$Bz{\cdot}I_2$ complex, for example, Plyler and Mulliken[11] used a 4 mm. cell to study I_2 absorption. The enhanced benzene bands in $Bz{\cdot}I_2$ complex at 992 and 850 cm.$^{-1}$ are measured to have intensities of roughly 200 and 400 darks, respectively, while the I_2 absorption in the same complex is indeed less, around 120 darks.[15]

A consideration which may be significant here is that part of the intensity of the $I_2{\cdot}Bz$ band must be due to solvent effects. That this can be important is shown by the data of Person, *et al.*,[8a] on ICl in various solvents. The vapor intensity is reported as 650 darks, while the intensity in the inert solvents CCl_4, *n*-heptane and *n*-hexane, are all around 1000 darks. The intensity in benzene is 1900 darks, but the Bz·ICl complex is considerably stronger (K = 4.76 cm. moles^{-1}) than the $Bz{\cdot}X_2$ complexes.

It is of interest to note that the "electronic vibration" intensity is large compared to the normal or "permanent dipole" contribution. The spectroscopic values of dative coefficient appear larger than those inferred from binding energy and dipole moment data. Using a lower dative coefficient would decrease the calculated intensities and hence lessen the agreement with experimental data.[16] However, the relative importance of the "electronic vibration" intensity to the "permanent dipole" intensity would increase with decreasing dative coefficient since the first goes as the square and the latter as the fourth power of the dative coefficient.

We wish to express our appreciation to Dr. R. E. Erickson, to our anonymous reviewer for a number of helpful suggestions and to Professor Person for sending us copies of his work before publication.

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(15) In a previous paper (ref. 2) the 992 cm.$^{-1}$ benzene band in the benzene–iodine complex has been assigned an intensity of 770 ± 300 darks on the basis of a crudely measured peak intensity, an estimated normal half width and an assumed Lorentz shape. A recent direct measurement made in this Laboratory yields the value 190 ± 40 darks.

(16) For example, using the value b = 0.21, calculated from the observed dipole moment (assuming the overlap integral S = 0 consistent with the other calculations here) would reduce the calculated intensity by a factor

$$\left(\frac{0.21}{0.37}\right)^2 = \frac{1}{3}$$

[Contribution from the Oak Ridge National Laboratory, Chemistry Division, Oak Ridge, Tennessee]

Anion Exchange Studies. XXXI. Adsorption of Zn(II) and Ga(III) from HCl Solutions in the Temperature Range 25 to 150°[1]

By Kurt A. Kraus and Richard J. Raridon[2]

Received November 30, 1959

Adsorption functions of Zn(II) and Ga(III) have been determined by the preloaded column technique in the temperature range 25 to 150° in HCl solutions. Large changes in adsorbabilities with temperature have been observed. Adsorbability of negatively charged complexes decreases rapidly with increasing temperature and for $GaCl_4^-$, $\Delta\bar{H}$ for the ion exchange reactions is *ca.* −14 kcal. (extrapolated to $m_{HCl} = 0$). The shape of the adsorption functions changes rapidly with temperature. From these changes one can deduce that the degree of complexing of Zn(II) and Ga(III) increases rapidly with temperature at constant chloride concentration. Attempts were made to estimate the average heats of the complexing reactions. While these are largely of a qualitative nature, one may conclude that with increasing temperature stability constants change in a direction which increases the preponderance of neutral species or of species of low absolute charge.

From the adsorption functions of metals, one may deduce[3,4] information regarding the extent of complexing of the metals in the aqueous phase. Because of the high intrinsic selectivities of anion exchangers for some complexes, substantial adsorption may occur even when the fraction of the metal in the form of negatively charged complexes is small and when the average charge of the dissolved metal is positive. In an earlier paper,[4] some of the techniques were discussed in detail which may be used for computation of the average charge of the metals from anion exchange data and of the fraction of the metal present as negatively charged complexes in the aqueous phase.

With the development[5] of relatively simple equipment for measurement of ion exchange equilibria as a function of temperature up to 200°, it became of interest to illustrate the use of the anion exchange techniques for study of complexing reactions at high temperatures. Zinc(II) and Ga(III) in HCl were chosen for illustration since these elements have been studied in considerable detail at room temperature.[4]

Experimental

1. **Method and Equipment.**—Adsorbabilities were determined by the "pre-loaded column technique" with the high temperature column equipment previously described.[5] In this method, a sample of resin, uniformly loaded with the ion whose adsorption is to be studied, is placed in the column. At proper flow rates, eluent passing through the column leaves it equilibrated with the lower layers of the bed whose composition does not materially change if the number of column volumes of solution passed through the column is

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(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation. Previous papers: (a) XXVIII, F. Nelson, *J. Polymer Sci.*, **40**, 563 (1959); (b) XXIX, F. Nelson and K. A. Kraus, *J. Chromatography*, **3**, 279 (1960); (c) XXX, F. Nelson, R. A. Day, Jr., and K. A. Kraus, *J. Inorg. & Nuclear Chem.* (in press).

(2) Based on work submitted by R. J. Raridon to Vanderbilt University in partial fulfillment of the requirement for a Ph.D. degree. Work carried out at Oak Ridge National Laboratory under sponsorship of the Oak Ridge Institute of Nuclear Studies.

(3) K. A. Kraus and F. Nelson, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," Vol. VII, page 113, 131 (United Nations, 1956).

(4) K. A. Kraus and F. Nelson, "Anion Exchange Studies of Metal Complexes," in "The Structure of Electrolytic Solutions," Walter J. Hamer, Editor, John Wiley and Sons, Inc., New York, N. Y., 1959, p. 340.

(5) (a) K. A. Kraus, R. J. Raridon and D. L. Holcomb, *J. Chromatography* **3**, 178 (1960); (b) K. A. Kraus and R. J. Raridon, *J. Phys. Chem.*, **63**, 1901 (1959).

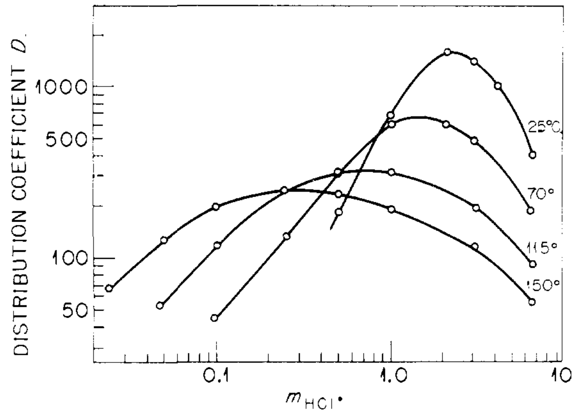

Fig. 1.—Adsorption of Zn(II) from HCl solutions as a function of temperature (Dowex-1X10, Cl^- form).

not excessive. Equilibrium was assumed established if the effluent concentration was independent of flow rate. From the concentration of material in the effluent and the known initial concentration in the resin bed, the distribution coefficient D (amount per kg. dry resin/amount per kg. water in solution) may be computed.

2. **Solutions and Radioactive Tracers.**—All analyses were carried out radiometrically using the tracers Zn^{65} ($T_{1/2}$ = 250 d.) and Ga^{67} ($T_{1/2}$ = 78 h). The liquid samples were collected in glass vials, counted in a well-type scintillation counter (NaI-Tl activated) and their size ascertained by weighing. From the values of activity per kg. of solution, the concentrations in terms of amount per kg. of water were computed using density values from the literature. The specific activity of the tracers was sufficiently large so that resins loading was always substantially less than 1% of capacity.

Zn^{65} tracer was obtained from the Radioisotopes Division of ORNL, with stated radiochemical purity greater than 98%.

The Ga^{67} tracer was prepared by cyclotron bombardment of zinc foil and separated and purified by anion exchange.[3] The bombarded zinc foil was dissolved in 8M HCl. The solution was passed through a small resin bed, pretreated with 8M HCl, whose total capacity was much less than would have been needed to adsorb the dissolved zinc. Thus, while some zinc is adsorbed, the bulk passes through this bed of limited capacity. However, because of its very high distribution coefficients, essentially all gallium is adsorbed by the resin. The loaded column was washed with a small amount of 1M HCl to remove Ga(III) from the resin while most of the adsorbed zinc was retained by the bed. Concentrated HCl was added to the effluent to raise its concentration again to 8M and a second adsorption–elution cycle carried out with a new, small resin column to remove the remaining zinc from the solution. Purity of the tracer was checked by following its decay for several half-lives.

Results and Discussion

(1) **Zn(II).**—The adsorption function of Zn(II) in HCl solutions was determined in the range $0.02 \leq m_{HCl} \leq 8$ (m is moles per 1000 g. of water) at 25, 70, 115 and 150°. Attempts to make measurements at higher temperatures were abandoned since in some tests ($m_{HCl} \approx 0.5$) drifts in the distribution coefficients with time occurred indicating decomposition of the exchanger.[5a] For example, at 175°, D varied by ~0.2% per minute. At 150°, there was no appreciable change of D in several hours.

Measurements were made with increasing and decreasing temperature. The results were averaged and are summarized in Fig. 1. The characteristic maximum of the distribution function which at 25° is located near m_{HCl} = 2 decreases significantly with increasing temperature and shifts to lower value of m_{HCl}. Further, the maximum broadens substantially and the slope at low HCl concentrations decreases with increasing temperatures.

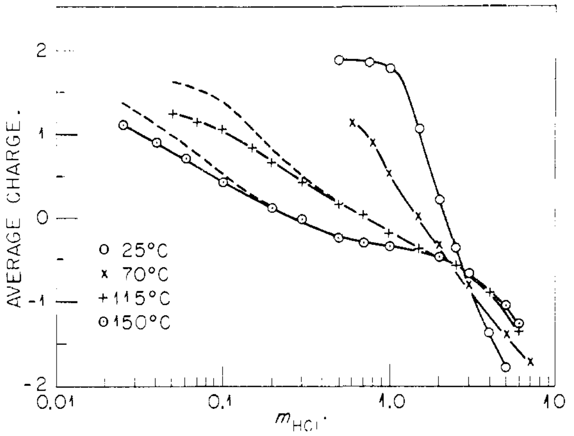

Fig. 2.—Chloride complexing of Zn(II) from anion exchange data. (Solid lines are d ln D/d ln m_{HCl}; broken lines are corrected for Debye–Hückel theory.)

(1.1) **Average Charge.**—As discussed earlier,[4] the slope S of a plot of log D *vs.* log m_{HCl} is closely related to the average charge $\bar{z}$ of all metal species in solution and hence to the average ligand number $\bar{l}$ which is given by

$$\bar{l} = \nu_0 - \bar{z} \qquad (1)$$

where ν_0 is the charge of the uncomplexed metal species. We may define $\bar{z}$ as

$$\bar{z} = \sum_{i=0}^{p} z_i F_i \qquad (2)$$

where z_i is the charge of the species $ZnCl_i$, F_i is the fraction of the metal as this species and p is the maximum number of chloride ions which can be coordinated. The relationship between $\bar{z}$ and the slope S, though complicated in the general case, simplifies to

$$S = \frac{d \ln D}{d \ln m_{HCl}} = \sum_i z_i F_i + \sum_i F_i \frac{d \ln G_i}{d \ln m_{HCl}} \qquad (3)$$

if resin invasion and activity coefficients in the resin phase change little with HCl concentration. In equation 3, G_i is the activity coefficient of the component involving the species $ZnCl_i$, *i.e.*, $G_i = g_{ZnCl_i} g_{Cl}^{2-i}$.

By graphical differentiation (Gerber Derivimeter Model D-1) of the curves, Fig. 1, the slopes S = d log D/d log m_{HCl} plotted in Fig. 2 (solid lines) were obtained. These should approximate the average charges of the species at low m_{HCl} since then presumably the simplifications, implied in equation 3, hold. For the more dilute HCl solutions, an attempt was made to correct for the (aqueous phase) activity coefficient term

$$\sum F_i \frac{d \ln G_i}{d \ln m_{HCl}}$$

assuming that G_i is given by the Debye–Hückel expression in the form

$$\log g_\pm = -\mathcal{S} z_i z_j \frac{\mu^{1/2}}{1 + 1.5\mu^{1/2}} \qquad (4)$$

where $\mathcal{S} = 1.8252 \times 10^6(\rho/\epsilon^3 T^3)^{1/2}$ (0.509 at 25°)

(see also ref. 5b). Since the individual values of F_i cannot be determined readily, the activity coefficient derivatives were weighted according to the average charge rather than F_i.[6]

The average charge $\bar{z}$ estimated in this manner (dotted lines, Fig. 2) is, at least at low HCl concentrations, a good indication of the extent of complexing of Zn(II). At low temperatures (25°), the average charge remains close to +2 up to almost $m_{HCl} = 0.5$, reflecting the small tendency for chloride complexing of Zn(II) under these conditions. (For more detailed discussion of complexing of Zn(II) at 25°, see ref. 4.) With increasing temperature, the average charge of Zn(II) decreases rapidly at any given m_{HCl} and, conversely, a given average positive charge (*e.g.* $\bar{z} = 1$) occurs at substantially lower values of m_{HCl} as the temperature increases. Clearly, Zn(II) at high temperatures becomes extensively complexed even at low HCl concentrations and the enthalpy change for the complexing reaction, in general, is large and positive.

(1.2) Complex Constants and Enthalpy Changes.—In order to obtain even a semi-quantitative estimate of the heat of the complexing reactions, it is necessary to evaluate as a function of temperature the stability constants k_{ij} defined as

$$k_{ij} = k_{ij}^{0}\,G_{ij} = \frac{(\mathrm{MCl}_j)}{(\mathrm{MCl}_i)(\mathrm{Cl})^{j-i}}\,G_{ij} \qquad (5)$$

where ( ) indicates concentration of species, k_{ij}^{0} is the concentration quotient and G_{ij} the appropriate activity coefficient quotient. Rearranging equation 1 to

$$\bar{i} = (\nu_0 - \bar{z}) = \Sigma i F_i = F_0 \Sigma i F_i / F_0 \qquad (6)$$

and remembering that[4]

$$\frac{1}{F_0} = \Sigma k_{oi}^{0} m_{Cl}^{i} \qquad (7)$$

one obtains the general relationship between $\bar{z}$ and the stability constants[7]

$$\sum_{i=0}^{i=p} (\nu_0 - \bar{z} - i) k_{oi}^{0}\, m_{Cl}^{i} = 0 \qquad (8)$$

In the case of Zn(II) where $\nu_0 = 2$ and where presumably $p = 4$, equation 8 simplifies to

$$\frac{2 - \bar{z}}{(z + 2)m_{Cl}} = \frac{\bar{z} - 1}{\bar{z} + 2}\,k_{o1}^{0} + \frac{\bar{z}}{\bar{z} + 2}\,k_{o2}^{0} m_{Cl} + \frac{\bar{z} + 1}{\bar{z} + 2}\,k_{o3}^{0}\, m_{Cl}^{2} + k_{o4}^{0}\, m_{Cl}^{3} \qquad (9)$$

Application of equation 9 to evaluation of the complex constants of Zn(II) is unfortunately greatly limited because of uncertainties in the activity coefficients and activity coefficient derivatives needed in the computation of $\bar{z}$. We therefore have used equation 9 only to estimate the stability constants $k_{o_1}^{0}$ and $k_{o_2}^{0}$ at 115 and 150° where the applicable data were obtained at reasonably low ionic strength. If one assumes that for $\bar{z} \geq 1$ negatively charged complex species are of negligible importance at these high temperatures, equation 9 simplifies to

$$k_{o2}^{0} \approx \frac{1}{m_{Cl}^{2}}\ (\text{at } \bar{z} = 1) \qquad (10a)$$

$$k_{o_1}^{0} \approx \frac{1}{m_{Cl}} - 3k_{o_2}^{0}\, m_{Cl}\ (\text{at } \bar{z} = 1.5) \qquad (10b)$$

From the values of m_{HCl} at which $\bar{z} = 1$, we obtain at 150°, $k_{o_2}^{0} = 400$ ($m_{HCl} = 0.05$) and at 115°, $k_{o_2}^{0} = 40$ ($m_{HCl} = 0.158$). With the Debye–Hückel extrapolation function (eq. 4), one obtains $k_{o_2} = 2 \times 10^3$ and 3.7×10^2 at 150 and 115°, respectively. This change in k_{o_2} corresponds to an apparent enthalpy change $\Delta\bar{H}_{o_2} = 15.7$ kcal. for the reaction $Zn^{++} + 2Cl^- \rightarrow ZnCl_2$ in the range 115 to 150°. Attempts to evaluate $k_{o_1}^{0}$ were abandoned because the residuals obtained after subtracting the term involving k_{02}^{0} (eq. 10b) were not sufficiently large to make these numbers meaningful.

We may compare the high temperature values of k_{o_2} with the value $k_{o_2} = 5 \times 10^2$ for Cd(II) at 25°.[8] Under the same condition k_{o_2} for Zn(II) must be several orders of magnitude smaller.[8] It is interesting to note that the large differences in complexing properties of Zn(II) and Cd(II) which exist at room temperature can be compensated with Zn(II) by a moderate (*ca.* 90°) increase in temperature.

(1.3) Average Enthalpy Change for Complexing Reactions.—As mentioned, detailed analysis of the data at higher m_{HCl} in terms of stability constants and enthalpy changes for the complexing reactions is premature because of lack of sufficient information regarding activity coefficients. Nevertheless, a qualitative picture of the enthalpy changes may be obtained by plotting against $1/T$ the log of the chloride concentration at which $\bar{z}$ has a given value. The slopes of such plots yield weighted average apparent enthalpy changes for the complexing reactions, as shown in eq. 11 which was obtained by differentiation of eq. 8

$$\left(\frac{\partial \ln m_{Cl}}{\partial\,(1/T)}\right)_{\bar{z}} = \left[\Sigma(\nu_0 - \bar{z} - i) m_{Cl}^{i} k_{oi}^{0}\,\frac{\Delta\bar{H}_{oi}}{R}\right] \Big/ \left[\Sigma i(\nu_0 - \bar{z} - i) k_{oi}^{0} m_{Cl_i}\right] = \left[\Sigma(\bar{i} - i)F_i\,\frac{\Delta\bar{H}_{oi}}{R}\right] \Big/ \left[\Sigma\, i(\bar{i} - i)F_i\right] \qquad (11)$$

Here $\Delta\bar{H}_{oi}$ is the apparent enthalpy change for the reaction $M^{+\nu_0} + iCl^- \rightarrow MCl_i^{\nu_0 - i}$. The second part of eq. 11 was obtained by the substitutions $\bar{i} = \nu_0 - \bar{z}$ and $m_{Cl}^{i} k_{oi}^{0} = F_i/F_0$.

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(6) This was achieved through replacing ΣF_i (d ln G_i)/(d ln m_{HCl}) by (d ln $\bar{G}_i$)/(d ln m_{HCl}) where $\bar{G}_i$ is the activity coefficient of the average component which is determined by the average charge $\bar{z}$ (or the average ligand number $\bar{i}$) *i.e.*, $\bar{G}_i = g_{ZnCl_{\bar{i}}}\ g_{Cl}^{2-\bar{i}}$. The activity coefficient derivative was evaluated through the Debye–Hückel equation (see eq. 4) considering the valence factor variable. This valence factor for log G_i is 6, 2, 0, 0, 2 for i = 0, 1, 2, 3 and 4, respectively, which corresponds to $\bar{z}_i$ = 2, 1, 0, −1 and −2. A smooth curve was drawn through these valence factors and its value read for each S of interest. This yielded an approximation of $\bar{z}$; the final values were obtained by a short iteration.

(7) Stability constants may also be obtained more directly from the slopes S. Setting $G_i' = d \ln G_i/d \ln m_{Cl}$ and $z_i = \nu_0 - i$ one obtains from equation 3

$$S = F_0\Sigma[(F_i/F_0)(\nu_0 - i + G_i')] \qquad (a)$$

This yields with equation 7

$$\Sigma[k_{oi}^{0}\, m_{Cl}^{i}\,(S + i - \nu_0 - G_i')] = 0 \qquad (b)$$

which with the relationship $G_{io} = g_M g_{Cl}^{i}/g_{MCl_i} = G_0/G_i$ simplifies to

$$\Sigma k_{oi}\, m_{Cl}^{i}\left(\frac{1}{G_i}\right)(S + i - \nu_0 - G_i') = 0 \qquad (c)$$

(8) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants," Part II, The Chemical Society (London), Special Publication No. 7 (1958).

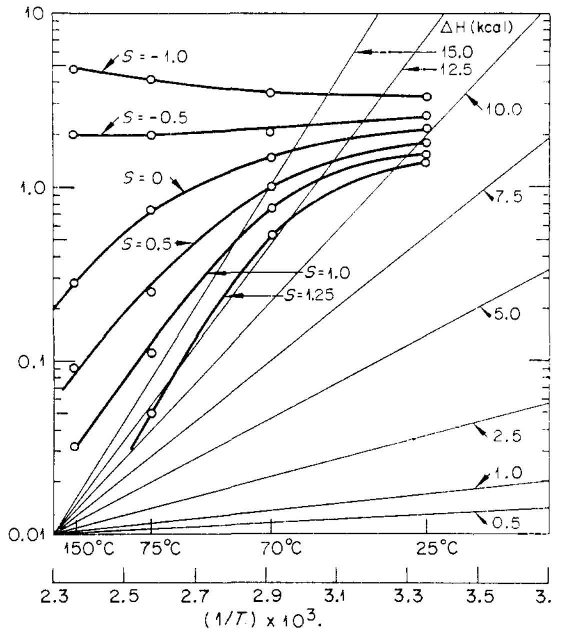

Fig. 3.—Estimation of heat of complex formation (Zn(II) in HCl).

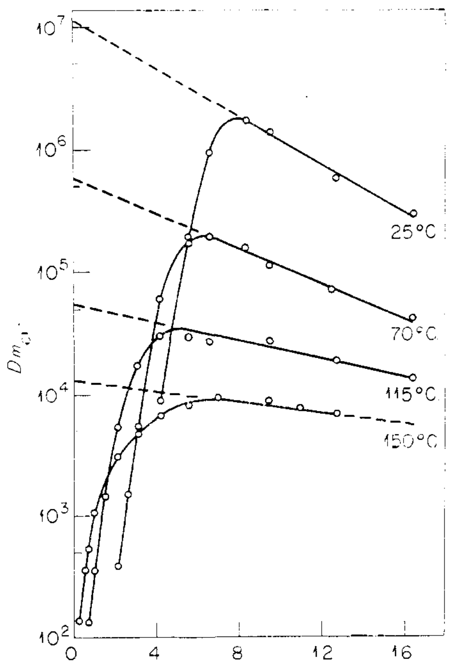

Fig. 4.—Adsorption of Ga(III) from HCl solutions as a function of temperature (Dowex-1X10, Cl⁻ form).

The meaning of the weighted enthalpy change of eq. 11 is not easy to see in general. However, the importance of the various terms becomes clearer if one considers an idealized system in which only two species are of importance at half-integral values of $\bar{z}$ (or $\bar{i}$), *i.e.*, if $F_0 = F_1 = 0.5$ at $\bar{z} = 1.5$; $F_1 = F_2 = 0.5$ at $\bar{z} = 0.5$; *etc.* Under these conditions, we find $\partial \ln m_{Cl}/\partial(1/T) = \Delta\bar{H}_{01}/R$ at $\bar{z} = 1.5$; $\partial \ln m_{Cl}/\partial(1/T) = \Delta\bar{H}_{02}/R - \Delta\bar{H}_{01}/R$ at $\bar{z} = 0.5$; and in general at $\bar{i} = i - 0.5$: $\partial \ln m_{Cl}/\partial(1/T) = \Delta\bar{H}_{0i}/R - \Delta\bar{H}_{0j}/R = \Delta\bar{H}_{ji}/R$ where $j = i - 1$.

Since in our case $\bar{z}$ is difficult to evaluate, we have substituted S for $\bar{z}$. A family of curves of log m_{HCl} *vs.* $1/T$ for S = 1.25, 1.0, 0.5, 0, −0.5 and −1.0 is given in Fig. 3. These slopes should be related, at least qualitatively, to the average (apparent) enthalpy changes which occur as a function of the average degree of complexing.[9] Clearly, the enthalpy change is largest when the average charge is large and positive; the slope at $S = 1.25$ suggests a $\Delta\bar{H}$ of *ca.* 15 kcal. at high temperatures. The enthalpy change decreases to almost zero at $S = -0.5$ and becomes slightly negative for more negative values of S. This implies that the enthalpy change for the first complexing reaction (corresponding to k_{01}) is large and positive, particularly at high temperatures and that $\Delta\bar{H}$ is negative when the complex species carries a negative charge, *e.g.*, when k_{34} describes the dominant equilibrium.

This leads to the interesting conclusion that with increasing temperature the stability constants vary in such a manner as to increase the stability of neutral species or those of low absolute charge. If this were general, it would imply that at very high temperatures the characteristics of highly charged electrolytes diminish in importance and that the solutes would behave increasingly like electrolytes of low charge and even like non-electrolytes. Fig. 3 implies a parabolic relationship between the log of constants and $(1/T)$. Since the curves presented flatten in a region where measurements were made at high supporting electrolyte concentrations, the meaning of this pseudo-parabolic shape is in doubt. However, it might imply that when the enthalpy change for complexing reactions leading to ions of lower charge is negative at low temperatures, a change in sign of ΔH at higher temperatures is likely and that the generalization regarding preponderance at high temperatures of species of low or zero charge is more broadly applicable.

(2) Ga(III).—Adsorbabilities of Ga(III) were determined in the range $0.2 \leq m_{HCl} \leq 16$ at 25, 70, 115 and 150°. Measurements were carried out with increasing and decreasing temperatures and the averaged results are summarized in Fig. 4.

As in the case of Zn(II), the adsorption function of Ga(III) varies drastically with temperature. At room temperature, adsorbabilities increase rapidly with increasing m_{HCl}; the distribution coefficients reach a maximum near $m_{HCl} = 8$ beyond which log D decreases approximately linearly with increasing m_{HCl}. Increasing temperature causes a shift of the adsorption maximum toward lower HCl concentrations and adsorbabilities at high m_{HCl} decrease greatly.

(2.1) Enthalpy Change for the Ion Exchange Reaction.—As described earlier,[3,4] in the region where the distribution coefficients decrease with

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[9] The meaning of this plot may be deduced by differentiation of eq. c (footnote 7) with respect to $(1/T)$ which yields

$$\left(\frac{\partial \ln m_{Cl}}{\partial(1/T)}\right)_S = \left[\Sigma(S + i - \nu_0 - G_i')F_i\,\frac{\Delta\bar{H}_{0i}}{R} + \Sigma F_i\,\frac{\partial G_i'}{\partial(1/T)}\right] \Big/ \left[\Sigma(S + i - \nu_0 - G_i')iF_i\right]$$

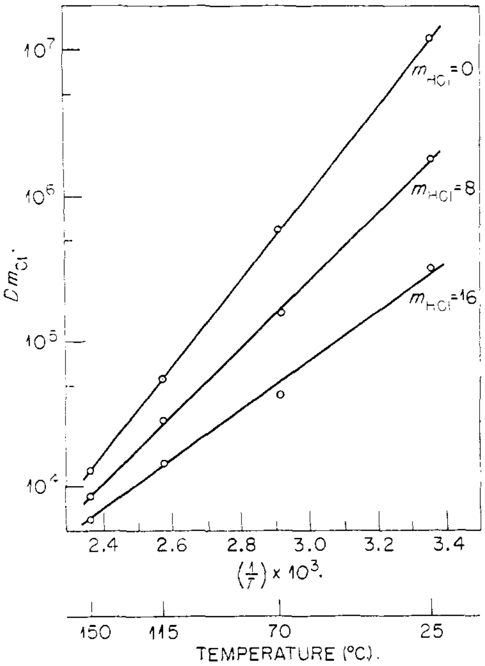

Fig. 5.—Adsorption of $GaCl_4^-$ at constant m_{HCl} as a function of temperature (Dowex-1X10, Cl^- form).

m_{HCl}, Ga(III) in the aqueous phase probably exists principally as the species $GaCl_4^-$. The change of distribution coefficients with temperature at high HCl concentration thus presumably reflects changes in the intrinsic adsorbability of this complex and the data in principle should permit computation of the apparent enthalpy change for the ion exchange reaction.

The equilibrium constant for the reaction is

$$K \equiv 1 = \frac{(GaCl_4^-)_{(r)}(Cl^-)}{(GaCl_4^-)(Cl^-)_{(r)}} G = K^0 G \qquad (12)$$

where

$$G = \frac{g_{GaCl_4(r)} g_{Cl}}{g_{GaCl_4} g_{Cl(r)}} \qquad (13)$$

$$K^0 = \frac{(GaCl_4^-)_{(r)}(Cl^-)}{(GaCl_4^-)(Cl^-)_{(r)}}$$

In conformity with our usual selection of standard states, K has been set identically equal to unity at all temperatures. Estimation of the apparent enthalpy change presupposes evaluation of the concentration quotient K^0 as a function of temperature which in turn requires knowledge of the distribution coefficients in the region where F_{GaCl_4} is unity and knowledge of the chloride concentration of the resin phase. At high chloride concentrations in the aqueous phase, there is invasion of electrolyte and hence $(Cl^-)_{(r)}$ may be substantially greater than the capacity of the resin. Since electrolyte uptake data are not available at high temperatures, this effect was ignored temporarily and the apparent enthalpy change was estimated from a plot of log $D\ m_{HCl}$ vs. $1/T$ rather than of log K^0 vs. $1/T$. With these reservations, one concludes (see Fig. 5) that the enthalpy change $\Delta\bar{H}$ is approximately constant throughout this temperature range and is of the order of −8 kcal. at $m_{HCl} = 16$, −10.6 kcal. at $m_{HCl} = 8$ and −14 kcal. at $m_{HCl} = 0$. The latter value was obtained by extrapolating (straight lines) the values of log Dm_{HCl} pertaining at high m_{HCl} to $m_{HCl} = 0$ (dashed lines Fig. 4).

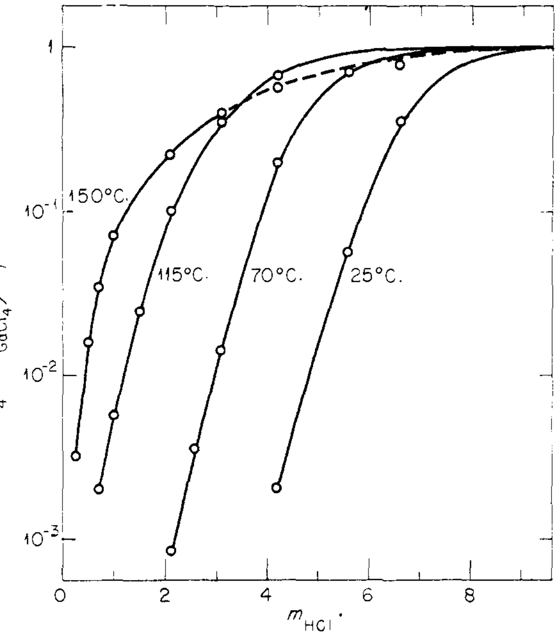

Fig. 6.—Formation of $GaCl_4^-$ in HCl solutions as a function of temperature (Dowex-1X10, Cl^- form).

While these estimates of $\Delta\bar{H}$ are considerably uncertain, they nevertheless establish that $\Delta\bar{H}$ is large and negative for this ion exchange equilibrium in contrast to many "normal" ion exchange equilibria.[5] Indeed, $\Delta\bar{H}$ here is of the order of magnitude one usually expects for chemical reactions.

The species $GaCl_4^-$ belongs to a small group of complexes (including $FeCl_4^-$ and $AuCl_4^-$) which are extremely strongly adsorbed by the anion exchange resin. One extrapolates from the data at high m_{HCl} that K^0 at 25° is of the order of 10^6 at $m_{HCl} = 0$. This corresponds to an excess free energy change $\Delta\bar{F}^e = -8$ kcal. Combining this value with the estimated $\Delta\bar{H} = -14$ kcal., one obtains $\Delta\bar{S} = -20$ e.u., a surprisingly large negative entropy change for an ion exchange reaction. These values may be compared with those for the Br^- (tracer) − Cl^- exchange reaction where $\Delta\bar{F}^e$ = ca. −0.5 kcal., $\Delta\bar{H} = -1.2 \pm 0.3$ kcal. and $\Delta\bar{S} = -2.0 \pm 0.9$ e.u. in the temperature range 25 to 150°.[5a]

(2.2) Average Enthalpy Change for the Complexing Reactions.—The adsorption function of Ga(III) at 25° has been interpreted[4] in terms of the ion fraction $F_4 = (GaCl_4^-)/m_{Ga}$ of Ga(III) converted to the species $GaCl_4^-$ (m_{Ga} is the stoichiometric concentration of Ga(III) in the aqueous phase). The fraction F_4 may be computed through the relationship

$$F_4 = D \frac{(Cl^-)}{(Cl^-)_{(r)}} \Big/ K^0 \approx D \frac{m_{Cl}}{m_{Cl(r)}} \Big/ K^0 \qquad (14)$$

which is obtained by rearranging eq. 12 after numerator and denominator have been multiplied by m_{Ga}.

The method of ion (or species) fractions had been chosen previously for Ga(III) since many of

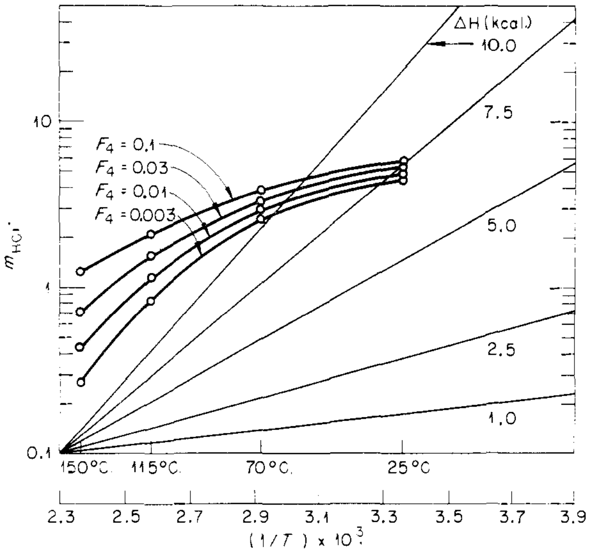

Fig. 7.—Estimation of heat of complex formation (Ga(III) in HCl).

the simplifications needed for slope analysis do not apply at the extremely high electrolyte concentrations where the pertinent points for Ga(III) are obtained. Further, with this element the predominantly adsorbed species ($GaCl_4^-$) seems well established. In contrast, the adsorbed species of Zn(II) has not been established with certainty and the relative preponderance of the species $ZnCl_3^-$ and $ZnCl_4^=$ as a function of m_{HCl} remains in doubt.

Since these considerations still apply, we shall attempt analysis of the adsorption functions of Ga(III) as a function of temperature in terms of F_4 although, because of uncertainties in resin invasion, K^0 cannot at present be determined at high temperatures. As in the estimation of the heats of adsorption, we shall again assume that log ($K^0 \cdot m_{Cl(r)}$) is a linear function of m_{HCl}, *i.e.*, that F_4 is given by the ratio of Dm_{Cl} *vs.* the extrapolated values of Dm_{Cl} for $F_4 = 1$, the dashed lines in Fig. 4. Such analysis leads to the values of F_4 shown in Fig. 6, which, though approximate and perhaps even to some extent incorrect (note *e.g.* the unexpected crossing of the 150° curve with the lower temperature curves), demonstrate the rapid increase with temperature of complexing of Ga(III). They substantiate the general comments regarding heats of complexing made in the discussion of Zn(II).

To obtain a qualitative estimate of the apparent enthalpy changes for the complexing reactions, we shall examine the values of m_{HCl} at which F_4 has a given value. The slope of a plot of log m_{HCl} *vs.* $1/T$ gives a weighted average of the heats of the complexing reactions as shown by differentiation at constant F_4 of the relationship

$$\frac{1}{F_4} = \Sigma k_{4i}{}^0 m_{Cl}{}^{i-4} \qquad (15)$$

which yields

$$0 = \Sigma(i-4)F_i\left(\frac{\partial \ln m_{Cl}}{\partial(1/T)}\right)_{F_4} + \Sigma F_i\left(\frac{-\Delta\bar{H}_{4i}}{R}\right) \qquad (16)$$

and hence

$$\left(\frac{\partial \ln m_{Cl}}{\partial\,(1/T)}\right)_{F_4} = \Sigma F_i\,\frac{\Delta\bar{H}_{i4}}{R}\Big/\Sigma(4-i)F_i \qquad (17)$$

In Fig. 7 a family of curves is given of log m_{HCl} *vs.* $1/T$ for F_4 = 0.1, 0.03, 0.01 and 0.003. At high temperatures and low values of F_4, $\Delta\bar{H}_{i_4}$ for the complexing reaction is near 10 kcal. and presumably will become even larger as the measurements are extended to lower values of F_4.

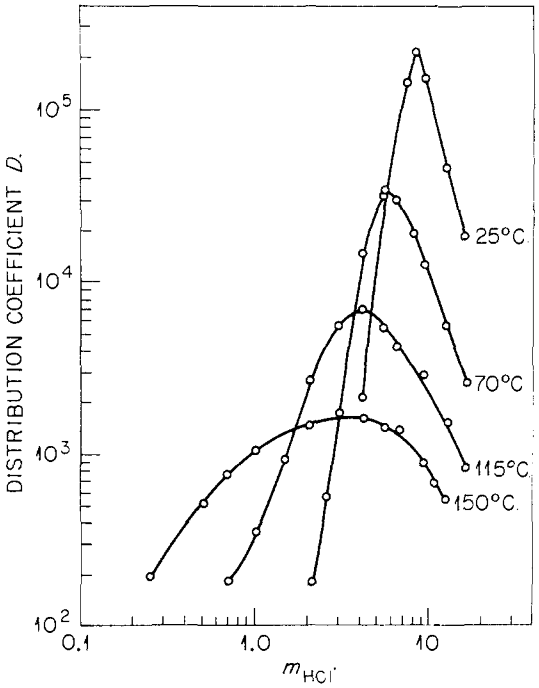

Fig. 8.—Adsorption of Ga(III) from HCl solutions as a function of temperature (Dowex-1X10, Cl^- form).

In addition to the rapid increase in degree of complexing of Ga(III) with temperature, the pattern of complexing of Ga(III) seems to change. It was pointed out earlier[4] that at 25° complexing of Ga(III) seems to proceed in essentially a single step from Ga^{+++} (or $GaCl^{++}$) to $GaCl_4^-$. Examination of a plot of log D *vs.* log m_{HCl}, Fig. 8, shows that this perhaps unusual situation does not persist at high temperatures and that intermediate species ($GaCl_2^+$ or $GaCl_3$) may assume importance. Thus a rather broad maximum in the log D *vs.* log m_{HCl} curve exists at 150° suggesting that the average charge remains close to zero over a substantial range of chloride concentrations. Further, the slope at low m_{HCl} remains moderately shallow. Thus S = *ca.* 1 at m_{HCl} = 0.7 and S is still substantially less than 2 at m_{HCl} = 0.25. The increasing importance of intermediate species with increasing temperatures of course is expected if, as mentioned earlier, the apparent enthalpy changes $\Delta\bar{H}_{ij}$ ($j = i+1$) become increasingly positive as the charge of the species MX_i increases.