and H. J. Rothe[16] and G. Neumann[17] have disclaimed, appears to be impossible through evaporation of neutral solutions.

C. **Acknowedgment.**—I wish to thank the Carnegie–Fisk Foundation for the support of this investigation.

NASHVILLE, TENNESSEE

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[16] H. Remy and H. J. Rothe, *J. prakt. Chem.*, [2] **114**, 144 (1926).

[17] G. Neumann, *Ann.*, **244**, 336 (1888).

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

Thermodynamics of Coprecipitation: Dilute Solid Solutions of AgBr in AgCl[1]

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The importance of the thermodynamic properties of dilute AgBr–AgCl solid solutions to the coprecipitation of small amounts of bromide ion by AgCl was evaluated by accurately measuring the "carrying" of 35.9 h Br^{82} activity. From the magnitude and temperature variation of the equilibrium distribution coefficient ($D = X_{AgBr}m_{Cl^-}/m_{Br^-}$) the *excess* free energy, entropy and enthalpy of solid solution formation in the Henry's law region ($X_{AgBr} = 10^{-4}$ to 10^{-2}) at 30° were found to be 287 cal. mole^{-1}, -1.4 e.u. and -139 cal. mole^{-1}, respectively. The observed enthalpy agreed with an estimate computed from Born–Mayer crystal lattice theory. The negative, excess entropy was attributed to a lowering of the vibrational randomness of a bromide ion when placed in a nearly pure AgCl lattice. Measurements on other systems revealed that interaction in the solid solution may sometimes be decisive in determining the "carrying-down" of traces by precipitates.

The process of coprecipitation whereby a substance soluble by itself is coseparated with an insoluble precipitate has been of general importance to radiochemical analysis, to the isolation of substances initially present in very low concentrations, such as radium and other radioactive species useful as tracers, and to conventional gravimetric analysis. The principles involved in most cases appear to be partly understood,[2a,b,3] although the difficulty of obtaining equilibrium, or reproducible and ideal conditions with non-equilibrium (*i.e.*, heterogeneous) type coprecipitations, has frequently prevented a demonstration of their applicability. When true equilibrium is established, the distribution of a microcomponent between crystals and a saturated solution is governed by the law of Berthelot–Nernst, provided the composition of both phases remains constant. A more general, exact quantitative description based on thermodynamic considerations may be applied, and it has been the object of our research to demonstrate this by accurate measurements of the "carrying down" of small quantities of bromide ion by silver chloride precipitates. From measurements of distribution coefficients and their temperature variations it was possible to estimate partial molar free energies, entropies and enthalpies of interaction for a bromide ion present at high dilution in a silver chloride crystal. These thermodynamic quantities are then interpreted on the basis of an "atomistic" picture which emphasizes the importance of structure in solid solutions for coprecipitation phenomena.

Theory

The distribution of an ion between a homogeneous solid solution and its equilibrium saturated aqueous solution may be regarded formally as an exchange reaction for which a mass law constant may be written (*viz.*, for the coprecipitation of bromide ion with insoluble silver chloride)

$$AgCl + Br^- \rightleftarrows AgBr + Cl^-$$

and

$$K_a = (AgBr)(Cl^-)/(AgCl)(Br^-) \qquad (1)$$

where the parenthesized quantities denote thermodynamic activities, a. The relations of these activities to the compositions of the solid and fluid phases will be defined by the Gibbs chemical potentials. Compositions of the aqueous solutions will be given in molalities, m, and the reference state will be taken as the infinitely dilute solution (*i.e.*, pure solvent). Binary solid solution compositions will be expressed in mole fractions, X, and pure, crystalline silver chloride and bromide each will be taken as standard states. Choosing AgBr as solute (2) and AgCl as solvent (1) and denoting the fluid phase by primes, the chemical potential, $\bar{F}_2'$, of AgBr in an aqueous solution *in equilibrium with the solid solution* is

$$\bar{F}_2' = \bar{F}_2^{0\prime}(\text{T,P}) + RT \ln a' \qquad (2)$$

and its potential in the solid solution will be

$$\bar{F}_2 = \bar{F}_2\,(\text{T,P}) + RT \ln X_2 f_2 \qquad (3)$$

where f_2 is the activity coefficient.

Imposing the Gibbs equilibrium condition: $\bar{F}_2 = \bar{F}_2'$ leads to

$$\ln\,(X_2 f_2/a_2') = -(\bar{F}_2^0 - \bar{F}_2^{0\prime})/RT \qquad (4)$$

Similarly, for component (1)

$$\ln\,[(1 - X_2)f_1/a_1'] = -(\bar{F}_1^0 - \bar{F}_1^{0\prime})/RT \qquad (5)$$

Combining equations (4) and (5)

$$\ln[(X_2 f_2)a_1'/(1 - X_2)f_1 a_2'] = -[(\bar{F}_2^0 - \bar{F}_2^{0\prime}) - (\bar{F}_1^0 - \bar{F}_1^{0\prime})]/RT \qquad (6)$$

The right hand member of equation (6) may be simplified by the expressions for the chemical potentials of the pure components in equilibrium with their own saturated solutions, respectively

$$\bar{F}_{20}' = \bar{F}_2^{0\prime}(\text{T,P}) + RT \ln a_{20}' = \bar{F}_{20} \equiv \bar{F}_2^0 \qquad (7a)$$

and

$$\bar{F}_{10}' = \bar{F}_1^{0\prime}(\text{T,P}) + RT \ln a'_0 = \bar{F}_{10} \equiv \bar{F}_1^0 \qquad (7b)$$

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[1] Presented before Division of Physical and Inorganic Chemistry, 115th Meeting, American Chemical Society, March 27–April 1, 1949, San Francisco, California.

[2] (a) V. G. Khlopin, *Trav. Inst. Etat Radium, U.R.S.S.*, **4**, 34 (1938); (b) O. Hahn, "Applied Radiochemistry," Cornell Univ. Press, Ithaca, N. Y., 1933.

[3] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, Ch. VIII.

so that

$$(X_2f_2)a'_1/(1 - X_2)f_1a'_2 = a'_{10}/a'_{20} \equiv K_0 \qquad (8)$$

where the quantities a'_{20} and a'_{10} signify the thermodynamic activity (solubility) products for pure AgBr and AgCl, respectively. For sufficiently dilute solid solutions, $X_2 \ll 1$ and $f_1 \equiv 1$

$$(X_2f_2)a'_1/a'_2 = K_0 \qquad (9)$$

According to equation (3)

$$f_2 = \exp\{[\bar{F}_2 - \bar{F}_2(\text{ideal})]/RT\} \qquad (10)$$

hence

$$X_2a'_1/a'_2 = K_0 \exp(-\Delta\bar{F}_2/RT) \qquad (11)$$

where $\Delta\bar{F}_2$, the excess free energy, is the partial molar free energy change involved in transferring one mole of bromide ion from a large quantity of ideal solid solution to the real solid solution of the same mole fraction. The magnitude of $\Delta\bar{F}_2$ will be a measure of the deviation of the actual equilibrium solid solution from ideality. Equation (11) may be written, after replacing ionic activities by molality—mean ionic activity coefficient products and dropping primes, by Equation (12) which also serves to define the experimentally observed distribution coefficient, D

$$D \equiv (X_{\text{AgBr}}m_{\text{Cl}^-}/m_{\text{Br}^-}) = K_0(\gamma_{\pm\text{MBr}}/\gamma_{\pm\text{MCl}})^2 \exp(-\Delta\bar{F}_{\text{AgBr}}/RT) \qquad (12)$$

Evidently, the coprecipitation of small amounts of bromide ion, initially present in aqueous solutions, by a silver chloride precipitate is determined by the product of: (a) a constant intrinsic factor, K_0, given by the solubility (activity) product ratio of AgCl to AgBr; (b) a "solution interaction" factor given by the ratio of the thermodynamic activity coefficients of the 1–1 electrolytes *MBr and MCl in the mixed aqueous solution in equilibrium with the solid solution;* and (c) the thermodynamic properties of the AgBr–AgCl solid solution. All of the quantities appearing in equation (12) may be determined independently by experiment. The exponential factor may be evaluated by combining measurements of D, K_0 and $(\gamma_{\pm\text{MCl}}/\gamma_{\pm\text{MBr}})^2$, or by means of heat of solution and heat capacity (entropy) determinations. An example of the latter is afforded by the work of Eastman and Milner[4] who have reported an *integral* free energy of formation of 81 cal./mole for a AgBr–AgCl solid solution where $X_{\text{AgBr}} = 0.728$. Calorimetric measurements become quite inaccurate, however, when the mole fraction of AgBr is small.

Several investigators[5–8] have attempted to evaluate the exponential factor for alkali halide solid solutions using the Born crystal lattice theory. Generally,[5,6,8] the entropy of mixing has been assumed to be given by the usual statistical formula (*i.e.*, "regular" solutions assumed). Theoretical calculations for the AgBr–AgCl solid solution have not been published. The X-ray diffraction measurements of Wilsey[9] show, however, that there is complete miscibility at room temperature, and that Vegard's law is obeyed, suggesting that this solid solution does not depart strongly from ideality.

A thermodynamic discussion of the coprecipitation of naturally occurring radioactive isotopes by insoluble "carriers" has also been given by Ratner.[10] In this treatment the standard state for the macrocomponent was taken as its own pure crystal, while the infinitely dilute solid solution was taken as the reference state for the microcomponent. This choice gives $\Delta\bar{F}_2$ as the work of transfer of the microcomponent from its own crystal to the infinitely dilute solid solution. The advantages of the type of choice we have made have been enumerated by Hildebrand.[11]

Ratner has given a discussion of the role of the aqueous solution in determining coprecipitation of traces upon which we can scarcely improve; however, he was unable to evaluate the importance of the thermodynamic properties of the solid phase. Later, necessary solubility product, thermodynamic activity coefficient and distribution coefficient data were obtained for the coprecipitation of Ra^{++} and Pb^{++} ions by $Ba(IO_3)_2$.[12,13] Unfortunately, the experimental difficulties and inaccuracies in this work were such that even in the best case it was not possible to determine whether or not $\Delta\bar{F}$ was temperature dependent.

Experimental

In view of the inaccuracies and uncertainties in the theoretical calculation of enthalpies and free energies of solid solution formation, it was decided to evaluate $\Delta\bar{F}_{\text{AgBr}}$ by means of equation (12). Since the AgBr–AgCl solid solution appeared to be nearly ideal,[9] small excess partial molar free energies were expected. Accordingly, to estimate $\Delta\bar{F}_{\text{AgBr}}$ reliably accurate values of D, K_0 and $(\gamma_{\pm\text{MCl}}/\gamma_{\pm\text{MBr}})$ were needed. Fortunately, accurate, self-consistent activity product determinations for both pure AgCl and AgBr had been performed over a range of temperatures[14] so that K_0 was considered known to within ±0.2%. Further, activity coefficient data for mixed aqueous HCl–HBr solutions were available[15] which indicated that the ratio $(\gamma_{\pm\text{HCl}}/\gamma_{\pm\text{HBr}})$ could be estimated to within ±1%. Application of the theory of the propagation of precision indexes to equation (12) shows then that D must be measured with a probable error of less than 1% to know $\Delta\bar{F}_{\text{AgBr}}$ to within ± 1%. Further, the temperature must be held constant to better than ±0.3°.

Previous measurements of the coprecipitation of bromide with silver chloride[16–18] employed conventional methods for the analysis of the solid solution, and, when the ratio of chloride to bromide was very large, the bromide determinations were accurate to only 10% at best. To achieve good accuracy in this work, the well-known, gamma-ray emitting, 35.9 h Br^{82} radioisotope was used as an analytical tool. This tracer, which may be obtained in high specific activity by a Szilard–Chalmers' enrichment,[19] was prepared as follows: Purified $KBrO_3$, irradiated in the Oak Ridge pile

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

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[7] W. E. Wallace, *ibid.*, **17**, 1095 (1949).

[8] G. S. Durham and J. A. Hawkins, *ibid.*, **19**, 149 (1951).

[9] R. B. Wilsey, *J. Franklin Inst.*, **200**, 739 (1935).

[10] A. P. Ratner, *J. Chem. Phys.*, **1**, 789 (1933).

[11] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, pp. 12–13.

[12] A. Polessitsky and A. Karataewa, *Acta Physicochim.* (*U.R.S.S.*), **8**, 259 (1938).

[13] A. Polessitsky, *ibid.*, **8**, 864 (1938).

[14] B. B. Owen and S. R. Brinkley, THIS JOURNAL, **60**, 2233 (1938).

[15] B. B. Owen, *ibid.*, **59**, 2277 (1937).

[16] F. W. Kuster, *Z. anorg. Chem.*, **19**, 81 (1899).

[17] H. F. Yutzy and I. M. Kolthoff, THIS JOURNAL, **59**, 916 (1937).

[18] H. Flood, *Kg. Norske Videnskab Selskabs. Skrifter*, **2**, 23 (1941).

[19] G. E. Boyd, J. W. Cobble and Sol Wexler, THIS JOURNAL, **74**, 237 (1952).

for two hours and allowed to "cool" for one day, was dissolved in distilled water (*ca.* 1 g. of $KBrO_3$/20 ml.), acidified with concentrated HNO_3 and the solution extracted immediately with purified CCl_4. The phase separation was performed after not more than one minute of shaking to minimize the loss of active bromine by exchange with bromate in the acid aqueous layer. The organic layer was washed twice with water, after which the Br^{82} was extracted into an aqueous sulfurous acid solution. Aliquots from this solution were employed in the distribution measurements after boiling to remove SO_2. The radiochemical purity of the preparations was established by γ-ray decay measurements, as well as by conventional aluminum and lead absorption curves.

Reagent grade hydrochloric acid was further purified by double distillation from $KMnO_4$, rejecting the first and last quarters of the distillate.[20] Merck and Co., Inc., reagent grade $AgNO_3$ was used without further purification. Silver perchlorate was prepared by adding a slight excess of concentrated $HClO_4$ to a concentrated aqueous solution of $AgNO_3$, heating until perchloric acid fumes were given off, and then cooling and filtering. The $AgClO_4$ was dried and freed of excess $HClO_4$ by heating to 150° in a vacuum.

The procedure for the distribution measurements was to put 4 *N* HCl solution, double distilled water and 5 to 20 ml. of radiobromine solution containing 3–10 γ total bromine per ml. into a three-necked, round-bottom 500-ml. reaction flask made of low actinic Pyrex glass (Corning 7740). Efficient mixing was obtained using a motor driven glass propeller which passed into the flask through a close fitting ground-glass bearing (Ace Trubore stirrer 8242). The flask was submerged in a 50-liter water thermostat held constant to within $\pm 0.03°$ of the desired temperature. After one hour of stirring, 10 cc. of air-free $AgNO_3$ solution (1.183 g. of $AgNO_3$/ml.), previously brought to the same temperature, was rapidly emptied into the reaction vessel to give a final mixture of approximately 200 ml. of one molar HCl solution plus one gram of solid AgCl. At temperatures of 50° and above consistent results could not be obtained unless air was very carefully excluded, and $AgClO_4$ instead of $AgNO_3$ was used. A stream of purified nitrogen, freed of oxygen by copper turnings at 700°, was passed through the flask during the following operations: The liquid contents were boiled for about two minutes before thermostating the flask. The precipitating silver salt solution was also boiled, brought to temperature under nitrogen, and then rapidly introduced into the reaction vessel through the nitrogen inlet. Next, a rapid stream of gas was passed to flush out any air introduced during the precipitation step. Finally, the gas outlet was closed and the contents were stirred under about one cm. pressure of nitrogen for about one day, after which analyses for radiobromine in the precipitate and supernatant liquid were made. Ten-ml. aliquots of the latter were drawn out in pipets calibrated to deliver at the temperature of the experiment. The reaction flask was then emptied, the precipitate caught on a sintered glass filter, washed with water, and dried for two hours in air at 130°. Three approximately 100-mg. aliquots of the dried precipitate were accurately weighed into 30-ml. test-tubes for a comparison of their radiobromine content with that of aliquots of the supernatant similarly contained.

Accurate radioactivity assays were made using a 4π geometry ionization chamber of 20-liters volume filled with 40 atmospheres of argon.[21] The ion currents produced were amplified by means of a dynamic condenser electrometer whose output was fed into a continuous recording Brown electronic potentiometer which indicated the instantaneous values of the activity. The walls of the sample thimble were sufficiently thick that only γ-radiations were detected. Because of its great stability, linearity in response and wide range, this ionization chamber–electrometer arrangement was well-suited for exact work using radioactive tracers. The sequence of radioactivity determinations was: background, one measurement of each of the three liquid samples, one or two measurements of each of the three precipitate samples, repeat liquid samples and back-ground. Since the supernatant liquid and precipitate aliquots occupied differing volumes, a *ca.* 0.3% geometry correction was applied.

The statistical error in the radioactivity assay was evaluated by numerous measurements on standard one and ten microgram radium sources procured from the National Bureau of Standards. An error of about 0.3% was estimated for the measurement of the *ratio* of radiobromine in the precipitates to that in the equilibrium solutions. The statistical error was, of course, somewhat smaller for the average value from several independent experiments.

The supernatant was next subjected to a chloride analysis: 4-ml. aliquots, taken in a calibrated pipet, were diluted with 20 ml. of water containing 2 ml. of 1 *M* K_2CrO_4. The acid was neutralized and then chloride was titrated with standardized silver nitrate solution.

The analysis for bromine in the initial HCl, or in the tracer solution, was made by a method in which free bromine is made to react with fluorescein to give eosin.[22] The optical transmissions of the resultant solutions were measured with a Beckman model DU spectrophotometer, and these compared with standards prepared by adding known amounts of bromine to pure HCl solutions. The tracer solutions were analyzed by comparison with standards made up from doubly distilled water.

Numerical values for the distribution coefficients, *D* (*cf.* eqn. (12)) of bromide were computed from the experimentally determined radioactivities and concentrations by

$$D = \frac{(\mathrm{Br^{82}\ activity/g.\ solid})(\mathrm{mmoles\ Cl^-/ml.\ liquid})}{(\mathrm{Br^{82}\ activity/ml.\ liquid})(\mathrm{mmoles\ Cl^-/g.\ solid})}$$

Experimental Results

The distribution coefficient was found independent of the mole fraction of AgBr in AgCl in the range between 10^{-2} and 10^{-4} indicating that the dilute solid solution obeyed Henry's law. Below a mole fraction of 10^{-4} down to 10^{-5} a decrease of about 2% in *D* was observed for which as yet no entirely satisfactory explanation has been found. Accordingly, the data summarized in Table I are for the Henry's law region of the solid solution, and serve to indicate the precision achieved, among other things.

The distribution experiments were subject to a number of possible errors, the most serious being the uncertainty that equilibrium had been reached, particularly at 30° and below. The lower precision of the value at 30° (Table I) is attributed to this cause. Oxidation and loss of bromine from solution was an ever present possible source of error at the highest temperatures, or when extremely low bromide concentrations were employed. Since these types of complication were particularly difficult to detect, reliable values seemed assured only when a relatively large number of experiments were made at each temperature.

Activity (solubility) product ratio values, K_0, for the various temperatures (Table I) were computed from an equation obtained on combining the relations for the activity products for AgCl and and AgBr given by Owen and Brinkley[14]

$$\log K_0 = \log \frac{K_a(\mathrm{AgCl})}{K_a(\mathrm{AgBr})} = 203.6/T - 11.6716 + 0.043244T - 5.0131 \times 10^{-5}\ T^2$$

This equation is strictly valid only from 5 to 45°. It has been used, however, up to 60°.

Mean ionic activity coefficient ratios for the mixed HBr–HCl solution (Column 6, Table I) were computed taking the activity coefficient for HCl as that of its own pure one molal solution at

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(20) E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, 1932, p. 322.

(21) C. J. Borkowski, *Anal. Chem.*, **21**, 348 (1949).

(22) F. D. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 370.

TABLE I

EXPERIMENTAL DISTRIBUTION COEFFICIENTS, D, FOR THE COPRECIPITATION OF MICRO-QUANTITIES OF BROMIDE BY SILVER CHLORIDE PRECIPITATES FORMED IN 1.0 M HYDROCHLORIC ACID SOLUTIONS AT VARIOUS TEMPERATURES

Temp., °C.	Range of D values	Average D^a	Average deviation, %	K_0	$(\gamma_{\pm HBr}/\gamma_{\pm HCl})^2$	$\exp(-\Delta\bar{F}_{AgBr}/RT)$	$\Delta\bar{F}_{AgBr}$, cal. mole^{-1}
30	208.0–215.0	211.4 (12)	1.10	315.7	1.078	0.622	287
35	185.8–187.8	187.3 (6)	0.48	280.1	1.081	.618	295
40	166.8–167.8	167.8 (6)	.24	249.5	1.089	.618	299
45	149.8–150.6	150.7 (7)	.19	223.5	1.095	.615	309
50	136.1–137.1	137.4 (9)	.22	201.2	1.103	.615	312
55	122.1–122.7	123.0 (3)	.19	182.8	1.110	.605	328
60	112.0–113.1	113.1 (6)	.53	169.4	1.116	.610	329

[a] Number of independent experiments averaged given in parentheses.

the desired temperature[23] while values for HBr were computed from the equation[15]

$$\log \gamma_{HBr(HCl)} = \log \gamma_{HBr} - (1 - X)m\alpha_{HBr(HCl)}$$

where the mean ionic activity coefficient, $\gamma_{HBr(HCl)}$, for HBr in an HCl solution is related to the coefficient, γ_{HBr}, for a pure HBr solution at the same total molality, m, to the fraction, X, of mixed electrolyte that is HBr (here $X = 0$), and to the parameter, $\alpha_{HBr(HCl)}$. The temperature variation of the latter from 0 to 45° for $m = 0.5$ was[15]

$$\alpha_{HBr(HCl)} = 0.0180 - 0.62 \times 10^{-4}\ T$$

A value of $\alpha_{HBr(HCl)}$ at 25° only for $m = 1.0$ was reported. However, Owen and Cooke have stated that this parameter may be considered constant between $m = 0.5$ and 1.0, and that this approximate equality probably is maintained over a considerable temperature range. We have employed their equations up to 60°.

Derived values for the excess free energy, $\Delta\bar{F}_{AgBr}$, are given in the last column of Table I. It was possible to fit the temperature variation of this quantity to an equation of the form

$$\Delta\bar{F}_{AgBr} = -139 + 1.41T$$

with an average deviation of 0.6%. The excess partial molar entropy, $\Delta\bar{S}_{AgBr}$, and enthalpy, $\Delta\bar{H}_{AgBr}$, for the transfer of a bromide ion from an ideal to the actual equilibrium solid solution of the same mole fraction (*i.e.*, 10^{-2} to 10^{-4}) are then -1.41 cal. mole^{-1} deg.$^{-1}$ and -139 cal. mole^{-1}, respectively. The distribution coefficient measurements were not sufficiently accurate to give the variation of the entropy and enthalpy with temperature so that the foregoing are average values.

Discussion

Several general statements may be made about Table I. The efficiency of the coprecipitation of small amounts of bromide by AgCl falls off markedly with increasing temperature, an observation in harmony with the findings of others[17,18] for mole fractions above 0.1. The magnitude of the distribution coefficient and its temperature variations are determined largely by the magnitude and temperature coefficient, respectively, of the intrinsic factor, K_0, or, less exactly, of the solubility ratio. It is manifest that the equilibrium coprecipitation of small amounts of bromide ion by silver chloride will be considerably lowered at temperatures approaching 100°. The solid solution factor acts to lower the coprecipitation by about 40% from that expected if an ideal mixture had been formed. The observation that the solid solution obeyed Henry's law in the mole fraction range examined would indicate that the bromide ions were separated on the average by distances exceeding the range of their coulomb forces. Assuming the bromide ions to be located at random, this distance would be 16 Å., or about five lattice spacings. In the Henry's law region the solid solution deviated in a positive sense from Raoult's law, for the transfer of a mole of bromide ion from an ideal to the real solid solution at the same mole fraction occurred with a partial molal free energy increase. This positive, excess free energy is a consequence of a negative excess entropy which more than counterbalances the lowering of the total energy (*i.e.*, $\Delta\bar{H} \backsimeq \Delta\bar{E}$) in the transfer of a bromide ion. Clearly, the dilute solid solution is neither ideal, ($\Delta\bar{F}_{AgBr} = 0$), nor is it "regular" ($\Delta\bar{S}_{AgBr} = 0$) as has been claimed[18] for $X_{AgBr} > 0.17$.

The observed negative entropy may be given a qualitative interpretation. The substitution of a larger bromide ($r_{Br^-} = 1.951$ Å.) for a smaller chloride ($r_{Cl^-} = 1.806$ Å.) ion in an essentially pure AgCl lattice should increase the forces acting on the former (relative to the ideal solid solution) with a consequent raising of its vibrational frequency and energy levels. This reduction in vibrational randomness will be accompanied by a lowering of the *entropy*. Conversely, a *vibrational entropy* increase should occur on the substitution of a smaller for a larger spherically symmetric ion. Excess entropies may arise from other sources, as in the replacement of non-spherical ions where orientational effects and/or changes in internal degrees of freedom may occur. An *excess mixing entropy* is to be expected when lattice vacancies are involved, or when the replacing particle may take up more than one position in the solvent lattice. For example, in the solid solution formed by $PbCl_2$ in AgCl an ordering of the vacant lattice sites created should be reflected in the excess entropy. Vacancy effects may be responsible for the anomaly observed in this work when $X_{AgBr} < 10^{-4}$, for near room temperatures the mole fraction of "holes" may approach 10^{-5}. Further experimental work in this region will be of greatest interest.

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(23) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 547.

The enthalpy (or energy) change to be expected in the transfer of a mole of bromide ion from an ideal to a real solution in AgCl will depend upon the variations in each of the different types of lattice energy involved. Substitution of a larger for a smaller spherically symmetric ion causes a large energy increase owing to the strong dependence of the repulsive potential on ionic radius, while the large, slowly varying coulombic energy dominates in the substitution of a smaller ion. In addition, with the AgBr–AgCl solid solution, lattice energy calculations (Table II) show that increases in the van der Waals–London potential (dipole–dipole and quadrupole–dipole = 0.47×10^{-2} erg molecule^{-1}) are important and determine the sign of the excess energy, for these exceed the sum of the increases (0.40×10^{-12} erg molecule^{-1}) in the repulsive and coulombic potentials. Even though the absolute magnitudes of the theoretical lattice energy values are subject to error, the energy of imperfect solution (given by the differences between the totals for columns 2 and 3, Table II) may be estimated to a fair approximation. Thus, $\Delta\bar{E}$ for the solution of very small amounts of AgBr in AgCl was computed as -0.039×10^{-12} erg/molecule, or -560 cal./mole. Although this theoretical energy is about four times too large, it is of the same sign as, and, when the uncertainties are considered, agrees with the experimental value of -139 cal./mole as well as might be expected. A more refined calculation, such as that for alkali halide solid solutions,[8] should give improved agreement.

TABLE II

THEORETICAL ENERGIES OF IMPERFECT SOLUTION ($\times 10^{12}$ ERGS/MOLECULE) AT 0°K.[a]

Type of interaction	AgBr in AgCl	AgBr	AgCl in AgBr	AgCl
Coulomb	−14.372	−13.814	−13.81	−14.39
Dipole–dipole	− 2.042	− 1.681	− 1.38	− 1.69
Quadrupole–dipole	− 0.407	− 0.302	− 0.23	− 0.31
Repulsion	3.015	2.051	1.51	2.22
Zero point	0.08	0.06	0.06	0.08
Total	−13.726	−13.686	−13.85	−14.09

[a] Values computed following J. E. Mayer, *J. Chem. Phys.*, 1, 327 (1933).

TABLE III

THERMODYNAMIC SOLID SOLUTION FACTORS IN VARIOUS COPRECIPITATING SYSTEMS NEAR ROOM TEMPERATURES

Solid solution	T, °C.	$D_{\text{obsd.}}$	K_0	$\Delta\bar{F}_2$, cal./mole	$\Delta\bar{H}_2$, cal./mole	$\Delta\bar{S}_2$, cal./mole/deg.
AgBr in AgCl[a]	30	211.4	315.7	+287	−139	−1.41
AgCl in AgBr[a]	30	0.0036	0.0031	−70	(+350)	(+1.41)
AgCl in TlCl[a]	40	4.2	7.2×10^5	*ca.* +7500	.....	......
$Pb(IO_3)_2$ in $Ba(IO_3)_2$[b]	25	25	3.2×10^3	+2800	....	......
$Ra(IO_3)_2$ in $Ba(IO_3)_2$[c]	25	1.42	1.32	−39 (?)	.....	......
$RaSO_4$ in $BaSO_4$[d]	20	1.8	5.9	+700	.....	......

[a] This work. [b] Ref. 13. [c] Ref. 12. [d] Ref. 2b, p. 88.

While the deviation of the AgBr–AgCl solid solutions from ideality was not a primary factor in determining coprecipitation, this may not always be the case (*cf.* Table III).[24] The incorporation of Ag^+ by TlCl and Pb^{++} by $Ba(IO_3)_2$ afford examples where interaction in the solid solution is decisive. Here, despite extremely favorable solubility ratios, the distribution coefficients are relatively small because of large, positive excess free energies of solid solution. It seems likely that both the sign and magnitude of the free energy are determined by a large positive excess enthalpy (or energy), although the positive excess entropy from substituting a smaller for a large ion will also contribute. This increase in potential energy of a Ag^+ or Pb^{++} ion in the solid solution over that in its own pure crystal arises from the *increase* in the sum of the electrostatic and van der Waals energies which is larger than the decrease in repulsion.

The coprecipitation of radium by insoluble barium salts involves the substitution of a larger Ra^{++} (r = 1.52 Å.) for a smaller Ba^{++} ion (r = 1.43 Å.). Again, as with the silver halides, the change in the van der Waals energy is crucial, although the lowering is not sufficient to overcome the increased repulsion, so that zero or positive excess free energies result from the combination of a negative excess entropy and a positive excess enthalpy. The van der Waals energy might be expected to be larger for insoluble iodates than for sulfates; hence, the gain on substituting radium for barium in $Ba(IO_3)_2$ will be larger than in $BaSO_4$. This seems to be supported by experiment (Table III) which showed that the excess free energy of solid solution for the former, although uncertain because of experimental difficulties, was probably near zero, while a value of + 700 cal./mole was observed for the latter.

In conclusion it may be said that, thermodynamically, there are no inherent conditions of isomorphism, similarity of lattice parameters, bond types, etc., necessary for coprecipitation. An important requirement for a good "carrier," in addition to a favorable solubility ratio (K_0), is that the excess free energy of solid solution formation be small or negative; this is most frequently met in the classical criteria of similarity in ionic size and lattice character.

OAK RIDGE, TENN.

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[24] Details on the preliminary measurements on dilute solid solutions of AgCl in AgBr and in TlCl may be found in the doctoral thesis of the junior author (F. V.) (University of Chicago, September, 1948).