metal–ligand orientation. Similar phenomena were noted by Johnston and Freiser[9] and by Basolo, *et al.*[10,11]

However, as the length of the alkyl chain increases, the chelates, in general, tend to become more stable. Approximate thermodynamic values were calculated using the temperature dependence of the equilibrium constants. These values indicate that this increase in stability is caused by an increase in entropy.

[9] W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, **11**, 1 (1954).

[10] F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5243 (1952); **76**, 211 (1954).

[11] F. Basolo, R. K. Murmann, and H. T. Chen, *ibid.*, **75**, 1478 (1953); **76**, 956 (1954).

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Solutions of Gallium(I) Salts in Aqueous Base[1]

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The characteristic reaction of the so-called gallium dichloride with water has been known for a considerable time. With ample amounts of water a strongly reducing, flocculent, orange-brown to black precipitate is produced together with smaller amounts of hydrogen and gallium. The precipitate evolves hydrogen slowly on standing or rapidly on addition of acids with ultimate solution of the product.[2] Although the identity of this precipitate has never been carefully studied, the supposition has been made that it is gallium(II) hydroxide produced by hydrolysis of the reactant $GaCl_2$, since the empirical formula for the latter suggests a dipositive state.[3] However, subsequent studies have amply shown that the gallium dihalides are actually gallium(I)–gallium(III) salts $Ga^+(GaX_4^-)$[4–6] and that the above reaction with water is characteristic of gallium(I) since it occurs not only in the presence of the GaX_4^- anion but also with $AlCl_4^-$, $AlBr_4^-$, Br^-, and I^-.[4,7] Because of the strong reducing character of the gallium(I) oxidation state, very little information has been reported regarding its solution properties. Recently Schug and Sadowski[8] have inferred from stoichiometric evidence that hot, concentrated (11 *M*) perchloric acid reacts with metal to yield hydrogen plus the Ga^+ intermediate and that this rapidly reduces the perchlorate ion. The present paper reports some characterization of the more stable solutions obtained with gallium(I) salts in aqueous base.

Table I

Pseudo-First-Order Rate Constants for the Decomposition of Alkaline Solutions of $Ga(GaCl_4)$ at 22–24°

NaOH, *M*	Additive, *M*	Rate constant, $sec.^{-1} \times 10^5$
0.998	. . .	3.73 ± 0.1
1.99	. . .	8.37 ± 0.2
1.99	0.05 Ga(III)	8.21 ± 0.1
1.99	0.3 I^-	8.54 ± 0.1
4.00	. . .	~27 ± 9
0.990	1.00 $NaClO_4$	4.177 ± 0.04
0.992	2.98 $NaClO_4$	5.06 ± 0.06
1.986	2.00 $NaClO_4$	9.93 ± 0.3
2.982	1.02 $NaClO_4$	14.7 ± 0.5

Solution of a gallium(I) salt such as Ga_2Cl_4 in aqueous NaOH gives, as with pure water, a black to dark orange precipitate, but this readily redissolves and the solution proceeds through shades of orange and yellow to colorless in a few 10-min. periods. The initially vigorous reaction, probably largely due to the hydrolysis of the $GaCl_4^-$ ion, produces some 5 to 25% (depending on sample size) of the total possible hydrogen by reduction of water and also 5 to 20% of the theoretical amount of metal through disproportionation (data for 2 *M* OH^-). It should be emphasized that separation of metal is observed *only* during the initial reaction with water. The resulting solution evolves hydrogen *homogeneously* and not from the walls of the glass container, so that the quiescent liquid becomes highly supersaturated ("pinpoint hydrogenation"). The rate of hydrogen evolution from vigorously stirred solutions 1 to 4 *M* in NaOH indicates the net reaction $[Ga^+] + 2H_2O + 2OH^- \rightarrow Ga(OH)_4^- + H_2$ is first order in gallium(I). Data obtained after the solution process appears complete were in kinetic agreement with those taken after the solution lost its light yellow to orange color 15 to 40 min. later. The rate constants obtained for solutions initially 3.5 to 10 m*M* in gallium(I) are summarized in Table I.[9] Comparison of these for solutions maintained at a fixed, total concentration of 2 or 4 *M* by $NaClO_4$ indicates that the reaction also is first order in hydroxide (0.95 to 1.0 observed) over the range studied. Gallium(III) was found to be without significant effect on the rate although at the 0.05 *M* level it virtually eliminates production of metal during the initial solution. As an indication of the stability of these solutions, the rate constant in 1.00 *M* base corresponds to a half-life of 5.2 hr. The observed linear dependence on hydroxide concentration, contrary to that for a reaction involving proton reduction, suggests that the reaction effectively takes place through an interaction of OH^- with the solvated Ga^+ ion to inductively affect transfer of the $4s^2$ electrons to water of solvation, forming hydrogen either directly (and probably intramolecularly) or *via* a hydride intermediate. Attempts

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[1] The Lower Oxidation States of Gallium. IV. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] E. Eineck, "Das Gallium," Voss, Leipzig, 1937; Edwards Bros., Ann Arbor, Mich., 1944, p. 79.

[3] L. S. Foster, *Inorg. Syn.*, **4**, 111 (1953).

[4] J. D. Corbett and R. K. McMullan, *J. Am. Chem. Soc.*, **78**, 2906 (1956); R. K. McMullan and J. D. Corbett, *ibid.*, **80**, 4761 (1958).

[5] L. A. Woodward, G. Garton, and H. Roberts, *J. Chem. Soc.*, 3623 (1957); L. A. Woodward, N. N. Greenwood, J. R. Hall, and I. J. Worrall, *ibid.*, 1505 (1958).

[6] G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.*, **4**, 84 (1957).

[7] J. D. Corbett and A. Hershaft, *J. Am. Chem. Soc.*, **80**, 1530 (1958).

[8] K. Schug and A. Sadowski, *ibid.*, **83**, 3538 (1961).

[9] There appears to be a decrease in rate after several half-lives at the highest base concentration although this was not investigated further.

to detect hydrogen atoms or other intermediate radicals were negative; emulsion polymerization of styrene in 0.05 *M* NaOH using Dreft as the emulsifying agent gave only faint amounts of turbidity with gallium(I), although a peroxydisulfate–sulfite mixture was found to initiate this system satisfactorily. In contrast to the behavior in base, a solution of Ga_2Cl_4 in 0.3 *M* $HClO_4$ produced a negligible quantity of hydrogen after the 12 min. necessary to get the initial precipitate into solution, although an orange-brown color persisted for more than an hour.

Careful neutralization of the basic solutions provides the interesting result that *all* of the reduced gallium is reversibly precipitated as a flocculent, *white* precipitate. The reduced gallium is relatively stable in this form and may be kept for more than 1 week stored under water. On slow addition of acid the solid begins to evolve hydrogen at about pH 5. The solution is slow even at a pH of 1 to 2, and the system is free of reducing strength before solution is complete. The manner in which the reduced gallium is so precipitated is not known, although it is possible that such a small $d^{10}s^2$ ion as Ga^+ could be truly amphoteric.

A considerable number of reducing reactions of the basic solutions of Ga_2Cl_4 were investigated. These were made up to be between 0.5 and 1 *M* in Ga^+ and near 1 *M* in free base (presuming $Ga(OH)_4^-$ is formed from $GaCl_4^-$) so that indications of the reduction potential would be more significant. In addition to reactions expected with the stronger oxidizing agents, the gallium(I) solutions readily reduce, to the metallic element unless otherwise noted, 1 *M* NaOH solutions of Tl^+, AsO_2^-, $Cd(CN)_4^{2-}$ (+ 1 *M* CN^-), and 1 *M* NaOH saturated with solid PbO, $Cd(OH)_2$, TlI, CdS, SnO_2, and, with warming, Fe_2O_3 (to Fe_3O_4) and $Zn(OH)_2$. Reaction is not found with CrO_2^-, SO_3^{2-}, SeO_3^{2-}, as well as ClO_4^- and SO_4^{2-}, presumably due to kinetic limitations for all but CrO_2^- (*vide infra*). From the standard potential for $Zn(OH)_2$–Zn,[10] the weakest couple for which reaction is observed, an E_B^0 value of 1.24 v. or greater is obtained for $[Ga^+] + 4OH^- = Ga(OH)_4^- + 2e$. With 1.29 v. for Ga–$Ga(OH)_4^-$,[11] the Ga–Ga(I) potential is ≤ 1.39 v.

The fleeting existence of Ga^+ in acid makes any estimate of the oxidation potential somewhat more difficult. Reactions with Ga^+ in acid were tested by addition of the neutral reagent to the reducing precipitate at pH 5–7 followed by slow acidification; the majority of the observed reactions occurred at pH 0 to 2. Reductions of stronger oxidizing agents under these conditions include $Cr_2O_7^{2-}$ to Cr^{3+}, SeO_3^{2-} to Se (and H_2Se), SO_3^{2-} to H_2S, and the kinetically more difficult ClO_4^- to Cl^- and SeO_4^{2-} to Se (and H_2Se). The element also was obtained from Sn^{2+}, As(III), Cd^{2+} solutions, and solid $PbCl_2$. No reaction under these conditions was detected with the solids $PbSO_4$, TlCl, TlI and solutions of Fe^{2+}, Ni^{2+}, and Cr^{3+}. Although uncertainties as to the effective pH and the state of the product gallium(III) exist in some cases, the reduction of Cd^{2+} occurs at a sufficiently high acidity that a like, lower limit of $\sim$0.40 v. can be assigned to Ga^+–Ga^{3+}. With the known E^0 value for Ga–Ga^{3+},[10] a maximum of $\sim$0.79 v. then can be established for Ga–Ga^+.

It will be noted that there is a 0.6 v. difference between the (maximum) values so estimated for the Ga–Ga(I) couple in acid and in base. A plausible explanation is that the gallium(I) state is this much more stable in base due to a specific reaction with the hydroxide ion, as also might be inferred from the precipitation behavior discussed earlier. The above potentials also indicate that gallium(I) should be stable with respect to disproportionation in either acid or base. However, potentials deduced for Ga(I)–Ga(III) are minimal and values only 0.13 and 0.05 v. larger, respectively, would give an equilibrium constant of unity for the disproportionation. Such a macroscopic decomposition reaction is, however, not observed other than during the initial solution process. Furthermore, it is difficult to see how a rate-determining disproportionation reaction in base could be first order in gallium(I) even if atomically dispersed metal so produced were to react rapidly with the solvent.

More direct methods for the production of the basic gallium(I) solutions also have been investigated. The equilibration of liquid metal with a solution 2 *M* in NaOH and 0.05 *M* in Ga(III) for 24 hr. does not give any detectable reaction, and reduction of basic gallate solutions 1 to 3 *M* in NaOH on a platinum cathode is similarly negative. However, anodic oxidation of liquid gallium into well stirred 1 *M* NaOH (at 35° and 17 to 170 ma./cm.^{2}) produces definite amounts of gallium(I), although the (undetermined) efficiency does not appear particularly large. Subsequent concentration of the reducing strength by precipitation of the mixed oxide then allows the preparation of moderately concentrated solutions far more easily than *via* a gallium(I) salt.

In conclusion, relatively stable solutions of gallium(I) are obtained by solution of gallium(I) salts such as Ga_2Cl_4 or by anodic oxidation of gallium metal in aqueous base. These solutions homogeneously evolve hydrogen in a reaction that is first order in Ga(I) and in OH^- and zero order in Ga(III) over the range of at least 1 to 4 *M* OH^-. A stable white precipitate containing all of the reducing strength is obtained on neutralization of basic solutions of Ga_2Cl_4; further reaction of this solid to give H_2 and Ga(III) takes place relatively rapidly at pH $\leq$ 5. The reducing reactions of the basic solutions and of the precipitate at pH

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(10) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 158ff.

(11) Calculated from data given in "Stability Constants," compiled by J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, Part II, the Chemical Society, London, 1958, p. 21, and E^0 for Ga–Ga^{3+}. The E_B^0 of *ca.* 1.22 v. given by Latimer (ref. 10) appears to be low since the acid ionization constant (K_{s4}^*) estimated for the hydrous oxide [$Ga(OH)_3(s) + H_2O = Ga(OH)_4^- + H^+$] is only 0.25% of that given for the better characterized ionization of hydrous aluminum oxide, whereas the gallium compound is well recognized to be more acidic. A like value of E_B^0, 1.29 ± 0.02 v., also is obtained if pK_{sp} is taken as −35.0 to −36.5 ("Stability Constants") and pK_{s4}^* is assumed to be 1 to 2 units more positive than that given by Latimer for aluminum.

0–2 indicate $E_B{}^0$ and E^0 for the Ga(I)–Ga(III) couple are ≥ 1.24 and $\sim\geq 0.40$ v., respectively.

Experimental

The cell for kinetic studies was made from a 40/50 standard taper joint sealed at both ends. The internal stirrer consisted of a glass rod with a bar magnet sealed crosswise near the top and glass stirring blades fused on near the bottom, and was mounted between a dimple in the cell top and the narrow opening of a capillary stopcock in the bottom piece. With Ga_2Cl_4 in the evacuated cell, solvent was admitted through the bottom stopcock, the apparatus pressurized with N_2 previously equilibrated with the solvent, and then opened to a gas buret. The H_2 evolution was measured at constant pressure to ±0.01 ml. for one to four half-lives and corrected for the vapor pressure of the solution. The final reducing strength C_t was determined by addition of standard I_3^- solution to an aliquot, acidification, and back titration. In the few cases where C_t was uncertain, the rate was evaluated independent of this from plots of C' *vs.* the graphically derived dC'/dt. Since impurities in commercial $NaClO_4$ were found to react with iodine solutions, this was prepared from reagent grade NaOH and $HClO_4$, and its concentration determined by titration before and after exchange of the solution with Dowex-50 in the acid cycle.

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Second Wien Effect in Aqueous Mercuric Chloride Solution[1]

BY MANFRED EIGEN AND EDWARD M. EYRING

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Onsager[2] suggested in his classic treatment of the second Wien effect[3] that the equilibrium

$$HgCl_2 \underset{k_R}{\overset{k_D}{\rightleftharpoons}} HgCl^+ + Cl^- \qquad (1)$$

would make a particularly interesting experimental rate study because of the hydrodynamic effect of the large cation on the specific rate k_R of the recombination reaction. Bailey and Patterson[4] subsequently measured a fractional increase in high field conductance of about 1.7% for an aqueous 9.3×10^{-3} *M* solution of $HgCl_2$ at 25° as the field was increased from 40 to 100 kv./cm. They tentatively attributed the observed effect to reaction 1 but could not exclude the possibility that hydrolysis plays a significant role.

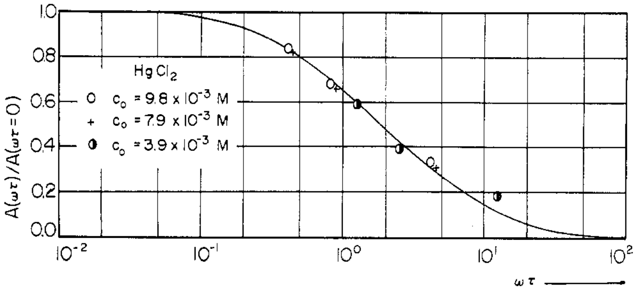

Fig. 1.—Experimental dispersions of the field effect in aqueous mercuric chloride solutions. Each set of three points corresponds to the three different pulse lengths (frequencies) $\omega_1 = 4 \times 10^5$ sec.$^{-1}$, $\omega_2 = 8 \times 10^5$ sec.$^{-1}$, and $\omega_3 = 3.8 \times 10^6$ sec.$^{-1}$ reading from left to right.

For $HgCl_2$ solutions of similar concentrations we have obtained extrapolated values of $\Delta\Lambda/\Lambda_0$ (Table I) of about the same size as those noted by Bailey and Patterson. Our technique[5] though less suitable than Patterson's instrument for making absolute Wien effect measurements, also permits the determination of a relaxation time τ, which for a simple dissociation equilibrium according to eq. 1 would read

$$\tau = (k_D + 2k_R x_e)^{-1} \qquad (2)$$

The symbol x_e in eq. 2 denotes the equilibrium concentration of one of the reacting ionic species which is assumed to be equal for Cl^- and $HgCl^+$. Even if the equilibrium constant *K* is not known, it frequently is possible to determine both the specific rate for dis-

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[1] Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J. September, 1962.

[2] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[3] M. Wien and J. Schiele, *Z. Physik*, **32**, 545 (1931). The second Wien effect or dissociation field effect is a marked, non-ohmic increase in the electrical conductance of a solution of a weak electrolyte when a high intensity electric field is applied. Effectively, the field displaces the equilibrium

$$\text{molecules} \rightleftharpoons \text{ion pairs} \rightleftharpoons \text{free ions}$$

to the right by pulling apart some of the ion pairs. In the range 40 to 100 kv./cm. the increase in conductance for a weak electrolyte will be proportional to the absolute value of the field intensity and, depending on concentration, can be as large as 10% of the conductance in the absence of a strong field. Earlier (1927) Wien reported a first Wien effect in solutions of both strong and weak electrolytes. This more modest increase in electrical conductance with increasing field gradient arises primarily from the destruction of the ionic atmosphere by the high field with a consequent increase in ion mobility. We denote the absolute change of equivalent conductance arising from both Wien effects by $\Delta\Lambda/\Lambda_0 \equiv (\Lambda_X - \Lambda_0)/\Lambda_0$, where Λ_X is the equivalent conductance of the solution at field x and Λ_0 is the equivalent conductance of the same solution at zero field. Since our experimental comparison system cancels most of the ion atmosphere effect in our mercuric chloride solutions, our observed $\Delta\Lambda/\Lambda_0$ is presumed to arise solely from a second Wien effect. Onsager[2] quantitatively described the second Wien effect by the equation

$$\Delta\Lambda/\Lambda_0 = [(1 - \alpha)/(2 - \alpha)]b\Delta E$$

where $\alpha = ci/c_0$ is the degree of dissociation, *ci* is the concentration of each of the recombining ions, c_0 is the total solute concentration, *E* is the electric field intensity, and *b* is a known function of ion mobilities, ion charge, solvent dielectric constant, and temperature.

[4] F. E. Bailey, Jr., and A. Patterson, Jr., *J. Am. Chem. Soc.*, **74**, 5759 (1952).

[5] M. Eigen and J. Schoen, *Z. Elektrochem.*, **59**, 483 (1955). We apply a high voltage pulse having the form of a critically damped, harmonic oscillation across a balanced, symmetric, bifilar-concentric bridge. The sample and reference cells are identical (2.0-mm. electrode distance, cell constant 0.053 cm.$^{-1}$). In the reference cell there is a dilute aqueous solution of HCl to cancel the first Wien effect in the sample cell. The remaining two arms of the bridge are cells with considerably greater electrode distances containing aqueous NaCl. The field intensity in these cells never exceeds a few kv./cm. The bridge and an auxiliary Wagner grounding circuit are the damping resistance in an RLC resonant circuit. We use half-wave, high voltage pulses of three different lengths: 2.5, 1.25, and 0.26 μsec. In a determination of the relaxation time τ of the mercuric chloride equilibrium for a given concentration of the salt in the sample cell we begin by applying a series of 1.25 μsec. pulses of increasing voltage to the bridge. The bridge is balanced oscillographically, and from the measured conductance at each voltage we plot the linear dependence of $\Delta\Lambda/\Lambda_0$ on $|E|$ over the range E = 40 to 100 kv./cm. Similar straight line plots are obtained with the 0.26 and 2.5 μsec. pulses. In case of a relaxation process these three straight lines are not superimposed; such a dispersion of the second Wien effect is shown in Fig. 1. The ordinate $A(\omega\tau)/A\cdot(\omega\tau = 0)$ is a reduced amplitude of the conductivity change during the sinusoidal high voltage pulse, and the ω in the abscissa $\omega\tau$ is the reciprocal of the duration of the critically damped harmonic oscillation, *i.e.*, the circular frequency in sec.$^{-1}$.