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BASIC CHEMISTRY OF GALLIUM:
THE STABILITY OF GALLIUM HALIDE COMPLEX IONS
IN AQUEOUS SOLUTIONS

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Personnel

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THE STABILITY OF GALLIUM HALIDE COMPLEX IONS IN AQUEOUS SOLUTION

The present report describes experiments which have been made in an attempt to measure the affinity in water solution of gallium ion for fluoride ion, chloride ion, and bromide ion. For the $\text{Ga}^{+++}\text{-F}^-$ system, qualitative experiments only have been done, which suffice to afford a comparison of stability with the fluoride complexes of ferric ion and gallium ion. For the $\text{Ga}^{+++}\text{-Cl}^-$ and $\text{Ga}^{+++}\text{-Br}^-$ systems, quantitative measurements have been made. In both of these systems, however, the affinity of gallium ion for the halide ions is so low that values for the association constants could not be determined. The experiments do however place rather low upper limits on these equilibrium quotients:
$$\frac{(\text{GaX}^{++})^1}{(\text{Ga}^{+++})(\text{X}^-)}.$$

A. ASSOCIATION OF GALLIUM ION AND FLUORIDE ION

Lacroix²⁾ has shown that a higher concentration of OH^- is necessary to precipitate $\text{Ga}(\text{OH})_3$ from a solution containing Ga^{+++} when F^- is present than when it is absent. The data are too incomplete to establish the nature of the complex ions which are present. From Lacroix's observations on the precipitation of $\text{Ga}(\text{OH})_3$ in the presence of F^- , the ratio of free Ga^{+++} to Ga^{+++} present in complexes may be calculated. For a solution about 8×10^{-3} M in total Ga^{+++} and in total F^- , the ratio of free Ga^{+++} to Ga^{+++} present in complex ions is 0.22. The affinity of Ga^{+++} for F^- thus appears to be much less than that of Al^{+++} or Fe^{+++} for F^- . Under the same conditions, the ratio of $\frac{(\text{Fe}^{+++})}{(\text{FeF}^{++})}$ or $\frac{(\text{Al}^{+++})}{(\text{AlF}^{++})}$ would be about 0.02³⁾ and that of (Fe^{+++}) or (Al^{+++}) to the total present as complex ions even less. Lacroix²⁾ has made a comparison of the $\text{Ga}^{+++}\text{-F}^-$ and $\text{Al}^{+++}\text{-F}^-$ systems in the presence of OH^- , and has concluded that the affinity of F^- for Ga^{+++} is less than for Al^{+++} .

1) It will be assumed that the association of gallium ion with halide ions is stepwise, as has been observed in the $\text{Al}^{+++}\text{-F}^-$, $\text{Fe}^{+++}\text{-F}^-$, $\text{Fe}^{+++}\text{-Cl}^-$ systems (references cited below) and in other systems.

2) Lacroix, Ann. chim. (12), 4, 5-83 (1949).

The qualitative experiment performed here consisted of comparing the solubility of LaF_3 in $\text{Fe}(\text{NO}_3)_3$ and in $\text{Ga}(\text{ClO}_4)_3$. It was found that a sample of LaF_3 would dissolve completely in $4M$ $\text{Fe}(\text{NO}_3)_3$, while the solubility in $4M$ $\text{Ga}(\text{ClO}_4)_3$ was only slight. This experiment also places the affinity of Fe^{+++} for F^- as being much in excess of that of Ga^{+++} for F^- . Since the amount of Fe^{+++} or Ga^{+++} exceeded that of F^- , the equilibrium quotient which applies to the data presumably has the form $\frac{(\text{MF}^{++})}{(\text{M}^{+++})(\text{F}^-)}$. For FeF^{++} , this quotient at $\mu = 0.5$ has a value³⁾ of about 5×10^5 .

B. ASSOCIATION OF GALLIUM ION AND CHLORIDE ION

Three methods have been used for the study of the association of chloride ion and gallium ion: measurement of the effect of Ga^{+++} on the e.m.f. of the $\text{Ag}, \text{AgCl} - \text{H}^+$, H_2 cell, measurement of the bleaching by Ga^{+++} of solutions containing ferric chloride complex ions, and study of Raman effect in solutions containing Ga^{+++} and Cl^- at high concentration. The first two methods set an upper limit on the quotient $\frac{(\text{GaCl}^{++})}{(\text{Ga}^{+++})(\text{Cl}^-)}$ of about 0.5. The Raman spectrum method shows that a complex does exist in concentrated solution, but these experiments have not as yet yielded quantitative information.

1. Potentiometric Methods

Experimental. The following cell pair without transference was used in the potentiometric experiments:

The cells, made of pyrex glass, had openings at the top for the introduction of electrodes, solutions, stirrers and gas outlet tubes.

Hydrogen was introduced into each cell by a bubbling tube. Both cells had a common hydrogen outlet tube in order to maintain the same hydrogen pressure in each. Before it was introduced into a cell, the hydrogen (electrolytic, water-pumped) was

³⁾Based on values for $\text{Fe}^{+++} - \text{F}^-$ equilibrium constants obtained by Dodgen and Rollefson, J.A.C.S. 71, 2600 (1949), and for $\text{Al}^{+++} - \text{F}^-$ obtained by Brosset and Gustover, Chem.Zent. I, 1300 (1943).

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passed over copper oxide at 260°C and through a three-stage bubbler system containing solutions identical in composition with that initially present in the cells.

Great care was found to be necessary for the preparation of reproducible Ag-AgCl electrodes of the accuracy desired. Among the precautions which were necessary were protection of the electrodes from mechanical shock and from contact with grease.⁴⁾ An electrode pair was constructed which generated a reproducible e.m.f. of the order of 0.2 millivolt. The hydrogen electrodes which were prepared differed by less than 0.01 millivolt.

A Leeds and Northrup K-1 type potentiometer was used with a Bureau of Standards calibrated standard cell. Changes in e.m.f. of less than 0.001 millivolt could be detected when the galvanometer was observed by a telescope. Cells and hydrogen bubblers were immersed in a constant temperature bath maintained at $24.96 \pm 0.05^\circ$.

The experiments were conducted as follows. The cells contained initially a solution of HClO_4 and NaCl of identical compositions. The e.m.f. generated by the cell pair under these conditions was measured, then successive portions of $\text{Ga}(\text{ClO}_4)_3$ solutions were added to one of the cells at intervals. After the addition of each portion of $\text{Ga}(\text{ClO}_4)_3$ solution, about an hour elapsed before the e.m.f. readings settled down to steady values. Readings were then recorded for a period of 40 to 60 minutes before the next addition of $\text{Ga}(\text{ClO}_4)_3$ took place.

Results and Conclusions. The change in e.m.f. produced in the cell pair by the addition of a quantity of $\text{Ga}(\text{ClO}_4)_3$ solution to one of the cells depends on the changes in concentrations of the various substances, on the change in ionic strength (and ionic composition), and on the extent of association of gallium ion with chloride ion.

⁴⁾Brown and MacInnes, J.A.C.S. 57, 1357 (1933).

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The following equation, which relates the effective variables, may be derived:

$$K = \frac{V + \Delta V}{g \Delta V} \left[1 - \left(\frac{V + \Delta V}{V} \right)^2 \left(\frac{aV}{aV + r \Delta V} \right) \frac{10^{\epsilon'}}{r^2} \right]$$

where $K = \frac{(GaCl^{+++})}{(Ga^{+++})(Cl^-)}$ (parentheses are used to denote concentrations),

V = initial volume.

ΔV = volume of solution added.

g = concentration of Ga^{+++} in solution added.

a = concentration of H^+ in solution added.

ϵ' = observed change in e.m.f. divided by $\frac{RT}{nF}$ (= 0.05915).

$r = \frac{\gamma_{\pm} (HCl \text{ final})}{\gamma_{\pm} (HCl \text{ initial})}$

In Table I are summarized the data obtained, together with the values of K calculated on the assumption that $r = 1$. The calculations are not appreciably affected by expressing the dilution in terms of molality rather than molarity, as was done.

Table I

Measurement of Association of Chloride and
Gallium Ion by e.m.f. Method

Initial composition of the solutions in each cell: 0.338M $HClO_4$, 0.00100M NaCl.
Composition of the gallium perchlorate solution: 0.1014M $Ga(ClO_4)_3$, 0.1956M $HClO_4$.
Initial volume of solution in the cells, 198.24 ml. Initial e.m.f. difference, 0.172 $\pm$ 0.02 millivolt.

	Overall vol. $Ga(ClO_4)_3$ aq added, ml	Overall change in e.m.f., mv	K calculated, assuming $r = 1$
1	0.916	0.14 $\pm$.02	-2.4
2	1.996	0.344 $\pm$.02	- .85
3	3.080	0.571 $\pm$.02	+ .15
4	3.686	0.689 $\pm$.02	+ .35
5	4.552	0.847 $\pm$.02	+ .35

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Since the association of Ga^{+++} and Cl^- is so slight ($K < \text{ca. } 0.5$), the bulk of the change in e.m.f. produced by the addition of $\text{Ga}(\text{ClO}_4)_3$ solution is due simply to the increase in volume, and calculation of the values of K depends on a small difference between relatively large quantities. The irrational negative values for K calculated from the data for the first two increments of $\text{Ga}(\text{ClO}_4)_3$ solution can be attributed to uncertainties in dilution and in the measurement of small differences in e.m.f. The estimated uncertainty in the value of K for the last experiment is about 0.5.

In calculating the values of K recorded in Table I, no allowance was made for the change in activity coefficient of HCl . To minimize effects due to this cause, the composition of the solution used was chosen to be near that for which a minimum is observed in the curve of $\gamma^{\pm} \text{HCl}$ vs. concentration. In addition, the ionic strength in every case changes only slightly, increasing from 0.339 initially to 0.355 in the most extreme case of experiment 5. However, a change in activity coefficient of HCl can be expected even if ionic strength is maintained constant, since the ionic composition changes. The net change in ionic composition on the addition of the gallium perchlorate solution is to decrease the HClO_4 content slightly, and increase that of $\text{Ga}(\text{ClO}_4)_3$. For the concentration region under investigation, a decrease in HClO_4 concentration decreases $\gamma^{\pm} \text{HCl}$ 5). The effect of the increase in $\text{Ga}(\text{ClO}_4)_3$ in the presence of excess HClO_4 is not known. HCl , NaClO_4 , $\text{Na}_2\text{S}_2\text{O}_6$, and BaCl_2 all decrease $\gamma^{\pm} \text{HCl}$ in the ionic strength region under investigation. It seems probable that $\text{Ga}(\text{ClO}_4)_3$ behaves similarly. If $\gamma^{\pm} \text{HCl}$ decreases on the addition of $\text{Ga}(\text{ClO}_4)_3$, the values of K would be reduced on recalculation, taking into account the change in $\gamma^{\pm} \text{HCl}$. In any case, it seems safe to accept from the e.m.f. measurements an upper limit of 1 for the value of the quotient $\frac{(\text{GaCl}^{++})}{(\text{Ga}^{+++})(\text{Cl}^-)}$ at $\mu = .35$ and 25° .

5) Murdock and Barton, J.A.C.S. 55, 4074 (1933).

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2. Spectrophotometric Method

In the spectrophotometric method used for investigating the affinity of gallium ion for chloride ion, the change in color produced when Ga^{+++} is added to a solution containing ferric chloride complexes was measured. For visible light the absorption coefficient of FeCl^{++} (and other ferric chloride complexes) is much greater than that of Fe^{+++} , Ga^{+++} or GaCl^{++} ; thus if the affinity of Ga^{+++} for Cl^- is high enough, a decrease in color of the ferric - chloride solution should be observed when Ga^{+++} is added. Since the equilibrium quotients governing the association of ferric ion and chloride ion are known,⁶⁾ quantitative measurement of the color change should yield a value of the dissociation constant of the gallium chloride complex ions.

It was observed that a solution containing Fe^{+++} , H^+ , Na^+ , ClO_4^- and Cl^- is more highly colored than is one of the same ionic strength, acidity, ferric ion concentration, and chloride concentration, but which contains Ga^{+++} in place of Na^+ . However, it was also shown that a solution made up as above but containing Al^{+++} in place of Ga^{+++} has an extinction almost exactly the same as that of the corresponding solution containing Ga^{+++} . This observation makes reasonable the conclusion that the bleaching effect of both Ga^{+++} and Al^{+++} is due to the change in ionic composition produced by replacing NaClO_4 by $\text{Ga}(\text{ClO}_4)_3$ or $\text{Al}(\text{ClO}_4)_3$ and is not a specific effect due to the formation of complex ions. If complex ion formation were the cause of the bleaching, the effects of Ga^{+++} and Al^{+++} could hardly be expected to be the same. The view that ion atmosphere effects rather than complex ion formation are responsible for the observed bleaching is supported by the fact that $\text{La}(\text{ClO}_4)_3$ produces almost quantitatively the same effect as Ga^{+++} or Al^{+++} (the data for $\text{La}(\text{ClO}_4)_3$ are not reported in detail, however, since the concentrations of the solutions were known only to about 5%).

⁶⁾Rabinowitch and Stockmayer, J.A.C.S. 64, 335 (1942).

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Accepting the assumption that Al^{+++} does not form an appreciable amount of chloride complex in the solutions under investigation, a comparison of the data for Ga^{+++} and Al^{+++} (see Table II) taking the maximum difference in extinction for the two solutions allowed by the precision of the measurements, sets an upper limit of about 0.7 on the quotient $\frac{(GaCl^{++})}{(Ga^{+++})(Cl^{-})}$.

Experimental. $Ga(ClO_4)_3$ was prepared by the reaction of Ga with 70% perchloric acid, $Fe(ClO_4)_3$ by dissolving $Fe(OH)_3$ in perchloric acid. Both substances were recrystallized from perchloric acid. Stock solutions of both substances were made up and analyzed. Sodium perchlorate solution was prepared and analyzed. All solutions were made up with distilled water from the laboratory tap (conductance, ca. 2×10^{-6} ohms $^{-1}$) and were filtered before being used.

A Beckman Model DU spectrophotometer was used for the measurements of optical density. The instrument was fitted with a cell compartment thermostatted at a temperature of $25.95 \pm 0.05^\circ C$. Care was taken that the solutions reached temperature equilibrium before measurements were made.

Results. Table II presents the data obtained. Comparison of solutions B and C with solution A shows that Ga^{+++} and Al^{+++} produce an appreciable bleaching effect. Comparison of B with C shows that the bleaching produced by the two ions is the same within experimental error.

To calculate an upper limit for $\frac{(GaCl^{++})}{(Ga^{+++})(Cl^{-})}$ from the data, the extinction coefficients for $FeCl^{++}$, $FeCl_2^{+}$, $FeOH^{++}$ and Fe^{+++} are required. These were taken from the paper by Rabinowitch and Stockmayer.⁶⁾ The value of the equilibrium quotient $\frac{(FeCl^{++})}{(Fe^{+++})(Cl^{-})}$, calculated from the data of Table II for solution A, is 3.7. That obtained by Rabinowitch and Stockmayer⁶⁾ for the same ionic strength (but not the same ionic composition) is 4.2.

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Table II

The Bleaching Effect of Ga⁺⁺⁺ and Al⁺⁺⁺
on Ferric-Chloride Solutions

Temperature 25.95 ± 0.05 . Cell thickness 1 cm. $\lambda = 4000 \text{ \AA}$. Concentration is expressed in moles per liter.

<u>Solution</u>	<u>A</u>	<u>B</u>	<u>C</u>
Fe(ClO ₄) ₃	0.0483	0.0483	0.0483
Al(ClO ₄) ₃	- -	0.0504	- -
Ga(ClO ₄) ₃	- -	- -	0.0507
NaClO ₄	0.304	- -	- -
HClO ₄	0.587	0.604	0.587
NaCl	.0104	.0104	.0104
Optical density = $\log I_0/I$	0.216 ± 0.003	0.203 ± 0.002	0.206 ± 0.002

3. Raman Study

The Raman spectrum method consists of looking for Raman lines which may be attributed to the complex ions under investigation. It has the advantage over the other two methods employed and described above that a property of the complex ion is measured directly.

Thus far, only a single preliminary experiment has been made. A solution was prepared by dissolving GaCl₃ in concentrated HCl (the solution was 0.4M in GaCl₃) and submitted to L. F. Maranville and H. M. Smith for examination in a Raman spectrograph.⁷⁾ A definite Raman peak at 337 cm^{-1} was observed. This peak cannot be attributed to H⁺-Cl⁻ interactions, nor to Ga⁺⁺⁺-H₂O interactions, and is presumably produced by a Ga⁺⁺⁺-Cl⁻ complex.

The system is being investigated further by the Raman method.

⁷⁾ This spectrograph was constructed under the direction of Dr. T. F. Young, Department of Chemistry, University of Chicago.

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C. STUDIES OF GALLIUM BROMIDE COMPLEX ION FORMATION

The method which was used in the study of the $\text{Ga}^{+++}\text{-Br}^-$ interaction is the same as the spectrophotometric method applied to the $\text{Ga}^{+++}\text{-Cl}^-$ system. The data obtained are reported in Table III.

Table III
The Bleaching Effect of Ga^{+++} and Al^{+++} on
Ferric-Bromide Solutions

Temperature 25.95 ± 0.05 . Cell thickness 1 cm. $\lambda = 4000 \text{ \AA}$. Concentration is expressed in moles per liter.

<u>Solution</u>	<u>A</u>	<u>B</u>	<u>C</u>
$\text{Fe}(\text{ClO}_4)_3$	0.0483	0.0483	0.0483
NaBr	.0100	.0100	.0100
HClO_4	.587	.587	.604
NaClO_4	.304	- -	- -
$\text{Ga}(\text{ClO}_4)_3$	- -	0.0507	- -
$\text{Al}(\text{ClO}_4)_3$	- -	- -	0.0504
Optical density = $\log I_0/I$	0.148 ± 0.001	$0.142 \pm .001$	$0.142 \pm .001$

The data show that Ga^{+++} and Al^{+++} exert a bleaching effect on the ferric-bromide solutions, and that the bleaching effects produced are identical for the two cations. Thus the system is similar in behavior to the ferric-chloride system, and a similar conclusion seems reasonable here also: that the effect of Al^{+++} and of Ga^{+++} are due to the changes they produce in activity coefficients rather than to association with Br^- to form complex ions. If this interpretation is accepted, the data set an upper limit of 0.3 on the equilibrium quotient $\frac{(\text{GaBr}^{++})}{(\text{Ga}^{+++})(\text{Br}^-)}$. This upper limit is arrived at by setting the optical densities of the Ga^{+++} and Al^{+++} at the maximum difference permitted by the data: 0.141 for solution B and 0.143 for solution C, and attributing the difference to

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association of Ga^{+++} with Br^- . Since the association of Fe^{+++} and Br^- is slight (as shown below), the calculation is not appreciably affected by the value of $K_{\text{FeBr}^{++}}$.

Doubt still exists about the value of the equilibrium quotient $\frac{(\text{FeBr}^{++})}{(\text{Fe}^{+++})(\text{Br}^-)}$. The value of 0.5 at $\lambda = 1.09$ recorded by Rabinowitch and Stockmayer⁶) required making an assumption about the value of $\epsilon_{\text{FeBr}^{++}}$, the extinction coefficient for FeBr^{++} . The reason for this is that ferric ion and bromide ion associate only slightly. Even at the highest concentration of ferric ion used by them, 0.1M, the formation of FeBr^{++} did not alter the concentration of Br^- appreciably, and the measurements of extinction yielded only the value of the product $K_{\text{FeBr}}\epsilon_{\text{FeBr}^{++}}$.

In an attempt to separate the factors $\epsilon_{\text{FeBr}^{++}}$ and $K_{\text{FeBr}^{++}}$, the extinctions of solutions containing ferric ion at concentrations varying to 0.5M and bromide ion at a constant, low concentration have been measured. In order to keep ion atmosphere effects constant, $\text{Al}(\text{ClO}_4)_3$ was added as the $\text{Fe}(\text{ClO}_4)_3$ content was reduced. The data obtained in this series of experiments are presented in Table IV.

Table IV

Extinction of Ferric Bromide Solutions
at Varying Concentrations of

Fe^{+++} and Constant $\text{Al}^{+++} + \text{Fe}^{+++}$ Concentration

Temperature = 25.95 ± 0.5 . Cell thickness 1 cm. $\lambda = 4000 \text{ \AA}$. Concentration is expressed in moles per liter.

<u>Solution</u>	<u>X</u>	<u>Y</u>	<u>Z</u>
$\text{Fe}(\text{ClO}_4)_3$	0.483	0.242	0.145
$\text{Al}(\text{ClO}_4)_3$	- -	0.236	.330
HClO_4	.978	.978	.978
NaBr	.00600	.00600	.00600
Optical density	$1.410 \pm .005$	$.698 \pm .005$	$.417 \pm .003$
<u>Optical density</u> <u>(Fe^{+++})</u>	$.292 \pm .001$	$.288 \pm .002$	$.288 \pm .002$

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The data of Table IV show that the optical density is proportional to the concentration of ferric ion even when this is as high as 0.48M. Thus, even at 0.48M ferric ion, that concentration of bromide ion is not appreciably affected by the formation of FeBr^{++} . These results impose an upper limit of about 0.1 on the equilibrium quotient $K_{\text{FeBr}^{++}}$ for the conditions of the experiments.

It is of course possible to interpret the data of Table IV also on the assumption that ferric ion associates strongly with bromide ion, and that the proportionality of optical density and (Fe^{+++}) is maintained because Al^{+++} has an exactly equivalent affinity for Br^- . This interpretation is very unlikely, however, particularly in view of the observations of Table III which would in turn require that Ga^{+++} and Al^{+++} associate equally strongly with Br^- . The more reasonable interpretation of the data is that none of the cations Fe^{+++} , Al^{+++} or Ga^{+++} associate strongly enough with Br^- even at 0.5M concentration to affect its concentration appreciably.

The upper limit of 0.1 which our data for high concentrations of ferric ion set on $K_{\text{FeBr}^{++}}$ is lower by a factor of five than the value chosen by Rabinowitch and Stockmayer as probable for this quotient. To arrive at a lower limit for $K_{\text{FeBr}^{++}}$, one may proceed as was done by Rabinowitch and Stockmayer by assigning to $\epsilon_{\text{FeBr}^{++}}$ a "maximum" value of 10,000, and then calculating $K_{\text{FeBr}^{++}}$ from the experimentally determined product $K_{\text{FeBr}^{++}} \epsilon_{\text{FeBr}^{++}}$. A serious discrepancy exists between the values we have measured for this product and that reported by Rabinowitch and Stockmayer. Thus for solution A described in Table III, the product $K_{\text{FeBr}^{++}} \epsilon_{\text{FeBr}^{++}}$ is 242; while for conditions not widely different Rabinowitch and Stockmayer report 2,880. When 242 is used for the value of the product $K_{\text{FeBr}^{++}}$.

FeBr^{++} , the lower limit placed on $K_{\text{FeBr}^{++}}$ is 0.02. Our data therefore indicate that $K_{\text{FeBr}^{++}}$ at $\mu = 1.3$ at 25° lies in the range 0.02 to 0.1. It should be noted that if the value for $K_{\text{FeBr}^{++}} \epsilon_{\text{FeBr}^{++}}$ reported by Rabinowitch and Stockmayer is used, the lower limit for $K_{\text{FeBr}^{++}}$ is calculated as 0.3, and is greater than the upper limit for this quotient established by the data of Table IV.

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D. DISCUSSION

Results on the stability of the halide complexes of gallium ion are of interest in connection with the general problem of correlating the stability of the complex ions with the electronic structure and other properties of the cations and anions. Data are still too sparse to suggest points of view which will rationalize the observations. The discussion attempted here will seek only to point out some of the interesting features which exist.

Qualitative observations, and a few quantitative observations, indicate that for cations with 8 electrons in the outside shell, the affinity for halide ions decreases in the order $F^- > Cl^- > Br^- > I^-$. This trend continues even for some of the transition metal ions, ferric ion⁶⁾ and manganic ion.⁸⁾ For cations with 18 electrons in the outer orbit, this order is often reversed. Thus, for Cu^+ the quotients for the equilibria of the form $\frac{(CuX_2^-)}{(Cu^+)(X^-)^2}$ have the values⁹⁾ 3.4×10^5 , 8.4×10^5 , 7.2×10^8 , for $X^- = Cl^-$, Br^- , and I^- , respectively. Thermodynamic data¹⁰⁾ for solutions of zinc halides, however, suggest that with Zn^{++} the affinity is restored to $Cl^- > Br^- > I^-$. The qualitative comparison of stability of fluoride and chloride complex of Ga^{+++} shows that the affinity of fluoride for gallium ion exceeds that of chloride ion; i.e., the reversal in trend brought about presumably by the increases in charge going from Cu^+ to Zn^{++} continues to Ga^{+++} . For the succeeding periods of elements, a relatively greater stability of iodide complexes as compared to chloride complexes is observed even when the charge is +2.¹¹⁾

8) Taube, J.A.C.S. 70, 2398 (1948).

9) Latimer, Oxidation Potentials, Prentice-Hall, 1938.

10) Stokes, Trans. Far. Soc. XLIV, 137 (1948).

11) For Cd^{++} , Ido Leden Z.P.C. 188, 160 (1941), for Hg^{++} , Latimer, Oxidation Potentials, Prentice-Hall, 1938.

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It is also of interest to note that Cu^+ , in spite of its large radius and low charge, has a greater affinity for chloride ion and for bromide ion than do Fe^{+++} , Ga^{+++} , or Zn^{++} . Stated in an equivalent way, the observations are perhaps less startling: H_2O competes more favorably against bromide or chloride ion when the cation is Fe^{+++} , Ga^{+++} , or Zn^{++} than when it is Cu^+ .

E. SUMMARY

The complex ions of Ga^{+++} and F^- are sufficiently stable so that the solubility of LaF_3 in $\text{Ga}^{+++}_{\text{aq}}$ is appreciable. The affinity of Ga^{+++} for F^- is considerably less, however, than that of Al^{+++} or Fe^{+++} for F^- .

At $\mu = 0.35$ and 25° , the quotient $\frac{(\text{GaCl}^{++})}{(\text{Ga}^{+++})(\text{Cl}^-)}$ has an upper limit of about 1.

At $\mu = 1.3$ and 25° , the corresponding quotient for the gallium bromide complex ion has an upper limit of 0.3.

The quotient $\frac{(\text{FeBr}^{++})}{(\text{Fe}^{+++})(\text{Br}^-)}$ lies in the range 0.02 to 0.1 at $\mu = 1.3$ and 25° .

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