that the vapor is an equilibrium mixture of several forms must be considered. The composition of such a mixture would necessarily depend on the pressure, which in this case is the vapor pressure. Any wide variation in this composition would be reflected in the heat of vaporization, which would result in abnormal curvature of a log p *vs.* $1/T$ plot. The experimental data do not reasonably permit a variation in the slope of this line by more than a few per cent. between one atmosphere and one-tenth atmosphere pressure. This lack of curvature limits the concentration of the lowest polymer (P_8O_{20}) to something less than 5% at one atmosphere, if the variation of the association equilibrium constant in this temperature range be considered of secondary importance to the change of the degree of association with pressure. The molecular formula P_4O_{10} must therefore be nearly correct. On this basis the calorimetric value of the heat of vaporization becomes 17,600 ± 2,600 cal. per gram mole. This deviates considerably from the value 22,800 obtained here and 22,600 calculated from the data of Hoeflake and Scheffer.

Considerable importance is attached to the fact that phosphorus pentoxide vapor will condense only as the low temperature form. This indicates, at least, that the transition occurs only through the solid phase.

Acknowledgments.—The authors are indebted to P. H. Emmett, S. B. Hendricks, R. T. Milner and P. H. Royster for their advice and encouragement. Special mention should be made of the skillful glassblowing of Leonardo Testa in the construction of the Jackson type gages.

Summary

1. The vapor pressure of phosphorus pentoxide has been found to be entirely reproducible and independent of the rate of distillation of the sample.

2. The data are interpreted to show that phosphorus pentoxide exists in a low temperature and a high temperature crystalline form and as a liquid. The atmospheric sublimation temperature of the low temperature form was found to be 358.9°. The triple point between the high temperature crystalline form, the gas and the liquid was found to be at a pressure of 45.6 cm. of mercury and at a temperature of 565.6°. The rate of transition from the low to the high temperature form is undetectable below 360°.

Washington, D. C. Received February 23, 1937

[Contribution from the School of Chemistry of the Institute of Technology, University of Minnesota]

Aging of Fresh Precipitates. XII. The Equilibrium between Mixed Crystals of Silver Chloride and Bromide and Solutions

By H. C. Yutzy[1] and I. M. Kolthoff

It is well known[2] that solid silver chloride and bromide form a complete series of mixed crystals. Küster,[3] preparing the mixed crystals by precipitation from solutions at 19°, was the first to study the equilibrium conditions existing between solid and solution. Various studies, more or less related to the subject, are found in the literature.[4-6] In connection with a study of the aging of precipitated silver chloride it was desirable to know the equilibrium conditions of distribution at 27 and 98°.

The relation between the distribution constant K and the composition of the liquid and the solid phase is found from the following considerations.

$$\mathrm{Cl^-\,(crystal) + Br^-\,(solution)} \rightleftarrows \mathrm{Br^-\,(crystal) + Cl^-\,(solution)}$$

in which Cl (crystal) and Br (crystal) denote the chloride and bromide in the mixed crystals. At equilibrium it is found that

$$K' = \left(\frac{a\ \mathrm{Br^-}}{a\ \mathrm{Cl^-}}\right)_{\text{crystal}} \left(\frac{a\ \mathrm{Cl^-}}{a\ \mathrm{Br^-}}\right)_{\text{solution}} = \left(\frac{f_{\mathrm{Br^-}}\ N_{\mathrm{Br^-}}}{f_{\mathrm{Cl^-}}\ N_{\mathrm{Cl^-}}}\right)_{\text{crystal}} \left(\frac{f_{\mathrm{Cl^-}}\ N_{\mathrm{Cl^-}}}{f_{\mathrm{Br^-}} N_{\mathrm{Br^-}}}\right)_{\text{solution}} \qquad (1)$$

in which a represents the activity of the particular component, f the activity coefficient, N the mole fraction. With the justifiable assumption that $f_{\mathrm{Cl^-}} = f_{\mathrm{Br^-}}$ in the solution (or that their ratio is constant over a wide range of ionic strengths) expression (1) can be written as

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[1] From a thesis submitted to the Graduate School of the University of Minnesota in partial fulfilment of the requirements of the degree of doctor of philosophy, 1936.

[2] R. B. Wilsey, *J. Franklin Inst.*, **200**, 739 (1925).

[3] F. W. Küster, *Z. anorg. allgem. Chem.*, **19**, 81 (1899).

[4] A. Thiel, *ibid.*, **24**, 1 (1900).

[5] O. Ruff and E. Ascher, *ibid.*, **185**, 369 (1929).

[6] E. D. Eastman and R. T. Milner, *J. Chem. Phys*, **1**, 444 (1933).

$$\left(\frac{\text{moles Br}^-}{\text{moles Cl}^-}\right)_{\text{crystal}} \left(\frac{\text{moles Cl}^-}{\text{moles Br}^-}\right)_{\text{solution}} = K' \left(\frac{f_{\text{Cl}^-}}{f_{\text{Br}^-}}\right)_{\text{crystal}} = K \qquad (2)$$

K being called the distribution coefficient.

The value of K calculated by Küster[3] from his experiments was found to vary continuously with the composition of the precipitate. On the basis of equation (2) this variation is attributed to deviations from the ideal state in the solid as exemplified by a variation of the ratio of ($f_{\text{Cl}^-}/f_{\text{Br}^-}$) solid.

The above expressions and the method of approach which are given in the thesis[1] are almost identical with those described by Flood[7a] and Flood and Bruun.[7b] In addition, the latter authors concluded that K is equal to the ratio of the solubility products and equal to K' at a mole ratio of chloride to bromide in the solid of 1.

Experimental

In previous work, mainly that of Küster, analysis of the system was made by filtering off the mixed crystals, and analyzing them by use of the classical indirect gravimetric method—one admittedly inaccurate when the ratio of chloride to bromide is very large or very small. In our experiments, the residual bromide in the aqueous solution was determined by the method of D'Ans and Höfer,[8] with slight modifications.[9] Since the amounts of the various constituents which had been added were known, this allowed the calculation of the compositions of the two phases. This procedure enabled us to analyze with fair accuracy systems in which the gravimetric method would be extremely inaccurate. The reagents used were all reagent grade, ground and dried. The solutions were made up in distilled water and analyzed: the silver nitrate and chloride solutions gravimetrically, the bromide solutions by the above volumetric method. Application of the latter method to the sodium chloride showed that this salt contained less than 0.003% NaBr.[9]

Quite generally the experiments were performed by adding a measured volume of standard silver nitrate to a mixture of a chloride and bromide solution of known composition. After precipitation the solution was made up with water to a known volume and the suspensions shaken for various periods of time. After a given time the bromide content of the solution was determined in the centrifugate. Changes in the order of addition of the reagents have been made in order to see whether the same equilibrium was found when starting under different conditions.

Since Küster[3] did not make sure that he had reached equilibrium (in some experiments he stirred for only two and one-half hours) his experiment number 11 was repeated, adhering closely to his directions but extending the time of shaking from two and one-half hours to one week and analyzing for bromide by our method. Over this period of time the final bromide concentration remained constant (3.6×10^{-3} M), indicating that in this particular case equilibrium was reached within two and one-half hours of shaking. From the results a value of $K = 488$ (19°) was calculated, whereas Küster reported $K = 469$, a satisfactory agreement.

Küster always used a total volume of 1000 ml., whereas in our later work a volume of 100 or 225 ml. of suspension was used. Therefore it was thought desirable to make a few experiments at 19° using a volume of 100 ml. of suspension. After precipitation the suspension was shaken for three days and an aliquot part of the supernatant liquid analyzed for bromide. As an example of the calculations, the composition of the solutions and the derived values are given in Table I. In these cases 25 ml. of 0.2791 M silver nitrate was added to the chloride–bromide mixture.

TABLE I

EQUILIBRIUM AT 19°. TOTAL VOLUME 100 ML.

2 M NaCl, taken, ml.	0.1 M KBr taken, ml.	Millimoles at equilibrium Cl^- in soln.	 Cl^- in ppt.	 Br^- in soln.	 Br^- in ppt.	Mole fraction AgBr in solid	K
25	35	46.4	3.58	0.103	3.40	0.487	428
10	55	18.4	1.60	.115	5.38	.772	538

The corresponding values of K, interpolated from Küster's data, are 410 and 525, respectively. Apparently, there is no appreciable effect of volume changes upon the value of K. A tenfold change in volume resulted in values agreeing within the experimental error. This agreement justifies our assumptions that the variation of K is not to be attributed to a change of the ratio of the activity coefficients of chloride and bromide in solutions but to a change of the ratio in the solid, when the composition of the latter is altered.

Equilibrium at 27 ± 1°

In the first set of experiments a measured volume of 0.2791 M sodium chloride was introduced into a 250-ml. brown glass bottle, then equal volumes of water and of 0.2791 M silver nitrate were added, the latter as the solution was stirred vigorously. After stirring for two minutes, measured volumes of more concentrated sodium chloride and of potassium bromide were added and, if necessary, water to make the volume up to 225 ml. The glass stopper was put in place, sealed in with paraffin and the bottle shaken violently for a given period of time at 27 ± 1°. The bromide concentration in the centrifugate was determined by the volumetric method. For the sake of brevity, only the mole percentages of bromide in the solid, the final bromide concentration in the solution and the values of K after various periods of shaking are reported in Table II. For details about the composition of the original suspension and the analyses the reader is referred to the thesis of the junior author.[1] In all cases equilibrium was established within twenty-four hours of shaking. It should be noted that a small error in the determination of the final bromide concentration has a relatively large effect upon the value of K. This is especially true when the final bromide concentration is extremely small as in series IV where it was of the order of 3×10^{-6} M. At this small concentration the analytical determination is accurate

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(7) (a) H. Flood, *Z. anorg. allgem. Chem.*, **229**, 76 (1936); (b) Flood and B. Bruun, *ibid.*, **229**, 85 (1936).

(8) J. D'Ans and P. Höfer, *Z. angew. Chem.*, **47**, 73 (1934).

(9) I. M. Kolthoff and H. C. Yutzy, *Ind. Eng. Chem., Anal. Ed.*, **9**, 75 (1937).

TABLE II

VALUES OF K AT 27° AFTER VARIOUS PERIODS OF SHAKING

The following figures correspond to the amounts of silver chloride taken and the original chloride concentrations in the various suspensions, the latter having a volume of 225 ml.: I, 1 g., 0.888 *M;* II, 1 g., 0.444 *M;* III, 0.08 g., 0.884 *M;* IV, 1 g., 0.0888 *M;* V, 0.08 g., 0.0884 *M;* VI, 0.08 g., 0.884 *M*.

		I			II			III	
Time of shaking	Bromide concn. in solution, $M \times 10^4$	Mole fraction of AgBr in solid	K	Bromide concn. in solution, $M \times 10^4$	Mole fraction of AgBr in solid	K	Bromide concn. in solution, $M \times 10^4$	Mole fraction of AgBr in solid	K^a
0	22.2	0	...	22.4	0	...	22.1	0	...
1 hour	2.83	0.0622	201	1.98	0.0652	156	15.1	0.286	234
3 hrs.	2.41	.0638	252	1.48	.0667	215			
6 hrs.	2.33	.0642	261						
12 hrs.	2.53	.0635	238						
21 hrs.	2.46	.0636	246	1.24	.0675	260	14.2	.322	296
63 hrs.	2.49	.0635	243	1.30	.0673	247	14.1	.326	308
1 week	2.46	.0638	246	1.28	.0674	252	13.8	.338	327
1 month	2.56	.0634	235				13.8	.338	327
Equilibrium value		.0635	235	1.28	.0674	252		.338	327
		IV			V			VI	
0	2.22	0	...	2.21	0		2.35	0	
1 hour	0.0253	0.00709	250						
3 hrs.	.0228	.00709	287	0.413	0.0725	168	1.66	0.0288	158
6 hrs.									
12 hrs.									
21 hrs.	.0211	.00709	300	.319	.0765	230	1.46	.0371	234
63 hrs.							1.46	.0371	234
1 week	.0257	.00709	246	.301	.0777	245	1.48	.0362	224
1 month	.0311	.00707	204	.308	.0768	239			
Equilibrium value		.00707	204		.0768	239		.0362	224

[a] In Series III and VI the solubility of the small amount of precipitate in the strong sodium chloride solution has been considered. Estimated from the data of Forbes and Cole[10] the solubility of silver chloride in 0.88 M sodium chloride is about 7×10^{-5} M. Application of a corresponding correction resulted in a change in K of only 3 to 4%. The solubility of the mixed crystals is smaller than that of silver chloride; since the above calculation yielded only a small correction for K it was not necessary to consider the solubility of the mixed crystals instead of that of silver chloride.

to only 10%. With a final bromide concentration of 2×10^{-6} M the method is accurate to 1%. Series I was repeated in the presence of nitric acid, the concentration of the acid in the suspension being 0.04 M, the same as used by Küster. The time–distribution curve of the bromide was practically identical with that in series IV, the final mole fraction of silver bromide in the solid being 0.00707 and K equal to 227.

Series I was repeated but instead of starting with a fresh precipitate of pure silver chloride the silver nitrate was added to a mixture of 25 ml. 0.2791 M sodium chloride, 50 ml. of 0.01 M potassium bromide and 25 ml. of water. After precipitation the conditions were made identical with those of series I. The time–distribution curve became practically identical with that of Series I after twenty-four hours; the final mole fraction of silver bromide in the solid being 0.0635 and K equal to 240. Series IV was also repeated in this way—precipitating together the mixture of chloride and bromide. Again, the time–distribution curve was practically identical with that of Series IV, the final mole fraction of silver bromide in the solid being 0.00707 and the final bromide concentration in the solution 2.8×10^{-6} M and K equal to 227. From these experiments it is evident that in all cases a true state of equilibrium was reached as the same final values were found, whether the original solid phase was pure silver chloride or a mixed crystal containing virtually all the bromide in the system.

The results of the determination of K at higher mole fractions of silver bromide are reported in Table III. In all cases 25 ml. of 0.2791 M silver nitrate corresponding to 1 g. of silver chloride was used as precipitating agent. After mixing of the reagents and making up to the indicated volume with water, the suspensions were shaken for one week at 27 ± 1°, centrifuged and the supernatant solutions analyzed for bromide. Equilibrium was approached from two sides, starting either with fresh silver bromide (a) or silver chloride (b). In all cases, except in the last sets in which the final mole fraction of bromide was very large (0.925), the true state of equilibrium was practically reached after a week of shaking.

With the high mole fraction of bromide in the precipitate true equilibrium was not reached after a month of shaking, although it seems to have been approached closely after one week when starting with silver bromide. In the latter case inhomogeneous mixed crystals too rich in chloride are formed during the early stages of aging as a result of recrystallization. Upon further aging these inhomogeneous crystals recrystallize faster than those formed in the reverse precipitation which soon become too rich in bromide and have a smaller solubility than the mixed crys-

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(10) G. S. Forbes and H. I. Cole, THIS JOURNAL, 43, 2492 (1921).

TABLE III

VALUES OF K AT HIGHER MOLE FRACTIONS OF AgBr ($27 \pm 1°$)

Order of pptn.	Total halide in system		Total volume, ml.	Final amt. of bromide in solution, mm.	Mole fraction of AgBr in solid	K	Average of K
	Cl^-, mm.	Br^-, mm.					
a	50	3.5	230	0.1265	0.483	343	343
b	50	3.5	230	.1265	.483	343	
a	50	3.5	100	.121	.484	359	364
b	50	3.5	100	.118	.484	369	
a	20	5.5	230	.1373	.768	443	426
b	20	5.5	230	.1475	.767	410	
a	20	5.5	100	.135	.771	456	441
b	20	5.5	100	.143	.770	426	
a	6.5	6.5	230	.1293	.913	476	476
b	6.5	6.5	230	(.1197)	(.914)	(524)[d]	
a[c]	2.0	6.5	100	.0402	.925	457	457
a[c]	2.0	6.5	100	.0389	.923	473	473
b	2.0	6.5	100	(.0208)	(.925)	(675)[d]	
b[c]	2.0	6.5	100	(.0292)	(.925)	(647)[d]	

[a] Silver nitrate added to the bromide, then chloride added. [b] Silver nitrate added to the chloride, then bromide added. [c] Shaken for one month instead of one week. [d] Not at equilibrium.

tals containing more chloride. Moreover, freshly precipitated silver bromide has a larger surface than a similar precipitate of silver chloride, the larger surface of the former favoring more rapid recrystallization. It may be noticed that in the last four cases reported in Table III the mole fractions of silver bromide in the solid are practically the same. Thus the same value of K would have been found in these four cases, if the analyses had been made according to the indirect method of Küster;[3] evidently the amount of bromide left in the solution is a much more sensitive indicator of the state of equilibrium. In order to ascertain that equilibrium had been reached in most of the experiments previously reported, a series of experiments was run by precipitating the bromide first and performing the shaking for one week in a medium 1 M in ammonia. The latter is a fair solvent for silver halides and hence should promote recrystallization. In the final analyses the amount of dissolved silver was determined by precipitation and weighing as silver iodide and was taken into account in the calculation of the composition of the solid. For the sake of brevity the details[1] are not reported separately, but the results are included in Table IV, the latter giving a summary of all the data found. From the good agreement it may be concluded that the figures reported in Table III and obtained by the method of precipitation "a" (Tables II, III and IV) correspond to the state of true equilibrium and that ammonium does not affect the value of K.

TABLE IV

EQUILIBRIUM VALUES OF K AT $27 \pm 1°$

Mole fr. of AgBr	0.00707	0.0362	0.0635	0.0674	0.0768
K	204	224	235	252	239
Mole fr. of AgBr	0.102	0.338	0.483	0.697	0.768
K	257[x]	327	354	395[x]	426
Mole fr. of AgBr	0.770	0.913	0.917	0.925	0.923
K	441	476[y]	466[x]	457[y]	473[y,z]

[x] In 1 M ammonia. [y] Silver bromide precipitated first, one week of shaking. [z] One month of shaking.

In Fig. 1 the values of K are plotted against the mole fraction of silver bromide in the solid. Within the experimental error K is found to increase linearly with the mole fraction N_{AgBr} of silver bromide in the solid. The values of K calculated from Küster's data at 19° have also been plotted in a similar way.

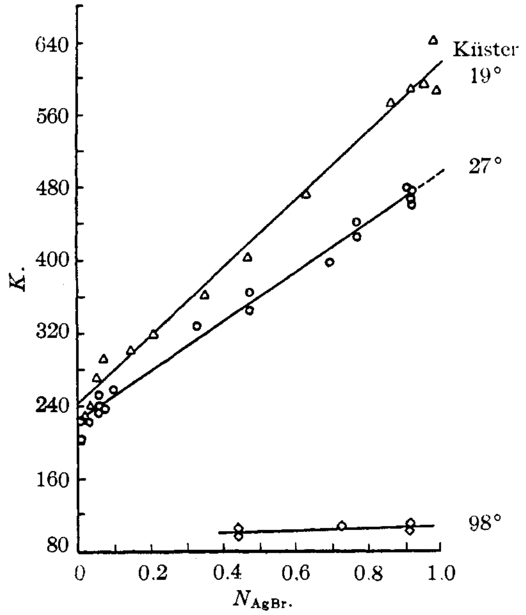

Fig. 1.—Value of K as function of N_{AgBr} at 19 (Küster), 27 and 98°.

The Value of K at 98°.—The experiments were carried out in a similar way to that reported in Table III. Immediately after precipitation and making up to volume, the bottles were heated in a water-bath to 100° (five to ten minutes), stoppered with collodion coated corks and placed in a rotator in an oven held at $98 \pm 2°$ for a week. Then the bottles were cooled, centrifuged and samples taken for analysis for bromide. The results are given in Table V and also plotted in Fig. 1.

TABLE V

EQUILIBRIUM VALUES OF K AT $98 \pm 2°$. TOTAL VOLUME, 100 ML.

Order of pptn.	Total halide in system		Final amt. of bromide in soln. in millimoles	Mole fraction of AgBr in solid	K	$K_{av.}$
	Cl^-, mm.	Br^-, mm.				
a	50	3.5	0.382	0.447	98	100
b	50	3.5	.367	.448	103	
a	20	5.5	.447	.724	106	106
b	20	5.5	(.397)	(.730)	(124)	
a	2.0	6.5	.139	.913	102	106
b	2.0	6.5	.132	.914	110	

[a] Silver nitrate added to bromide, then chloride added.
[b] Silver nitrate added to chloride, then bromide added.

Evidently, practically the same values were obtained independent of the manner of precipitation, indicating that distribution equilibrium had been obtained in all cases. At mole fractions of silver bromide between 0.45 and 0.91 a constant value of K of 104 ± 4 was found within the experimental error.

TABLE VI

COMPARISON OF K WITH RATIO OF SOLUBILITY PRODUCTS AND SOLUBILITIES OF SILVER CHLORIDE AND BROMIDE

Medium	t, °C.	S. P. AgCl	S. P. AgBr	sol. $\frac{\text{AgCl}}{\text{AgBr}}$	$\frac{\text{S. P. AgCl}}{\text{S. P. AgBr}}$	K	N_{AgBr}
Water	25	1.70×10^{-10}(12,13)	6.4×10^{-13}(12)	16.3	265	374[a]	0.5
						265[a]	.15
Water	100	2.10×10^{-8}(14)	3.25×10^{-10}	8	65	104	.45–0.9
Ethanol	25	1.16×10^{-14}(15)	1.06×10^{-16}				
		0.92×10^{-14}(16)	0.76×10^{-16}	10.8	116	110	.069

[a] Estimated from our data at 27°.

Experiments in Ethanol at 27 ± 2°.—A few experiments were made in absolute ethanol instead of in water as a liquid medium. Silver chloride was precipitated from aqueous medium at 27°, washed with water and then with absolute ethanol. After air had been drawn through to remove most of the adhering liquor the precipitate was divided among several bottles containing 210 ml. of a solution in absolute ethanol, 0.00237 M in sodium bromide and 0.466 M in lithium chloride. The bottles were shaken for various periods of time at 27° and centrifuged. The bromide was determined in the solution and silver in the precipitate. The values of K calculated from the results after various periods of shaking were 27.9 after two hours, 64.4 after a day and 109.5 after nine weeks. The mole fraction of silver bromide in the precipitate after nine weeks was 0.069.

Discussion

1. From the results reported in Table II it is seen that upon shaking of freshly precipitated silver chloride with an aqueous solution containing chloride and bromide a maximum is found in the amount of bromide in the precipitate after a certain period. During the early stages of aging, heterogeneous mixed crystals too rich in bromide are formed which eventually become homogeneous after repeated recrystallizations upon subsequent shaking. Qualitatively, the phenomenon is comparable to the heterogeneous distribution of thorium B through lead sulfate during the early stages of aging of the latter,[11] although in the latter case no maximum was found.

2. If silver chloride and bromide would form an ideal system of solid solutions it is easily derived (compare Flood and Bruun[7]) that under equilibrium conditions

$$\left(\frac{a\ \text{Cl}^-}{a\ \text{Br}^-}\right)_{\text{solution}} \left(\frac{N\ \text{Br}^-}{N\ \text{Cl}^-}\right)_{\text{solid}} = \frac{\text{S. P. AgCl}}{\text{S. P. AgBr}} = K'$$

(compare eq. 1 and 2)

In this equation mole fractions have been written instead of activities in the solid state, whereas S. P. denotes the solubility (activity) product. Actually it is seen from Fig. 1 that at 19 and 27° K increases with increasing mole fraction of bromide in the solid, the slope of the line being less at 27° than at 19°. It appears that the system approaches an ideal one with increasing temperature and it seems to behave as such at 98°.

In Table VI are given the ratios of the solubilities and of the solubility products of silver chloride and bromide in water at 25 and 100° and in ethanol at 25°. In water at 100° and in ethanol at 25° ($N_{\text{AgBr}} = 0.069$) the agreement between K and the ratio of the solubility products is within the experimental error. In water at 27° K is a linear function of the mole fraction of silver bromide in the solid, the value of K found being equal to the ratio of the solubility products at $N_{\text{AgBr}} = 0.15$.

3. Although according to Hildebrand's[17] own statement it is doubtful whether the system silver chloride–bromide can be considered as a "regular solution,"[18] this concept was applied by Flood and Bruun[7] to this particular case. On this basis it was inferred by the latter authors that log K should be a linear function of N_{AgBr}. They plotted log K *versus* $(2N_{\text{AgBr}} - 1)$ for Küster's data and actually found the relation $\log K = 0.19\,(2N_{\text{AgBr}} - 1)$ to hold within the experimental error. Our own data at 27° give a slope of 0.17, although our experimental data fit better the simple relation $K = K_0 + aN$, as plotted in Fig. 1.

Using the equations given by Hildebrand[18] (pp. 69, 70) in describing a regular solution, we may calculate the slope, approximately, in the following way. According to Hildebrand

$$RT \ln a_2/N_2 = bN_1^2 = RT \ln \gamma_2 \qquad (3)$$

$$\overline{H}_1 = bN_2^2;\ \overline{H}_2 = bN_1^2 \qquad (4)$$

in which γ is the activity coefficient, $\overline{H}$ partial

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[11] I. M. Kolthoff and Chas. Rosenblum, THIS JOURNAL, **58**, 116 (1936).

[12] A. S. Brown and D. A. McInnes, *ibid.*, **57**, 459 (1935); W. R. Carmody, *ibid.*, **54**, 188 (1932); E. Neumann, *ibid.*, **54**, 2195 (1932); S. Popoff and E. Neumann, *J. Phys. Chem.*, **34**, 1853 (1930).

[13] A. Thiel, *Z. anorg. allgem. Chem.*, **24**, 57 (1900); K. Hess and K. Jellinek, *Z. physik. Chem.*, **A162**, 153 (1932).

[14] W. Böttger, *ibid.*, **56**, 83 (1906).

[15] A. McFarlane and H. Hartley, *Phil. Mag.*, **13**, 425 (1932).

[16] F. K. V. Koch, *J. Chem. Soc.*, 1551 (1930).

[17] J. H. Hildebrand, "Solubility of Non-electrolytes," A. C. S. Monograph, Second Edition, Reinhold Publishing Corporation, 1936, p. 66.

[18] J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

molal heat of mixing, b a constant, N the mole fraction in the mixed crystal.

From the above relations and the conventional between partial molal quantities it is found that

$$b = H/N_1N_2 \qquad (5)$$

in which H is the heat of mixing per mole.

From equation (2) in the present paper it is found that

$$\log K = \log K' + \log (f_{\text{Cl}}/f_{\text{Br}})_{\text{crystal}} \qquad (6)$$

From Hildebrand's expressions it follows that

$$RT \ln f_{\text{Cl}} = bN^2_{\text{Br}}$$
$$RT \ln f_{\text{Br}} = bN^2_{\text{Cl}}$$

and

$$\log_{10} \left(\frac{f_{\text{Cl}}}{f_{\text{Br}}}\right) = \frac{0.4343b}{RT} (2N_{\text{Br}} - 1) \qquad (7)$$

Combination of equations (6) and (7) leads to

$$\log K = \log K' + \frac{0.434b}{RT} (2N_{\text{Br}} - 1) \qquad (8)$$

Hence, if log K is plotted as a function of $(2N_{\text{AgBr}} - 1)$, the slope of the line should be

$$\frac{0.4343b}{RT} = \frac{0.4343}{RT} \frac{H}{N_1N_2}$$

Eastman and Milner[6] give the change in heat content in the formation of one mole of a mixed crystal, in which $N_{\text{AgBr}} = 0.728$ and $N_{\text{AgCl}} = 0.272$ as 81 ± 10 calories.

Taking this as the heat of mixing the calculated slope is

$$\frac{0.4343}{1.99 \times 298} \times \frac{81}{0.728 \times .272} = 0.30 \pm 0.04$$

The calculated value deviates from the experimentally found slope (0.19 Küster, 18°; 0.17 Yutzy and Kolthoff, 27°) by more than the estimated error. Thus the consideration of the solid phase as a "regular solution" seems questionable.

Summary

1. The distribution coefficient K of bromide between solution and mixed crystals of silver chloride and bromide has been determined at 27 and 98° in aqueous medium and at one mole fraction of silver bromide in ethanol at 27°.

2. At 27° K changes as a linear function of the mole fraction of silver bromide in the solid. Evidence has been given that the mixed crystals cannot be considered as "regular solutions." At 98° the value of K becomes practically independent of N_{AgBr}, and the solid approaches the behavior of an ideal solution.

3. The value of K is approximately equal to the ratio of the solubility products as pointed out by Flood and Bruun[7] and not to the ratio of the solubilities of the components.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 1, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity of Silver Nitrite from 15 to 300°K. The Heat of Solution at 298°K. of Silver Nitrite, Barium Nitrate and Thallous Nitrate. The Entropy of Silver Nitrite, Thallous Ion, Nitrate Ion and Nitrite Ion

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The determination of the entropy of silver nitrite enables a calculation to be made of the entropies of both nitrate and nitrite ions. The entropy of nitrate ion can also be obtained by three other independent methods, making use of existing data on sodium nitrate, potassium nitrate and barium nitrate, combined with a value of the heat of solution obtained in this investigation. In the present paper we shall also present two methods of calculating the entropy of thallous ion.

Material.—The silver nitrite was a C. P. sample prepared in this Laboratory. It was recrystallized from distilled water and the product dried in a vacuum desiccator for several days. The final product was analyzed for nitrite by titration with permanganate solution, and for silver by thermal decomposition. Calcd. Ag, 70.10; nitrite, 29.90. Found: Ag, 69.89, 69.95, 69.90, 69.96; nitrite, 29.79, 29.74. The barium nitrate was a Mallinckrodt reagent grade sample, which was dried and used without further purification. The thallous nitrate was the same as that used by Latimer and Ahlberg.[1]

Heat Capacity Measurements.—The experimental method followed the general procedure described by Latimer and Greensfelder.[2] Specific

[1] Latimer and Ahlberg, THIS JOURNAL, **54**, 1900 (1932).

[2] Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).