

with 0.3 *M* lanthanum perchlorate resulted in the separation of the two species. The species with the absorption maximum at 225 *mμ* was eluted as a discrete band in front of the lanthanum just as the Ru<sup>3+</sup> described by Cady. The species with the peak at 290 *mμ* eluted only as a diffuse band with lanthanum and resisted all attempts to "push" it.

The most plausible explanation of the above results was suggested to us by E. E. Mercer. The Ru(III) produced by the reduction of Ru(IV) at -0.4 V is a polymeric species. Reduction of that species at -0.6 V results in the formation of monomeric Ru(II) which is rapidly oxidized to monomeric Ru<sup>3+</sup> by perchloric acid.

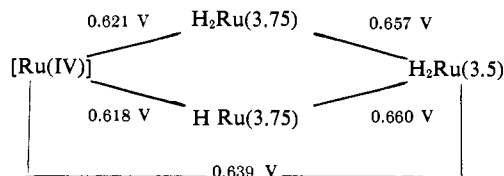
### Summary

Ru(IV) in perchloric acid media is a tetrameric species with a charge of +4 which can be reduced reversibly at a gold electrode by two, one-electron processes to tetrameric species with formal oxidation states of 3.75 and 3.5. Because approximately one hydrogen ion is involved as a reactant in each of these reactions, the reduced species can be formulated as [H Ru(3.75)]<sup>4+</sup> and [H<sub>2</sub>Ru(3.5)]<sup>4+</sup>. A more complete description requires the assumption of the species [H<sub>2</sub>Ru(3.75)]<sup>5+</sup> as well.

Tetrameric [H<sub>2</sub>Ru(3.5)]<sup>4+</sup> is then reduced by a two-electron process, the details of which are not known, to a transient species of Ru(III) (presumably also tetrameric). The transient form of Ru(III) undergoes a spontaneous conversion to a stable polymeric form of Ru(III). The lifetime of the transient Ru(III) is greater

than 10 sec but less than 30 min. Stable Ru(III) can be reoxidized irreversibly back to the original tetrameric Ru(IV), but there do not appear to be any well-defined reversible steps in this process. Stable Ru(III) can also be reduced to Ru(II) which is spontaneously oxidized by perchloric acid to monomeric Ru<sup>3+</sup>.

The potential diagram for the processes involved in the reduction of Ru(IV) to H<sub>2</sub>Ru(3.5) at ionic strength 1 *M*, referred to the normal hydrogen electrode, is shown below. The signs follow the IUPAC conventions. The potential for the reduction of H<sub>2</sub>Ru-



(3.5) to the transient form of Ru(III) determined by cyclic voltammetry in 0.1 *M* H<sup>+</sup> and ionic strength 1 *M* was 0.40 V *vs.* the normal hydrogen electrode. No study of the acid dependence of this process has been made so the number of hydrogen ions involved is not known.

**Acknowledgments.** We wish to acknowledge the assistance of F. G. McNatt and J. W. Crooks with the experimental work. The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

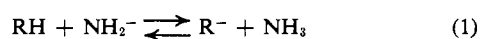
## Liquid Ammonia Solutions. VII. Solutions of Carbon Acids

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**Abstract:** The reaction of a series of hydrocarbon acids with potassium amide in liquid ammonia has been investigated using spectrophotometric techniques reported previously. The acidity and spectroscopic characteristics of di(*p*-tolyl)methane and 4,4'-dimethoxydiphenylmethane permit the ionization constants of these substances to be determined; at -34.5°, the ionization constants of di(*p*-tolyl)methane and di(4-methoxyphenyl)methane are  $7.33 \times 10^{-28}$  and  $2.53 \times 10^{-29}$ , respectively.

Weakly acidic carbon and nitrogen acids such as diphenylmethane and aniline can be deprotonated in liquid ammonia solutions containing amide ions, the strongest base that can exist in this solvent. In the case of carbon acids, *i.e.*, compounds that donate a proton by fission of a carbon-hydrogen bond, the equilibrium described by eq 1 is established when the conju-



$$K = (a_{\text{R}^-})(a_{\text{NH}_3}) / (a_{\text{RH}})(a_{\text{NH}_2^-}) \quad (2)$$

gate base formed by deprotonation with amide ion is of comparable strength to the latter. The relative

strengths of hydrocarbon acids should be related to the equilibrium constants defined in the usual manner (eq 2). Since many of the conjugate bases (R<sup>-</sup>) are highly colored in liquid ammonia solution, it should be possible to monitor the position of equilibrium 1 using the absorption band(s) characteristic of the conjugate base, the band characteristic of the amide ion,<sup>1</sup> or both. We present here the results of a spectrophotometric investigation of the equilibria established between a series of carbon acids and potassium amide in anhydrous liquid ammonia.

(1) R. E. Cuthrell and J. J. Lagowski, *J. Phys. Chem.*, **71**, 1298 (1967).

**Table I.** Absorbance Maxima, Half-Widths, and Extinction Coefficients of the Potassium Salts of Carbon Acids in Liquid Ammonia at  $-34.5^\circ$ 

Potassium salt	Band center, $\text{cm}^{-1}$ ( $\text{\AA}$ )	Width at half-height, $\text{cm}^{-1}$	$\epsilon \times 10^{-4}$ , $\text{l. mol}^{-1} \text{cm}^{-1}$
Xanthene	$17,604 \pm 7$ ( $5861 \pm 2$ )	$630 \pm 10$	...
	$19,553 \pm 62$ ( $5114 \pm 16$ )	$2650 \pm 80$	...
	$21,865 \pm 125$ ( $4574 \pm 26$ )	$3800 \pm 80$	$1.70 \pm 0.01$
Triphenylmethane	$19,946 \pm 37$ ( $5014 \pm 9$ )	$2920 \pm 30$	$3.08 \pm 0.06$
	$23,399 \pm 185$ ( $4274 \pm 34$ )	$3970 \pm 440$	...
	$22,696 \pm 16$ ( $4406 \pm 3$ )	$2700 \pm 200$	$4.90 \pm 0.02$
Diphenylmethane	$22,534 \pm 24$ ( $4438 \pm 4$ )	$3110 \pm 50$	$4.57 \pm 0.13$
Di( <i>p</i> -tolyl)methane	$23,307 \pm 18$ ( $4290 \pm 3$ )	$2700 \pm 200$	$3.00 \pm 0.01$

## Experimental Section

The spectra of anhydrous liquid ammonia solutions of the carbon acids and their potassium salts were determined using essentially the same apparatus and techniques described previously.<sup>2</sup> The optical cell (path length, 0.957 cm), the dilution vessels in the spectrophotometric dewar, and all sample-transfer equipment which came into contact with liquid ammonia solutions were treated with  $10^{-3} M \text{KNH}_2$  solutions at  $-78^\circ$  and rinsed several times with anhydrous liquid ammonia to remove adsorbed water which could not be removed by evacuation of the system under high vacuum.<sup>3</sup>

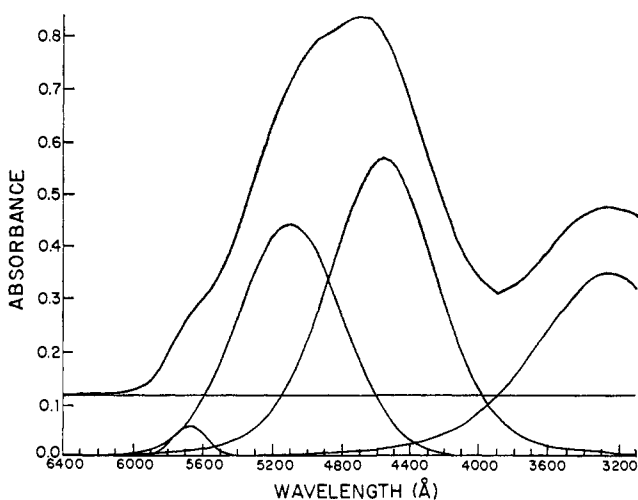


Figure 1. The spectrum of a mixture of xanthene and potassium amide in liquid ammonia at  $-34.5^\circ$ . The upper curve is the experimental envelope which has been resolved into the lower set of bands.

All equipment prepared in this manner was rigorously protected from atmospheric recontamination.

All carbon acids were the highest purity commercially available; these substances were recrystallized to a constant melting point and analyzed for carbon and hydrogen using conventional micro-combustion techniques. The samples used in this work had melting points that were consistent with those reported in the literature and analyses that were within the usually defined limits.<sup>4</sup>

Potassium amide was prepared from the catalytic decomposition of potassium metal-anhydrous ammonia solutions, and the product was recrystallized several times from anhydrous ammonia. All chemicals were stored in a drybox, the helium atmosphere of which was equilibrated with the liquid eutectic mixture of the Na-K system.<sup>5</sup>

The spectra of liquid ammonia solutions containing the hydrocarbon acid, and of mixtures of the hydrocarbon acid and potassium

amide, were determined at  $-34.5^\circ$  using a Cary Model 14 recording spectrophotometer. The spectra were digitized with a Pencil Follower (Edwin Industries) and resolved into their component bands using a computer program kindly supplied by D. D. Tunnicliff of Shell Development Co. and modified by P. F. Rusch of these laboratories for use on a CDC 6600.<sup>4</sup> An example of the experimentally obtained spectrum and of the resolved spectrum of a mixture of a carbon acid and potassium amide in liquid ammonia appears in Figure 1. In every case the resolved bands could be summed to give the experimental envelope to within the accuracy of the spectrophotometer.

Since it was important to monitor the concentration of the amide ion in liquid ammonia solutions of potassium amide, the spectral characteristics reported for this species<sup>1</sup> were redetermined by following the decrease in the intensity of the band in potassium amide solutions upon addition of weighed amounts of ammonium chloride; the molar extinction coefficient at the band maximum ( $\epsilon_{\text{max}}$ ) at  $-34.5^\circ$  is  $3.02 \pm 0.05 \times 10^3$ .

## Results and Discussion

All of the carbon acids studied are slightly soluble in liquid ammonia over the temperature range  $-33$  to  $-40^\circ$ . The solubility of these compounds [except di(4-dimethylaminophenyl)methane] is approximately 5 mg/100 ml of ammonia at  $-35^\circ$ . The solubility of di(4-dimethylaminophenyl)methane is about 1 mg/ml under the same conditions. Each of the carbon acids shows spectral features characteristic of the phenyl ring,<sup>6</sup> *i.e.*, a band at 260–270  $m\mu$  with an estimated molar extinction coefficient ( $\epsilon_{\text{max}}$ ) of  $1-5 \times 10^3$ .

The carbon acids readily dissolve in anhydrous ammonia solutions of  $\text{KNH}_2$  to give colored solutions (presumably arising from the formation of the corresponding potassium salts) which exhibit intense absorption bands in the region 425–500  $m\mu$  (Table I). In general, the spectra consist of overlapping bands characteristic of the free carbon acid, the conjugate base, and excess  $\text{KNH}_2$ . The relative band intensities are dependent upon the analytical mole ratio of carbon acid to  $\text{KNH}_2$ .

A comparison of the spectra of xanthene, triphenylmethane, and diphenylmethane in pure liquid ammonia with the spectra of solutions of these compounds containing  $\text{KNH}_2$  indicates that they do not undergo detectable ionization. However, these three compounds are sufficiently acidic that they react essentially completely ( $>99\%$ ) with potassium amide, and the equilibria established cannot be determined accurately spectrophotometrically. In the cases of di(*p*-tolyl)methane and di(4-methoxyphenyl)methane, it is possible to estimate the equilibrium constants for eq 1 from the spectral parameters of each parent acid, its conjugate base (Table I), and  $\text{KNH}_2$ .

(6) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, p 125.

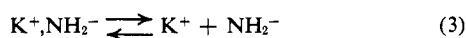
(2) R. E. Cuthrell, E. C. Fohn, and J. J. Lagowski, *Inorg. Chem.*, **4**, 1002 (1965).

(3) D. F. Burow and J. J. Lagowski, *Advances in Chemistry Series*, No. 50, American Chemical Society, Washington, D. C., 1965, p 125.

(4) For a more detailed description, see J. H. Takemoto, Ph.D. Dissertation, The University of Texas at Austin, 1968.

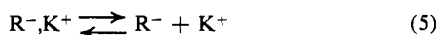
(5) D. F. Burow, Ph.D. Dissertation, The University of Texas, 1966.

The results of conductivity studies and spectrophotometric investigations indicate that dilute potassium amide solutions in liquid ammonia contain potassium ions, solvated amide ions, and solvent-separated ion pairs in equilibrium (eq 3).<sup>1</sup> Weak carbon acids react



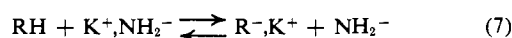
$$K_d = (a_{\text{K}^+})(a_{\text{NH}_2^-}) / (a_{\text{K}^+, \text{NH}_2^-}) \quad (4)$$

with potassium amide to yield the potassium salt of the conjugate bases (eq 1), which can exist as either ion pairs or the free ions (eq 5). A final equilibrium expres-



$$K_d' = (a_{\text{R}^-})(a_{\text{K}^+}) / (a_{\text{R}^-, \text{K}^+}) \quad (6)$$

sion could be written for the species in this system (eq 7),



but since it is the sum of eq 1, 3, and the reverse of eq 5, it is mathematically superfluous.

A direct comparison of the relative strengths of hydrocarbon acids can be made on the basis of their equilibrium constants (eq 2) for reaction 1. Practically, this can be achieved if it is assumed that the activities of the species in equilibria 1, 3, and 5 can be replaced by their concentrations in the dilute solutions ( $10^{-4}$ – $10^{-5}$  *M*) studied here and that the activity of the solvent is a constant. Under these conditions, eq 2 becomes

$$K' = \frac{K}{a_{\text{NH}_3}} = [\text{R}^-] / [\text{NH}_2^-][\text{RH}] \quad (8)$$

where the brackets have their usual meaning. Ion pairs cannot be distinguished spectrophotometrically from the corresponding free ions in liquid ammonia,<sup>1,7</sup> but the analytical concentrations of potassium amide ( $[\text{K}^+\text{NH}_2^-]_0$ ) and the potassium salt of the weak acid ( $[\text{R}^-\text{K}^+]_0$ ) can be expressed in terms of the absorbance of these species at a characteristic wavelength (eq 9 and 10); the subscripts 1 and 2 refer to the amide ion and

$$[\text{K}^+\text{NH}_2^-]_0 = [\text{NH}_2^-] + [\text{K}^+, \text{NH}_2^-] = A_1 / \epsilon_1 l \quad (9)$$

$$[\text{R}^-\text{K}^+]_0 = [\text{R}^-] + [\text{K}^+, \text{R}^-] = A_2 / \epsilon_2 l \quad (10)$$

carbanion, respectively. In addition, the free potassium ion concentration ( $[\text{K}^+]_0$ ) is given by eq 11. The quan-

$$[\text{K}^+]_0 = [\text{R}^-] + [\text{NH}_2^-] \quad (11)$$

ties  $[\text{K}^+, \text{NH}_2^-]$ ,  $[\text{K}^+, \text{R}^-]$ , and  $[\text{K}^+]$  can be eliminated from eq 4, 5 (in which concentrations have been substituted for activities), 9, 10, and 11 to give eq 12 and 13.

$$[\text{NH}_2^-]^2 + [\text{NH}_2^-](K_d + [\text{R}^-]) - K_d A_1 / \epsilon_1 l = 0 \quad (12)$$

$$[\text{R}^-]^2 + [\text{R}^-](K_d' + [\text{NH}_2^-]) - K_d' A_2 / \epsilon_2 l = 0 \quad (13)$$

The results of conductivity measurements on solutions of  $\text{KNH}_2$  yield a value of  $0.70 \times 10^{-4}$  for  $K_d$  at  $-33.2^\circ$ .<sup>8</sup> Although conductivity data are not available for the potassium salts of di(*p*-tolyl)methane or di(4-methoxyphenyl)methane, a reasonable estimate can be obtained from structurally similar compounds. Assuming that

anions of the diphenylmethane-type carbon acids have structures and conductivities similar to those of the diphenylamide ion, the dissociation constant for  $\text{KN}(\text{C}_6\text{H}_5)_2$  as determined from conductivity data ( $5.0 \times 10^{-3}$  at  $-33.2^\circ$ )<sup>8</sup> can be used as a good approximation for  $K_d'$ . Using these assumptions, and under the conditions of our experiments, eq 12 and 13 are a pair of nonlinear equations of the type  $X^2 + X(Y + A) + B = 0$ . At a given analytical mole ratio of  $\text{KNH}_2:\text{RH}$ , unique experimentally determinable values of  $A_1$  and  $A_2$  can be obtained. Since  $K_d$ ,  $K_d'$ ,  $\epsilon_1$ ,  $\epsilon_2$ , and  $l$  are known constants, eq 12 and 13 can be solved for  $[\text{NH}_2^-]$  and  $[\text{R}^-]$  using a computer version<sup>4</sup> of the Newton-Raphson method.<sup>9</sup> Knowing  $[\text{NH}_2^-]$  and  $[\text{R}^-]$ , it is then possible to evaluate  $[\text{RH}]$  from the analytical concentration of  $\text{RH}$  and  $A_1$ . Since the concentration of each of the species in eq 8 is known,  $K'$  can be determined directly. Data for this type of analysis for di(*p*-tolyl)methane and di(4-methoxyphenyl)methane appear in Table II.

Table II. Spectrophotometric Data for Di(*p*-tolyl)methane and Di(4-methoxyphenyl)methane

$[\text{RH}]_0$ $\times 10^6$ , <i>M</i> <sup>a</sup>	<i>A</i> <sub>1</sub> <sup>b</sup>	<i>A</i> <sub>2</sub> <sup>c</sup>	$[\text{R}^-]$ $\times 10^6$ , <i>M</i> <sup>d</sup>	$[\text{NH}_2^-]$ $\times 10^6$ , <i>M</i> <sup>d</sup>	$[\text{RH}]$ $\times 10^6$ , <i>M</i> <sup>e</sup>	$K' \times 10^{-3}$
Di( <i>p</i> -tolyl)methane						
0.60	0.259	0.887	0.58	11.3	0.21	244
2.06	0.861	0.242	1.94	4.39	1.20	368
2.97	1.217	0.379	2.74	5.88	2.29	203
6.6	2.45	0.144	5.5	2.3	11.0	220
4.62	1.902	0.878	4.23	10.0	38.5	110
Av = (2.29 ± 0.66) × 10 <sup>-5</sup>						
Di(4-methoxyphenyl)methane						
1.11	0.142	0.652	0.485	9.37	6.21	8.34
1.87	0.126	0.189	0.435	4.00	14.4	7.55
2.23	0.177	0.238	0.610	4.70	16.1	8.06
2.39	0.273	0.561	0.934	8.34	14.5	7.72
0.801	0.144	0.949	0.387	11.9	4.13	7.88
Av = (7.91 ± 0.27) × 10 <sup>-5</sup>						

<sup>a</sup> Initial analytical concentration. <sup>b</sup> Absorbance at  $\lambda_{\text{max}}$  for  $\Sigma([\text{R}^-] + [\text{K}^+\text{R}^-])$ . <sup>c</sup> Absorbance at  $\lambda_{\text{max}}$  for  $\Sigma([\text{NH}_2^-] + [\text{K}^+\text{NH}_2^-])$ . <sup>d</sup> Calculated from eq 12 and 13. <sup>e</sup> Calculated from  $[\text{RH}]_0$  and  $A_1$ .

$K'$  can be converted into conventional ionization constants,  $K_a$ , using the familiar relationship shown in eq 14, where  $K_s$  is the autoprotolysis constant for

$$K' = K_a / K_s \quad (14)$$

liquid ammonia. Using the value  $3.3 \times 10^{-33}$  for  $K_s$  at  $-33^\circ$ , which was determined from thermodynamic arguments,<sup>10</sup>  $K_a$  for di(*p*-tolyl)methane and di(4-methoxyphenyl)methane is calculated to be  $7.33 \times 10^{-28}$  ( $\text{p}K_a = 27.1$ ) and  $2.53 \times 10^{-29}$  ( $\text{p}K_a = 28.6$ ), respectively.

The data reported here, together with the equilibrium constants reported previously for nitroacetanilides (at  $-55.6^\circ$ ), bring to four the number of acids for which equilibrium constants in anhydrous ammonia have been determined. A much larger body of nmr data (at  $31^\circ$ ) exists from which the relative acidities of a series of

(7) (a) R. E. Cuthrell, E. C. Fohn, and J. J. Lagowski, *Inorg. Chem.*, **5**, 111 (1966); (b) J. T. Nelson, R. E. Cuthrell, and J. J. Lagowski, *J. Phys. Chem.*, **70**, 1492 (1966).

(8) C. A. Kraus and W. W. Hawes, *J. Am. Chem. Soc.*, **55**, 2776 (1933).

(9) D. D. McCracken and W. S. Dorn, "Numerical Methods and Fortran Programming," John Wiley and Sons, Inc., New York, N. Y., 1964, p 144.

(10) L. V. Coulter, J. R. Sinclair, A. G. Cole, and G. C. Roper, *J. Am. Chem. Soc.*, **81**, 2986 (1959).

compounds have been determined,<sup>11</sup> but, unfortunately, the data available at this point do not provide a method for relating the meager quantitative data to the more

(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).

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.

## Gas Chromatographic Evaluation of Equilibria in Fused Salts. I. The Tetrachloroaluminate and Tetrachloroferrate Systems<sup>1,2</sup>

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**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  $290^\circ$  in  $KFeCl_4$  and in  $KAlCl_4$ ;  $TlCl + SbCl_3 \rightleftharpoons TlSbCl_4$ ,  $K_f = 0.8 \pm 0.2$  at  $315^\circ$  in  $TlAlCl_4$ ;  $2FeCl_4^- \rightleftharpoons Fe_2Cl_7^- + Cl^-$ ,  $K_d = 4 \times 10^{-4}$  at  $290^\circ$  in  $KFeCl_4$ ;  $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$ ,  $K_d = 3 \times 10^{-4}$  at  $289^\circ$  in  $KAlCl_4$ ; and  $K_d = 6.5 \times 10^{-3}$  at  $315^\circ$  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<sup>4</sup> in 1960. Inorganic fused-salt liquid phases allow the gas chromatographic elution and separation of metal halides boiling at temperatures as high as  $800^\circ$ . In recent work from this laboratory<sup>5</sup> 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  $450^\circ$ .  $LiCl$  (Baker's Analyzed, 99.2%) was dried at  $450^\circ$  for 24 hr in the presence of dry  $HCl$  gas.  $TlCl$  (Fisher) was vacuum dried at  $400^\circ$ . 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.<sup>6</sup> 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-