tions of K_2 and of $[X_s]$ for each value of D; K_1 is found from

$$D = \frac{K_D}{\frac{1}{K_1K_2[X]_s^2} + \frac{1}{K_2[X]_s} + 1} \qquad (3'')$$

The values in Table II were thus calculated. Using the values of K_m in this table and of $K_D = D_{max}$, D at all values of $[X]_s$ can be calculated; agreement within the experimental error is obtained with all experimental results. Specifically, it is possible to calculate D_{max} for the value of $[X]_s$ which satisfies

$$2 + K_1[X]_s - K_1K_2K_3[X]_s^3 - 2K_1K_2K_3K_4[X]_s^4 = 0 \qquad (9)$$

Equation 9 is obtained by maximizing D in eq 3 with respect to $[X]_s$ and shows that, when D reaches its maximum, the amount of free halide is exactly equal to the amount of KX added to a system containing no zinc nitrate. In each case, D_{max} as calculated was found to agree within experimental error with the D_{max} value used as K_D. This assumption thus being valid, the values of K_D can be given as in Table III.

Table II

	150°	165°	180°	200°
K_1(Cl)	$(3.4 \pm 0.9)10^7$	$(6.0 \pm 1.0)10^6$	$(1.1 \pm 0.3)10^6$	$(1.5 \pm 0.4)10^5$
K_2(Cl)	$(2.0 \pm 0.5)10^7$	$(3.4 \pm 0.8)10^6$	$(6.5 \pm 2.0)10^5$	$(8.0 \pm 2.0)10^4$
K_1(Br)	$(2.9 \pm 0.7)10^7$	$(5.0 \pm 1.0)10^6$	$(9.5 \pm 2.0)10^5$	$(1.3 \pm 0.4)10^5$
K_2(Br)	$(1.8 \pm 0.5)10^7$	$(3.0 \pm 0.7)10^6$	$(6.0 \pm 1.0)10^5$	$(7.0 \pm 2.0)10^4$
K_1(I)	$(2.4 \pm 0.6)10^7$	$(4.3 \pm 0.9)10^6$	$(8.5 \pm 2.0)10^5$	$(1.1 \pm 0.3)10^5$
K_2(I)	$(1.6 \pm 0.4)10^7$	$(2.7 \pm 0.7)10^6$	$(5.0 \pm 1.0)10^5$	$(6.5 \pm 2.0)10^4$

Table III

	150°	165°	180°	200°
Chloride	12.9 ± 0.4	7.4 ± 0.2	4.4 ± 0.1	2.2 ± 0.1
Bromide	24.0 ± 0.7	18.9 ± 0.6	15.5 ± 0.5	11.9 ± 0.4
Iodide	39.0 ± 1.0	35.0 ± 1.0	32.0 ± 1.0	28.0 ± 1.0

The agreement between results obtained at total zinc concentrations varying between 3×10^{-4} and 1×10^{-5} m in the salt phase shows that no polynuclear zinc halide species are formed in a nitrate melt. Figure 2 shows the dependence of K_1, K_2, K_3, K_4, and K_D on temperature. The linearity of log D with the inverse of the temperature shows ΔH to be constant in the range 150–200° for both the partition and the complex formation reactions. The values of $-\Delta H$ in Table IV can be deduced from $d \ln K/d(1/T) = -\Delta H/R$. (In these equations, the participating NO_3^- groups have been omitted for reasons of simplicity.)

Table IV

Reaction	ΔH, kcal/mole X = Cl	 X = Br	 X = I
$Zn^{2+} + X^- \rightleftarrows ZnX^+$	11 ± 1	11 ± 1	11 ± 1
$ZnX^+ + X^- \rightleftarrows ZnX_2$	11 ± 1	11 ± 1	11 ± 1
$ZnX_2^- + X^- \rightleftarrows ZnX_3^-$	1.1 ± 0.4	0.6 ± 0.3	...
$ZnX_3^- + X^- \rightleftarrows ZnX_4^{2-}$	1.1 ± 0.2	...	...
$(ZnX_2)_s \rightleftarrows (ZnX_2)_o$	3.6 ± 0.1	1.4 ± 0.1	0.75 ± 0.09

It would seem that ZnX_2 is very stable, the halogens being bound to the zinc by covalent bonds which can be broken only at higher temperatures. On the other hand, the ligands which serve to form tetracoordinated Zn complexes, whether they are aromatic molecules or halide or nitrate ions, seem to be readily interchangeable, even at 150°.

It may be noted that, by extrapolation of the $K_1 = K_2$ and $K_3 = K_4$ values for chloride to 309° (Figure 2), the melting point of $NaNO_3$, the values obtained are approximately: $K_1 = 25$, $K_2 = 13$, $K_3 = 3.3$, and $K_4 = 1.7$. Calculations show that this is one of the numerous sets of constants which agree well with Van Artsdalen's[10] cryoscopic results, the latter being quite sensitive to the products K_1K_2 and K_3K_4, but allowing wide variation in K_1 and K_3 if both values are varied in the same proportion.

Acknowledgment.—Thanks are due to Professor Y. Marcus and Dr. M. Givon for helpful discussions and to Mr. S. Shamash for technical assistance.

Contribution from the Radiochemistry Department, Soreq Nuclear Research Centre,
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Solvent Extraction from Molten Salts. VI.[1] Mixed Zinc Halides

By M. ZANGEN

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The over-all distribution ratio D for zinc species between a polyphenyl eutectic mixture and molten $LiNO_3$–KNO_3 eutectic was determined for $ZnCl_2$–$ZnBr_2$, $ZnCl_2$–ZnI_2, and $ZnBr_2$–ZnI_2 mixtures of varying composition, at 150, 165, 180, and 200°. At the lower temperatures, the plot of D *vs.* R (=the ratio Br_{total}/Cl_{total}, I_{total}/Cl_{total}, or I_{total}/Br_{total}) showed a maximum, which was not found at 180 and 200°. The results show that K_o, the equilibrium constant for the reaction $ZnA_2 + ZnB_2 \rightleftarrows 2ZnAB$ in the organic phase, remains essentially constant at varying temperature, while K_s, the equilibrium constant for the same reaction in the salt phase, strongly increases with temperature. The values of K_{AB}, the distribution coefficient of ZnAB, and of ΔH for the extraction of this species were determined.

Introduction

Unlike the case of Cd(II) and Hg(II), little work seems to have been done on mixed-halide complexes of Zn(II) even in aqueous phase. After the somewhat unexpected results obtained for mixed Hg(II) halides in molten salts,[2] it seemed interesting to obtain, by the

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[1] Previous paper in series: M. Zangen, *Inorg. Chem.*, **7**, 133 (1968).

[2] M. Zangen, *Israel J. Chem.*, **2**, 91 (1964).

same methods, some data on the stability of mixed Zn(II) halides in molten nitrate and in an aromatic solvent.

Experimental Section

As in previous work[1,2] the molten salt phase consisted of the eutectic mixture $LiNO_3$-KNO_3, mole ratio 3:4 (mp ~120°). The nitrate mixture was fused and homogenized at 350°, after which dry nitrogen was bubbled through for 6 hr at 250° to remove water. The organic phase consisted of a eutectic mixture of biphenyl, *o*-terphenyl, and *m*-terphenyl in the mole ratio 37:48:15 (mp 25°).

Solutions (10^{-3} *m*) of zinc chloride, bromide, and iodide in the polyphenyl phase, containing Zn^{65} tracer (γ, 245 days), were prepared as described in part V.[1] Mixtures in varying proportion of any two of these solutions were added to test tubes containing the nitrate eutectic mixture; in all experiments, the mass ratio of the salt phase to the organic phase, $q = m_o/m_s$, was very near 3.5. Equilibration and phase separation were as previously[1] described. The radiometric determination of D = (counts/min per g of polyphenyl phase)/(counts/min per g of salt phase), obtained in an NaI crystal well-type γ spectrometer, gives the over-all distribution ratio for zinc species. D is determined within 3% relative error.

Results

Figure 1a–c shows the variation of D with $R = Br_{tot}/Cl_{tot}$, I_{tot}/Cl_{tot}, and I_{tot}/Br_{tot}, respectively, at 150, 165, 180, and 200°. In all cases, the distribution ratios at very high or very low values of R approach the values found in part V for the pure zinc halides. While no maximum is found at 180 and 200°, all plots at 150 and 165° show maxima (although shallower at 165°).

Detailed experimental results are given in an appendix.[3]

Discussion

If the investigated system of Zn(II) species were in all points similar to that of Hg(II), the only species in the system would be $(ZnA_2)_o$, $(ZnAB)_o$, $(ZnB_2)_o$, $(ZnA_2)_s$, $(ZnAB)_s$, and $(ZnB_2)_s$, where A and B represent two different halogens and the subscripts o and s the organic and salt phase, respectively. However, since it was shown[1] that the zinc dihalides are partly dissociated in the molten salt phase, especially at higher temperatures, the species $(ZnA^+)_s$, $(ZnB^+)_s$, $(Zn^{2+})_s$, $(A^-)_s$, and $(B^-)_s$ have to be taken into account and

$$D = \frac{[ZnA_2]_o + [ZnAB]_o + [ZnB_2]_o}{[ZnA_2]_s + [ZnA^+]_s + [ZnAB]_s + [ZnB_2]_s + [ZnB^+]_s + [Zn^{2+}]_s} \quad (1)$$

However, it seemed very difficult to draft (let alone to solve) equations concerning parameters that would express all 11 species. Therefore, a method of successive approximations was used.

(I) As a first step, the dissociation of zinc dihalides is neglected; approximate values $K_{AB} = [ZnAB]_o/[ZnAB]_s$, $K_s = [ZnAB]_s^2/[ZnA_2]_s[ZnB_2]_s$, and $K_o = [ZnAB]_o^2/[ZnA_2]_o[ZnB_2]_o$ are then calculated from the following equations, valid in the case of Hg(II).

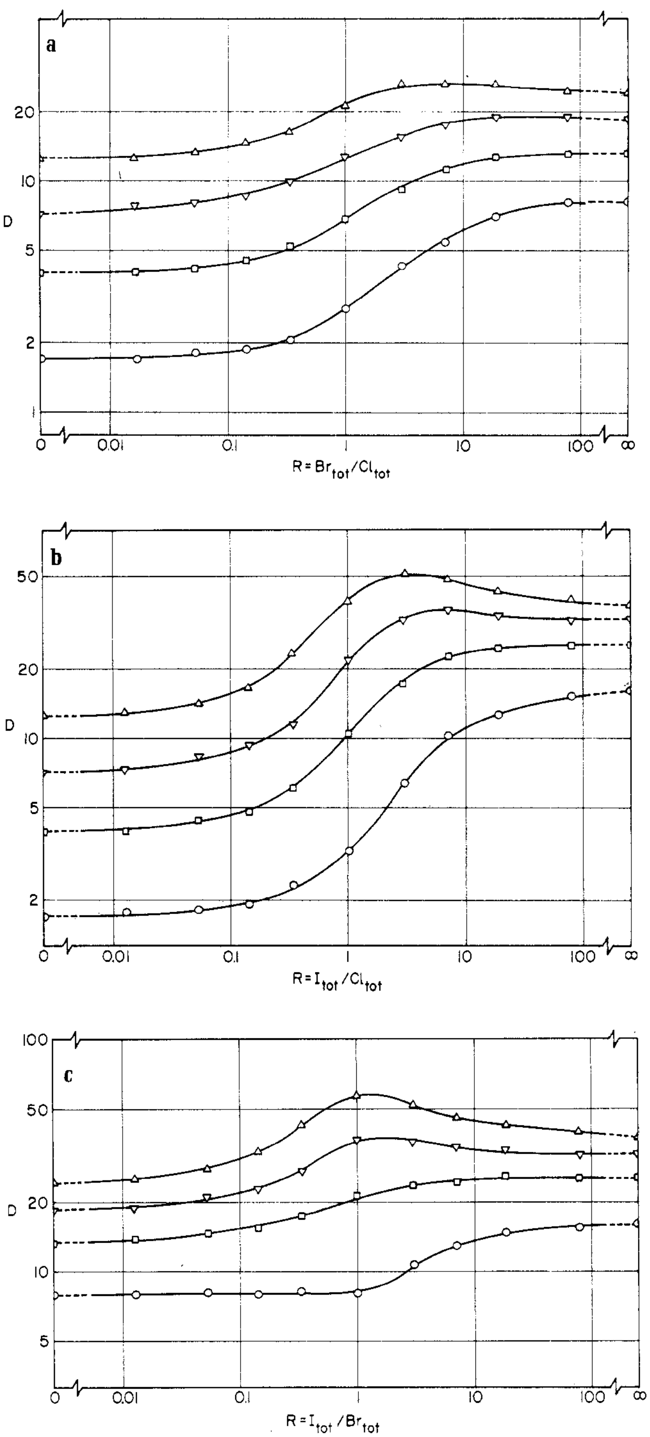

Figure 1.—Over-all distribution ratio for zinc halide species between polyphenyl eutectic and molten(K, Li)NO_3 eutectic as a function of the ratios bromide/chloride (a), iodide/chloride (b), and iodide/bromide (3): 150°, △; 165°, ▽; 180°, □; 200°, ○.

(a) If the plot of D *vs.* R shows no maximum

$$P_{AB} = \frac{2RPP_A}{2RP_A - (1 - R)(P - P_A)} \quad (2)$$

for $R \ll 1$ and

$$P_{AB} = \frac{2PP_B}{2P_B + (R - 1)(P_B - P)} \quad (3)$$

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[3] This appendix has been deposited as Document No. 9646 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

for $R \gg 1$

$$K_s = \frac{[P_A(P_B - P) - P_B(P - P_A)]^2}{(P - P_{AB})^2 P_A P_B} \qquad (4)$$

for $R = 1$, where $P_A = q + K_A$, $P_B = q + K_B$, $K_A = [ZnA_2]_o/[ZnA_2]_s$, $K_B = [ZnB_2]_o/[ZnB_2]_s$ (both these constants having been derived in part V), $P_{AB} = q + K_{AB}$, and $P = q + D$.

(b) If there is a maximum in the plot of D *vs.* R

$$K_{AB} = \frac{R_{max}K_A(D_{max} - K_B) - K_B(D_{max} - K_A)}{R_{max}(D_{max} - K_B) - (D_{max} - K_A)} \qquad (5)$$

$$K_s = \frac{4[R_{max}(D_{max} - K_B) - (D_{max} - K_A)]^2}{(R_{max} - 1)^2(D_{max} - K_A)(D_{max} - K_B)} \qquad (6)$$

where R_{max} is the ratio B_{total}/A_{total} for which the maximum distribution ratio, D_{max}, is found. In both cases

$$K_o = K_s\frac{K_{AB}^2}{K_A K_B} \qquad (7)$$

(II) From the found values of K_s and K_{AB}, approximate values of $[ZnA_2]_s$ and $[ZnB_2]_s$ are calculated, again using equations that neglect the dissociation of these species

$$[ZnA_2]_s' = \frac{A_{tot}}{m_o}\left[4P_AP_B - \frac{1}{2}K_s(1 - R)P_{AB}^2 - P_{AB}V\right]/(8P_A^2P_B - 2K_sP_AP_{AB}^2) \qquad (8)$$

$$[ZnB_2]_s' = \frac{A_{tot}}{m_o}\left[4RP_AP_B + \frac{1}{2}K_s(1 - R)P_{AB}^2 - P_{AB}V\right]/(8P_AP_B^2 - 2K_sP_BP_{AB}^2) \qquad (9)$$

where $V = [4K_sRP_AP_B + {}^1/_4K_s^2(1 - R)^2P_{AB}^2]^{1/2}$ and the prime indicates a temporary value.

(III) $(ZnA_2)_s$ and $(ZnB_2)_s$ are now assumed to be partially dissociated, and the concentrations of Zn^{2+}, ZnA^+, ZnB^+, ZnA_2, ZnB_2, A^-, and B^- are calculated from

$$K_{1A} = \frac{[ZnA^+]}{[Zn^{2+}][B^-]}, \quad K_{2A} = \frac{[ZnA_2]}{[ZnA^+][A^-]},$$

$$K_{1B} = \frac{[ZnB^+]}{[Zn^{2+}][B^-]}, \quad K_{2B} = \frac{[ZnB_2]}{[ZnB^+][B^-]}$$

which were derived in part V, and from the balance equations

$$2[ZnA_2]_s' = [A^-]_s + [ZnA^+]_s + 2[ZnA_2]_s$$

$$2[ZnB_2]_s' = [B^-]_s + [ZnB^+]_s + 2[ZnB_2]_s$$

$$[ZnA_2]_s' + [ZnB_2]_s' = [Zn^{2+}]_s + [ZnA^+]_s + [ZnB^+]_s + [ZnA_2]_s + [ZnB_2]_s$$

(IV) The sum $[Zn^{2+}] + [ZnA^+] + [ZnB^+]_s$ is now subtracted from the total concentration of zinc species in the salt melt, Zn_{tot}/m_oP, and the value which D would have at each point if the ionic species were nonexistent is calculated

$$D^* = \frac{Zn_{tot}D}{Zn_{tot} - \{[Zn^{2+}] + [ZnA^+] + [ZnB^+]\}m_oP}$$

(V) Using D^* instead of D, second approximation values of K_{AB} and K_s, derived either from eq 2–4 or from eq 5–6, and of $[ZnA_2]_s'$ and $[ZnB_2]_s'$, derived from eq 8 and 9, are calculated. The cycle III–IV–I–II is repeated until $[ZnA_2]_s'$ and $[ZnB_2]_s'$ remain constant within 2%, which result is generally obtained after three or four cycles.

By this method the values of Table I were found.

TABLE I

	150°	165°	150°	200°
log K_{ClBr}	2.24 ± 0.1	1.67 ± 0.1	1.18 ± 0.02	0.53 ± 0.02
log K_{ClI}	2.31 ± 0.1	1.80 ± 0.1	1.24 ± 0.02	0.69 ± 0.02
log K_{BrI}	2.41 ± 0.1	1.93 ± 0.1	1.46 ± 0.02	1.14 ± 0.02
log K_s(Cl–Br)	−1.04 ± 0.2	−0.29 ± 0.2	0.42 ± 0.1	1.30 ± 0.1
log K_s(Cl–I)	−1.18 ± 0.2	−0.42 ± 0.2	0.37 ± 0.1	1.15 ± 0.1
log K_s(Br–I)	−1.28 ± 0.2	−0.55 ± 0.2	0.19 ± 0.1	0.98 ± 0.1
log K_o(Cl–Br)	0.93 ± 0.3	0.91 ± 0.3	0.94 ± 0.1	0.93 ± 0.1
log K_o(Cl–I)	0.78 ± 0.3	0.76 ± 0.3	0.70 ± 0.1	0.75 ± 0.1
log K_o(Br–I)	0.59 ± 0.3	0.54 ± 0.3	0.52 ± 0.1	0.61 ± 0.1

Back calculation of the partition data from the final equilibrium constants yields agreement with experimental results well within the experimental error, as shown by the full lines in Figure 1a–c. However, such agreement is still obtained in most cases upon variation of the constants within the given uncertainty limits.

As can be seen from Table I, the formation constant of the mixed complexes in the aromatic solvent does not change with temperature and (especially in the case of K_{BrI}) remains of the same order of magnitude as the "statistical" formation constant, $K_{stat} = 4$. In the salt melt, however, the stability of the mixed complexes appears to increase strongly with temperature. The stabilization constant, defined as $K_{stab} = K_s/K_{stat}$,[2,4] can be seen to vary by a factor of ~200 between 150 and 200°.

The extensive change in the relative stability of the mixed complex in the salt with respect to the organic phase is also expressed in the values of K_{AB}, which are much higher (by a factor of 20–50) at 150° than at 200°. The temperature dependence of K_s and K_{AB} is shown in Figure 2, log K_s and log K_{AB} being essentially linear with the inverse of the temperature. $\Delta H°$, both for the formation of the mixed complex in the salt phase and for its extraction into the aromatic solvent, is, therefore, constant between 150 and 200° and can be calculated from van't Hoff's equation.

However, owing to the complexity of the equations governing the system, the obtained values, shown in Table II, should be considered mainly as an indication of the order of magnitude.

TABLE II

Reaction	ΔH°, kcal/mole, for		
	A = Cl, B = Br	A = Cl, B = I	A = Br, B = I
$ZnA_2 + ZnAB_2 \rightarrow 2ZnAB$	−43 ± 20	−43 ± 20	−42 ± 20
$(ZnAB)_s \rightleftarrows (ZnAB)_o$	31 ± 10	30 ± 10	26 ± 10

In the work on mixed mercury(II) halides,[2] which was carried out at 150° only (experiments at other tem-

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[4] Y. Marcus, I. Eliezer, and M. Zangen, "Transactions of the Tihany Symposium on Coordination Chemistry," Hungarian Academy of Science, 1964, p 105.

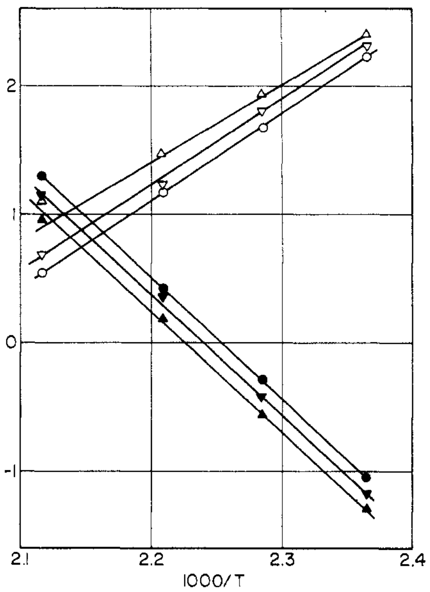

Figure 2.—Values of equilibrium constants as a function of temperature; full symbols indicate K_s(A–B) and empty symbols indicate K_{AB} for the mixed halide systems: chloride–bromide, O; chloride–iodide, ▽; bromide–iodide, △.

peratures are in progress), low stability in the salt phase was found for HgClI and HgBrI, but not for HgClBr. This low stability was attributed to steric effects, taking into account the two nitrate ions which are assumed to complex the neutral mercury halide in the (nitrate) melt phase.[5] In the case of the smaller Zn(II) ion, such a steric effect should be expected also in the case of ZnClBr, as was found in this work. However, the magnitude of this effect and its disappearance at higher temperatures still remains unexplained. Apparently, as was pointed out in the preceding paper,[1] pure zinc dihalides are so stable that the zinc–halogen bonds cannot be broken at lower temperatures even in order to exchange one halide for another. It may be pointed out that the $\Delta H°$ values involved in the replacement of a halide by a nitrate[1] are of the same order of magnitude as those involved in the formation of the mixed halide complex.

Acknowledgment.—Thanks are due to Mr. S. Shamash for technical assistance.

(5) M. Zangen and Y. Marcus, *Israel J. Chem.*, **2**, 49, 155 (1964).

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Synthesis of Thallium Platinate at High Pressure[1]

BY HENRY R. HOEKSTRA AND STANLEY SIEGEL

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The double oxide $Tl_2Pt_2O_7$ has been prepared by reaction of Tl_2O_3 with platinum metal or PtO_2 at 1000° and 40 kbars pressure. The brown solid is insoluble in aqua regia and is thermally stable to 750° at atmospheric pressure. The cell is face-centered cubic with $a = 10.132 \pm 0.004$ A and the structure is assumed to be of the cubic pyrochlore type based on space group Fd3m. The measured density is 11.12 g/cm^3 and the computed value is 11.63 g/cm^3, with $Z = 8$. Fifteen diffraction lines were observed and used in a least-squares refinement to determine the one unknown coordinate. The R factor is 3.6% based on observed maxima only. Each platinum is bonded octahedrally to six oxygens at 2.08 ± 0.04 A, each thallium to six oxygens at 2.32 ± 0.04 A and two oxygens at 2.19 ± 0.002 A. Some general aspects of the pyrochlore structure are discussed. The infrared spectrum of $Tl_2Pt_2O_7$ (to 200 cm^{-1}) has four sharp maxima at 684, 562, 449, and 363 cm^{-1}.

Introduction

Information concerning the preparation and properties of anhydrous platinum oxides is scanty and often contradictory. Three oxides (PtO, Pt_3O_4, and PtO_2) and two double oxide compositions ($M^IPt_3O_4$ and $M_2^IPtO_3$, where M is lithium or sodium) have been reported in relatively recent publications.

Moore and Pauling[2] treated $PtCl_2$ with KNO_3 and on the basis of very meager crystal data, concluded that the product was PtO, isostructural with the corresponding palladium oxide. The existence of PtO has been questioned by later workers.[3] Galloni and Roffo[4] determined the structure of several crystals of a cubic oxide which had been obtained from a platinum wire electrode. The assigned formula was Pt_3O_4, but confirmatory analysis was not possible on the small sample, and its true composition remains in doubt. Ariya, *et al.*,[5] reported that the oxidation of platinum sponge at oxygen pressures to 310 bars produced only one thermodynamically stable oxide, Pt_3O_4. Its structure, however, was not that of the Galloni compound. Platinum dioxide has been prepared by fusing H_2PtCl_6 with an alkali metal nitrate.[3,6]

Waser and McClanahan[7] report that cubic $NaPt_3O_4$

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission. Paper presented at 153rd National Meeting of American Chemical Society, Miami Beach, Fla., April 1967.

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(5) S. M. Ariya, M. P. Morozova, G. S. Markevich, and A. A. Reikhardt, *Sb. Statei Obshchei Khim. Akad. Nauk SSSR*, **1**, 76 (1953); see *Chem. Abstr.*, **48**, 12533 (1954).

(6) R. Adams and R. L. Shriner, *J. Am. Chem. Soc.*, **45**, 2171 (1923).

(7) J. Waser and E. D. McClanahan, *J. Chem. Phys.*, **19**, 413 (1951); **20**, 199 (1951).