

The accuracy of the calculation of the fugacities is dependent primarily upon the determination of the slopes of the curves of Δ against N . These slopes in turn are dependent upon the magnitudes of Δ . With such small magnitudes of Δ as were found (the maximum $\Delta = 4.6$) it is estimated that the probability of a greater error than 1.5% is very slight. Independent calculations by both authors differed in most instances by less than 0.3% and in only two instances approached a difference of 1.5%.

Summary

The fugacities and free energies of hydrogen and nitrogen in their mixtures have been calculated from the experimental results of Bartlett. Maximum deviation from the Lewis and Randall assumption of a perfect solution does not exceed about 20% with pressures up to 1000 atmospheres.

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

THE SOLUBILITY OF LEAD BROMIDE IN AQUEOUS SALT SOLUTIONS AND THE CALCULATION OF THE ACTIVITY COEFFICIENT FROM SOLUBILITY MEASUREMENTS¹

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Lewis and Randall² found that the activity coefficient of lead bromide was about the same as that of cadmium bromide, and was less than that of barium chloride, potassium sulfate and similar salts. Lead bromide must not, therefore, be considered a typically strong electrolyte. It is moderately soluble and its solubility can be accurately measured. A determination of the solubility of this salt in the presence of several strong and moderately strong electrolytes was undertaken, with the hope that the deviations of the activity coefficients from those predicted by the principle of the ionic strength would be large, and that we might thus find a further experimental basis for prediction as to the behavior of mixtures of electrolytes.

Solubility of Lead Bromide in Aqueous Salt Solutions at 25°

Lead bromide was prepared from dilute solutions of recrystallized lead nitrate and sodium bromide by metathesis. The salt was purified by recrystallization and was

¹ Presented at the Joint Session of California Section of the American Chemical Society and the Pacific Division of the American Association for the Advancement of Science at Stanford University, California, June 26, 1924. Referred to by Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

² Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 424.

considered pure when successive determinations of the solubility gave constant values. The added salts were ordinary chemically pure materials purified by recrystallization. The solvent solutions were made up by weight. All compositions are expressed as moles per 1000 g. of water, vacuum corrections being employed. So-called conductivity water was used.

Sufficient lead bromide, so that about 25 g. of the solid phase would remain after equilibrium was established, was placed in a long-necked flask (250-cc. Pyrex distilling flask body) and washed several times with water or the solution to be used as a solvent. About 200 cc. of the solvent solution was then added and the flask sealed by drawing off the neck near its end. Equilibrium was approached from undersaturation and supersaturation in each case.

The flasks were fastened to a rotating shaft (about 30 r.p.m.) suspended in a water thermostat maintained at $25 \pm 0.01^\circ$. With the neck of the flask at an angle, the solid filled the neck at one phase of the rotation and was replaced by the residual air at another. Lead bromide is slowly soluble in the higher concentrations of added salt and the method of shaking here described proved to be quite efficient.

After the period of rotation shown in Col. 3 of Table I, the flask was removed from the rotator and placed in a rack in the thermostat. The tip of the flask was then broken and the solution filtered by blowing it out at the rate of about 5 cc. per minute through a tube whose lower end was submerged in the solution and was lightly plugged with absorbent cotton, the first 25 cc. being discarded. Weighed portions were then taken for analysis.

For the determination of bromide a slight excess of a known silver nitrate solution was added (weight buret); the solution was heated to coagulate the silver bromide, allowed to cool and acidified with a small amount of nitric acid. The slight excess of silver was estimated by volumetric titration (Volhard) with a very dilute solution of potassium thiocyanate.

Lead was determined as lead peroxide. Bromide was removed as bromine by successive evaporations with nitric acid, the nitrates were dissolved in water and the solution acidified by the addition of 10 cc. of nitric acid (sp. gr., 1.42) per 100 cc. of solution. This solution was electrolyzed (four to eight hours) at 6 volts between a platinum disk cathode and a 300cc. platinum dish as anode. In order to secure an adherent deposit, the surface of the dish was sand-blasted. The deposit was washed free of soluble salts *in situ* before opening the circuit, then with water and three successive portions of absolute alcohol. The deposit was dried at $180\text{--}200^\circ$ in an electric oven for two hours, cooled and weighed. The resulting peroxide varied from a rich brown-red to black, the color varying according to the thickness of the deposit.

The composition of the solid phase in equilibrium with the solutions was determined by direct analysis for lead and bromine as above. Weighed moist samples were taken, dried to constant weight at 110° and then analyzed. Corrections were made for the amount of solution in contact with the solid phase and the composition was calculated for dry solid phase.

The solubility of lead bromide in water, as determined directly by evaporation of the solution, was 0.02674 mole per 1000 g. of water; as calculated from the bromide by comparison with silver solution, 0.02683; and as calculated from the lead weighed as lead peroxide, 0.02684 mole per 1000 g. of water.

The molality of the added salt is shown in the first column of Table I. The second column shows the molality of the lead bromide in the ordinary sense, that is, as calculated from the molality of the ion not present as a constituent of the solvent solution, the third the time of rotation, the

fourth the logarithm of the mean molality of the lead and bromide ions and the last the square root of the ionic strength.

TABLE I

SOLUBILITY OF LEAD BROMIDE IN AQUEOUS SALT SOLUTIONS AT 25°									
Added salt, moles per 1000 g. of H ₂ O	Soly., moles per 1000 g. of H ₂ O	Time of rotation, days	Log (1/m _±)	μ ^{1/2}	Added salt, moles per 1000 g. of H ₂ O	Soly., moles per 1000 g. of H ₂ O	Time of rotation, days	Log (1/m _±)	μ ^{1/2}
None	0.02680	4-10	1.3723	0.282					
In lead nitrate, Pb(NO ₃) ₂					In barium nitrate, Ba(NO ₃) ₂				
0.0020	0.02664	4	1.3634	0.293	0.002	0.02737	4	1.3664	0.297
.0050	.02644	4	1.3520	.307	.005	.02808	4	1.3509	.315
.0100	.02622	4	1.3340	.330	.01	.02883	4	1.3395	.341
.0200	.02612	4	1.3001	.372	.02	.03034	4	1.3173	.389
.0500	.02663	4	1.2202	.479	.05000	.03370	8	1.2717	.501
.1000	.02954	4	1.1169	.624	.09045	.03691	14	1.2322	.618
.1326	.03159	14	1.0612	.692	.1000	.03780	12	1.2219	.693
.2000	.03544	12	0.9757	.841	.2000	.04385	12	1.1574	.855
.3134	.04333	14	.8573	1.035	.2105	.04428	14	1.1532	.874
.5000	.05342	14	.7332	1.288	.3513	.05008	14	1.0997	1.097
.703	.06522	14	.6279	1.519	.4116 ^c	.05337	14	1.0720	1.222
.9521	.07754	14	.5354	1.737					
1.6547	.1268	21	.3138	2.310					
1.964 ^a	.1346	14	.2727	2.510					
In cadmium bromide, CdBr ₂					In potassium bromide, KBr				
0.0010	0.02637	4	1.3674	0.286	0.001	0.02645	4	1.3714	0.283
.0020	.02591	4	1.3643	.289	.002	.02611	4	1.3718	.283
.0050	.02466	4	1.3539	.298	.0050	.02500	4	1.3734	.283
.0100	.02307	4	1.3321	.315	.0100	.02345	4	1.3732	.283
.0200	.01999	4	1.2977	.346	.0200	.02043	4	1.3737	.285
.0500	.01450	14	1.2059	.440	.0500	.01380	4	1.3594	.303
.1000	.01117	14	1.0860	.577	.1000	.00859	4	1.3097	.347
.1305	.01038	14	1.0281	.650	.2000	.00694	12	1.1661	.470
.2000	.00939	14	0.9280	.793	.3740	.00687	14	0.9955	.628
.3236	.00969	14	.7890	1.000	.3887 ^d	.00700	14		
.5000	.01072	14	.6505	1.238	.5902 ^d	.00707	14		
.5607	.01143	21	.6083	1.310	.8041 ^d	.00740	14		
1.000	.01597	12	.3939	1.745	1.200 ^d	.01137	14		
1.692	.02445	21	.1803	2.270					
4.182 ^b	.06508	21	.2170	3.570					

^a Solid phase, PbBr₂ and Pb(NO₃)₂.

^b Solid phase, PbBr₂ and CdBr₂·4H₂O.

^c Solid phase, PbBr₂ and Ba(NO₃)₂.

^d Solid phase, KBr·2PbBr₂.

The solubility of lead bromide has also been determined by Von Ende³ and by Herz and Hellebrandt,⁴ who expressed their results in moles per liter

³ Von Ende, *Z. anorg. Chem.*, **26**, 129 (1901).

⁴ Herz and Hellebrandt, *Z. anorg. allgem. Chem.*, **130**, 188 (1923).

at 25°. Their results are summarized in Table II, in which the first column gives the concentration of the added salt, the second the solubility in the ordinary sense in moles per liter, the third the logarithm of the mean concentration and the fourth the square root of the ionic strength in concentration units.

TABLE II

SOLUBILITY OF LEAD BROMIDE IN AQUEOUS SALT SOLUTIONS AT 25°				SOLUBILITY OF LEAD BROMIDE IN AQUEOUS SALT SOLUTIONS AT 25°							
Added salt, Soly., moles per liter, <i>c</i>		moles per liter		Log 1/ <i>c</i> ±	μ _s ^{1/2}	Added salt, Soly., moles per liter, <i>c</i>		moles per liter		Log 1/ <i>c</i> ±	μ _s ^{1/2}
In nitric acid, HNO ₃ (Von Ende ³)				In barium bromide, BaBr ₂ (Herz and Hellebrandt ⁴)							
None	0.02628	1.3797	0.281	0.225	0.00607	0.9624	0.832				
0.001	.02659	1.3746	.283	.455	.01091	.6745	1.182				
.01	.02735	1.3624	.304	.91	.04443	.2639	1.692				
.05 ^a	.03025	1.3199	.375	1.38	.1604	-0.0609	2.150				
.051	.03004	1.3216	.376	1.835	.4140	-0.3077	2.597				
In calcium bromide, CaBr ₂ (Herz and Hellebrandt ⁴)				In sodium bromide, NaBr (Herz and Hellebrandt ⁴)							
None	0.02625	1.3803	0.281	0.73	0.00860	0.7727	0.869				
0.26	.00667	0.9073	.893	1.47	.02247	.4292	1.240				
.52	.01205	.6217	1.255	2.20	.07043	.1375	1.553				
1.04	.0438	.2289	1.803	2.93	.1958	-0.1115	1.875				
1.565	.1175	-0.0411	2.246	3.67	.3936	-0.2977	2.202				
2.085	.5187	-0.3827	2.795	4.40	.7337	-0.4675	2.569				
In strontium bromide, SrBr ₂ (Herz and Hellebrandt ⁴)											
0.26	0.00673	0.9060	0.883								
.52	.01273	.6134	1.264								
1.04	.04367	.2294	1.798								
1.56	.1559	-0.0880	2.269								
2.08	.5687	-0.4010	2.819								

^a 0.01 *N* HNO₃ + 0.04 *N* KNO₃.

Herz and Hellebrandt⁴ also determined the solubility of lead bromide in calcium, strontium, barium, potassium and sodium chlorides, but the solid phase probably contained lead chloride. In their determinations in potassium bromide, the solid phase was probably a complex, in which case we cannot determine the concentration of the various constituents in the solution. The values of Table II are shown as the upper curves in Fig. 3.

Calculation of the Activity Coefficient from Solubility Measurements

The effective molality of a salt such as lead bromide in a mixture of electrolytes is determined by the mean molality of its ions rather than by the molality of either the lead ion or of the bromide ion. If the dissolved salt is in equilibrium with a solid salt, its activity is fixed and hence the mean activity coefficient is proportional to the reciprocal of the mean molality

of the ion.⁵ The ratio, therefore, of the reciprocal of the mean molality to the extrapolated reciprocal of the mean molality at zero concentration (proportionality factor of Lewis and Randall) gives the activity coefficient of the salt in the mixture.

Methods for Determining the Proportionality Factor.—Lewis and Randall⁶ plotted the reciprocal of the mean molality, $1/m_{\pm}$ against the z^{th} root⁷ of the ionic strength. The plots were found to give approximately straight lines, and by graphical extrapolation of the curves so obtained to zero ionic strength the value of the proportionality factor was directly found. These results did not differ greatly from those obtained by the methods we will describe.

In a second method, they obtained the ratio of the reciprocal of the mean molality of the unknown salt to known activity coefficients of salts of similar types at corresponding values of the ionic strength. These ratios were plotted against a function of the ionic strength and the limiting value of the ratio at zero ionic strength was taken as the proportionality factor.

The proportionality referred to above may be expressed in the form

$$\log \gamma + \text{const.} = \log (1/m_{\pm}) \quad (1)$$

We have plotted in Fig. 1 the logarithm of the mean molality of thallos chloride⁸ against the square root of the ionic strength, for various molalities of added salt. We also give, in Fig. 2, the final average curves for the

⁵ See ref. 2, Chap. 28. For the convenience of those who desire to follow the discussions of other authors, we give the notation now being used by several authors. (a) Lewis and Randall, ref. 2; (b) Brönsted, *THIS JOURNAL*, **42**, 761 (1920); (c) Noyes, *ibid.*, **46**, 1080, 1098 (1924); (d) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

NOTATION OF VARIOUS AUTHORS

	L. and R.	B.	N.	D. and H.
Activity of solvent	a_1
Activity of solute	a_2, a_3, \dots	ξc
Activity of ions	a_+, a_-, a_{\pm}	ξ_1, ξ_2
Activity coefficient	$\gamma_+, \gamma_-, \gamma$	f_1, f_2, f	α_A, α_B	f_1, f_2, f_1
Moles per 1000 g. H ₂ O	m	...	c	γ'
Moles per liter	c	m	c	γ
Equiv. per liter	...	c
Valency	z_+, z_-	z_1, z_2	ν_A, ν_B	z_1, z_2, z_i
Ions per molecule	ν, ν_+, ν_-		z_A, z_B	ν_1, ν_2, ν_i

The symbol f was proposed and has always been used for the fugacity, which is an intensive quantity. The activity coefficient is a number without dimensions, and the symbol γ is preferred in accord with the custom of using α , β and γ for quantities without dimensions.

⁶ Lewis and Randall, *THIS JOURNAL*, **43**, 1112 (1921); ref. 2.

⁷ $z_+ + z_- = z$, the sum of the valencies of the two ions formed by the dissociation; e. g., $z = 2$ for TlCl ; $z = 3$ for PbBr_2 and $z = 4$ for CaSO_4 . Lewis and Randall (unpublished) also plotted $\log (1/m_{\pm})$ against the z^{th} root of the ionic strength.

⁸ See Randall and Chang, *THIS JOURNAL*, **50**, 1535 (1928). The full data of other authors will be published in another place.

logarithm of the activity coefficient of typical strong electrolytes as taken from an unpublished summary of all data. In plotting Fig. 2, $1/2 \log \gamma$ was taken for uni-bivalent salts, $1/3 \log \gamma$ for uni-trivalent salts, $1/4 \log \gamma$ for bi-bivalent salts, $1/6 \log \gamma$ for bi-trivalent salts and $1/9 \log \gamma$ for tri-trivalent salts, etc. In this way the curves of the salts of the various ionic types superimpose. This is also in accordance with the theoretical implications of the Debye and Hückel theory.⁹

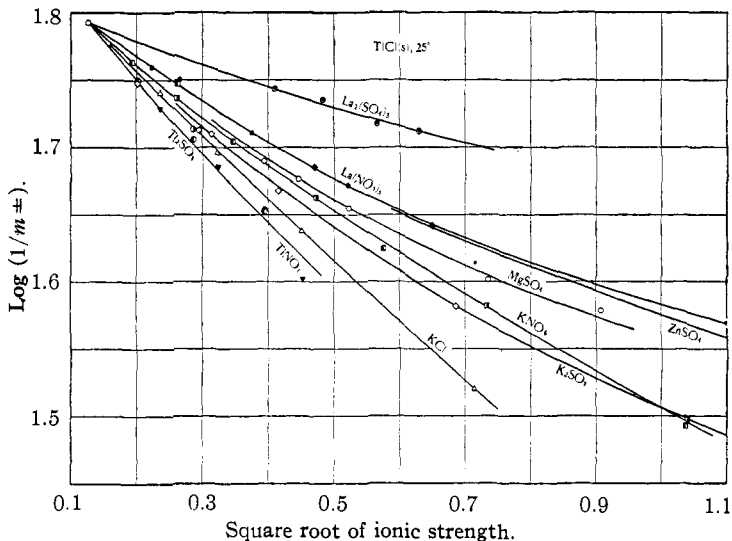


Fig. 1.—Solubility of thallos chloride in aqueous salt solutions at 25°.

If the added salt has the same characteristics as the saturating salt, that is, the same constants in a theoretical or empirical equation, or the same activity coefficient, then the curves of Fig. 1 would continue through the point of zero added salt, in the region of undersaturated solutions without a departure, but if the added salt has different characteristics, then there will be a more or less sharp departure. If Figs. 1 and 2 are made on transparent paper, using the same scale, then we may superimpose the plots, and if, as in the case of thallos chloride, the curve of $\log \gamma$ of thallos nitrate¹⁰ superimposes on the curve of this same salt added to thallos

⁹ See "The Theory of Strong Electrolytes, A Discussion," *Trans. Faraday Soc.*, 23, 333-542 (1927).

¹⁰ No actual measurements of the curve for thallos nitrate are available. (a) Lewis, *THIS JOURNAL*, 34, 1631 (1912), combined conductivity and transference data and showed that thallos and silver nitrates had smaller activity coefficients than potassium nitrate. (b) Onsager, *Physik. Z.*, 28, 277 (1927), in his treatment of conductivity data, considers thallos nitrate to be an "associated" electrolyte. His functions stand in the same order as the activity coefficients of the salts. His curves show thallos chloride to be slightly lower than the nitrate.

chloride, we may confidently expect it to have about the same characteristics as thallos chloride and then choose the log proportionality factor as the intersection of the log γ curve on the axis of the log $(1/m_{\pm})$ curve. Thus we find log p.f. = 1.8630 ± 0.002 for thallos chloride. In some cases the curve of log $(1/m_{\pm})$ will not superimpose upon any of the standard curves, but the curve may be between two of these curves. We then make such an estimate as will be most likely.

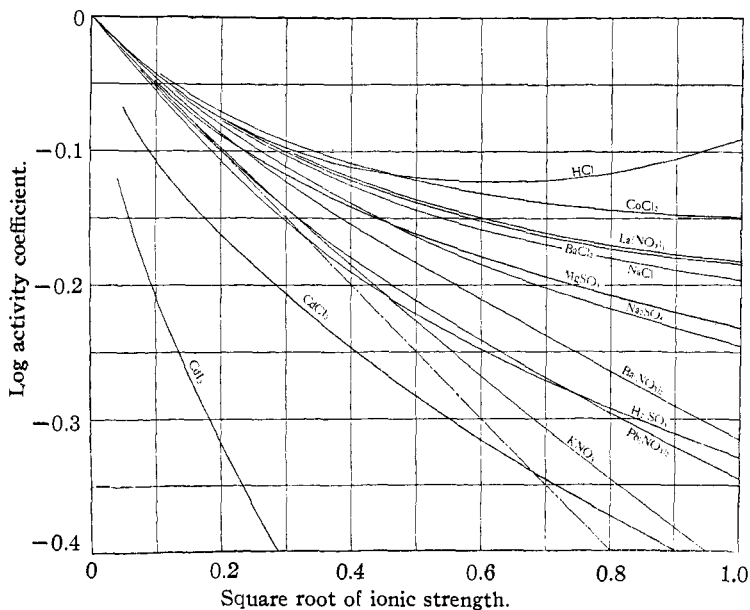


Fig. 2.—Activity coefficient of aqueous solutions of electrolytes.

In a number of cases concentrations have been expressed in moles per liter. In these cases we can convert the ionic strengths of the reference salts to ionic strengths in concentration units, γ_c . The activity of an ion is the same whether moles per liter or molality is used. If, therefore, we divide the activity by the concentration instead of by the molality, we obtain an activity coefficient in concentration units, γ_c , such that $a_{\pm} = (m\gamma_{\pm})^{\nu} = (c\gamma_{c\pm})^{\nu}$. Reference plots of log γ_c against μ_c can be obtained by multiplying the values of log γ by m/c for the temperature in question. For infinite dilution, therefore, log $\gamma_c = 0.0013$ at 25° and 0.0051 at 50° , if we are to retain our definition¹¹ that $a_{\pm} = m_{\pm}$ at infinite dilution.¹¹ The difference between log γ and log γ_c will, in general, be

¹¹ Debye and Hückel (ref. 5 d) have tacitly assumed the standard state so that the activity of an ion is equal to its concentration at infinite dilution. Thus their unit activity is equal to $1/c$ times the activity at a small concentration c , so small that $a_{\pm}' \approx c$. Their activity coefficient is, therefore, the number by which we multiply the concentration to find the activity referred to their tacitly assumed standard state. Because

come larger at greater concentrations. The value of $\log p.f.$ is obviously the same as when molalities are used, since the activity of the solid salt is constant and defined with reference to activities which become equal to molalities in infinitely dilute solutions.

Brönsted and LaMer¹² have plotted $\log S/S^\circ$ against the square root of the ionic strength where S° is the solubility in pure water and S the solubility in the salt solution when no common ion is present. They then extrapolated to zero concentration and determined $\log \gamma$ by a method which is somewhat similar to the method here suggested.

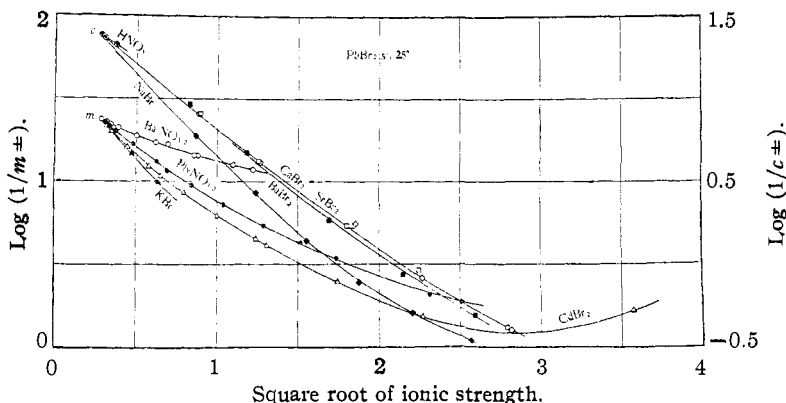


Fig. 3.—Solubility of lead bromide in aqueous salt solutions at 25°.

We show the values of $1/2 \log (1/m_{\pm})$ for lead bromide, taken from Table I, in Fig. 3 plotted against $\mu^{1/2}$. We have attempted to estimate the activity coefficient by superimposition of a portion of the data of Table I, drawn on the same scale as Fig. 2, upon that figure. The data for the activity coefficients of cadmium chloride, bromide and iodide are conflicting, and the curves drawn in Fig. 2 for these substances are provisional. We have been unable to apply the methods suggested above to the data for lead chloride, bromide or iodide and to obtain activity coefficients which would be consistent with the measured potentials of the halide electrodes and the measured free energies of the lead halides.

We have examined in the above manner all the available data for the the composition of their standard state varies with the temperature, that is, the number of moles of water in a liter changes with the temperature, it is not possible to use exact thermodynamic equations which are true only for constant composition. The difference in the free energy of an ion in the two standard states is given by the equation

$$\text{Ion } (a' = 1, \text{ Debye and Hückel}) = \text{Ion } (a=1, \text{ Lewis and Randall}); \\ \Delta F_{298}^{\circ} = 1364.9 \times \log 0.0013 = -1.7 \text{ cal.}; \quad \Delta F_{223}^{\circ} = -7.5 \text{ cal.} \quad (2)$$

It is obviously most important in any tabulation of activities or of activity coefficients to so define the quantities that they will refer, as we have done, to a single standard state whether the experimental results are given in molalities or in concentrations.

¹² Brönsted and LaMer, THIS JOURNAL, 46, 555 (1924).

solubility of slightly soluble salts in the presence of electrolytes. The method of treatment here suggested seems to be justified if the saturating salt is not associated in the Bjerrum¹³ sense, if the association is not large or if the solubility is very small. The application of the method to the data for thallos chloride represents perhaps the limit of the possibilities and, with salts such as lead iodide, erroneous results can easily be obtained.

An interesting phenomenon is observed in the case of the lowering of the solubility of lead bromide by small additions of potassium bromide. The effect of the common ion in lowering the solubility (in the old fashioned sense) is so great that the total ionic strength of the solution is actually slightly lowered and the value of $\log (1/m_{\pm})$ is slightly increased. Such a phenomenon is general when a uni-univalent salt is added to a uni-bivalent salt or a uni-trivalent salt, etc., with the common univalent ion. The phenomenon will also be observed when a salt with a bivalent ion is added to a saturating salt in which the common bivalent ion is combined with an ion of higher valence than in the added salt. In such cases the value of $\log (1/m_{\pm})$ at the ionic strength of the solution containing added salt, which is the same as the ionic strength of the pure saturated solution, need not be the same as the value of $\log (1/m_{\pm})$ of the pure saturated solution.

Summary

The solubility of lead bromide in aqueous salt solutions has been determined at 25°.

A refined technique for such determinations is described.

The determination of the activity coefficient by graphical treatment of solubility data is discussed. Specific applications of a convenient graphical method are made in the case of thallos chloride and lead bromide.

The solubility method, while satisfactory when the saturating salt is "non-associated," or when the solubility is very small, may lead to considerable errors with fairly soluble "associated" substances such as lead bromide.

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¹³ Bjerrum, *Det. Kgl. Danske Videnskab Math.-fys. Medd.*, 7, No. 9 (1926).