

evidence, but this evidence has gained further support by the recent work of Bayes<sup>11</sup> on the photolysis of carbon suboxide.

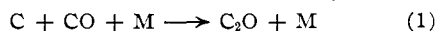
**Conclusions.**—The experimental results may be summarized by

(a)  $C_3O_2$  reacts extremely fast with oxygen atoms with CO as a chief product. To a small fraction, however,  $C_2O$  and  $CO_2$  are formed.

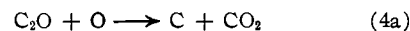
(b) The radical  $C_2O$  reacts in two alternative ways with oxygen atoms. The faster reaction yields C and  $CO_2$ , whereas  $2CO$ , one in an excited triplet state, are formed to a smaller extent.

(c) Ozone reacts with  $C_3O_2$  in a different way than oxygen atoms. The reaction with ozone is extremely slow.

These results strongly support the suboxide mechanism<sup>8</sup> proposed for the radiolysis of carbon-oxygen systems. They also show that, of the two chain reactions 1, 4a; and 2, 5b, only the first



(11) K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).



can occur because of the very fast reaction of  $C_2O$  with O-atoms.

In irradiated CO, however, reaction 2 may also occur due to the high concentration of CO. A chain reaction will not take place in this case since the terminating reaction 3 dominates.

The chemical kinetics of the carbon suboxide reactions are of great importance not only for the radiolytic but also photochemical and combustion processes in carbon-oxygen systems. They must be taken into consideration in any study of the chemistry of planetary atmospheres containing substantial amounts of carbon monoxide and carbon dioxide.

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## The Evaluation of Thermodynamic Association Constants in Solutions with an Application to Molten Salt Solutions

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The evaluation of thermodynamic association constants in solution is discussed and is applied to molten salt systems. The calculated association constants  $K_1$ ,  $K_2$  and  $K_{12}$  for the formation of the species  $AgCl$ ,  $AgCl_2^-$  and  $Ag_2Cl^+$ , respectively, in molten  $KNO_3$  at  $385^\circ$  are  $460 \pm 15$ ,  $169 \pm 20$  and  $20 \pm 10 \left(\frac{\text{moles}}{\text{mole } KNO_3}\right)^{-1}$ . A recalculation of the association constants,  $K_1$ , for the species  $CdCl^+$  and  $PbCl^+$  from cryoscopic, polarographic and from solubility data in nitrate melts indicates that the greater part of the very large discrepancies in the published values of  $K_1$  is a result of the incorrect analysis of the data.

### Introduction

In this paper, the determination of thermodynamic association (formation) constants in solution is discussed. Although our methods of calculation are here applied to molten salt solutions only, they may be used with modifications for other types of solutions.

To be able to test theories of association a reliable determination of association constants is required. Many of the methods of evaluation used<sup>4-7</sup> often lead to uncertainties in the values of the association constants which are greater than the uncertainties warranted by the precision of the data, particularly when a single method is used for different systems without regard for the relative

magnitude of the association constants. It is the purpose of this paper to discuss methods which eliminate the uncertainties caused merely by the imprecise manipulation of data. We shall discuss the evaluation of formation constants for associations of  $Ag^+$  and  $Cl^-$  in molten  $KNO_3$  at  $385^\circ$  from our published data<sup>8</sup> supplemented with new data. As a further illustration we will show that the greater part of the very large apparent inconsistency in the published values for association constants for the formation of  $CdCl^+$  and  $PbCl^+$  in molten nitrates<sup>9-11</sup> may be removed by a new and improved analysis of the data.

No single method of calculation of association constants is possible, since each set of data or type of measurement requires a somewhat different analysis. We do, however, include the following guiding principles in our analysis which are not all included in the most common methods of calculation used.

A. The extrapolation function used in the evaluation of the association constants, the values of

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(4) I. Leden, *Z. physik Chem.*, **A188**, 160 (1941).

(5) S. Fronaeus, *Acta. Chem. Scand.*, **4**, 72 (1950).

(6) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

(7) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Company, New York, N. Y., 1961.

(8) J. Braunstein and M. Blander, *J. Phys. Chem.*, **64**, 10 (1960).

(9) E. R. Van Artsdalen, *ibid.*, **60**, 172 (1956).

(10) J. H. Christie and R. A. Osteryoung, *J. Am. Chem. Soc.*, **82**, 1841 (1960).

(11) F. R. Duke and M. L. Iverson, *J. Phys. Chem.*, **62**, 417 (1958).

which are calculated from the data, is defined so as to have a reasonably constant probable error. By doing this, simple statistical or graphical procedures can be used validly. The methods of Leden,<sup>4</sup> Fronaeus<sup>5</sup> and of DeFord and Hume,<sup>6</sup> by contrast, utilize functions in which the probable error increases with decreasing concentration of ligand and hence a simple unweighted extrapolation is not correct.

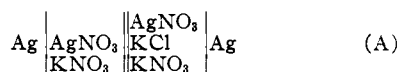
B. Whenever possible, the functions evaluated from the data are expressed as a power series in the *stoichiometric concentrations* of the solutes. This eliminates the need for successive approximations and makes the calculations simple and direct.

C. The formation constants are evaluated at infinite dilution of all solutes so as to be thermodynamic association constants.

### Experimental

Previous measurements of the activity coefficients of  $\text{AgNO}_3$  in the presence of  $\text{Cl}^-$  in  $\text{KNO}_3$  at  $385^\circ$  at four fixed concentrations of  $\text{AgNO}_3$  were supplemented by new measurements to improve the precision of the calculated association constants.

Electromotive force measurements of the cell at  $385^\circ$



have been described previously.<sup>8</sup> Additional data were obtained at this temperature. The experimental procedure was the same as described previously<sup>8,12,13</sup> except that the temperature was measured to  $\pm 1^\circ$  with a chromel-alumel thermocouple calibrated at the freezing points of Bi, Cd and Zn.

The difference  $\Delta E$  between the e.m.f. of the cell (A) and the e.m.f. of this cell in the absence of  $\text{KCl}$  is given in Table I at mole ratios of  $\text{AgNO}_3$  ( $R_{\text{AgNO}_3}$ ) equal to  $0.776 \times 10^{-3}$ ,  $1.49 \times 10^{-3}$  and  $2.79 \times 10^{-3}$ .

The mole ratio,  $R_i$ , is defined as  $\frac{n_i}{n_{\text{KNO}_3}}$  where  $n_i$  is the number of moles of the component  $i$ . The cation fraction of  $\text{Ag}^+$  is  $N_{\text{Ag}^+} = \frac{n_{\text{Ag}^+}}{n_{\text{Ag}^+} + n_{\text{K}^+}}$  and the anion fraction of  $\text{Cl}^-$  is

$N_{\text{Cl}^-} = \frac{n_{\text{Cl}^-}}{n_{\text{Cl}^-} + n_{\text{NO}_3^-}}$ . The ratios  $\frac{R_{\text{AgNO}_3}}{N_{\text{Ag}^+}} = \frac{R_{\text{KCl}}}{N_{\text{Cl}^-}} = (1 + \frac{R_{\text{AgNO}_3}}{R_{\text{AgNO}_3} + R_{\text{KCl}}})$  are close to unity in dilute solutions of  $\text{Ag}^+$  and  $\text{Cl}^-$ . The activity coefficients of  $\text{AgNO}_3$  are defined by the equations  $\mu_{\text{AgNO}_3} = \mu_{\text{AgNO}_3}^0 + RT \ln \gamma_{\text{AgNO}_3} N_{\text{Ag}^+} N_{\text{NO}_3^-} = RT \ln \gamma_{\text{AgNO}_3} R_{\text{AgNO}_3}$ . In dilute solutions  $\gamma_{\text{AgNO}_3} \cong \gamma_{\text{AgNO}_3}^0$  and consequently at low concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$

$$\frac{F\Delta E}{2.303RT} \cong \log \gamma_{\text{AgNO}_3} \cong \log \gamma_{\text{AgNO}_3}^0$$

where the standard states are chosen such that the activity coefficients are unity at infinite dilution of all solutes in  $\text{KNO}_3$ . In the equations that follow we shall not distinguish between  $\gamma$  and  $\gamma^0$ .

**The Method of Calculations.**—If one has a dilute solution of the solutes AD and BC in a molten salt BD, or in a "blanketing" electrolyte, then the total stoichiometric concentration of the  $\text{A}^+$  and  $\text{C}^-$  ions in a system in which associations of the  $\text{A}^+$  and  $\text{C}^-$  ions,  $\text{A}^+ + \text{C}^- \rightleftharpoons \text{AC}$ ,  $\text{A}^+ + \text{AC} \rightleftharpoons \text{A}_2\text{C}^+$ ,  $\text{AC} + \text{C}^- \rightleftharpoons \text{AC}_2^-$ , etc., may occur is

$$R_{\text{AD}} = R'_A + R'_{\text{AC}} + R'_{\text{A}_2\text{C}} + 2R'_{\text{A}_3\text{C}} + \dots \quad (1)$$

$$R_{\text{BC}} = R'_C + R'_{\text{AC}} + 2R'_{\text{A}_2\text{C}} + R'_{\text{A}_3\text{C}} + \dots \quad (2)$$

where the concentration units are the mole ratios  $R_i$  ( $R_i = n_i/n_{\text{BD}}$ ). The prime (') denotes the "free" species  $i$  and  $R_{\text{AD}}$  and  $R_{\text{BC}}$  are the stoichiometric concentrations of  $\text{A}^+$  and  $\text{C}^-$ . The conventional definitions for the association quotients of the species  $i$  are

(12) M. Blander, F. F. Blankenship and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959).

(13) D. G. Hill, J. Braunstein and M. Blander, *ibid.*, **64**, 1038 (1960).

$$K_1 = \frac{R'_{\text{AC}}}{R'_A R'_C} \quad (3)$$

$$K_2 = \frac{R'_{\text{A}_2\text{C}}}{R'_{\text{AC}} R'_C} \quad (4)$$

$$K_{12} = \frac{R'_{\text{A}_3\text{C}}}{R'_{\text{AC}} R'_A} \text{ etc.} \quad (5)$$

In a region of concentrations low enough so that the species obey Henry's law,  $K_i$  are true constants. By considering the activities of the solute components AD and BC, using equations 1 through 5 and introducing the usual convention that  $\gamma_{\text{AD}} = R'_A/R_{\text{AD}}$  and  $\gamma_{\text{BC}} = R'_C/R_{\text{BC}}$  (or that the activities of AD or BC are proportional to the concentrations of "free"  $\text{A}^+$  or  $\text{C}^-$  ions, respectively), one obtains the relations

$$\frac{1}{\gamma_{\text{AD}}} = 1 + K_1 \gamma_{\text{BC}} R_{\text{BC}} + K_1 K_2 \gamma_{\text{BC}}^2 R_{\text{BC}}^2 + 2K_1 K_{12} \gamma_{\text{AD}} \gamma_{\text{BC}} R_{\text{AD}} R_{\text{BC}} + \dots \quad (6)$$

$$\frac{1}{\gamma_{\text{BC}}} = 1 + K_1 \gamma_{\text{AD}} R_{\text{AD}} + K_1 K_{12} \gamma_{\text{AD}}^2 R_{\text{AD}}^2 + 2K_1 K_2 \gamma_{\text{AD}} \gamma_{\text{BC}} R_{\text{AD}} R_{\text{BC}} + \dots \quad (7)$$

The activity coefficients  $\gamma_{\text{AD}}$  and  $\gamma_{\text{BC}}$  in (6) and (7) refer to the deviations from ideality which are caused only by association and not to deviations from ideality of the species which may be present.

TABLE I  
CHANGE OF E.M.F. (VOLTS) OF THE CELL

Ag $\left  \begin{array}{c} \text{AgNO}_3 \\ \text{KNO}_3 \end{array} \right  \left  \begin{array}{c} \text{AgNO}_3 \\ \text{KCl} \\ \text{KNO}_3 \end{array} \right  \text{Ag}$					
WITH THE ADDITION OF KCl TO THE RIGHT HAND HALF CELL <sup>a</sup>					
Temperature = $350^\circ$					
$R_{\text{KCl}} \times 10^3$	$-\Delta E(\text{v.})$	$-\log \gamma_{\text{AgNO}_3}$	$R_{\text{KCl}} \times 10^3$	$-\Delta E(\text{v.})$	$-\log \gamma_{\text{AgNO}_3}$
0.207	0.0041	0.031	0.395	0.0066	0.051
0.814	.0156	.119	1.185	.0193	.148
1.368	.0259	.198	2.018	.0329	.252
2.000	.0369	.283	3.135	.0503	.385
2.815	.0494	.378	3.917	.0615	.471
4.275	.0727	.556			

$R_{\text{AgNO}_3} = 0.776 \times 10^{-3}$			$R_{\text{AgNO}_3} = 1.493 \times 10^{-3}$		
$R_{\text{KCl}} \times 10^3$	$-\Delta E(\text{v.})$	$-\log \gamma_{\text{AgNO}_3}$	$R_{\text{KCl}} \times 10^3$	$-\Delta E(\text{v.})$	$-\log \gamma_{\text{AgNO}_3}$
1.560	0.0196	0.150			
2.103	.0273	.209			
2.544	.0344	.264			

<sup>a</sup> These values supplement previously published results at  $R_{\text{AgNO}_3}$  equal to  $0.279 \times 10^{-3}$ ,  $0.724 \times 10^{-3}$ ,  $2.20 \times 10^{-3}$  and  $3.50 \times 10^{-3}$ .

Our methods of calculation utilize equations 6 and 7 or the logarithms of  $(1/\gamma)$  as a starting point. We expand  $\gamma_{\text{BC}}$  and  $\gamma_{\text{AD}}$  on the right hand side of (6) and (7) by iteration to obtain a series in the stoichiometric concentrations  $R_{\text{AD}}$  and  $R_{\text{BC}}$  with combinations of the  $K_i$  as coefficients of the individual terms. The series or its logarithm is compared with a Maclaurin expansion of the function  $f(R_{\text{AD}}, R_{\text{BC}})$ , about  $R_{\text{AD}}$  and  $R_{\text{BC}}$  both equal to zero

$$f(R_{\text{AD}}, R_{\text{BC}}) = f(0,0) + R_{\text{AD}} \left( \frac{\partial f}{\partial R_{\text{AD}}} \right)_0 + R_{\text{BC}} \left( \frac{\partial f}{\partial R_{\text{BC}}} \right)_0 + \frac{1}{2} R_{\text{BC}}^2 \left( \frac{\partial^2 f}{\partial R_{\text{BC}}^2} \right)_0 + \frac{1}{2} R_{\text{AD}}^2 \left( \frac{\partial^2 f}{\partial R_{\text{AD}}^2} \right)_0 + R_{\text{AD}} R_{\text{BC}} \left( \frac{\partial^2 f}{\partial R_{\text{AD}} \partial R_{\text{BC}}} \right)_0 + \dots \quad (8)$$

Alternately, the variables in the power series may be taken as  $R_{\text{BC}}$  and  $a_{\text{AD}}$  (or other pairs of the activities and stoichiometric concentrations of the solute components). The particular expansion used is chosen in such a manner that the subsequent extrapolation will be nearly linear. The linearity depends on the relative magnitude of the association constants in the particular system so that a single re-

liable method of evaluation for all systems is not possible and the "best" method may be determined most directly by graphical methods. The  $K_1$  are obtained by evaluating the derivatives of  $f$  at infinite dilution of the solutes.

**Calculation of Formation Constants from Our E.m.f. Data.**—The components  $\text{AgNO}_3$  and  $\text{KCl}$  in  $\text{KNO}_3$  correspond to AD and BC in equations 6 and 7. The function  $-\log \gamma_{\text{AgNO}_3}$ , calculated from the data has much less curvature than the function  $1/\gamma_{\text{AgNO}_3}$  and hence is more suitable for this analysis. (In a subsequent paper, a system is considered for which the function  $1/\gamma$  has less curvature than the function  $\log \gamma$  because of the relative magnitudes of the association constants.) Taking the logarithm of  $(1/\gamma_{\text{AD}})$  and expanding the individual terms one obtains the relation

$$-\ln \gamma_{\text{AD}} = K_1 R_{\text{BC}} + (K_1 K_2 - \frac{1}{2} K_1^2) R_{\text{BC}}^2 + (2K_1 K_{12} - K_1^2) R_{\text{AD}} R_{\text{BC}} + \dots \quad (9)$$

From equations 8 and 9

$$\lim_{\substack{R_{\text{AD}}=0 \\ R_{\text{BC}}=0}} \left( \frac{\partial \ln \gamma_{\text{AD}}}{\partial R_{\text{BC}}} \right) = -K_1 \quad (10)$$

$$\lim_{\substack{R_{\text{AD}}=0 \\ R_{\text{BC}}=0}} \left( \frac{\partial^2 \ln \gamma_{\text{AD}}}{\partial R_{\text{BC}}^2} \right) = (K_1^2 - 2K_1 K_2) \quad (11)$$

$$\lim_{\substack{R_{\text{AD}}=0 \\ R_{\text{BC}}=0}} \left( \frac{\partial^2 \ln \gamma_{\text{AD}}}{\partial R_{\text{AD}} \partial R_{\text{BC}}} \right) = (K_1^2 - 2K_1 K_{12}) \quad (12)$$

Equations 10–12 may be used to evaluate the association constants contained in them.

$K_1$  and  $K_{12}$  were evaluated in two ways from our data. In the first, a large scale plot of  $-\log \gamma_{\text{AgNO}_3}$  versus  $R_{\text{KCl}}$  at several constant values of  $R_{\text{AgNO}_3}$  was made. The limiting slope of these plots at  $R_{\text{KCl}} = 0$ , which we call  $S_1$ , was obtained graphically using a line ruled on a Lucite strip as a straight-edge. The values of these limiting slopes are plotted as a function of  $R_{\text{AgNO}_3}$  in the lower part of Fig. 1. The extrapolated intercept is equal to  $K_1/2.303$  and leads to a value of  $K_1 = 460 \pm 15$ . The limiting slope of the plot in Fig. 1 is equal to  $(2K_1 K_{12} - K_1^2)/2.303$ . For large values of  $K_{12}$ , this slope is relatively small and  $K_{12}$  may be calculated from it. Since, in this case,  $K_{12}$  is small, large errors can be introduced into the  $K_{12}$  by relatively small errors in these slopes. To avoid this, the slopes plotted in Fig. 1 were multiplied by  $(1 + K_1 R_{\text{AgNO}_3})$  and are plotted in Fig. 1

A partially unexpanded form of equation 9 is

$$-\ln \gamma_{\text{AD}} = \frac{K_1}{(1 + K_1 R_{\text{AD}} + \dots)} R_{\text{BC}} + \frac{(K_1 K_2 - \frac{1}{2} K_1^2) R_{\text{BC}}^2}{(1 + K_1 R_{\text{AD}} + \dots)^2} + \frac{2K_1 K_{12}}{(1 + K_1 R_{\text{AD}} + \dots)} R_{\text{BC}} R_{\text{AD}} + \dots \quad (13)$$

from which it can be shown that

$$\lim_{\substack{R_{\text{AD}}=0 \\ R_{\text{BC}}=0}} \left( \frac{\partial [(1 + K_1 R_{\text{AD}}) S_1]}{\partial R_{\text{AD}}} \right) = 2K_1 K_{12}$$

where  $S_1 = \lim_{\substack{R_{\text{BC}}=0 \\ R_{\text{AD}}=0}} \left( \frac{\partial \ln \gamma_{\text{AD}}}{\partial R_{\text{BC}}} \right)$ . The slope of the function plotted in the upper part of Fig. 1 is  $\frac{2K_1 K_{12}}{2.303}$ , and a value of  $K_{12} = 20 \pm 10$  was obtained. It is important to note that although the evaluation of slopes can be subject to large error here, as well as in other methods of calculation, the fact that  $-\log \gamma_{\text{AgNO}_3}$  must go through the origin leads to a considerably smaller error in  $S_1$  than in the evaluation of slopes without a fixed point.

The second procedure consisted of least squares fitting values of  $\log \gamma_{\text{AgNO}_3}$  at fixed concentrations of  $R_{\text{AgNO}_3}$  to the equation

$$-\log \gamma_{\text{AgNO}_3} = A R_{\text{KCl}} + B R_{\text{KCl}}^2 \quad (15)$$

where the least squares code assumed a constant probable error in  $\log \gamma_{\text{AgNO}_3}$ . The intercept of a plot of  $A$  and the intercept and slope of the plot of  $A(1 + K_1 R_{\text{AgNO}_3})$  versus  $R_{\text{AgNO}_3}$  led, within the indicated error, to the values of  $K_1$  and  $K_{12}$  derived using the derivatives obtained graphically. The graphical evaluation, as is proper for evaluating  $K_1$  and  $K_{12}$ , gives more importance to the experimental results at

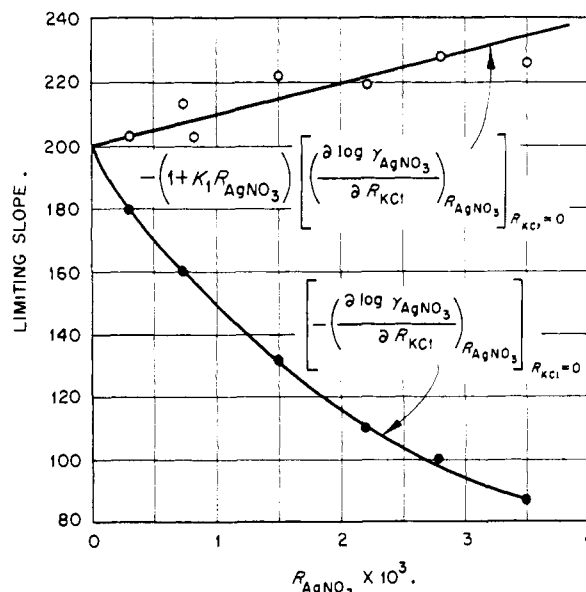


Fig. 1.—Graphical extrapolation of slopes to infinite dilution of solutes to evaluate  $K_1$  and  $K_{12}$ .

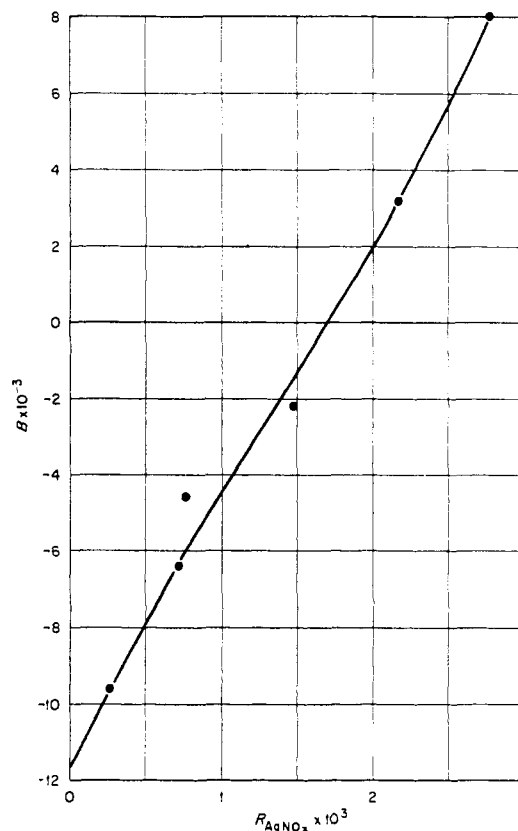


Fig. 2.—Graphical extrapolation of the coefficients  $B$  to infinite dilution to evaluate  $K_2$ .

low values of  $R_{\text{KCl}}$  than the least square evaluation. This indicates that the results at all concentrations are self consistent. Using an equation which included a cubic term led to more scatter in the values of  $A$  and  $B$  and of the  $K_1$  obtained in the extrapolation, although the  $K_1$  were within the range indicated.  $K_2$  was evaluated from the value of the zero intercept,  $B_0$ , of a plot of  $B$  versus  $R_{\text{AgNO}_3}$ , ( $B_0 = 1.17 \times 10^4$ ) shown in Fig. 2. The limit of  $B$  is

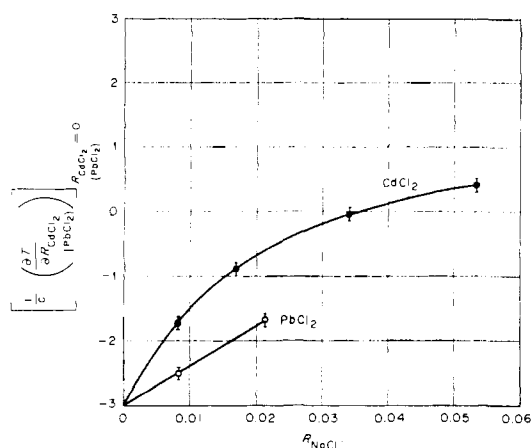


Fig. 3.—Extrapolation of the limiting slopes of the freezing point depressions from the data of Van Artsdalen for the evaluation of  $K_1$ .

equal to  $(K_1K_2 - \frac{1}{2}K_1^2)/2.303$  from which a value of  $K_2 = 169 \pm 20$  was obtained. It should be noted that the relative error of  $K_2$  will be much smaller than the relative error of  $B_0$ .

**Calculation of  $K_1$  from Cryoscopic, Polarographic and Solubility Data.**—Reported values of the formation constants for  $\text{CdCl}^+$  and  $\text{PbCl}^+$  in molten nitrate melts show large differences. In this section we discuss the recalculation of these formation constants based on methods which utilize the principles discussed in the introduction.

Van Artsdalen<sup>9</sup> has reported measurements of the freezing point lowering of molten  $\text{NaNO}_3$  and of mixtures of  $\text{NaNO}_3$  with  $\text{NaCl}$  by  $\text{CdCl}_2$ . If one interprets his freezing point lowering measurements in terms of the formation of species  $\text{CdCl}^+$ ,  $\text{CdCl}_2$ ,  $\text{CdCl}_3^-$  etc., then the "cryoscopic number" or the number of particles effective in freezing point lowering per molecule of  $\text{CdCl}_2$  is given by

$$\frac{3R_{\text{CdCl}_2} - R_{\text{CdCl}^+} - 2R_{\text{CdCl}_2^-} - 3R_{\text{CdCl}_3^-} - \dots}{R_{\text{CdCl}_2}}$$

from which one can show that the limiting slope (*i.e.*, at  $R_{\text{CdCl}_2} = 0$ ) of the freezing point lowering of  $\text{NaNO}_3$ - $\text{NaCl}$  mixtures is proportional to

$$3 - K_1R_{\text{NaCl}} + (K_1^2 - 2K_1K_2)R_{\text{NaCl}}^2 + \dots$$

which is the limiting value of the "apparent cryoscopic number."

Figure 3 is a plot of limiting slopes obtained from the data of Van Artsdalen. A value of  $K_1 = 190 \pm 50$  listed in Table II was estimated from the limiting slope of this plot which compares with the apparent value of zero (0) obtained by Van Artsdalen by curve fitting part of his data. It should be noted that our value of  $K_1$  is obtained by extrapolation to infinite dilution and is a thermodynamic association constant. It may be seen that if the value of  $K_1$  were zero, the limiting slope of the graph in Fig. 3 must be zero, which cannot be inferred from the data. Unfortunately measurements at very low concentrations of  $\text{NaCl}$  were not obtained, making a more precise evaluation of  $K_1$  difficult. Because of the uncertainty in  $K_1$  values of  $K_2$  are unreliable. A correction for the fact that these measurements are not isothermal would probably be much smaller than the estimated error in  $K_1$ . The  $K_1$  for the formation of  $\text{PbCl}^+$  in  $\text{NaNO}_3$  listed in Table II were evaluated in the same way.

Christie and Osteryoung<sup>10</sup> presented polarographic data from which they calculated formation constants for  $\text{CdCl}^+$ ,  $\text{CdCl}_2$  etc. in molten mixtures of  $\text{LiNO}_3$ - $\text{KNO}_3$  (38.56 mole %  $\text{LiNO}_3$ ) at  $180^\circ$  using the method of calculation of DeFord and Hume. The method of DeFord and Hume is useful when reliable data are obtained at low ligand and low central cation concentrations and if the relative values of the formation constants are such that the extrapolations are linear at low concentrations of ligand. The function used by Christie and Osteryoung is

$$F_0 = \sum_i \beta_i R_x^i$$

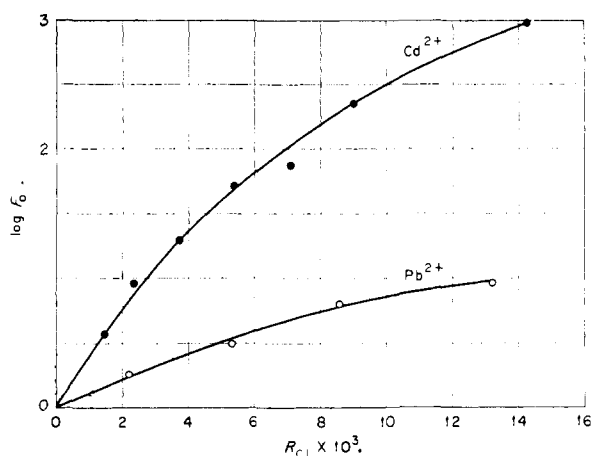


Fig. 4.—Evaluation of apparent values of the association constants for  $\text{CdCl}^+$  and  $\text{PbCl}^+$  from the data of Christie and Osteryoung.

where  $\beta_i = \prod_1^i K_i$ . The quantities  $F_1, F_2$  etc., which are re-

lated to  $F_0$  and from which  $K_1, K_2$ , etc., were evaluated by extrapolation exhibit enough curvature so that the extrapolations are unreliable because measurements were not obtained at low enough ligand concentrations.

TABLE II

CALCULATED VALUES OF  $K_1 \left( \frac{\text{MOLES}}{\text{MOLE SOLVENT}} \right)^{-1}$

Solvent	Temp. (°C.)	Species	$K_1^a$
$\text{NaNO}_3^{(9)}$	307	$\text{CdCl}^+$	$190 \pm 50$ (0)
		$\text{PbCl}^+$	$60 \pm 20$ (0)
$\text{LiNO}_3$ - $\text{KNO}_3^{(10)}$	180	$\text{CdCl}^+$	$[900 \pm 200]$ $\{[(2260)]\}$
		$\text{PbCl}^+$	$[270 \pm 80]$ $\{[(480)]\}$
$\text{NaNO}_3$ - $\text{KNO}_3^{(11)}$	250	$\text{CdCl}^+$	$[250]$ $\{[(220)]\}$
	300	$\text{CdCl}^+$	$[300]$ $\{[(260)]\}$
	250	$\text{PbCl}^+$	$[200]$ $\{[(200)]\}$
	300	$\text{PbCl}^+$	$[65]$ $\{[(65)]\}$

<sup>a</sup> ( ), reported in the papers cited; [ ], values of  $K_1$  in brackets are not obtained by extrapolation to infinite dilution and are apparent association constants.

$\log F_0$ , which is analogous to the quantity  $-\ln \gamma_{AD}$  in equation 6, is plotted in Fig. 4 versus  $R_{\text{CdCl}_2}$ . If  $R_{\text{CdCl}_2} (2K_{12} - K_1) \ll 1$  in this system then a value of  $K_1 = 900 \pm 200$  is calculated from the limiting slope of this plot. This is a minimum value, and a correct value (using our method or the method of DeFord and Hume) would require extrapolation to zero concentration of  $\text{Cd}$ . Apparent (minimum) values of  $K_1$  for  $\text{CdCl}^+$  and  $\text{PbCl}^+$  calculated by our method are tabulated in Table II. The quantities in parentheses in Table II are the apparent values of  $K_1$  reported by Christie and Osteryoung. The uncertainties in  $K_1$  preclude obtaining reliable values of the higher constants.

Duke and Iverson,<sup>11</sup> from measurements of the solubility of cadmium and lead chromates in a nitrate melt containing chloride ions, deduced values of  $K_1$  for the formation of  $\text{CdCl}^+$  and  $\text{PbCl}^+$ . The limiting value of the increase in the solubility,  $S$ , of a relatively insoluble salt  $\text{CdCrO}_4$  or  $\text{PbCrO}_4$  caused by the addition of alkali chloride,  $(dS/dR_{\text{Cl}})$  is given by

$$\frac{2}{S_0} \left( \frac{dS}{dR_{\text{Cl}}} \right)_{R_{\text{Cl}}=0} = \frac{K_1 + 2K_1K_{12}S_0 + \dots}{1 - K_1S_0 + K_1K_{12}S_0^2 + \dots} \quad (16)$$

Values of  $K_1$  calculated using equation 16 under the assumption that  $K_{12}$  may be neglected are given in Table II. These values are given in brackets because the slopes could not be extrapolated to infinite dilution of all solutes but rather to a saturated solution of cadmium (or lead) chromate. If  $\text{CrO}_4^{2-}$  ion associates with  $\text{Cd}^{2+}$  (or  $\text{Pb}^{2+}$ ) ions the values of

$K_1$  calculated from (16) will differ from the values which would be obtained by extrapolation to infinite dilution of all solutes, but the magnitude of this effect cannot be estimated from the data of Duke and Iverson. The correction  $\left(\frac{1}{1 + K_1 S_0 + \dots}\right)$  in equation 16 although appreciable probably is much smaller than the other uncertainties in the evaluation of  $K_1$ . Since  $S_0$  for  $\text{PbCrO}_4$  is much smaller than for  $\text{CdCrO}_4$ , the calculation of Duke and Iverson of  $K_1$  for  $\text{PbCl}^+$  did not differ significantly from that calculated using equation 16.

### Discussion

Refined methods of calculation of  $K_1$  are important in order to be able to systematize measured association constants and to correlate these constants with theory. The evaluation of  $K_1$  for the formation of the species  $\text{Ag}^+\text{-Cl}^-$  in  $\text{KNO}_3$  at  $385^\circ$  made in this paper confirms, within the experimental error, the value calculated from the relation<sup>13</sup>

$$K_1 = Z(\exp(-\Delta E_1/RT) - 1) \quad (17)$$

where values of  $Z$  and  $\Delta E_1$  have been published.<sup>8,12</sup> We will check values of  $K_1$  at the other temperatures in a similar manner.

Duke and Garfinkel<sup>14</sup> in a recent paper presented limited data on activities of  $\text{AgNO}_3$  in the molten solvent  $\text{NaNO}_3\text{-KNO}_3$  (54-46 mole %) to which either  $\text{Cl}^-$  or  $\text{Br}^-$  ions have been added. Their method of calculation requires modification to lead to the thermodynamic association constants and their evaluation of association constants from part of their data and from the data of Blander<sup>12</sup> is subject to a computational error which may be larger than the experimental error. Equation 9 of their paper is incomplete and should be

$$\frac{1}{\gamma_{AD}} = 1 + K_1 R_{BC} + K_1 K_2 R_{BC}^2 + (2K_1 K_{12} - K_1^2) R_{AD} R_{BC} + \dots \quad (18)$$

and their function  $\theta$  should be

$$\theta = K_1 + K_1 K_2 R_{BC} + (2K_1 K_{12} - K_1^2) R_{AD} + \dots \quad (19)$$

(It should be noted that the units of concentration, of  $K_i$  and of  $\theta$  used here differ from those used by Duke and Garfinkel. This will have no effect on the conclusions.)

The limit of  $\theta$  at  $R_{BC} = 0$  is

$$\lim_{R_{BC} \rightarrow 0} \theta = K_1^{APP} = K_1 [1 + (2K_{12} - K_1) R_{AD} + \dots] \quad (20)$$

where  $K_1^{APP}$  is an apparent value of  $K_1$  and is re-

(14) P. R. Duke and H. M. Garfinkel, *J. Phys. Chem.*, **65**, 416 (1961).

ported by Duke and Garfinkel as  $K_1$ . The second term in parentheses in equation 20 can be neglected only if  $(2K_{12} - K_1) R_{AD} \ll 1$  which is the necessary condition for approximating  $K_1$  by  $K_1^{APP}$ . From their data for the association of  $\text{Ag}^+$  and  $\text{Cl}^-$  in  $\text{NaNO}_3\text{-KNO}_3$  this correction appears to be small ( $<3\%$ ) and  $K_1$  probably is only slightly higher than ( $K_1^{APP}$ ).

This correction term is relatively large when applied to the data of Blander<sup>12</sup> because of the higher silver concentration in the data from which  $K_1^{APP}$  was calculated. The apparent value of the first association constant,  $K_1^{APP}$ , at  $436^\circ$  calculated by Duke and Garfinkel from the data of Blander differs from the value calculated by Blander using equation 17 mainly because Duke and Garfinkel did not apply the above correction of extrapolation to zero concentration of  $\text{Ag}^+$  ion and hence did not obtain the thermodynamic association constant.

For evaluating  $K_1$  for the association of  $\text{Ag}^+$  and  $\text{Br}^-$  ions from the data of Duke and Garfinkel more data are necessary. The method of Duke and Garfinkel is equivalent to using the value of the slope,  $S_1$ , at the lowest concentration of  $\text{AgNO}_3$  studied. As is obvious from Fig. 1 and equation 20 the limit of this slope extrapolated to zero concentration of AD is larger than the slope at any finite concentration. Unless it can be shown that  $K_{12}$  is of the order of  $1/2 K_1$  in the bromide containing system and hence that the species  $\text{Ag}_2\text{Br}^+$ , which Duke and Garfinkel neglect, is an important species in solution,  $K_1$  in the bromide containing system may be 6-10% higher than their quoted values. To check this requires more data than are presented by them.

In Table II are given the recalculated values of  $K_1$  and, in parentheses, the values reported in the literature for the formation of  $\text{CdCl}^+$  and  $\text{PbCl}^+$  in molten nitrates. Considering the differences in temperatures and the small differences between the solvents, our recalculated values are reasonably self consistent. A large part of the apparent anomalies in the reported values of  $K_1$  for these systems is then due to the incorrect methods of calculation. Since the uncertainties in the higher  $K_i$  are a magnified reflection of uncertainties in  $K_1$ , we did not attempt to calculate the higher  $K_i$  in these systems.

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