5	*ca.* 0.98	3.2	No pptn. in a year
6.9	4.9	0.95	6.6	Slow pptn., complete sepn. in months
22.3	15.5	.84	17	Momentary sol stage, complete sepn. in hr.
42.6	29.8	.74	29	Crystals in few sec.
18700	13000	.05	8700	Cryst. barely recognizable, jelly-like material

$Ba(NO_3)_2$ and Na_2SO_4 solutions of varying concentrations were mixed as rapidly as possible to avoid local supersaturations and examined visually for the time of appearance of barium sulfate crystals. (Available spectrophotometric and photronic devices gave results that lagged behind the visual technique by several minutes.) The results are shown in Table V and Fig. 3. For supersaturation ratios above 12, the time of appearance of crystals was sharp and well defined. For ratios below 12, the number of scintillating crystals seemed to increase slowly with time, giving no sharp transition point. As a result, supersaturation ratios less than 9.6 were not observed. The plot of $\sqrt{K^0_{ss}/K^0_{SP}}$ *versus* time extrapolated to zero time should give the ratio needed for instantaneous formation of particles. This value should be no higher than that obtained by the chemical reaction method, since local inhomogeneities of mixing can only lower the supersaturation value for particle formation. The extrapolated value is 21.2 which agrees much more closely than expected with the previously determined value of 21.5. Since concentrations less than this value will also bring about the production of large numbers of particles of the stable phase, but not without a time lag, the upper limit of supersaturation determined by these methods may be called a "limiting value."

This supersaturation ratio for $BaSO_4$ exhibits a notable increase over that calculated for sulfur of 1.2 (see ref. 5), indicating that decreased solu-

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(11) W. H. Rodebush, *Chem. Revs.*, **44**, 275 (1944).

TABLE V

DIRECT MIXING OF $Ba(NO_3)_2$ AND Na_2SO_4

$Ba(NO_3)_2$, 10^4 m./l.	Na_2SO_4, 10^4 m./l.	$10^3\mu$	γ	$\sqrt{K^0_{ss}/K^0_{SP}}$	Time, min.
3.6	2.6	3.6	0.72	19.3	1.50; 1.75
2.54	1.95	1.4	.85	17.3	3.50; 3.25
2.3	1.77	1.2	.87	16.0	5.0
2.03	1.56	1.09	.88	14.3	6.75; 7.0
1.81	1.39	0.96	.90	13.1	10.0
1.69	1.30	.85	.91	12.3	12.0; 13.5; 13.5
1.27	0.98	.67	.93	9.5	Slow pptn. (*ca.* 40 min.)

bility, high net charge, increased interfacial tension and orientation effects may all raise the value of the supersaturation necessary for rapid spontaneous condensation of colloidal particles.

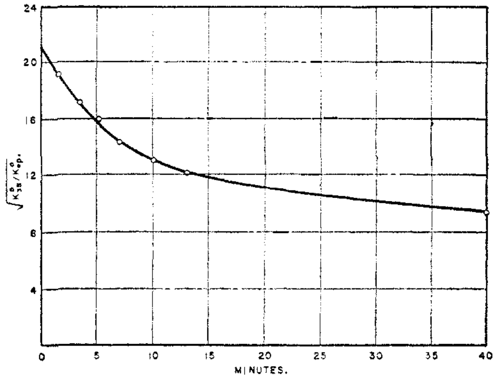

Fig. 3.—Time of appearance of crystalline phase as a function of $K^0{}_{ss}/K^0{}_{SP}$; direct mixing of $Ba(NO_3)_2$ and Na_2SO_4.

As an intermediate case between a substance having a relatively low surface tension (sulfur = 66 dynes/cm.) and $BaSO_4$, where the surface tension is roughly equal to 1500 dynes/cm.,[12] one may take as an example AgCl. The concentration of ions necessary before particle formation takes place is roughly 2.5 times that of the solubility product.[13] AgCl has surface tension estimated to be 150 dynes/cm.

From the Kelvin–J. J. Thompson relationship between the ratio of the vapor pressure of a spherical drop of radius r^* as against a plane surface, one may estimate the size of the stable nucleus formed in these three systems. That is

$$RT \ln P_{r^*}/P = 2\sigma v/r^*$$

σ = surface tension, R = gas constant, T = temp. in A°.
P_{r^*} = vapor pressure of spherical drop of radius, r^*
P = vapor pressure of plane surface
V = molal volume

Replacing these relative pressures by activities and defining the chemical potential of an electrolyte as equal to the sum of the chemical potentials of the constituent ions, one obtains

$$RT/M \ln a_{r^*}/a = 2\sigma/\rho_{r^*}$$

Replacing activity with solubility one obtains

$$iRT/M \ln S_{r^*}/S = 2\sigma/\rho_{r^*}$$

where M = molecular weight; ρ = density; i = van't Hoff factor equal in the limit of zero concentration to one for sulfur, two for AgCl and the sparingly soluble sulfates.[14] The "critical" radii calculated from the above equation, assuming that the surface tension given may be substituted for the interfacial tension involved, for S, AgCl and $BaSO_4$ are

Substance	S_{r^*}/S_0	σ	r^*, micron
S (from organic solvent)	1.2	66	0.005
AgCl	1.4	150	.005
$BaSO_4$	22	1500	.01

These calculations are approximately 10 times larger than the radii calculated for vapor–liquid condensation.[15]

The number of molecules in a particle of radius equal to 0.0075 μ are too many to be accounted for on the basis of the single fluctuation theory visualized for gases (see ref. 7). The mechanism which is indicated by nuclei of these sizes is rather the stepwise association reaction suggested by several investigators.[16] They assume that nuclei do not suddenly come into existence as a result of a single density fluctuation, but rather arise from smaller embryos that change their sizes by losing or gaining atoms or ions at finite rates from the surrounding solution. The production of a nucleus from an embryo arises from the series of "bimolecular reactions" previously described.

The possibility of solute–solvent interaction must not be overlooked in condensed systems. Thus molecules of solvent may interact with subcritical size embryos, thereby forming mixed particles of a size r^*. The relatively large concentration of solvent molecules thus makes possible the formation of stable nuclei at very low supersaturation ratios of solute. The reaction giving rise to nuclei by this mechanism may be represented by the equations

$$nx \longrightarrow (x_n)_{r<r^*} + \text{solvent} \longrightarrow [(x_n) + \text{solvent}]_{r=r^*}$$

Since all particles formed in this manner would contain various amounts (n) of solute molecules, the entire system would equilibrate rapidly; *i.e.*

$$[x_n + \text{solvent}]_{r=r^*} \longrightarrow y(x_a)_{r>r^*} + \text{solvent}$$

where a is now a new variable, characteristic of the distribution of particle sizes, or a constant value in the case of monodispersed systems. The solvent, in effect, is a catalyst, that lowers the necessary free energy of transformation by making possible larger size embryos. Theoretical justification of these ideas have been formulated recently by Reiss.[17]

The Effect of Neutral Salts, Solubility and Temperature.—The addition of neutral salts, such as KNO_3, $Mg(NO_3)_2$ and $Sr(NO_3)_2$, all caused an apparent decrease in the supersaturation ratio. Although the value of the activity coefficient used in the calculations may be open to question in the

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(12) Hulett, *Z. physik. Chem.*, **37**, 385 (1901); **47**, 357 (1904).

(13) G. M. Pound, unpublished data, private communication.

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presence of specific ions, the strong adsorption of NO_3^- ion by sulfate precipitates suggests that mixed crystals possibly are formed with nitrate ion superimposed on the primary $BaSO_4$ lattice. This would allow a larger crystal (and consequently a smaller $\sqrt{K_{ss}/K_{SP}}$ for equilibrium) to be formed for a given sized MSO_4 skeleton. If the cation were also strongly adsorbed this tendency would be even more pronounced. The Paneth–Fajans rule of adsorption predicts no change in adsorbing tendency between K^+ and Mg^{++} and no change was found when $Mg(NO_3)_2$ was substituted for KNO_3 in the case of the precipitation of $SrSO_4$. Sr^{++} is predicted to be much more strongly adsorbed than Mg^{++} or K^+ and $Sr(NO_3)_2$. When substituted for $Mg(NO_3)_2$ in the precipitation of $BaSO_4$, it showed a larger decrease in the ratio at the same ionic strength. The effects of solubility and temperature on the observed supersaturation ratio are opposite to one another. Since the higher the solubility the larger is the concentration of ions, that is, in the supersaturated region, the larger is the possible size of any aggregate of ion pairs formed by collisions. This leads to a smaller ratio being required before the aggregate and supersaturation ratio are compatible. The more soluble sulfates of Sr^{++} and Pb^{++} showed a considerably lower supersaturation ratio at their precipitation point.

The increase in the supersaturation ratio with the decrease in temperature, in the case of $BaSO_4$, could well reflect the decrease in the number of collisions per unit concentration which in turn would require a larger concentration of ion pairs to form a given size nucleus.

Summary and Conclusions

1. The maximum limiting concentrations of sulfate ion that can coexist in aqueous solution with barium and strontium ions, respectively, without producing rapid visible precipitation detectable by Tyndall beam, have been investigated for a variety of conditions.
2. To avoid the possibility of local inhomogeneities in concentration as a result of the direct mixing of reagents leading to premature nucleation, sulfate has been generated homogeneously by chemical reactions in the presence of the cations.
3. The data are interpreted in terms of the ratio of the observed mean ion product at the limiting supersaturation $\sqrt{K_{ss}}$ to the corresponding value $\sqrt{K_{SP}}$ at saturation in respect to the stable crystalline phase; *i.e.*, to $\sqrt{K_{ss}/K_{SP}}$. These ratios are sensitive to ionic environment and consequently require correction to unit values of the activity coefficient, namely, to $\sqrt{K^0_{ss}/K^0_{SP}}$, the mean activity product ratio.
4. The uncorrected ratio for barium sulfate varies from 55 to 48; when corrected to unit activity coefficient, assuming the activity coefficient of barium sulfate behaves like that of zinc and cadmium sulfates, the ratio assumes a constant value of 21.5. This corrected ratio now varies little if at all with ionic strength except on the addition of specific foreign neutral salts. The ratio decreases with rising temperature.
5. The technique of direct mixing of reagents gives limiting supersaturation values which decrease uniformly with the elapsed time required for the appearance of the Tyndall beam. When extrapolated to an elapsed time of zero, the corrected ratio becomes 21.2 in excellent agreement with the preceding result.
6. The corrected ratio for strontium sulfate is 2.9.
7. The results of Von Weimarn when recalculated to unit activity coefficient become consistent with our values.
8. The problem of nucleation is discussed in the light of modern theories of phase transitions.

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[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO]

A Thermodynamic Study of Liquid Metallic Solutions. III. The Systems Bismuth–Gold and Thallium–Gold

BY O. J. KLEPPA*

In earlier communications dealing with the liquid systems lead–gold[1] and tin–gold[2] the author has pointed out the importance of gathering further information on liquid metallic mixtures. As in the earlier investigations the electromotive force method was used to obtain information on the chemical potentials and partial molal entropies of the binary solutions. In the two systems under investigation the reversible galvanic cells take the form

$$Bi(l)/Bi^{+++}/(Bi + Au)(l)$$

and

$$Tl(l)/Tl^{+}/(Tl + Au)(l)$$

Series of alloys containing from zero to about 80 atomic per cent. gold were investigated at temperatures from about 400° up to more than 800° for alloys rich in gold.

Experimental Procedure

(A) General.—The experimental procedure was analogous to the one used in the case of the system tin–gold,[2] with the following modifications.

In order to study alloys containing more than 55–60 atomic per cent. gold, a closed type silica or vycor cell was devised which could be used above 630°, the upper limit for use of Pyrex cells. Because of the impossibility of making gas-tight tungsten–silica and tungsten–vycor seals, the following two alterations of the closed type cell were used.

Type 1 cell (Fig. 1(a)) was made from silica or vycor tubing of 9–10 mm. o.d., and was fitted with two Pyrex–

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