Summary

The lead–uranium ratio of a uraninite from Lac Pied des Monts, Quebec, was determined as 0.135. The analytical results show 6.67% lead, 49.25% uranium, and a trace of thorium.

An isotopic determination on the lead obtained from this analysis was made by A. O. Nier at Harvard University. With these results available, the age of the Lac Pied des Monts uraninite can now be given with greater assurance and accuracy. Corrections for common lead made from Nier's determination change the percentage to 6.40 and the lead–uranium ratio to 0.130. The age of the mineral, calculated with these corrected figures, is 920 million years and compares favorably with the results calculated from the isotopic determination of the lead from this sample.

Two independent age determinations made by entirely different methods on the same specimen yield results in fairly good agreement.

LAS VEGAS, N. M. RECEIVED MAY 22, 1939

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Solubility of Mercuric Halides in Solutions of Potassium Halides. The Character of the Mercuric Halide Complex Ions. Evidence for Polymerization of Mercuric Chloride

BY A. B. GARRETT

The purpose of this paper is to present measurements of the solubility of mercuric halides in halide solutions and to calculate the equilibrium constants for the reactions involved in the formation of the complex mercuric halide ions; the values of these constants should indicate the character of the complex ions of mercury in the solutions studied.

The moderately low solubility of mercuric bromide and mercuric iodide makes possible a fairly direct determination of the character of the complex ions of these mercuric halides by means of solubility measurements. Additional information essential to this determination are these facts: (1) earlier work[1–6] has shown that the mercury halides are only slightly dissociated and (2) their solubility in halide solutions is predominantly specific to the concentration of the halide ion and not to the ionic strength. These facts make it possible to attribute the solubility of mercuric halides in halide solutions mainly to several or to all of the following reactions (using the bromide as an example)[7]

$$HgBr_2(\text{solid}) = HgBr_2(\text{solution}) \qquad (1)$$

$$HgBr_2 + Br^- = HgBr_3^- \qquad (2)$$

$$HgBr_2 + 2Br^- = HgBr_4^{=} \qquad (3)$$

The data necessary are those in low concentrations where one might reliably expect the limiting law to be applicable. Only a meager amount of such data is available from early work.[1–6]

Early work is at variance with respect to definite conclusions concerning the character of these halide ions. A number of workers[3,8–10] have claimed the formation $HgCl_3^-$, $HgBr_3^-$ or HgI_3^- whereas others[11–13] submit evidence for the $HgI_4^{=}$ ion. Job[11] claims the presence of $KHgCl_3$, K_2HgBr_4 and K_2HgI_4 in their respective solutions. Sherrill[4] even gives data on the ionization constants for all of these salts, *i. e.*, $KHgI_3$, K_2HgI_4, $KHgBr_3$, K_2HgBr_4, etc. Tananaev and Pilipenko[13] assumed the near 2 to 1 ratio of added potassium iodide to mercuric iodide indicated the formation of $HgI_4^{=}$ predominantly.

Procedure.—Baker C. P. quality and Mallinckrodt Analytical Reagent mercuric bromide and mercuric iodide were used. For a number of preparations the mercuric bromide was recrystallized from hydrobromic acid solution and heated at 115° for four hours to assure complete removal of any hydrogen bromide. The same procedure was followed with the mercuric iodide but the recrystallization was omitted.

Baker Analytical Reagent potassium bromide and potassium iodide were used.

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(1) Thomas, THIS JOURNAL, **61**, 920 (1939). This paper contains a very good bibliography on the mercuric chloride–chloride system.

(2) Herz and Paul, *Z. anorg. Chem.*, **82**, 431 (1913).

(3) Abegg (with Immerwahr and Jander), *Z. Elektrochem.*, **8**, 689 (1902); (with Sherrill) **9**, 550 (1903).

(4) Sherrill, *Z. physik. Chem.*, **43**, 727 (1903).

(5) Le Blanc and Noyes, *ibid.*, **6**, 389 (1890).

(6) Richards and Archibald, *ibid.*, **40**, 385 (1902).

(7) See latter section of this paper for additional equilibria that may exist in the $HgCl_2$–Cl system.

(8) Naude, *Z. physik. Chem.*, **125**, 98 (1927).

(9) Pernot, *Compt. rend.*, **185**, 950 (1927); *Ann. chim.*, [10] **15**, 5 (1931).

(10) Dunningham, *Proc. Chem. Soc.*, **30**, 8 (1914); *J. Chem. Soc.*, **105**, 368 (1914).

(11) Job, *Ann. chim.*, **9**, 113 (1928), from light absorption studies.

(12) Golse, *Compt. rend.*, **190**, 873 (1930), from studies on the equilibrium $AgNO_3 + HgI_2 + KI$.

(13) Tananaev and Pilipenko, *J. Applied Chem.* (U. S. S. R.), **10**, 549 (1937).

All work was done in conductivity water which was boiled free of oxygen, in an atmosphere of nitrogen, and at 25 ± 0.02°. Equilibrium was approached from undersaturation (u) and supersaturation (s). An equilibrium period of three days was established by the close approach of the (u) and (s) values. The data given are averages of these two values.

The samples were analyzed by precipitating the mercury as the sulfide. The halide content was determined by preparing the samples in standard halide solutions.

The *p*H of a number of the samples was measured with a glass electrode.

The Data

The data are given in Tables I to III. All values are expressed in moles per 1000 g. of water.

The water solubility was reinvestigated for the bromide since it is a critical value in the later treatment of the data. During this investigation it was revealed that repeated, careful washing was not enough to remove the impurity of hydrobromic acid. It seems only to be removed by oven drying and heating. The comparison of the data in Table I shows the consistent results obtained by such treatment and agree with values in the literature. Samples not receiving such treatment varied from 1.84×10^{-2} to 2.01×10^{-2} mole per 1000 g. of water.

TABLE I

WATER SOLUBILITY OF MERCURIC BROMIDE

	Moles of $HgBr_2$ per 1000 g. water
Baker C. P.	0.0167^s
Analyzed heated	.0167^u
four hours	.0169^s
at 115°	.0171^u
Average	0.0168$_5$
Baker C. P. Analyzed	0.0171^s
recrystallized from hydro-	.0170^u
bromic acid solution and	.0170^s
heated four hours at 115°	.0170^u
Average	0.0170
Best value	.0170
Other workers[a]	.0170

[a] Moles and Marquina, *Anales soc. españ. fís. quím.*, **22**, 551 (1924); Sherrill, ref. 4; Jander, ref. 3.

TABLE II

Moles KBr per 1000 g. H_2O	Moles $HgBr_2$ per 1000 g. H_2O	Moles KBr per 1000 g. H_2O	Moles $HgBr_2$ per 1000 g. H_2O
0.003006	1.86×10^{-2}	0.0607	5.85×10^{-2}
.00506	2.05	.0712	6.42
.00506	2.05	.0917	7.64
.00709	2.17	.1022	8.36
.01011	2.44	.155	11.78
.01011	2.32	.319	22.3
.01512	2.63	.417	28.7
.02024	2.95	.642	43.8
.0303	3.71	.868	58.6
.405	4.28	1.006	67.3

TABLE III

Moles per KI per 1000 g. water	Moles of HgI_2 per 1000 g. water
0.00400	1.50×10^{-3}
.01011	3.87×10^{-3}
.01011	3.71×10^{-3}
.0202	8.22×10^{-3}
.0403	1.78×10^{-2}
.0705	3.15×10^{-2}
.1020	4.70×10^{-2}
.3128	1.53×10^{-1}
.539	2.72×10^{-1}
.795	4.09×10^{-1}
1.131	5.86×10^{-1}
1.161	6.10×10^{-1}
Water solubility	1.3×10^{-4} mole/kg. H_2O Morse, *Z. physik. Chem.*, **41**, 731 (1902). 1.32×10^{-4} mole/kg. H_2O Tananaev and Pilipenko, ref. 13.

Tables IV and V give smooth data taken from a large scale graph. Column 3 of these tables gives the amount of the complex ion present at a given concentration of potassium halide. The value is obtained by assuming that the amount of complex ion equals the total mercury content minus the water solubility (equation 1). Column 4 of Tables IV and V gives the concentration of halide ion in solution calculated on the assumption that

TABLE IV

M_{KBr}	$M_{mercury}$	$M_{complex}$	M_{Br^-}	$K_2 = M_{complex}/M_{Br^-}$
0.000	0.0170			
.001	.0176			
.002	.0183	0.0013	0.0007	1.85
.004	.0196	.0026	.0014	1.85
.006	.0209	.0039	.0021	1.85
.008	.0222	.0052	.0028	1.86
.01	.0235	.0065	.0035	1.86
.03	.03650	.0195	.0105	1.85
.08	.0692	.0522	.0278	1.87
.10	.0825	.0655	.0345	1.89
.3	.213	.196	.104	1.88
.8	.543	.526	.274	1.91
1.0	.672	.655	.345	1.90

TABLE V

M_{KI}	$M_{mercury}$	$M_{complex}$	M_{I^-}	$K_2 = M_{complex}/M_{I^-}$
0.00	1.32×10^{-4}			
.01	3.79×10^{-3}	3.66×10^{-3}	6.34×10^{-3}	0.577
.04	1.65×10^{-2}	1.64×10^{-2}	2.36×10^{-2}	.694
.07	3.05×10^{-2}	3.04×10^{-2}	3.96×10^{-2}	.767
.1	4.60×10^{-2}	4.59×10^{-2}	5.41×10^{-2}	.848
.2	9.60×10^{-2}	9.59×10^{-2}	1.04×10^{-1}	.922
.4	2.00×10^{-1}	2.00×10^{-1}	2.00×10^{-1}	1.00
.6	3.05×10^{-1}	3.05×10^{-1}	2.95×10^{-1}	1.03
.8	4.10×10^{-1}	4.10×10^{-1}	3.90×10^{-1}	1.05
1.0	5.16×10^{-1}	5.16×10^{-1}	4.84×10^{-1}	1.07

the solubility of the mercuric halide can be accounted for by equations (1) and (2) only. Column 5 of Tables IV and V gives the ratio Hg complex/halide ion or in other words the equilibrium constant for equation (2) calculated on the assumption that equations (1) and (2) represent the only reactions taking place. The near constancy of the value of K_2 for the bromide suggests that the $HgBr_3^-$ ion is the main ion formed with the possibility of only a very small amount of the $HgBr_4^=$ ion. However, the value of K_2 for the iodide varies considerably, thus indicating that an additional reaction probably is present, namely, that represented by equation 3.

The calculation of K_2 is made quite accurately from the relationship

$$K_2 = \frac{m_{\text{Hg complex}^-}\,\gamma_{\text{Hg complex}^-}}{m_{\text{Br}^-}\,\gamma_{\text{Br}^-}}$$

and upon the reasonable assumption that the ratio $\gamma_{\text{Hg complex}^-}/\gamma_{\text{Br}^-}$ is unity throughout this range of concentrations.

The small variation in the value of K_2 (1.85 to 1.91) for mercuric bromide from 0.002 to 1 molal hardly justifies the calculation of the value of K_3 for reaction (equation(3)). Choosing the value of 1.85 as the most reliable value for K_2 as determined from low concentration measurements the value of ΔF_{298} is -365 cal. for equation (2).[14]

The variation in the value of K_2 for the iodide and the less than 2 to 1 ratio of potassium iodide–mercuric iodide complex indicate the necessity of including equation (3), together with equations (1) and (2), to explain the solubility of mercuric iodide in iodide solutions. The method of Garrett and Howell[15] for the calculation of the dissociation constants for mercuric hydroxide gives the values $K_2 = 0.48$, $\Delta F^\circ_{298} = +430$ cal., $K_3 = 35$ $\Delta F^\circ_{298} = -2100$ cal. for the iodides. This value of K_2 is in agreement with the extrapolation of the values of K_2 given in column 5 of Table V. These values of K_2 and K_3 indicate an appreciable amount of $HgI_4^=$ in solution.

The Mercuric Chloride–Chloride System

WITH ERNEST HOGGE

The mercuric chloride–chloride ion equilibrium has been investigated by Thomas.[1]

It is not easily possible to treat the data of these chlorides exactly due to the high molalities; however, this interesting observation is evident, namely, the concentration of the complex ion stands in almost a 1:1 ratio with the concentration of added chloride ion for reasonable concentrations of hydrochloric acid (to 1 molal) and for all concentrations of other salts (see Table VI). This suggests that equation (2) is sufficient to account for the increased solubility of mercuric chloride and that the most common complex chloride ion of mercuric chloride in all probability has the formula $HgCl_3^-$. The higher ratio of $m_{\text{HgCl}_2\text{ complex}}/m_{\text{added chloride}}$ at high solute concentrations suggests the possibility of the formation of a small amount of $HgCl_4^=$, but, on the other hand, this higher ratio may also be due to changing activity coefficients, which is expected at these high concentrations. It is virtually impossible to treat quantitatively any type of solution at such high concentrations; however, it may be concluded that the data in all the solutes used indicate the formation of $HgCl_3^-$ predominantly.

If it is true that the predominating ion is $HgCl_3^-$, then a quantitative treatment of the data becomes more possible due to the unit or near unit ratio of $\gamma_{\text{HgCl}_3^-}/\gamma_{\text{Cl}^-}$ in the equilibrium constant of K_2, for equation (2) over a wide range of concentrations. This should make possible a fairly reliable calculation of the value of K_2 from data even at 1 molal of added chloride ion (see Table VI, column 5). It is of interest to point out here the relatively large values of K_2 are indicative of a high ratio of $HgCl_3^-$ ion to free Cl^- ion; they also indicate that any other ion existing in the solution must be of relatively low concentration.

TABLE VI

[Thomas (ref. 1) revised]

m_{Cl}	s_{HgCl_2} in HCl	$m_{\text{HgCl}_2\text{ complex}}$ in HCl	$m_{\text{HgCl}_2\text{ complex}}$ in LiCl	Ratio $HgCl_2$ complex to free chloride ions = K_2	$m_{\text{HgCl}_2\text{ complex}}$ in $CaCl_2$	$m_{\text{HgCl}_2\text{ complex}}$ in $AlCl_3$
0.00	0.2702					
.1	.376	0.106	0.105		0.105	0.103
.2	.481	.211	.205		.208	.201
.3	.586	.316	.300		.303	.298
.5	.795	.525	.491	44	.492	.486
1.0	1.325	1.055	.960	24	.969	.965
2.0	2.420	2.150	1.907	21	1.937	1.926
3.0	3.557	3.287	2.375	23	2.915	2.906
4.0	4.726	4.456	3.864	28	3.894	3.862
5.0	5.901	5.631	4.862	35	4.874	4.774
6.0	7.054	6.784	5.861	42	5.853	
7.0	8.176	7.906	6.850	46		
8.0	9.264	8.994	7.827	45		
9.0	10.309	10.039				

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[14] This calculation and that for the iodides do not take into consideration a possibility of polymerization of mercuric bromide or mercuric iodide (see latter section of this paper for a discussion of this possible effect with mercuric chloride). No evidence of this effect in the bromide or iodide has come to our attention.

[15] Garrett and Howell, THIS JOURNAL, **61**, 1730 (1939).

An apparent anomaly still exists in these data at low concentrations of added chloride ion, namely, the data in Table VI show higher (about 5%) mercuric complex concentrations than can be accounted for on the basis of the 1:1 ratio of $HgCl_2:Cl^-$. This is outside the limit of experimental error and is consistent for all the salts used.

A very probable explanation of this apparent anomaly is the fact that a polymerization equilibrium may exist in mercuric chloride solutions. Such an equilibrium would make necessary the consideration of the following additional reactions in interpreting these data

$$x\mathrm{HgCl_2} \rightleftarrows (\mathrm{HgCl_2})_x \qquad (4)$$

and

$$(\mathrm{HgCl_2})_x + \mathrm{Cl^-} \rightleftarrows (\mathrm{HgCl_2})_x\mathrm{Cl^-} \qquad (5)$$

That a polymerization equilibrium does exist is supported by other independent evidence, namely, (1) measurements of rise of the boiling point of mercuric chloride solutions[16–19] and (2) freezing point lowering.[20,21] Such evidence is somewhat uncertain as individual cases but all of the evidence taken as a whole points strongly to the validity of this assumption of the existence of at least a small per cent. of polymerized mercuric chloride molecules in solution.

An additional observation that seems to lend further support to this assumption is the fact that the values of K_2 calculated from Thomas'[1] data go through a minimum (see column 5, Table VI) whereas the values of K_2 for similar data for the bromide and iodide vary in the direction that one might reasonably expect if there are no secondary equilibria such as polymerization.

It is obvious that more careful work is necessary on vapor pressure lowering, freezing point lowering, distribution ratios, etc., to verify this assumption of polymerization. However, it would be reasonable to conclude that from the data now at hand the amount of polymerized mercuric chloride molecules need only be in the order of 10% to account for the apparent anomalous behavior of mercuric chloride. This also leads one to the conclusion that the complex ion of mercuric chloride that one expects to predominate is the $HgCl_3^-$ ion but it does not exclude the possibility of smaller amounts of other ions such as $(HgCl_2)_xCl^-$, $HHgCl_4^-$ and $HgCl_4^=$.

It may also be observed that a near 1 to 1 ratio of mercuric chloride to added chloride ion would indicate only a small amount of free chloride ions in solution and thus suggest a highly stable complex ion. Other work pointing to the high stability of these complex ions is the work of LeBlanc and Noyes[21] on the effect of mercuric chloride on the rate of catalysis of methyl acetate with hydrochloric acid and the work of Richards and Archibald[22] on the effect of mercuric chloride on the conductivity of hydrochloric acid. These papers also indicate that the new compounds formed are strong electrolytes. Again one is led to the conclusion that the predominating ion is the $HgCl_3^-$ ion; otherwise one would expect the catalytic activity and the conductivity of the hydrochloric acid to be considerably altered due to the removal of hydrogen ions to form the $HHgCl_4^-$ ion which would be only slightly dissociated in such concentrated solutions.

This conclusion is further supported by the data on these other halides which suggest an appreciable amount of $HgI_4^=$, and only a very small amount (if any) of $HgBr_4^=$. A reasonable prediction would suggest a still smaller amount of $HgCl_4^=$. If this conclusion be justified, then one obtains an approximate value of $K_2 = 20$ from Thomas' data, and a value of $\Delta F^\circ_{298} = -1700$ cal. if one assumes no polymerization at this value of chloride ion concentration. This value indicates a fairly stable complex chloride ion, which is in agreement with other evidence.

Evidence of hydrolysis was obtained in the mercuric bromide–bromide system when it was found that the *p*H of the samples varied from 4.1 for water solubility to 4.8 for the salt samples from $m_{\mathrm{KBr}} = 0.01$ to 1.0 molal.

Acknowledgments.—The author is indebted to Mr. James Lemley and Dr. Claude Acker for aid in the experimental part of this paper.

Summary

The solubilities of mercuric bromide and mercuric iodide have been determined in potassium

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[16] Kahlenberg, *J. Phys. Chem.*, **5**, 367 (1901), whose data indicate molecular weights from 310 to 423 (theoretical mol. wt. 271).

[17] Beckmann, *Z. physik. Chem.*, **6**, 460 (1890), whose data indicate molecular weights from 275 to 342 except at high dilutions.

[18] Bourion and Rouyer, *Ann. chim.*, **10**, 263 (1928); *Compt. rend.*, **177**, 546 (1923), whose data indicate single and double molecules at 25°. These authors also give references to other evidence of polymerization.

[19] Tourneux, *Bull. soc. chim.*, [5] **1**, 1043 (1934).

[20] Raoult, *Compt. rend.*, **87**, 169 (1878), whose data indicate a molecular weight of 387.

[21] See ref. 5. A brief but significant summary of this work is given by Sherrill, ref. 4, who points out an interpretation of the data in terms of polymerized molecules.

[22] Richards and Archibald, *Z. physik. Chem.*, **40**, 385 (1902).

bromide and potassium iodide solutions. The water solubility of mercuric bromide has been redetermined.

The equilibrium constants for the formation of the complex ions of mercuric halides have been evaluated. These calculations indicate that $HgBr_3^-$, HgI_3^- and $HgI_4^{=}$ are formed. Earlier work indicated the formation of $HgCl_3^-$ with small amounts of $(HgCl_2)_x$ and $(HgCl_2)_xCl^-$.

The anomalous solubility of mercuric chloride in low concentrations of chloride solutions is accounted for on the basis of polymerization of mercuric chloride. Other evidence is cited to indicate the existence of polymerized mercuric chloride molecules.

A number of different independent arguments are presented to indicate that the chief ion formed in the chloride solutions is the $HgCl_3^-$ ion.

The equilibrium constants and ΔF°_{298} of several of these ions have been evaluated. They have been shown to be in agreement among themselves and with other known data.

The free energy of formation of the various halide ions from mercuric halide and the halide ions is $HgCl_3^-$, $\Delta F^\circ_{298} = -1700$ cal.; $HgBr_3^-$, $\Delta F^\circ_{298} = -365$ cal.; HgI_3^-, $\Delta F^\circ_{298} = +430$ cal.; $HgI_4^{=}$, $\Delta F^\circ_{298} = -2100$ cal.

COLUMBUS, OHIO RECEIVED JULY 7, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The Redistribution Reaction. I. The Random Intermolecular Exchange of Organic Radicals

BY GEORGE CALINGAERT AND HAROLD A. BEATTY

This is the first of a series of papers describing a hitherto unrecognized type of intermolecular exchange of organic radicals. The systematic study of this reaction has yielded simple laws governing its course, and supplies a ready interpretation of the small amount of related data scattered through the literature. The results obtained offer interesting suggestions regarding the behavior of the covalent bond as well as possibilities for new methods of probing into this field. The reaction also constitutes a new tool for the synthesis of several types of organic compounds. This first paper defines the nature of the reaction, using illustrations from the field of organo-metallic compounds, and constitutes a general introduction to subsequent papers which will cover specific phases of the subject.

Introduction.—A wide variety of reactions is known in which atoms or radicals linked by covalent bonds are transferred from one molecule to another through exchange with an atom or radical of another kind. For example, in the Jacobsen reaction, bromobenzene under the influence of aluminum chloride yields a mixture containing benzene and *p*-dibromobenzene, as well as other products. Likewise, under the influence of the same catalyst, toluene is converted into a mixture containing, in addition to toluene itself, benzene and several polymethylated benzenes. Reactions of this type are also known in the field of organo-metallic compounds. Dialkylzinc compounds have long been prepared by heating alkylzinc halides, which are converted into a mixture of the dialkyl compound and the zinc halide, the former being removed as formed, by distillation. A few cases also have been reported where the radicals exchanged were similar instead of dissimilar: for example, the interchange of methyl and ethyl radicals in organo-silicon compounds,[1] of phenyl and tolyl radicals in triarylbismuth compounds[2] and of halogen atoms in ethylene chlorobromide.[3]

Except in the last case, little or no indication has been given of the existence of an equilibrium, and in most cases a considerable amount of side reaction takes place. Also, the conditions used, namely, elevated temperatures or the presence of a powerful catalyst or both, suggest that the reactions are closely related to the irreversible decompositions of the compounds involved.

In the studies which will be reported in the present series of papers, it has been found that by a judicious choice of operating conditions and catalyst, it is possible to bring about an extensive

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[1] Dolgov and Volnov, *Zhur. Obshcheĭ Khim.*, Khim. Ser., **1**, 91 (1931).

[2] Challenger and Allpress, *J. Chem. Soc.*, **119**, 913 (1921); Challenger and Ridgway, *ibid.*, **121**, 104 (1922).

[3] Dougherty, THIS JOURNAL, **51**, 576 (1929).