

Complex Formation between Silver and Iodide Ions in Fused Potassium-Sodium Nitrate. III. Heterogeneous Equilibria Involving Solid and Liquid AgI Solutions

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A thermodynamic calculation method of treating data pertinent to the distribution of AgI between solid or liquid (K,Ag)I and a nitrate melt is described. The heterogeneous equilibrium constants are estimated and the stability constants β_{nm} for the proposed complexes in the nitrate phase are computed and compared to results from previous studies. From this comparison it is concluded that the species Ag^+ , AgI , AgI_2^- , AgI_3^{2-} and $\text{Ag}_2\text{I}_6^{4-}$ are present in the nitrate melt, whereas clearcut evidence for AgI_4^{3-} cannot be established.

The complex formation between Ag^+ and I^- in liquid equimolar (K,Na) NO_3 has recently been studied at this laboratory with different experimental methods.¹⁻³ One aim of these investigations is to compare the results concerning the iodide-rich complexes obtained with different experimental techniques in order to see whether or not the various kinds of experimental data can be satisfactorily described by one single model of the system.

Unfortunately, the conventional solubility method cannot be utilized in the whole concentration range of interest, since the solid silver iodide phase undergoes a phase transition to a reddish liquid at high iodide concentrations in the nitrate melt.¹ This phase transition has been treated in detail in a previous paper.³ The liquid iodide phase can be formulated as (K,Ag)I(l) and the solid phase as (K,Ag)I(s). As pointed out earlier,³ the solute in the solid solution cannot be proved to be exclusively either KI or NaI. It is obvious, however, that the same results would be obtained if NaI were dissolved to some extent in the solid, and there would be no difference in the numerical calculations (*vide infra*).

In this paper a simple thermodynamic calculation routine will be described and applied to the distribution equilibria between (K,Ag)I(s) or (K,Ag)I(l) and the nitrate melt in order to yield information on the nature and stability

of the complex species in the nitrate phase. The method may be regarded as an extension of the well established solubility method⁴ to heterogeneous equilibria involving non-ideal solid and liquid solutions, with both solute and solvent taking part in the complex formation equilibria under study.

EXPERIMENTAL

Chemicals, apparatus and analyses have been described elsewhere.³

Procedure. Weighed amounts of equimolar (K,Na)I and AgI were added to 50.00 g of equimolar (K,Na)NO₃. The distribution of silver and iodide between the two phases was determined in three series of measurements with different amounts of AgI in the systems, namely: 0.700 g AgI (series A), 2.200 g AgI (series B), and 4.50 g AgI (series C). For all three series the total concentrations of silver and iodide in the nitrate melt were determined. The composition of the iodide phase was determined for systems in series C only. The experimental technique was the same as described previously.³

CALCULATIONS

The following symbols are used:

C_{Ag} = total concentration of Ag⁺-ion in the nitrate melt.

C_{I} = total concentration of I⁻-ion in the nitrate melt.

[A] = denotes the concentration in the nitrate phase of species "A".

\bar{n} = $(C_{\text{I}} - [\text{I}^-])C_{\text{Ag}}^{-1}$, the ligand number.

β_{nm} = $[\text{Ag}_m\text{I}_n^{(n-m)-}][\text{Ag}^+]^{-m}[\text{I}^-]^{-n}$

K_n = $[\text{AgI}_n^{(n-1)-}][\text{AgI}_{(n-1)}^{(n-2)-}]^{-1}[\text{I}^-]^{-1}$

x_i = mol fraction of component "i" in the iodide phase.

a_i = activity of component "i" in the iodide phase.

f_i = $a_i x_i^{-1}$

x_i, a_i, f_i etc. denote quantities valid for the solid iodide phase.

x_i'', a_i'', f_i'' etc. denote quantities valid for the liquid iodide phase.

The indices 1 and 2 are used for AgI and KI, respectively.

R = $([\text{K}^+][\text{I}^-])^{-1}$

R_0 = value of R in a system where $x_2' = 0$

$R^*, []^*, ()^*$ etc. denote the values of the quantities in question at the point of phase transition.

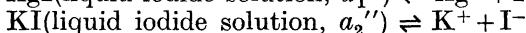
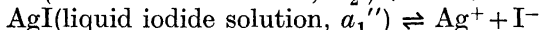
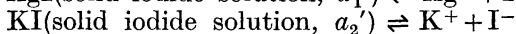
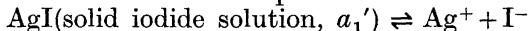
Sternberg and coworkers⁵ have performed emf measurements in liquid AgI-KI mixtures in the temperature range 400–680°C⁶ and have found considerable deviations from ideality in such systems. Nevertheless, the concentration product $[\text{Ag}^+][\text{I}^-]$ in a nitrate melt in equilibrium with a liquid AgI-KI phase may be calculated for each C_{I} . The evaluation of the stability constants for the complex species in the nitrate melt may then be extended to the concentration range $C_{\text{I}} \geq 0.5$ mol kg⁻¹. The calculation routine outlined below requires the following conditions to be met:

i. The true equilibrium state must be reached. For the distribution of a solute between a liquid and a solid solution it is often difficult to ascertain that this condition has been fulfilled. In the present case, however, there is no doubt that the figures of Table 1 refer to a true equilibrium state. Obviously the high temperature and the structure of α -AgI strongly promote the equilibration.

ii. The total composition of each phase must be known in the entire concentration range under study, since the calculations involve an integration of functions of the composition variables.

iii. The activity coefficients for K^+ and the solute species in the nitrate melt should be constant in the pertinent concentration range. This condition, originating from the definitions of the equilibrium constants (*vide infra*), has been discussed in a recent paper.²

Consider the following heterogeneous equilibria, where the species of the right hand members are present in the nitrate melt:



with the equilibrium constants

$$K_1' = [\text{Ag}^+][\text{I}^-]/a_1' \quad (1)$$

$$K_2' = [\text{K}^+][\text{I}^-]/a_2' \quad (2)$$

$$K_1'' = [\text{Ag}^+][\text{I}^-]/a_1'' \quad (3)$$

$$K_2'' = [\text{K}^+][\text{I}^-]/a_2'' \quad (4)$$

In eqn. (1) K_1' is identical with the conventional solubility product, $K_{s,0}$, determined by Elding and Leden,¹ since $a_1' = 1$ in pure α -AgI, which is taken as the standard state for AgI in the solid solution. From the Gibbs-Duhem equation we have

$$d \ln a_1' = -(x_2'/x_1') d \ln a_2' \quad (5)$$

Eqn. (2) yields

$$d \ln a_2' = d \ln [\text{K}^+][\text{I}^-]$$

and hence

$$\ln a_{1j}' = \int_{\ln R_0}^{\ln R_j} (x_2'/x_1') d \ln R \quad (6)$$

The index j is used to denote corresponding values of different quantities referring to the same actual system. From eqns. (1) and (6) we obtain

$$([\text{Ag}^+][\text{I}^-])_j = K_1' \exp \left[\int_{\ln R_0}^{\ln R_j} (x_2'/x_1') d \ln R \right] \quad (7)$$

Eqn. (7) may be used to evaluate $([\text{Ag}^+][\text{I}^-])$ in the region $C_I \leq C_I^*$. For systems with $C_I \geq C_I^*$ the following expression, analogous to eqn. (6), is valid

$$\ln (a_1'')_j - \ln (a_1'')^* = \int_{\ln R^*}^{\ln R_j} (x_2''/x_1'') d \ln R \quad (8)$$

Taking the hypothetical pure liquid AgI at 280°C as the standard state where $a_1'' = 1$, we define an activity scale for the liquid iodide phase in accordance

with normal conventions. The choice of standard state for the liquid iodide solution is, however, of no importance for the determination of the product $[\text{Ag}^+][\text{I}^-]$. From eqns. (3) and (8) we have

$$([\text{Ag}^+][\text{I}^-])_j = K_1''(a_1'')^* \exp \left[\int_{\ln R^*}^{\ln R_j} (x_2''/x_1'') \, d \ln R \right] \quad (9)$$

At the point of phase transition, $([\text{Ag}^+][\text{I}^-])^*$ can be expressed by means of both eqns. (1) and (3), and hence

$$K_1''(a_1'')^* = K_1'(a_1')^* \quad (10)$$

Eqn. (6) yields

$$(a_1')^* = \exp \left[\int_{\ln R_0}^{\ln R^*} (x_2'/x_1') \, d \ln R \right] \quad (11)$$

By combination of eqns. (9), (10), and (11) we obtain

$$([\text{Ag}^+][\text{I}^-])_j = K_1' \exp \left[\int_{\ln R_0}^{\ln R^*} (x_2'/x_1') \, d \ln R + \int_{\ln R^*}^{\ln R_j} (x_2''/x_1'') \, d \ln R \right]$$

which finally can be rewritten in the more general form

$$([\text{Ag}^+][\text{I}^-])_j = K_1' \exp \left[\int_{\ln R_0}^{\ln R_j} (x_2/x_1) \, d \ln R \right] \quad (12)$$

This expression is identical with eqn. (7). Consequently, the integration may be performed continuously, irrespective of the phase transition, even if a graph of x_2/x_1 vs. $\ln R$ displays a discontinuity at the transition point (*cf.* Fig. 1). Furthermore, the derivation of eqn. (12) is rather general and will apply to any phase transition. Hence, regarding the solid-liquid equilibria, the calculation method is not restricted to cases when a so called "continuous range of solid solution" is formed, but any phase transformation in the solid

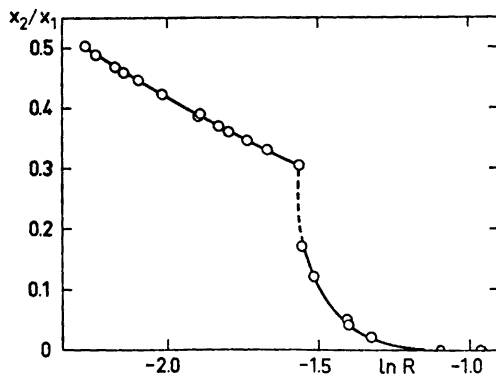


Fig. 1. A plot of x_2/x_1 vs. $\ln R$, calculated according to alt. I. The integration is performed along the smooth curve.

may occur as long as there is no change in the components of the solid solution and the proper values of x_2 and R are known.

For $R_i \leq R^*$ the exponential factor in the right hand member of eqn. (12) is proportional to a_1'' and may be written $\lambda_1 a_1''$. This quantity is directly obtained from the integration process and is tabulated in Table 1. A simple calculation gives $\lambda_1 = K_1''/K_1'$.

Table 1. Experimental data and calculated quantities (alternative I). Interpolated values are denoted i. Data above the line refer to systems (K,Ag)I(s)-nitrate melt; those below the line refer to (K,Ag)I(l)-nitrate melt.

Series	C_I mol kg ⁻¹	$C_{Ag} \times 10^2$ mol kg ⁻¹	x_1	a_1' or $\lambda_1 a_1''$	a_1''	f_1	a_2	f_2	$\frac{[Ag^+][I^-] \times 10^{10}}{(\text{mol kg}^{-1})^2}$	\bar{n}	$\frac{[I^-]}{\text{mol kg}^{-1}}$
C	0.492	0.789	1.00	1		1	0		6.20	3.20	0.467
C	0.561	0.937	1.00	1		1	0		6.20	3.25	0.531
C	0.715	1.672	0.98	0.9984		1.02	0.0067	0.3	6.19	3.32	0.659
C	0.773	1.994	0.96	0.9962		1.04	0.0072	0.18	6.18	3.34	0.706
C	0.779	2.065	0.95	0.9960		1.05	0.0073	0.14	6.18	3.35	0.710
C	0.881	2.690	0.89	0.9879		1.11	0.0081	0.07	6.12	3.37	0.790
A	0.908	2.819							6.10 i	3.38	0.813
C	0.923	2.969	0.85	0.9822		1.15	0.0085	0.06	6.09	3.38	0.823
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C	0.936	3.00	0.767	0.9806	0.49	0.63	0.39	1.68	6.08	3.39	0.834
A	0.942	3.01							6.07 i	3.39	0.840
B	0.961	3.23							6.04 i	3.39	0.851
B	0.998	3.43							5.97 i	3.40	0.881
A	1.046	3.78							5.88 i	3.41	0.917
C	1.048	3.74	0.752	0.9477	0.47	0.62	0.44	1.76	5.87	3.41	0.920
B	1.099	4.19							5.79 i	3.42	0.956
C	1.132	4.56	0.742	0.9271	0.46	0.62	0.46	1.80	5.75	3.42	0.976
A	1.139	4.47							5.73 i	3.43	0.986
C	1.198	4.79	0.735	0.9070	0.45	0.61	0.49	1.87	5.62	3.44	1.033
B	1.212	4.96							5.60 i	3.44	1.041
C	1.241	5.28	0.730	0.8974	0.44	0.61	0.51	1.89	5.56	3.44	1.059
A	1.255	5.42							5.55 i	3.44	1.068
B	1.310	5.94							5.47 i	3.45	1.105
C	1.329	6.03	0.720	0.8763	0.43	0.60	0.54	1.94	5.43	3.45	1.121
C	1.333	5.96	0.722	0.8742	0.43	0.60	0.55	1.96	5.42	3.45	1.127
B	1.404	6.72							5.33 i	3.46	1.171
C	1.533	8.10	0.703	0.8321	0.41	0.59	0.62	2.08	5.16	3.46	1.253
B	1.572	8.32							5.10 i	3.46	1.284
C	1.661	9.27	0.691	0.8047	0.40	0.58	0.67	2.16	4.99	3.47	1.339
B	1.715	10.01							4.93 i	3.47	1.368
C	1.755	10.39	0.685	0.7874	0.39	0.57	0.70	2.22	4.88	3.47	1.394
C	1.817	11.10	0.681	0.7761	0.38	0.56	0.72	2.26	4.81	3.48	1.431
B	1.856	11.77							4.78 i	3.48	1.446
C	1.954	12.93	0.672	0.7534	0.37	0.56	0.77	2.34	4.67	3.48	1.504
B ^a	1.995	13.36							4.62 i	3.48	1.530
C ^a	2.013	13.30	0.665	0.7408	0.37	0.55	0.79	2.37	4.59	3.48	1.550

^a Three-phase system (K,Ag)I(l)–(K,Na)I(s)-nitrate melt.

The activity of KI in the solid iodide solution might in principle be obtained by integrating some function based on the Gibbs–Duhem relation. Since no such function can be extrapolated to $x_2' = 0$ with an acceptable accuracy, another method has been tried. From the limiting value $\lim_{x_1' \rightarrow 0} f_2' = 1$ we obtain

$$\lim_{x_2' \rightarrow 0} [x_2' / ([K^+][I^-])] = K_2'^{-1} \quad (13)$$

Hence, K_2' may be estimated from a graphical extrapolation according to eqn. (13) and the activities a_2' can then be calculated from eqn. (2).

Similar methods may be utilized to obtain estimates of K_1'' and K_2'' , although the extrapolation range is considerably larger in these cases. The working equations are

$$\lim_{x_1'' \rightarrow 1} [x_1'' / ([Ag^+][I^-])] = K_1''^{-1} \quad (14)$$

$$\lim_{x_2'' \rightarrow 0} [x_2'' / ([K^+][I^-])] = K_2''^{-1} \quad (15)$$

The activities a_1'' and a_2'' are computed from eqns. (3) and (4).

RESULTS

In Table 1 the results from all three series of measurements have been collected. An inspection of the experimental data reveals that series with different amounts of AgI phase give the same corresponding values of C_I and C_{Ag} within the limits of error. This means, that deviations from the original K–Na balance (1:1) in the nitrate melt, originating from the potassium iodide migration into the AgI phase, are so small that they do not cause any observable changes in the relations between C_I and C_{Ag} .

The product $[Ag^+][I^-]$ was calculated from the data of series C by means of graphical integration according to eqn. (12). The value of K_1' was taken from Ref. 1. Recalling that systems of series C contain 0.2686 mol KNO_3 , 0.01917 mol AgI and 50.00 g $(K,Na)NO_3$, we obtain

$$R^{-1} = \left[\frac{0.2686}{0.0500} \text{ mol kg}^{-1} + \frac{C_I}{2} - \frac{x_2}{x_1} \left(\frac{0.01917}{0.0500} \text{ mol kg}^{-1} - C_{Ag} \right) \right] (C_I - \bar{n}C_{Ag})$$

With $\bar{n} = 3$ as a starting value, a first set of products $([Ag^+][I^-])_j$ was calculated and used to evaluate a set of stability constants yielding better values of \bar{n} and $[I^-]$. The calculations were iterated until the variables remained unaltered. Fig. 1 gives the graph of x_2/x_1 , versus the final values of $\ln R$.

For the determination of the stability constants the $(C_I; C_{Ag})$ data from series A and B were incorporated into the experimental material utilized. The corresponding values of $[Ag^+][I^-]$ were obtained by graphical interpolation between the values from series C.

From previous studies¹⁻³ it may be concluded that the concentrations of the species AgI_3^{2-} , AgI_4^{3-} , and $Ag_2I_6^{4-}$ or a combination of two of them give the

main contributions to C_{Ag} in the pertinent range of C_{I} . Since AgI_2^- is not quite negligible at the smallest C_{I} , a small correction has been applied, *viz.* $C_{\text{corr}} = C_{\text{Ag}} - [\text{AgI}_2^-]$. The correction term was calculated from the value of β_{21} of Ref. 1. Hence

$$C_{\text{corr}}[\text{Ag}^+]^{-1} = \beta_{31}[\text{I}^-]^3 + \beta_{41}[\text{I}^-]^4 + 2\beta_{62}[\text{Ag}^+][\text{I}^-]^6 \quad (16)$$

The stability constants were evaluated from eqn. (16) with standard graphical and least-squares methods.

It appeared that the experimental results could not be satisfactorily described by a model with only four mononuclear complexes. Hence, the last term of the right hand member of eqn. (16) cannot be omitted. Since the terms are all of a rather high order in $[\text{I}^-]$, it is, on the other hand, difficult to judge whether the AgI_4^{3-} term should be discarded or not. The calculations were performed both on the assumption that AgI_3^{2-} , AgI_4^{3-} and $\text{Ag}_2\text{I}_6^{4-}$ are present in significant amounts (alternative I) and on the assumption that AgI_3^{2-} and $\text{Ag}_2\text{I}_6^{4-}$ are the only prevailing species (alternative II). The calculated stability constants are found in Table 3. In Table 1 the ligand numbers *etc.* for all the experimental material (according to alternative I) are given. The thermodynamic quantities pertaining to the iodide phase and the distribution equilibria (*vide* Table 1) also refer to alternative I, but the changes in the numerical values of these quantities would be very small if they were derived according to alternative II instead.

When the concentrations $[\text{Ag}^+]$, $[\text{K}^+]$, and $[\text{I}^-]$ had been determined, the constants K_2' , K_1'' , and K_2'' were estimated by extrapolations according to

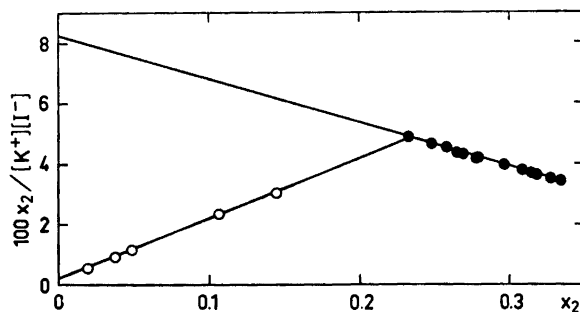


Fig. 2. Estimation of K_2' and K_2'' by extrapolation according to eqns. (13) and (15). Notations: $(\text{K,Ag})\text{I}(\text{s})$ (O); $(\text{K,Ag})\text{I}(\text{l})$ (●).

eqns. (13), (14), and (15). Fig. 2 gives an example of this extrapolation procedure. The results are collected in Table 2, where the cation exchange equilibrium constants $K_{12}' = K_1'/K_2'$ and $K_{12}'' = K_1''/K_2''$ have also been included. The standard free energy changes for the corresponding exchange reactions are calculated according to $\Delta G^\circ = -RT \ln K_{12}$ and the results are included in Table 2.

Table 2. The estimated heterogeneous equilibrium constants and free energy changes, K_1' from Ref. 1. The equilibrium constants for reactions I – IV are expressed in $(\text{mol kg}^{-1})^2$.

Equilibrium reaction	Equilibrium constant		ΔG° (kJ mol ⁻¹)
	Sym- bol	Value	
I. AgI(solid iodide solution) \rightleftharpoons Ag ⁺ + I ⁻	K_1'	$(6.2 \pm 0.1) \times 10^{-10}$	
II. AgI(liquid iodide solution) \rightleftharpoons Ag ⁺ + I ⁻	K_1''	$(1.25 \pm 0.08) \times 10^{-9}$	
III. KI(solid iodide solution) \rightleftharpoons K ⁺ + I ⁻	K_2'	$(5.6 \pm 0.6) \times 10^2$	
IV. KI(liquid iodide solution) \rightleftharpoons K ⁺ + I ⁻	K_2''	12.2 ± 0.4	
V. AgI(solid iodide solution + K ⁺ \rightleftharpoons KI(solid iodide solution) + Ag ⁺	K_{12}'	1.1×10^{-12}	127
VI. AgI(liquid iodide solution + K ⁺ \rightleftharpoons KI(liquid iodide solution) + Ag ⁺	K_{12}''	1.0×10^{-10}	106

DISCUSSION

Heterogeneous equilibria. The equilibrium constants of Tables 2 and 3 give a good description of the two-phase systems in the composition range investigated. The estimates of K_1'' and K_2'' , and hence a_1'' and a_2'' , may of course be subject to considerably larger errors than those quoted in Table 2, which are three standard deviations, estimated from the linear regression. No theoretical argument can justify a linear extrapolation to $x_2 = 0$ according to eqns.

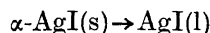
Table 3. Sets of stability constants in nitrate melts at 280°C.

	$\frac{\beta_{11} \times 10^{-3}}{(\text{mol kg}^{-1})^{-1}}$	$\frac{\beta_{21} \times 10^{-6}}{(\text{mol kg}^{-1})^{-2}}$	$\frac{\beta_{31} \times 10^{-7}}{(\text{mol kg}^{-1})^{-3}}$	$\frac{\beta_{41} \times 10^{-7}}{(\text{mol kg}^{-1})^{-4}}$	$\frac{\beta_{62} \times 10^{-16}}{(\text{mol kg}^{-1})^{-7}}$
Solubility data, Ref. 1	4.2 ± 0.3	3.6 ± 0.2	2.9 ± 0.3	—	—
This work, alt. I	—	—	2.4 ± 0.3	3.6 ± 0.7	1.6 ± 0.7
This work, alt. II	—	—	3.8 ± 0.6	—	3.1 ± 0.6
Emf data, Ref. 2: unsaturated melts	—	3.1 ± 0.3	2.27 ± 0.06	0.28 ± 0.06	1.9 ± 0.7
melts saturated with (K,Na)I, A ^a	—	<i>3.1</i>	<i>2.27</i>	<i>1.6</i>	<i>1.9</i>
B ^a	—	<i>3.1</i>	<i>2.27</i>	<i>0.28</i>	<i>0.64</i>
Probable values	4.2	3.1	2.3	≈ 1	1.9

^a Set of constants that describes the experimental data. The values in italics are taken from the emf data in unsaturated melts; the fourth is calculated from the data on saturated melts.

(13), (14), and (15), although the points fall on a straight line within the range of the experiments. A comparison with thermodynamic literature data can be made, however, in the following way.

The proportionality factor $\lambda_1 = K_1''/K_1'$ is related to the standard free energy change, ΔG° , for the process



at 280°C by the equation $\Delta G^\circ = RT \ln \lambda_1$. Hence an estimate of λ_1 may be obtained from an approximate value of ΔG° . Recently Hamer, Malmberg and Rubin⁷ published a set of calculated emf's for formation cells based on a critical compilation of thermodynamic data up to 1500°C. From their results the value $\Delta G^\circ = (3 \pm 1) \times 10^3 \text{ J mol}^{-1}$, valid at 280°C, may be estimated, yielding $\lambda_1 = 2.0 \pm 0.4$. From the constants in Table 2 we obtain $\lambda_1 = 2.0 \pm 0.2$. This agreement indicates that the linear extrapolations give estimates of the constants that may be better than just to the correct order of magnitude. Hence, we can regard the ΔG° values of Table 2 with some confidence, and it may be of interest to note that the liquid-liquid cation exchange reaction is associated with quite a large ΔG° -value, only 20 % smaller than that for the solid-liquid reaction.

In the solid (K,Ag)I solution the activity factor f_2' decreases very rapidly from the limiting value 1 to rather small values near the phase transition point (*vide* Table 1). These large deviations from ideality are in good agreement with the picture of the possible structure of the solid solution outlined in a previous paper.³ This pronounced non-ideal behaviour should be expected if the K^+ ions preferentially occupy the largest cation sites and simultaneously cause a considerable distortion of the iodide lattice.

The complex formation equilibria in the nitrate melt. Table 3 contains sets of over-all stability constants, obtained from different experimental methods. From a comparison of the results of this work with previous findings, it is evident that alternative II must be discarded, since the values of β_{31} and β_{62} both markedly disagree with results from conventional solubility¹ and emf² measurements.

In the set of constants according to alternative I, β_{31} is in good agreement with the values from both solubility and emf data, and β_{62} agrees well with the value obtained from emf measurements in unsaturated melts. The discrepancy with previous results is large for β_{41} . It has been pointed out before,² however, that the rather small value of β_{41} from emf measurements in unsaturated melts might emerge from systematic errors which might be caused by liquid junction potentials. This assumption was to some degree qualitatively supported by the ligand solubility data.³ Assuming reasonable values of β_{31} and β_{62} , the emf measurements in melts saturated with (K,Na)I also favour a model that includes a fourth mononuclear complex with β_{41} in the order of magnitude of $10^7 (\text{mol kg}^{-1})^{-4}$ (*vide* Table 3).

On the other hand, variations in activity coefficients of the solute species may be of importance at large C_I and C_{Ag} . Remembering that β_{41} is obtained more or less as a correction term in the calculations, we must conclude that the variations of the β_{41} values in Table 3 are too large to permit us to decide for certain whether or not a fourth mononuclear complex is really formed.

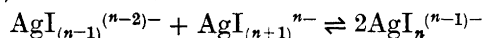
To sum up, the presence of three mononuclear species and the dinuclear complex $\text{Ag}_2\text{I}_6^{4-}$ has been proved by different experimental methods. The most probable values of the corresponding stability constants are given in Table 3. In addition, effects that might emerge from the presence of AgI_4^{3-} have been observed, but it follows from the magnitude of the equilibrium constants that the concentration of AgI_4^{3-} will never become large enough

Table 4. The stepwise stability constants and quotients.

Medium	Quantity	$n=1$	$n=2$	$n=3$	$n=4$
H ₂ O, 18°C, $I=0^{11}$	K_n/M^{-1}	3.8×10^6	1.4×10^5	87	0.27
H ₂ O, 25°C, $I=4 \text{ M}(\text{NaClO}_4)^9$	K_n/M^{-1}	(10^8)	(10^3)	600	4
(K,Na)NO ₃ (l), 280°C	$K_n/(\text{mol kg}^{-1})^{-1}$	4200	740	7	≈ 0.5
H ₂ O, 18°C, $I=0^{11}$	$K_n/K_{(n+1)}$	27	1600	320	
H ₂ O, 25°C, $I=4 \text{ M}(\text{NaClO}_4)^9$	$K_n/K_{(n+1)}$	(10^9)	(1.7)	150	
(K,Na)NO ₃ (l), 280°C	$K_n/K_{(n+1)}$	5.7	100	≈ 10	

to be measured with any accuracy. A reasonable estimate of β_{41} would be $10^7 (\text{mol kg}^{-1})^{-4}$.

The relative stability of the different complexes may be judged from the quotients $K_n/K_{(n+1)}$, *i.e.* the equilibrium constants for the reactions



Since $K_n/K_{(n+1)}$ is a dimensionless quantity, a direct comparison may be made between, *e.g.*, aqueous solutions and molten salt media. The stepwise stability constants K_n and the quotients are given in Table 4. The second complex is evidently the most stable one in the nitrate melt. In aqueous solution, this behaviour is in fact a rather general feature of Ag(I)-halide complex formation.

The abnormally high stability of AgI reported by Leden ^{8,9} is evidently erroneous. His much too high value of β_{11} was caused by too primitive experimental facilities.¹⁰ Lieser ¹¹ later found a sequence of stabilities in aqueous solution which is in good agreement with the general pattern (*cf.* Table 4). The values of K_3 and K_4 , and hence K_3/K_4 , obtained by Lieser, must be looked upon with some scepticism, however, since Lieser did not use a constant ionic medium but tried to estimate the activity coefficients for the solute species. The stability constants for the complexes richest in iodide may therefore be subject to considerable errors. A far more reliable value of K_3/K_4 can be calculated from the data of Leden ^{8,9} (*cf.* Table 4).

From the discussion above it is evident that no definite support can be found for the view ¹² that only three halide ions may be coordinated to silver(I) in nitrate melts. In fact, $K_3/K_4 \approx 10$ is a rather normal value for complexes formed stepwise.

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