compounds have been determined,[11] but, unfortunately, the data available at this point do not provide a method for relating the meager quantitative data to the more extensive list of relative pK_a values. Work directed toward this end is in progress.

Acknowledgment. We gratefully acknowledge the financial support of the Robert A. Welch Foundation and the National Science Foundation.

(11) (a) W. L. Jolly and T. Birchall, *J. Am. Chem. Soc.*, **88**, 5439 (1966); (b) T. Birchall and W. L. Jolly, *Inorg. Chem.*, **5**, 2177 (1966).

Gas Chromatographic Evaluation of Equilibria in Fused Salts. I. The Tetrachloroaluminate and Tetrachloroferrate Systems[1,2]

Richard S. Juvet, Jr.,[3] Vernon R. Shaw, and M. Aslam Khan

Contribution from the Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801. *Received January 6, 1969*

Abstract: Gas chromatography has been applied for the first time for the determination of complex stability constants in inorganic fused-salt systems. Specific retention volumes, partition coefficients, and other thermodynamic data for the volatile solutes $SbCl_3$, $NbCl_5$, and $TaCl_5$ in a series of alkali metal tetrachloroaluminate and tetrachloroferrate liquid phases show that complexes formed between the solute and solvent exhibit decreasing stability with change of liquid-phase alkali metal in the order potassium > thallium > sodium > lithium. Variations are due to differences in availability of complexing chloride ion resulting from the equilibrium $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$. Through measurements of the gas chromatographic partition coefficient of $SbCl_3$ as a function of added excess alkali metal chloride in the tetrachloroaluminate and tetrachloroferrate liquid phases, the following equilibria have been established: $KCl + SbCl_3 \rightleftharpoons KSbCl_4$, $K_f = 40 \pm 10$ at 290° in $KFeCl_4$ and in $KAlCl_4$; $TlCl + SbCl_3 \rightleftharpoons TlSbCl_4$, $K_f = 0.8 \pm 0.2$ at 315° in $TlAlCl_4$; $2FeCl_4^- \rightleftharpoons Fe_2Cl_7^- + Cl^-$, $K_d = 4 \times 10^{-4}$ at 290° in $KFeCl_4$; $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$, $K_d = 3 \times 10^{-4}$ at 289° in $KAlCl_4$; and $K_d = 6.5 \times 10^{-3}$ at 315° in $TlAlCl_4$ melt.

The first successful separation of transition metal compounds using nonvolatile inorganic fused salts as liquid phases was reported by Juvet and Wachi[4] in 1960. Inorganic fused-salt liquid phases allow the gas chromatographic elution and separation of metal halides boiling at temperatures as high as 800°. In recent work from this laboratory[5] the elution characteristics and thermodynamic measurements for 11 metal chlorides on 12 inorganic fused-salt liquid phases were reported, and preliminary evaluations of thermodynamic and retention data were combined to provide insight into the solution mechanism and the Lewis acid–base, solute–solvent interactions involved in metal chloride, inorganic fused-salt systems. Differences in chloride ion activity allow the separation of niobium pentachloride and tantalum pentachloride on a 2-in. long column containing the indium chloride–thallium chloride eutectic as liquid phase but not on a column containing the indium chloride–sodium chloride eutectic.

In the present investigation a series of alkali metal tetrachloroaluminates and tetrachloroferrates are studied as liquid phases to establish the effect of the metal cation on the stability of the complexes formed and the mechanism of complex formation of these materials with Lewis acids. Equations are developed which allow the determination of the stability constants of the chloro complexes formed in mixtures of the tetrachloroaluminate or -ferrate with controlled amounts of excess metal chloride. Gas chromatography is here applied for the first time for the determination of complex stability constants in inorganic fused-salt systems.

Experimental Section

Chemicals. Anhydrous reagent grade $AlCl_3$ (Mallinckrodt) and $FeCl_3$ (Matheson Coleman and Bell) were triply sublimed under anhydrous conditions. Analytical reagent grade NaCl and KCl (Mallinckrodt) were dried overnight at 450°. LiCl (Baker's Analyzed, 99.2%) was dried at 450° for 24 hr in the presence of dry HCl gas. TlCl (Fisher) was vacuum dried at 400°. Reagent grade $SbCl_3$ (Baker's Analyzed Reagent) was recrystallized from CCl_4 and dried under vacuum. $NbCl_5$ and $TaCl_5$ (K and K Corp.) were further purified by distillation under anhydrous conditions.

The tetrachloroferrate and tetrachloroaluminate liquid phases were prepared by mixing weighed amounts of alkali metal chloride with an excess of resublimed aluminum or iron chloride. After complete solution at elevated temperatures, dry chlorine or hydrogen chloride gas followed by nitrogen was passed through the melt for a period of 40 hr to convert any hydrolyzed product to the chloride and to remove excess aluminum or iron chloride. This procedure led to a product whose weight agreed with the theoretical value based on alkali metal chloride added to within 0.1%. Argentimetric analysis of the products for chloride ion gave results which agreed with calculated values for the tetrachloroaluminates and tetrachloroferrates within 0.1% of the stoichiometric amount.

The density of the fused salt melts are required in measurement of the thermodynamic partition coefficients. The density of the tetrachloroaluminates and -ferrates and mixtures of these compounds with excess metal halides were determined over the range of temperatures used in the gas chromatographic measurements using a density balance based on Archimedes' principle, similar in design to that described by White.[6] The platinum bob was en-

---

[1] Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[2] This work was supported by the National Science Foundation under Grant No. GP-5151X.

[3] Author to whom correspondence should be addressed.

[4] R. S. Juvet and F. M. Wachi, *Anal. Chem.*, **32**, 290 (1960).

[5] F. M. Zado and R. S. Juvet in "Gas Chromatography, 1966," A. B. Littlewood, Ed., Elsevier Publishing Co., New York, N. Y., 1967, pp 283–295.

[6] J. L. White in "Physicochemical Measurements at High Tem-

closed in glass to prevent reaction with the melt. The melts were heated in an aluminum block furnace with temperature control to within ±2° at 300°, a variation which introduced only negligible error in the evaluation of the partition coefficient.

Bio-Glas 2500, 80–100 mesh (Bio-Rad Laboratories, Richmond, Calif.), and in some cases acid-washed Chromosorb P, 60–80 mesh, which was dried overnight at 450°, were used as a solid support in these studies. The support was coated by mixing weighed amounts of solid support and fused-salt liquid phase at temperatures above the melting point of the melt with periodic shaking over a period of 1 hr. Owing to the relatively high density of the fused salts, liquid-phase loading of 50–70% by weight was used for Chromosorb P and 40–45% by weight for Bio-Glas 2500.

Samples ranging in weight from 0.1 to 0.5 mg were sealed in glass capillaries for introduction into the column with an F and M Model SI-4-2A solid sampler.

F and M Model 810 and MicroTek Model 2000R gas chromatographs were modified for use with the selective-nonselective flame photometer detector previously described.[7] The Beckman-type atomizer burner was constructed of stainless steel and was maintained, along with connecting tubing, above the column temperature and the boiling point of the solutes to prevent condensation. The helium carrier gas was predried over activated Linde 4A molecular sieves maintained at Dry Ice-acetone temperatures. In experiments with the tetrachloroferrate liquid phases, the carrier gas was further dried at 200° using a 3-in. precolumn containing sodium tetrachloroferrate coated on Bio-Glas 2500. This drying column effectively removed traces of moisture not trapped on the molecular sieve column and was positioned between the molecular sieve column and the injection port.

Inlet column pressure was measured with an open-end mercury manometer and outlet pressure was taken as atmospheric. Flow rates were accurately determined in the usual manner[8] with a flow meter attached to the detector burner tip.

Results and Discussion

Specific Retention Volumes and Heats of Solution. The specific retention volumes, V_g, for $SbCl_3$, $NbCl_5$, and $TaCl_5$ were evaluated on alkali metal tetrachloroaluminate and tetrachloroferrate liquid phases using the expression[9]

$$V_g = \frac{jF_c(t_R - t_a)}{w_L}\frac{273}{T_c}$$

where j is the gas compressibility term, $j = (^3/_2)[(p_i/p_o)^2 - 1]/[(p_i/p_o)^3 - 1]$, p_i and p_o are the column inlet and outlet pressures, respectively; F_c is the flow rate of the carrier gas at the column outlet and at the column temperature; t_R is the observed retention time of the solute; t_a is the retention time required for an insoluble solute such as air or CCl_4 to pass through the column; w_L is the weight of the liquid phase; T_c is the absolute temperature of the column. The specific retention volume is related to the heat of solution by the expression[9]

$$\log V_g = \frac{-\Delta H_s}{2.303RT_c} + c$$

where R is the molar gas constant, 1.987×10^{-3} kcal/(mole deg), and c is a constant. Heats of solution were measured directly from the slopes of the plots of log V_g *vs.* $1/T_c$ shown in Figure 1.

More significant for the present discussion is the heat of mixing, ΔH_m, defined by the expression

$$\Delta H_m = \Delta H_s + \Delta H_v$$

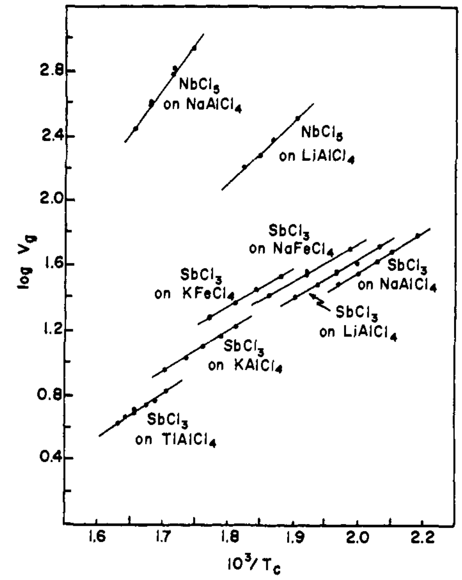

Figure 1. Logarithm specific retention volume *vs.* $1/T_c$ plot for $SbCl_3$ and $NbCl_5$ on various alkali metal tetrachloroaluminate and -ferrate liquid phases.

The heat of vaporization of the solutes, ΔH_v, has the values: $SbCl_3$, 10.4 kcal/mole;[10] $NbCl_5$, 13.2 kcal/mole;[11] and $TaCl_5$, 13.6 kcal/mole.[11] Values for the measured specific retention volume, the heat of solution, and the heat of mixing are summarized in Table I.

Table I. Thermodynamic and Retention Data for Solutes on Tetrachloroaluminate and Tetrachloroferrate Liquid Phases

Solute	Liquid phase	V_g, ml/g	ΔH_s, kcal/mole	ΔH_m, kcal/mole
		At 220°		
$SbCl_3$	$LiAlCl_4$	50.1	−10.7	−0.3
	$NaAlCl_4$	45.6	−10.7	−0.3
	$KAlCl_4$	56.8[a]	−11.4	−1.0
	$TlAlCl_4$	40.5[a]	−11.7	−1.3
	$NaFeCl_4$	64.3	−10.8	−0.4
	$KFeCl_4$	80.5	−11.0	−0.6
		At 275°		
$NbCl_5$	$LiAlCl_4$	163	−17.3	−4.1
	$NaAlCl_4$	1600[a]	−25.2	−12.0
	$KAlCl_4$	Not eluted	. . .	. . .
$TaCl_5$	$LiAlCl_4$	450	. . .[b]	. . .[b]

[a] Value extrapolated to temperature indicated for comparison. [b] Accurate values not obtained owing to variations in retention with sample size.

For $SbCl_3$ in $LiAlCl_4$ and $NaAlCl_4$ the heat of mixing is that of ideal solution behavior within the expected experimental error of ±0.3 kcal/mole. If an interaction between the solute and melt takes place, such as complex formation, the interaction is very weak. With $KFeCl_4$, $KAlCl_4$, and $TlAlCl_4$ the larger heats of mixing suggest somewhat stronger interaction between the solute and solvent. Greater retention and heat of mixing is observed for $SbCl_3$ on the tetrachloroferrates than on the corresponding tetrachloroaluminates.

Niobium pentachloride shows a heat of mixing of −4.1 kcal/mole in $LiAlCl_4$ and −12.0 kcal/mole in

---

peratures," J. O. Bockris, J. L. White, and J. D. Mackenzie, Ed., Butterworth & Co., Ltd., London, 1959, pp 193–207.

(7) F. M. Zado and R. S. Juvet, *Anal. Chem.*, **38**, 569 (1966).

(8) S. Dal Nogare and R. S. Juvet, "Gas-Liquid Chromatography," Interscience Publishers, New York, N. Y., 1962, pp 162–163.

(9) Reference 8, pp 70–81.

(10) K. K. Kelley, U. S. Bureau of Mines Bulletin, No. 383, U. S. Government Printing Office, Washington, D. C., 1935.

(11) K. M. Alexander and F. Fairbrother, *J. Chem. Soc.*, S223 (1949).

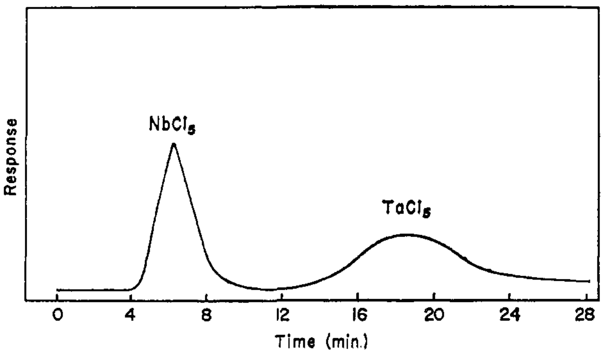

Figure 2. Chromatographic separation of $NbCl_5$ and $TaCl_5$ on $LiAlCl_4$ at 285°: column length, 6 in., 40% w/w $LiAlCl_4$ on Bio-Glas 2500; carrier gas flow rate, 30 ml of He/min; sample size, 1 mg.

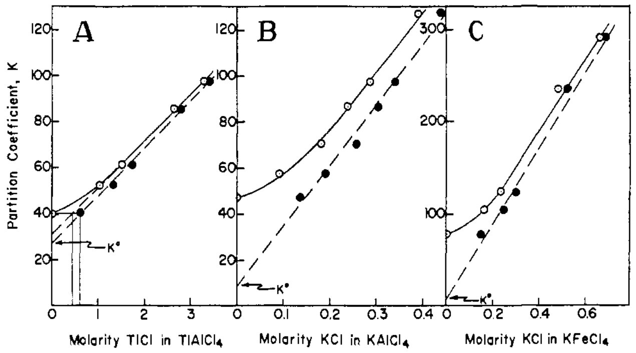

Figure 3. Variation in partition coefficient of $SbCl_3$ in tetrachloroaluminate and -ferrate melts with excess alkali metal chloride concentration: solid line, metal chloride added; dashed line, calculated total concentration of metal chloride.

$NaAlCl_4$, considerably stronger solute–solvent interactions than observed with $SbCl_3$. Large differences in the degree of complex formation between the various tetrachloroaluminates is also apparent in the vast differences in V_g. Complexation is so strong in $KAlCl_4$, $TlAlCl_4$, $NaFeCl_4$, and $KFeCl_4$ that $NbCl_5$ could not be eluted under the experimental conditions used. Tantalum pentachloride can be eluted only from the lithium salt and is well resolved from $NbCl_5$ on this liquid phase as is shown in Figure 2. From these data it is evident that the stability of antimony, niobium, and tantalum complexes with the alkali metal tetrachloroaluminate and -ferrate melts increases as the alkali metal cation increases in radius.

Equilibrium Measurements. The various alkali metal tetrachloroaluminates and -ferrates are thermally stable compounds and will, in fact, distil as the salts at temperatures ranging from 800 to over 1000° without decomposition to free aluminum chloride or ferric chloride.[12] Thus it can safely be assumed that the amount of free chloride ion from the reaction

$$2MAlCl_4 \rightleftharpoons 2MCl + Al_2Cl_6$$

is extremely small. Spectrophotometric studies[13] and an investigation involving the distribution of uranium between $KAlCl_4$ melts and molten aluminum,[14] however, has provided evidence for the existence of the species $Al_2Cl_7^-$. Such a structure would allow free Cl^- in the melt without loss of Al_2Cl_6 through the disproportionation reaction

$$2AlCl_4^- \overset{K_d}{\rightleftharpoons} Al_2Cl_7^- + Cl^- \qquad (1)$$

The disproportionation constant for this reaction, K_d, has been estimated by Morrey and Moore[14] for the $KAlCl_4$ system between 4×10^{-3} and 10^{-4}, corresponding to free chloride concentrations ranging from 0.5 to 0.08 *M*. The species $Fe_2Cl_7^-$ has not previously been reported. However, the similarity in structure of $FeCl_4^-$ and $AlCl_4^-$ suggests possible existence of this species, and strong experimental evidence for this assumption is reported below.

Alkali metal chloride complexes of $NbCl_5$, $TaCl_5$, and $SbCl_3$ are well known.[12,15] Formation of such complexes in the melt would result in substantial lowering of the vapor pressure of the volatile free metal chloride with a subsequent increase in retention. We will show below that it is the chloride ion present in equilibrium with the tetrachloroaluminate and -ferrate melts that is involved in complex formation, and trends observed in the retention of the solutes in the various melts are explained by differences in the effective equilibrium constants for the three equilibria

$$MAlCl_4 \rightleftharpoons M^+ + AlCl_4^- \qquad (2)$$

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$$

$$M^+ + Cl^- \rightleftharpoons MCl \qquad (3)$$

As the alkali metal cation, M^+, increases its radius, the charge separation between anion and cation becomes larger resulting in increased ionization in eq 2 and 3. Thus the concentration of free Cl^- in the melts should increase in the series $LiAlCl_4 < NaAlCl_4 < KAlCl_4 < RbAlCl_4 < CsAlCl_4$ and bring about stronger solute–solvent complexes in the same order.

Evidence for the conclusion that free chloride is the complexing ligand is given in Figure 3, which is a plot of the thermodynamic partition coefficient (defined by eq 6) of $SbCl_3$ in mixtures of various tetrachloroaluminates or tetrachloroferrates with added excess alkali metal chloride. From such plots it is possible to determine the stoichiometry and the stability constants of the complexes formed in the melt. In all cases studied, a curved line is obtained which becomes nearly linear at higher added chloride concentrations. Curvature at lower concentrations of added metal chloride is caused by repression of the ionization shown in eq 1 by the chloride added. If a complex had formed directly between $SbCl_3$ and the tetrachloroaluminate or tetrachloroferrate ions and if a more stable complex with chloride were formed in the presence of excess chloride, the plot predicted would be linear throughout. Thus, the shape of this curve in itself is evidence that it is the chloride ion in equilibrium with the tetrachloroaluminate and -ferrate that enters into complex formation with the volatile solutes.

It is convenient in deriving an expression for the stability constants of the complexes formed in the melt to define a quantity, $K°$, the thermodynamic partition coefficient for the uncomplexed solute which would have existed in the pure tetrachloroaluminate or tetrachloroferrate melts had the equilibrium shown in eq 1

---

(12) I. S. Morozov and D. Y. Toptygin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1832 (1959).

(13) H. A. Øye, D. M. Gruen, *Inorg. Chem.*, 3, 836 (1964); 4, 1173 (1965).

(14) J. R. Morrey and R. H. Moore, *J. Phys. Chem.*, 67, 748 (1963).

(15) J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Amer. Chem. Soc.*, 45, 963 (1923).

not existed. This hypothetical partition coefficient is given by

$$K^\circ = \frac{(C_X)_{liq}}{(C_X)_{gas}} \tag{4}$$

where $(C_X)_{liq}$ is the concentration of uncomplexed solute in the liquid phase and $(C_X)_{gas}$ is the concentration of solute in gaseous phase.

Equilibria between the solute, X, the complexing ligand, A, and possible complexes, XA and XA_2, are also considered.

$$X_{gas} \overset{K^\circ}{\rightleftharpoons} X_{liq}$$

$$X_{liq} + A \overset{K_1}{\rightleftharpoons} XA$$

$$XA + A \overset{K_2}{\rightleftharpoons} XA_2$$

The equilibrium constants for these reactions are given by

$$K_1 = \frac{C_{XA}}{C_X C_A} \qquad K_2 = \frac{C_{XA_2}}{C_{XA} C_A} = \frac{C_{XA_2}}{K_1 C_X C_A{}^2} \tag{5}$$

The observed thermodynamic partition coefficient, K, is given by

$$K = \frac{C_X + C_{XA} + C_{XA_2} + \ldots}{(C_X)_{gas}} \tag{6}$$

and is measured experimentally through the relationship[9]

$$K = V_g \rho_L T_c / 273$$

where ρ_L is the density of the melt.

Substitution of eq 4 and 5 into eq 6 leads to

$$K = K^\circ[1 + K_1 C_A + K_1 K_2 C_A{}^2 + \ldots] \tag{7}$$

This is similar in form to an expression derived by Purnell.[16]

If only a 1:1 complex is formed between the solute and the melt, eq 7 may be written in the form

$$(K - K^\circ)/K^\circ = K_1 C_A \tag{8}$$

For a 1:1 complex a plot of $(K - K^\circ)/K^\circ$ *vs.* C_A should yield a straight line passing through the origin with slope equaling K_1, the equilibrium constant.

If a 1:2 complex is formed exclusively, eq 7 may be written in the form

$$(K - K^\circ)/K^\circ = K_1 K_2 C_A{}^2 \tag{9}$$

while for a multicomplex system in which both XA and XA_2 exist in appreciable amounts in the melt the following relationship holds.

$$(K - K^\circ)/K^\circ C_A = K_1 + K_1 K_2 C_A \tag{10}$$

Thus the form in which the complex exists in the melt can be recognized by the appropriate plot and the partition coefficients measured.

The systems selected for this study were $SbCl_3$ as solute in solvents consisting of $KAlCl_4$ and $KFeCl_4$ with excess KCl and $TlAlCl_4$ with excess TlCl. $LiAlCl_4$, $NaAlCl_4$, and $NaFeCl_4$ would also have provided suitable solvents for such studies; however, the solubility of LiCl and NaCl in these melts is insufficient for precise measurements. Published phase diagrams of the TlCl–$AlCl_3$ system,[17] the KCl–$AlCl_3$ system,[18] and the KCl–$FeCl_3$ system[19] indicate alkali metal chloride-rich eutectics at 60 mole % TlCl, and 51.2 and 52.0 mole % KCl, respectively, allowing addition of substantial amounts of metal halides without need for excessive column temperatures.

Values for the heat of solution, the heat of mixing, the thermodynamic partition coefficient, and the specific retention volume of $SbCl_3$ in various tetrachloroaluminate and -ferrate melts are tabulated in Table II along with the melt density as a function of added metal halide. Graphs of the partition coefficient *vs.* MCl added are shown in Figure 3. In each case a systematic increase in both $-\Delta H_m$ and K occurs with increases in chloride concentration as the distribution of $SbCl_3$ is shifted through complexation toward larger liquid-phase concentrations.

Table II. Thermodynamic and Retention Data of $SbCl_3$ in Various Melt Mixtures

Liquid phase	Concn of MCl added, *M*	V_g, ml/g	ρ_L, g/cm^3	K	$-\Delta H_s$	ΔH_m
$KFeCl_4$	0.00 KCl	19.8	1.890	77.2	11.0	−0.6
(at 290°)	0.161	26.9	1.890	104.8	13.0	−2.6
	0.235	31.8	1.889	123.9	13.4	−3.0
	0.482	60.3	1.888	234.8	15.5	−5.1
	0.665	74.8	1.888	291.2	16.4	−6.0
$KAlCl_4$	0.00 KCl	13.8	1.667	47.3	11.4	−1.0
(at 289°)	0.0912	17.4	1.667	57.7	12.1	−1.7
	0.182	20.6	1.668	70.7	13.6	−3.2
	0.237	25.2	1.668	86.5	14.0	−3.6
	0.286	28.4	1.669	97.6	14.8	−4.4
	0.391	37.0	1.669	127.1	14.8	−4.4
$TlAlCl_4$	0.00 TlCl	6.5	2.890	40.5	11.7	−1.3
(at 315°)	1.029	8.1	3.010	52.5	12.9	−2.5
	1.517	9.3	3.063	61.4	13.1	−2.7
	2.639	12.5	3.182	85.7	13.9	−3.5
	3.295	13.9	3.252	97.4	14.7	−4.3

The curves in Figure 3 are linear at higher concentrations of added metal chloride but show curvature at the lower chloride concentrations. Curvature is caused by suppression of the disproportionation equilibria

$$2AlCl_4{}^- \rightleftharpoons Al_2Cl_7{}^- + Cl^-$$

$$2FeCl_4{}^- \rightleftharpoons Fe_2Cl_7{}^- + Cl^-$$

by the added chloride. At higher concentrations the equilibrium is suppressed to the point that contribution of chloride ion from the equilibrium is small and nearly constant, and a linear variation of K with concentration of metal chloride is observed.

Evaluation of Melt Disproportionation Constants. An accurate estimate of the degree of disproportionation of the tetrachloroaluminates and -ferrates may be made from Figure 3 through a series of successive approximations. A first approximation of the value of K° and the equilibrium chloride concentration may be made by

---

[16] J. H. Purnell in ref 5, pp 3–19.

[17] I. S. Morozov and A. T. Simonich, *Zh. Neorgan. Khim.*, 2, 1907 (1957).

[18] V. W. Fisher and A. L. Simon, *Z. Anorg. Allgem. Chem.*, 306, 1 (1960).

[19] C. M. Cook and W. E. Dunn, *J. Phys. Chem.*, **65**, 1505 (1961).

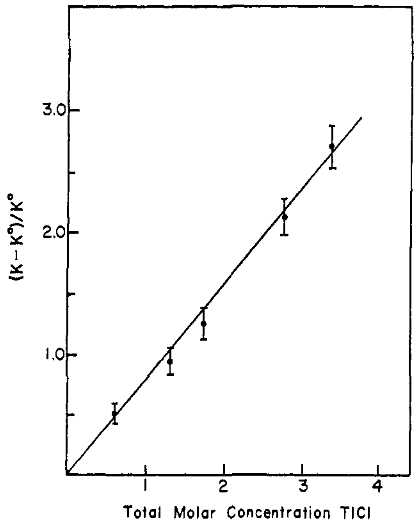

Figure 4. Graphical determination of formation constant for the reaction $SbCl_3 + TlCl \rightarrow TlSbCl_4$, according to eq 8 of the text.

extrapolation of the linear portion of Figure 3. The *y* intercept is a direct measure for the first approximation to $K°$, the thermodynamic partition coefficient which would have been found if no complexation with chloride ion had occurred since this line was constructed by extrapolating data in a region of the curve in which suppression of ionization in eq 1 is essentially complete. Of course, the observed partition coefficient is larger than $K°$ since, in the absence of added metal chloride, disproportionation does occur. A first approximation to the chloride present may be made by establishing the chloride concentration which would have to be added to the hypothetical undissociated melt to produce the observed partition coefficient as shown in Figure 3A. With this estimate of the chloride concentration in the melt, a first approximation of the dissociation constant, K_d, of eq 1 may be made from the known weight of melt and the fact that $(Al_2Cl_7^-) = (Cl^-)$ in the absence of added metal chloride.

$$K_d = \frac{(Al_2Cl_7^-)(Cl^-)}{(AlCl_4^-)^2}$$

With this estimate of K_d the total available chloride may be calculated for each of the experimental points on the plot. A linear extrapolation through these new points gives a more accurate value of $K°$ and K_d. Successive approximation calculations such as these are continued until constant values are obtained for $K°$ and K_d. The calculated total chloride concentrations in the melt mixtures are shown in Figure 3 with points connected by the dashed line.

Values for the disproportionation constants of the melt and the hypothetical thermodynamic partition coefficient, $K°$, are given in Table III. It is interesting to note that the K_d value found for $KAlCl_4$ is within the range 4×10^{-3} to 1×10^{-4} estimated by Morrey and Moore.[14]

Table III. Disproportionation Constants for Potassium and Thallium Tetrachloroaluminates and Potassium Tetrachloroferrate

Melt	Temp, °C	Equilibrium	K_d	$K°$
$KFeCl_4$	290	$(Fe_2Cl_7^-)(Cl^-)/(FeCl_4^-)^2$	4×10^{-4}	10 ± 3
$KAlCl_4$	289	$(Al_2Cl_7^-)(Cl^-)/(AlCl_4^-)^2$	3×10^{-4}	10 ± 3
$TlAlCl_4$	315	$(Al_2Cl_7^-)(Cl^-)/(AlCl_4^-)^2$	6.5×10^{-3}	27 ± 5

Evaluation of Solute Complex Formation Constants. From plots suggested by eq 8, 9, and 10 it is shown that $SbCl_3$ reacts with a single mole of chloride ion to form the species $SbCl_4^-$ in the melt. A plot of $(K - K°)/K°$ *vs.* the calculated TlCl concentration results in a straight line intersecting the origin (Figure 4) predicted in eq 8 for a 1:1 molar reaction. The slope of this line gives the formation constant, K_f, of the complex in the melt directly.

$$SbCl_3 + Cl^- \overset{K_f}{\rightleftharpoons} SbCl_4^-$$

Table IV lists the formation constants found for the tetrachloroantimonates in three different tetrachloroferrate and tetrachloroaluminate melts. It should be noted that the formation constant for potassium tetrachloroantimonate is identical, within experimental error, in both the potassium tetrachloroferrate and the potassium tetrachloroaluminate melts, as would be predicted. Errors in the values reported are primarily caused by uncertainties in the measurements of $K°$.

Table IV. Formation Constants for Tetrachloroantimonates in Various Melts

Melt	Temp, °C	Equilibrium	K_f, l./mole
$KFeCl_4$	290	$(KSbCl_4)/(SbCl_3)(KCl)$	40 ± 10
$KAlCl_4$	289	$(KSbCl_4)/(SbCl_3)(KCl)$	40 ± 10
$TlAlCl_4$	315	$(TlSbCl_4)/(SbCl_3)(TlCl)$	0.8 ± 0.2

Acknowledgment. The authors wish to thank Stephen N. Chesler for his assistance in the construction of the density balance used in these investigations. The generous support of the National Science Foundation under Grant GP-5151X is also gratefully acknowledged.