one hesitates to postulate a structure from the evidence available. It may be simply a double salt, but the spectra suggest that this is not the case. It is hoped that suitable crystals can be obtained for X-ray crystallographic determination of the structure. The products from different preparations are closely reproducible.

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CONTRIBUTION FROM THE RADIOCHEMISTRY DEPARTMENT, SOREQ NUCLEAR RESEARCH CENTRE,
ISRAEL ATOMIC ENERGY COMMISSION, YAVNE, ISRAEL

# Solvent Extraction from Molten Salts. V.[1] Zinc(II) Chloride, Bromide, and Iodide

BY M. ZANGEN

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The distribution ratio $D$ of zinc chloride, bromide, and iodide between a eutectic mixture of molten $LiNO_3$ and $KNO_3$ and a eutectic mixture of polyphenyls was determined radiometrically. Addition of small amounts of the corresponding potassium halide causes a slight increase in $D$. Further addition of potassium halide has no effect in the case of iodide, while $D$ is slightly decreased for the bromide and strongly for the chloride. This can be explained by formation of the inextractable anionic complexes $ZnCl_3^-$, $ZnCl_4^{2-}$, and $ZnBr_3^-$, for which the formation constants were calculated. Values were also calculated for the stability constants of the complexes $ZnX^+$ and $ZnX_2$. $\Delta H$ values for the various reactions in the range 150–200° are given.

## Introduction

Zinc chloride in the molten state, whether pure or mixed with molten alkali chloride, has been extensively investigated. Pure molten zinc chloride is said to consist of polymer molecules, $(ZnCl_2)_n$, in equilibrium with the ions $Zn^{2+}$, $ZnCl^+$, and $Cl^-$.[2] As to the mixtures with alkali halides, some authors[3-5] find evidence for the complex $ZnCl_4^{2-}$ only, while others claim the existence of $ZnCl_3^-$ alone[6] or in addition to $ZnCl_4^{2-}$;[7,8] in one instance,[9] evidence was found for a species $Cs_3ZnCl_5$, which might imply the existence of $ZnCl_5^{3-}$. The existence of some complex species of zinc and cadmium chloride in molten sodium nitrate was shown by Van Artsdalen,[10] who used cryoscopic measurements to determine stability constants; the method of calculation was later criticized,[11] but alternative calculations were made only in the case of cadmium chloride.

Very little work seems to have been done on zinc bromide and iodide in the molten state, but some evidence was found for the existence of both $ZnBr_3^-$ and $ZnBr_4^{2-}$ in fused $AsBr_3$.[12] It may be of interest to note that present knowledge of zinc halide complexes in aqueous solution presents the same picture: a large number of mostly conflicting data in the case of chloride, few data on bromide, and almost none on iodide.[13,14]

Previous work on solvent extraction of mercuric halides from molten nitrate[15] showed the possibility of using this tool to investigate the complex species in molten salts; this should be especially true in the case of zinc halides, which are expected to be structurally similar to mercuric halides.

## Experimental Section

As in the work with Hg(II) halides,[15] the molten-salt phase was the $LiNO_3$–$KNO_3$ eutectic mixture, mole ratio 3:4 (mp 120°). In some experiments, Zn halide and/or nitrate in various concentrations was also added. The nitrate mixture was fused and homogenized at 350°, after which dry nitrogen was bubbled through for 6 hr at 250° to remove any 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°).

A $Zn^{65}$ tracer ($\gamma$, 245 days) solution of high activity was obtained from Oak Ridge National Laboratory. This solution (5 $\mu$l) was added to larger amounts of analytically pure $ZnCl_2$, $ZnBr_2$, and $ZnI_2$ solutions, which were then evaporated to dryness. The dry zinc halides were made up to $10^{-3}$ $m$ solutions in the polyphenyl mixture and further diluted in some experiments.

Measured quantities of these polyphenyl solutions were added to Pyrex test tubes containing the nitrate eutectic mixture, in which varying amounts of the corresponding potassium halide had been dissolved. The weight to weight ratio of salt to polyphenyl was near 3.5 in all experiments.

The tube was sealed and tumbled for 15 min in an oil bath at constant temperature, regulated to ±1°, after which the phases were allowed to separate in the bath. The tube was then rapidly cooled to 30° and opened; the polyphenyl phase (liquid) was

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(1) Previous paper in series: M. Zangen, *J. Phys. Chem.*, **69**, 1835 (1965).

(2) J. O'M. Bockris, E. H. Crook, H. Bloom, and N. E. Richards, *Proc. Roy. Soc.* (London), **A255**, 558 (1960).

(3) M. A. Bredig and E. R. Van Artsdalen, *J. Chem. Phys.*, **24**, 478 (1956).

(4) B. F. Markov and R. V. Chernov, *Ukr. Khim. Zh.*, **27**, 34 (1961).

(5) R. A. Fleming and F. R. Duke, *J. Electrochem. Soc.*, **104**, 251 (1957).

(6) H. I. Moss, *Dissertation Abstr.*, **21**, 3283 (1960).

(7) R. L. Seifert, USAEC Report TID 6289, 1960.

(8) W. Bues, *Z. Anorg. Allgem. Chem.*, **279**, 104 (1955).

(9) B. F. Markov, I. D. Panchenko, and T. G. Kostenko, *Ukr. Khim. Zh.*, **22**, 287 (1956).

(10) E. R. Van Artsdalen, *J. Phys. Chem.*, **60**, 172 (1956).

(11) J. Braunstein, H. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).

(12) G. Jander and K. Gunther, *Z. Anorg. Allgem. Chem.*, **298**, 241 (1959).

(13) L. G. Sillén and A. E. Martell, "Stability Constants," The Chemical Society, London, 1964, pp 289–290, 324–325, 329–340.

(14) Aqueous zinc halide solutions were investigated by this author, using the solvent extraction method; results will be given in a separate publication.

(15) (a) M. Zangen and Y. Marcus, *Israel J. Chem.*, **2**, 49 (1964); (b) M. Zangen, *ibid.*, **2**, 91 (1964); (c) M. Zangen and Y. Marcus, *ibid.*, **2**, 155 (1964).

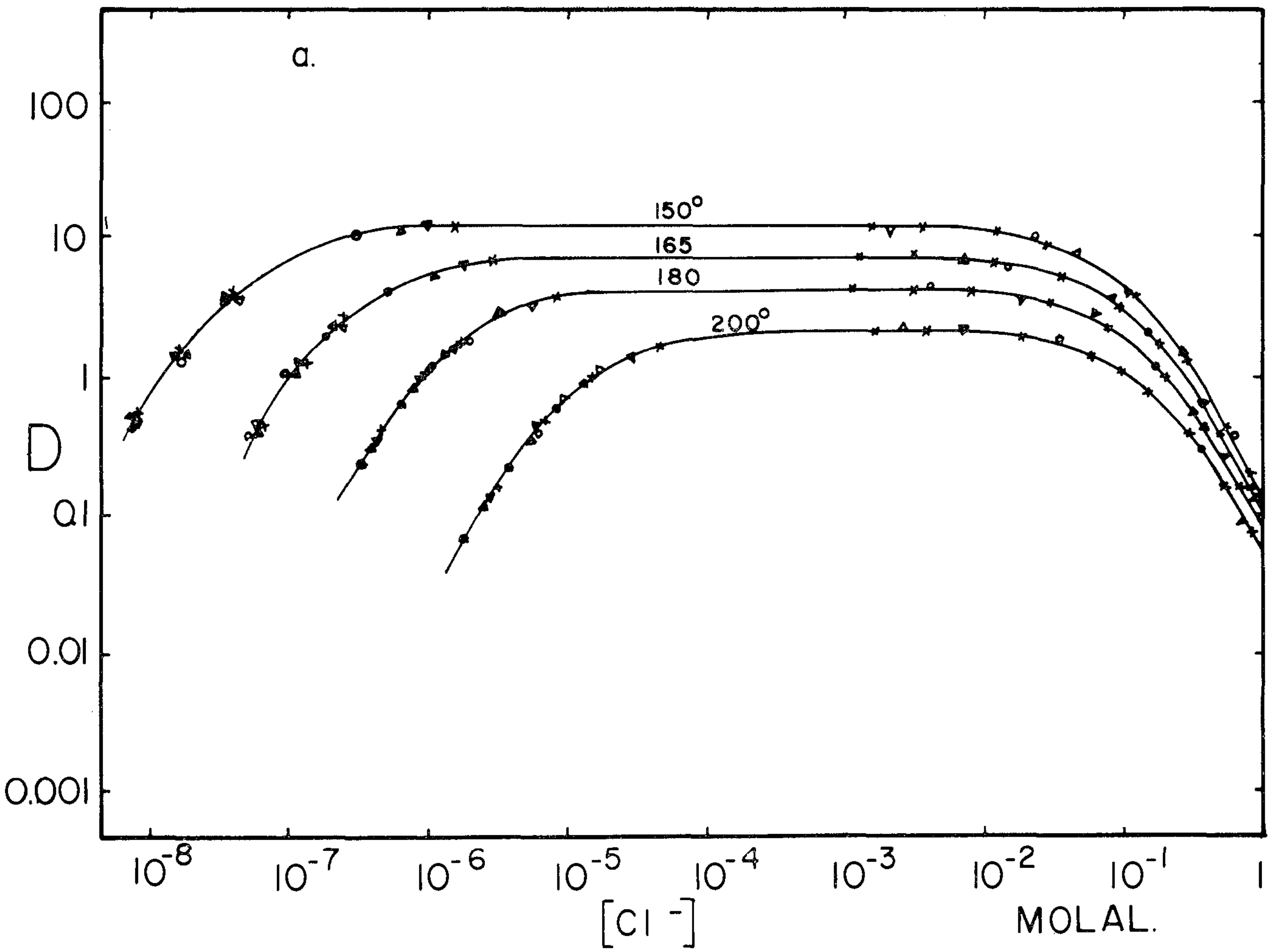

Figure 1a.—Distribution ratio of $ZnX_2$ as a function of free halide in the salt melt at 150, 165, 180, and 200° for X = Cl: ○, $(C_{Zn})_i = 10^{-1}$ *m*; △, $(C_{Zn})_i = 3 \times 10^{-5}$ *m*; ▽, $(C_{Zn})_i = 10^{-4}$ *m*; ×, $(C_{Zn})_i = 3 \times 10^{-4}$ *m*.

removed to another tube and the nitrate washed with benzene. The radiation in both phases was measured in an NaI crystal well-type $\gamma$ spectrometer and the molal distribution ratio was calculated as

$$D = \frac{\text{counts/min per g of polyphenyl phase}}{\text{counts/min per g of salt phase}}$$

Distribution ratios were obtained within ±3%.

## Results

Figure 1 shows the distribution ratio[16] of zinc chloride, bromide, and iodide as a function of concentration of free halide ($X^-$) in the salt melt, at 150, 165, 180, and 200°. At large excess of added potassium halide (KX) over total zinc present, $[X^-]$ was taken equal to [KX] added; otherwise it was calculated as shown below. It can be seen that in each case, *D* first increases with $[X^-]$, the increase becoming larger at higher temperature. Upon further addition of larger quantities of KX, a strong decrease in *D* is observed for the chloride and a slight decrease for the bromide, while in the case of iodide *D* remains unchanged.

## Discussion

As in the extraction of mercuric halides[15] it will be assumed that only the neutral species $ZnX_2$ exists in the organic phase, while, in addition, $Zn^{2+}$, $ZnX^+$, $ZnX_3^-$, and $ZnX_4^{2-}$ can exist in the salt melt. For simplicity, charges will not be written in the subsequent equations. The concentrations of the various species are interrelated by the constants

$$K_m = \frac{[ZnX_m]_s}{[ZnX_{m-1}]_s[X_s]} \tag{1}$$

and

$$K_D = \frac{[ZnX_2]_o}{[ZnX_2]_s} \tag{2}$$

where $1 \leq m \leq 4$, the subscripts s and o represent the salt melt and organic phases, respectively, and symbols in brackets represent the molalities of species. The distribution ratio will then be given by

$$D = \frac{K_D}{\dfrac{1}{K_1K_2[X]_s^2} + \dfrac{1}{K_2[X]_s} + 1 + K_3[X]_s + K_3K_4[X]_s^2} \tag{3}$$

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(16) A detailed table of data has been deposited as Document No. 9641 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.

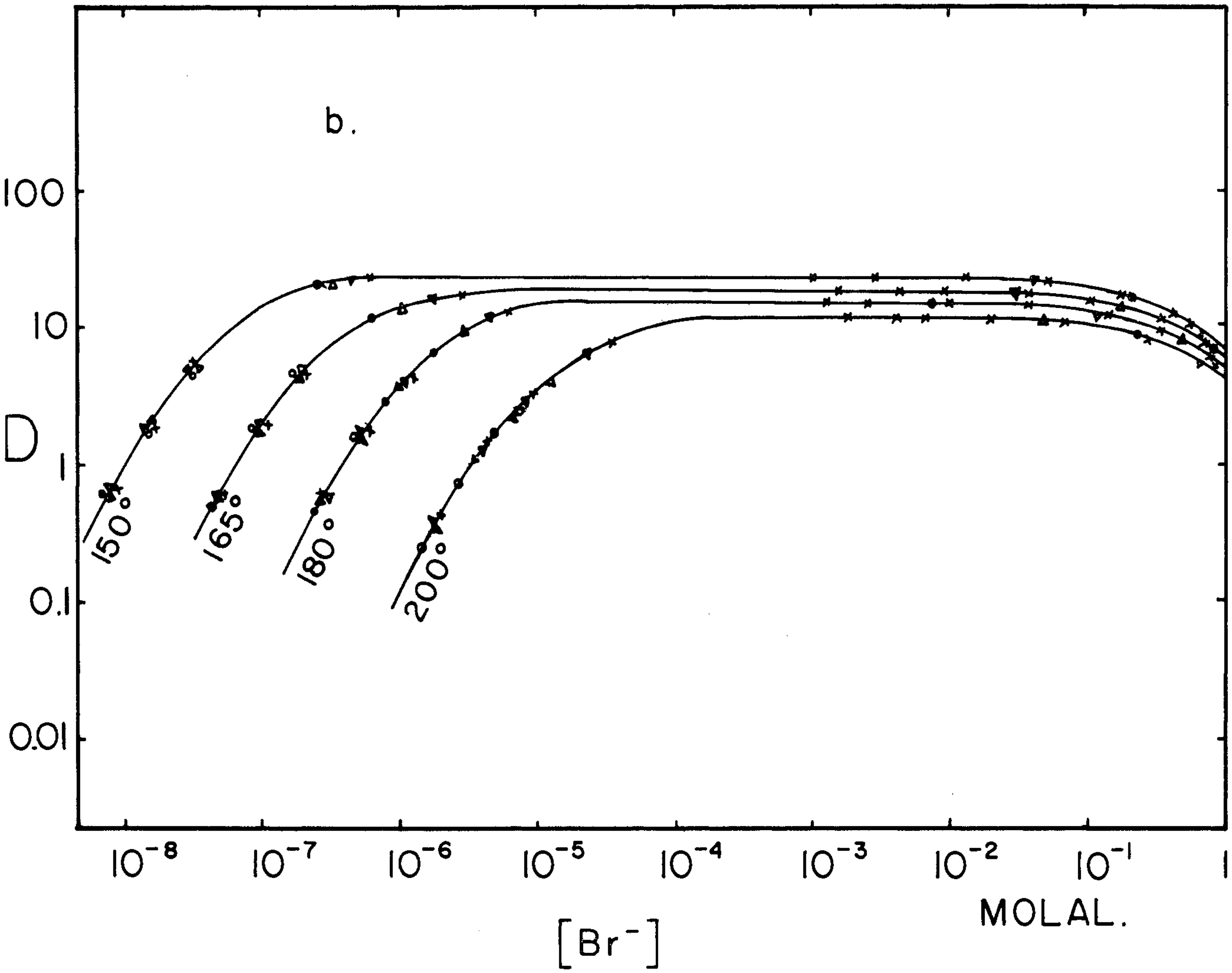

Figure 1b.—Same as Figure 1a, except X = Br.

The first two terms in the denominator are significantly decreased on addition of even small amounts of potassium halide, which accounts for the increase in $D$, as compared to the experiments where total X/total Zn = 2. Since, however, this increase is relatively small, it must be concluded that the terms $1/K_1K_2[\mathrm{X}]_s^2$ and $1/K_2[\mathrm{X}]_s$ are small even without addition of halide; this means that $K_1$ and $K_2$ must be very large, so that zinc dihalides are only slightly dissociated in the salt melt.

This dissociation can be completely disregarded in the experiments where no Zn salts were added to the salt melt (using only the $10^{-3}$ $m$ solution in the polyphenyl) and where [KX] added exceeds $10^{-2}$ $m$ (30 times the concentration of Zn), and we have then

$$D = \frac{K_\mathrm{D}}{1 + K_3[\mathrm{X}]_s + K_3K_4[\mathrm{X}]_s^2} \qquad (3')$$

By approximation, $K_\mathrm{D}$ is taken equal to $D_{\max}$, the maximum value of $D$, which was generally obtained at the lowest addition of potassium halide (near $10^{-3}$ $m$). Subsequent recalculations of $D_{\max}$ from this value of $K_\mathrm{D}$ and the obtained values of $K_m$ show deviations of less than half the experimental error, which proves the above approximation to be permissible. Graphical methods[15a] then allow determination of $K_3$ and $K_4$, and the values in Table I were found.

TABLE I

| Temp, °C | $K_3$(Cl) | $K_4$(Cl) | $K_3$(Br) |
|---|---|---|---|
| 150 | 11 ± 2 | 8 ± 2 | 2.6 ± 0.5 |
| 165 | 9 ± 2 | 7 ± 2 | 2.3 ± 0.5 |
| 180 | 8 ± 1 | 6 ± 1 | 2.0 ± 0.4 |
| 200 | 7 ± 1 | 4.5 ± 0.9 | 1.8 ± 0.4 |

The constants in Table I were used to calculate $[\mathrm{X}]_s$ from eq 3′ in the experiments where higher zinc concentrations did not allow the assumption $[\mathrm{X}]_s = [\mathrm{KX}]_\mathrm{added}$.

The balance equation for total zinc is

$$(C_\mathrm{Zn})_i w_s = (C_\mathrm{Zn})_s w_s + [\mathrm{ZnX_2}]_o w_o = (C_\mathrm{Zn})_s w_o(q + D) \qquad (4)$$

where $(C_\mathrm{Zn})_i$ is the initial molal concentration of all zinc species, calculated as if all were in the salt phase, $(C_\mathrm{Zn})_s$ is the molal zinc concentration in the salt phase, $w_o$ and $w_s$ are the weights of organic and salt phases, respectively, and $9 = w_s/w_o$.

Hence, the values of

$$[\mathrm{ZnX_2}]_s = (C_\mathrm{Zn})_i \frac{qD}{q + D} \qquad (5)$$

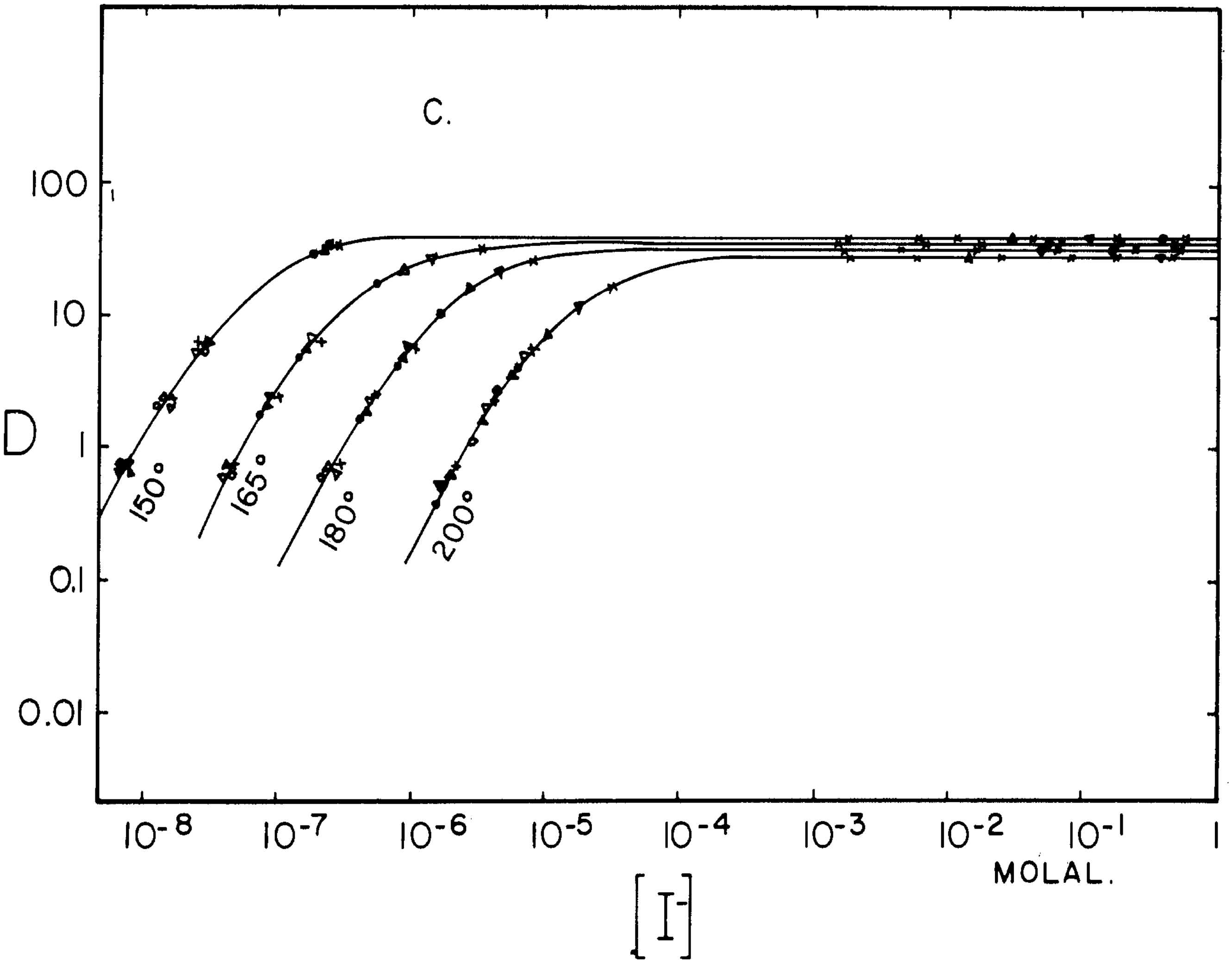

Figure 1c.—Same as Figure 1a, except X = I.

and

$$[\mathrm{ZnX_2}]_\mathrm{s} = [C_\mathrm{Zn}]_\mathrm{i}\frac{qD}{K_\mathrm{D}(q + D)} \qquad (5')$$

can be derived.

The accuracy of the constants $K_3$ and $K_4$ can now be checked by the expression of the balance equations for total halide

$$(C_\mathrm{X})_\mathrm{i}w_\mathrm{s} = 2[\mathrm{ZnX_2}]_\mathrm{o}w_\mathrm{o} + \\ \{[\mathrm{X}]_\mathrm{s} + [\mathrm{ZnX_2}]_\mathrm{s}(2 + 3K_3[\mathrm{X}]_\mathrm{s} + 4K_3K_4[\mathrm{X}]_\mathrm{s}{}^2)\}w_\mathrm{s} \qquad (6)$$

where $(C_\mathrm{X})_\mathrm{i}$ is the initial total concentration of halide in any form, calculated as if all were in the salt phase. Results were found to agree within experimental error.

No evidence was found for the existence of $\mathrm{ZnBr_4}^{2-}$, $\mathrm{ZnI_3}^-$, and $\mathrm{ZnI_4}^{2-}$. Since there is no reason why the coordination number of Zn(II) in the salt melt should change (between 2 and 4) because of the addition of different potassium halides, the nonexistence of $\mathrm{ZnBr_4}^{2-}$, $\mathrm{ZnI_3}^-$, and $\mathrm{ZnI_4}^{2-}$ must be attributed to steric effects. Taking into account the ionic radii of $\mathrm{Zn}^{2+}$, $\mathrm{Cl}^-$, $\mathrm{Br}^{2-}$, $\mathrm{I}^-$, and $\mathrm{NO_3}^-$, it can be seen that such steric effects can only exist if we assume the existence of $\mathrm{ZnX_2(NO_3)_2}^{2-}$ instead of $\mathrm{ZnX_2}$ and $\mathrm{ZnX_3(NO_3)}^{2-}$ instead of $\mathrm{ZnX_3}^-$. Only in this case will $\mathrm{Br}^-$ or $\mathrm{I}^-$ ions be hindered from approaching, respectively, $\mathrm{ZnBr_3(NO_3)}^{2-}$ or $\mathrm{ZnI_2(NO_3)_2}^{2-}$ near enough to establish bonds with the central Zn. This formulation of the $\mathrm{Zn}^-$ complexes which is analogous to previous conclusions regarding Hg(II)[1,15] leaves Zn(II) tetracoordinated in each case and accounts for the fact that $K_3$ and $K_4$ in the case of chloride were found practically equal, as they should be if both constants involve reactions where one nitrate is replaced by one chloride.

Since the dissociation of $\mathrm{ZnX_2}$ was found to be negligible in practically the whole range of measurable amounts of added KX, experimental results in this range cannot provide any data for the calculation of $K_1$ and $K_2$. Results suitable for this purpose are the distribution ratio obtained in the absence of added potassium halide and the experiments where part of the zinc was added as nitrate. In this case, the value of $[\mathrm{X}]_\mathrm{s}$ is so small that the existence of $\mathrm{ZnX_3}$ and $\mathrm{ZnX_4}$ can be neglected. The balance equation for halide is now

$$(C_\mathrm{X})_\mathrm{i}w_\mathrm{s} = 2[\mathrm{ZnX_2}]_\mathrm{o}w_\mathrm{o} + \\ \left\{[\mathrm{X}]_\mathrm{s} + [\mathrm{ZnX_2}]_\mathrm{s}\left(2 + \frac{1}{K_2[\mathrm{X}]_\mathrm{s}}\right)\right\}w_\mathrm{s} \qquad (7)$$

Eliminating $[\mathrm{ZnX_2}]_\mathrm{o}$ and $[\mathrm{ZnX_2}]_\mathrm{s}$ among eq 5, 5′, and 7, we obtain eq 8.

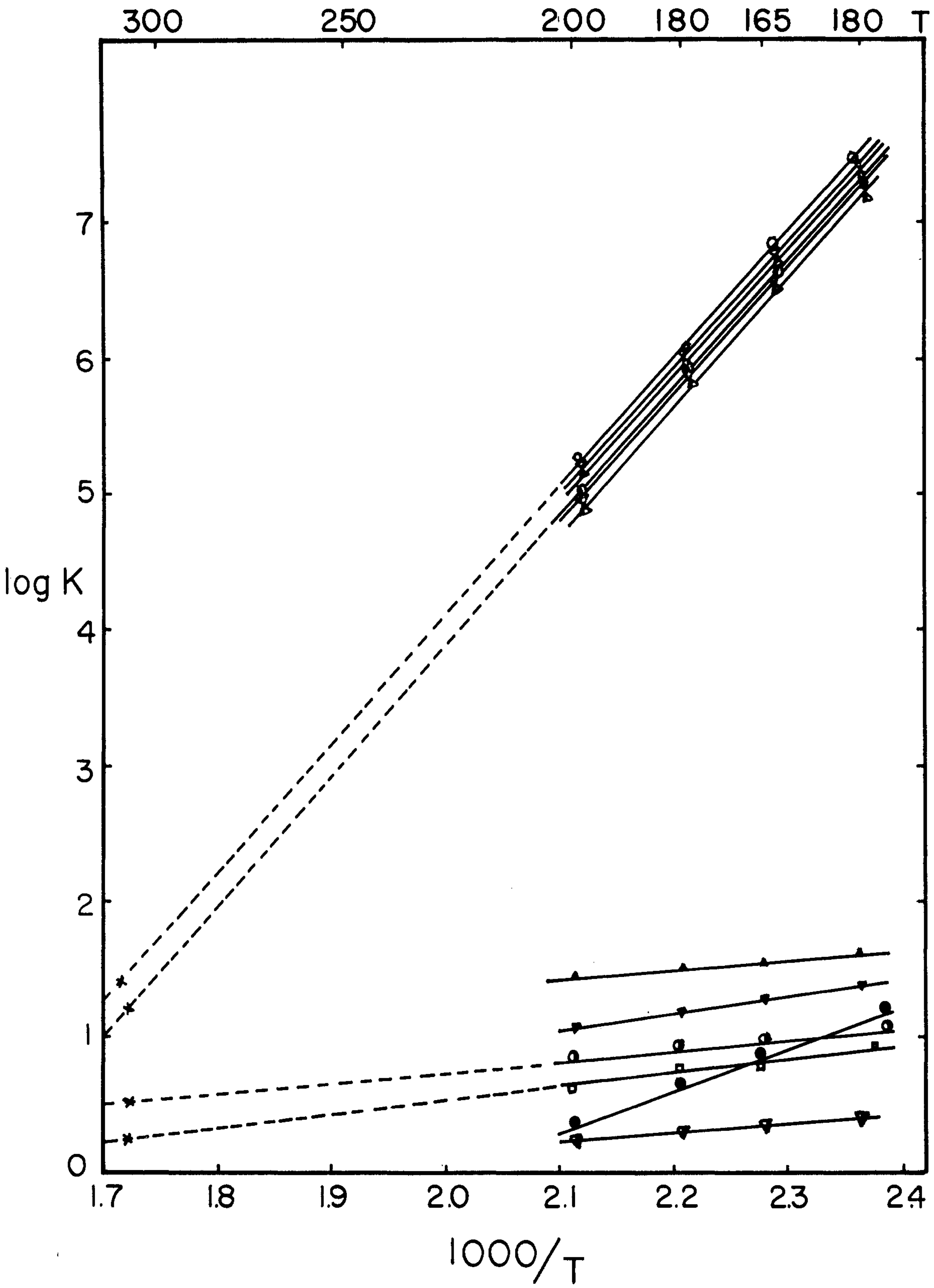

Figure 2.—Values of equilibrium constants as a function of temperature: X = Cl: $K_1$, ○; $K_2$, ◐; $K_3$, ◑; $K_4$, □; $K_D$, ●; X = Br: $K_1$, ▽; $K_2$, ▼; $K_3$, ▼; $K_D$, ▼; X = I: $K_1$, △; $K_2$, ▲; $K_D$, ▲.

$$[X]_s^2 + \left\{2\frac{D(K_D + q)}{K_D(D + q)}(C_{Zn})_i - (C_X)_i\right\}[X]_s + \frac{Dq(C_{Zn})_i}{K_DK_2(D + q)} = 0 \tag{8}$$

By using (interpolated) results where the same $D$ is obtained for different values of $(C_{Zn})_i$ and $(C_X)_i$, since $D_1 = D_2$ implies $[X]_{s1} = [X]_{s2}$, we obtain the equation

$$2\frac{D(K_D + q)}{K_D(D + q)}\{(C_{Zn})_{i1} - (C_{Zn})_{i2}\} - \{(C_X)_{i1} - (C_X)_{i2}\}[X]_s + \frac{Dq}{K_DK_2(D + q)}\{(C_{Zn})_{i1} - (C_{Zn})_{i2}\} = 0 \tag{8'}$$

Together with eq 8, this equation allows determinations 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 $3 \times 10^{-4}$ and $1 \times 10^{-5}$ $m$ 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 $\Delta H$ 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.

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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

*Received August 10, 1966*

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 $\Delta H$ 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).