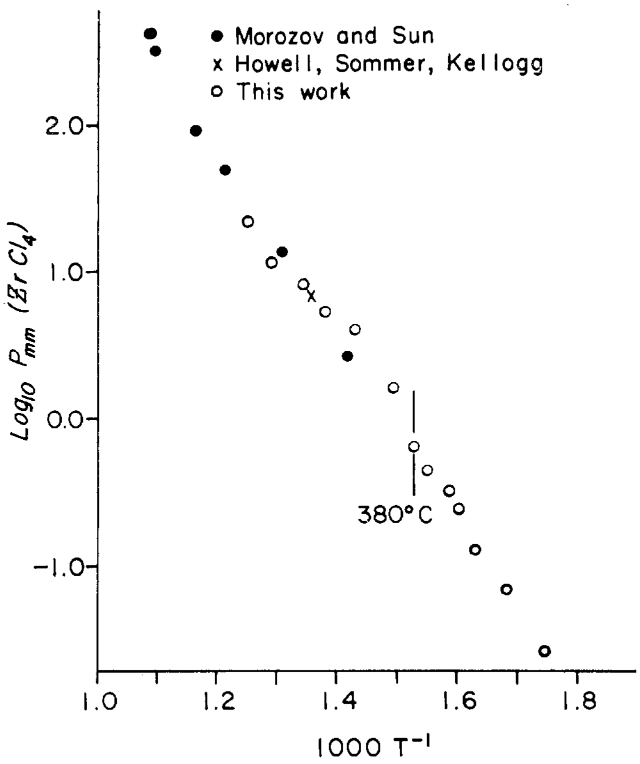

Fig. 1.—Decomposition pressures as a function of temperature.

In initial runs the sodium content of the deposit was also determined (by flame photometry). Amounts of sodium present were very small. In three runs at 500°, the apparent pressure of Na_2ZrCl_6 thus indicated was *ca.* 3×10^{-4} mm., somewhat over ten times the vapor pressure of NaCl.[8] Since contamination of the sublimate by small amounts of "dust" carried by the stream of argon could contribute quantities of sodium of the order of magnitude found, the value cited is suggested only as an upper limit for the partial pressure of the complex.

Results and Discussion

In experiments of type 1 calculated decomposition pressures of $ZrCl_4$ were found to depend on flow rate, which varied from 0.81 to 75.6 ml./min. (calculated at room temperature), with most experiments conducted at flows between 5 and 30 ml./min. A plot of $P(ZrCl_4)$ *vs.* flow rate gave reasonably smooth curves; pressures at flows of *ca.* 30 ml./min. were usually of the order of one-half values obtained by extrapolating to zero flow rate. The latter values were assumed to represent equilibrium pressures. The apparatus was designed so diffusion effects were negligible.

In experiments of type 2 a partial pressure of $ZrCl_4$ approximately twice the expected equilibrium value was introduced into the carrier gas by passing the argon over a sample of $ZrCl_4$, at a suitable temperature, prior to its contact with NaCl. A series of three runs, each at a different flow rate, was made at each of three temperatures, 300, 380, and 425°; in each case the initial reactant was pure NaCl. Only a very small dependence of the final pressure of $ZrCl_4$ with flow rate was observed when equilibrium was approached from the high pressure side; "zero flow" pressures agreed well with those of method 1.

Decomposition pressures appear independent of the relative amounts of sodium chloride and Na_2ZrCl_6 present. In (2) the composition of the solid remained close to pure NaCl; in (1) the solid phase contained around 50 mole % NaCl; the single value reported by Howell, Sommer, and Kellogg was determined over a solid corresponding to virtually pure Na_2ZrCl_6.

Results are listed in Table I and are shown graphically in Fig. 1. Considered independently of the work of others, our data suggest a possible transition in the vicinity of 390 to 400°, a temperature somewhat higher than that at which the stops were observed in phase studies (the transition temperature at *ca.* 380°, reported by both groups conducting phase studies, is marked on the figure).[2–4] Extrapolation of a least-squares line drawn through our five highest temperature points leads to pressures in the vicinity of 660° considerably below those observed by Morozov and Sun. However, we do not feel that the precision we have been able to attain is sufficiently good to justify a definite conclusion concerning the presence or absence of transitions. As can be seen in Fig. 1 our results are in general agreement with the decomposition pressures measured by other workers. A straight line correlating pressures of all investigators, ignoring possible transitions, gives a slope corresponding to a mean value of $\Delta H°$ of 27 kcal. for

$$Na_2ZrCl_6(s) = 2NaCl(s) + ZrCl_4(g)$$

The mean entropy change $\Delta S°$ (atm.) is 28 e.u. In view of the general consistency of the data the enthalpy and entropy changes associated with any transitions in this range are expected to be small.

Table I
Equilibrium Data

T, °K.	Type	P, mm.	T, °K.	Type	P, mm.
573	2	0.027	668	1	1.6
595	1	0.070	698	2	4.0
613	1	0.13	723	1	5.3
624	1	0.25	743	1	8.1
629	1	0.33	773	1	11.5
644	1	0.45	798	1	22.0
653	2	0.65			

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[8] A. N. Nesmeyanov and L. A. Sazonov, *Zh. Neorgan. Khim.*, **2**, 946 (1957).

Contribution from Arthur D. Little, Inc.,
Cambridge, Massachusetts

The Effect of Pressure on the Dissociation of Iron(III) Monochloride Complex Ion in Aqueous Solution[1]

By R. A. Horne, B. R. Myers, and G. R. Frysinger

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The ionization of weak electrolytes in aqueous solution is known to increase with the application of hydrostatic pressure due to the effects of ionic solva-

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tion and the attendant decreases in solvent volume.[2] Correspondingly, the dissociation of complex ions might be expected to increase with increasing pressure. Such has been found to be the case. The dissociation constants of $CoCl_4^{-2}$ and of $CuCl_4^{-2}$ roughly double as the pressure is increased from 15 to 23,000 p.s.i.[3]

Our interest in the corrosion of devices and structures situated on the ocean bottom (the bottom of the deepest ocean trenches corresponds to pressures of about 15,000 p.s.i.) prompted us to examine the pressure dependence of the dissociation of the chloride complex of a common constructional metal such as iron.

Experimental

The apparatus and experimental techniques employed have been described elsewhere.[4] The aqueous electrolytic solutions of the desired concentration were prepared and analyzed by standard procedures. The light yellow $Fe(ClO_4)_3$–$HClO_4$ solution, comparable in color intensity to the $FeCl_3$–HCl and $Fe(NO_3)_3$–HNO_3 solutions, was prepared by dissolving G. Frederick Smith Chem. Co. "non-yellow" $Fe(ClO_4)_3$ salt in aqueous $HClO_4$. Attempts to prepare $Fe(ClO_4)_3$–$HClO_4$ solutions by other methods yielded dark, highly hydrolyzed solutions.

Results and Discussion

The variation at 25° of the specific conductance of aqueous HNO_3, $HClO_4$, HCl, $Fe(NO_3)_3$–HNO_3, $Fe(ClO_4)_3$–$HClO_4$, and $FeCl_3$–HCl solutions is summarized in Tables I and II.

TABLE I

PRESSURE DEPENDENCE OF THE SPECIFIC CONDUCTANCE OF AQUEOUS HCl, $HClO_4$, AND HNO_3 SOLUTIONS

Specific conductance in ohm^{-1} $cm.^{-1}$ at 25.03 ± 0.02°

Pressure, p.s.i.	0.0505 *M* HCl	0.0489 *M* $HClO_4$	0.0513 *M* HNO_3
15	0.02016	0.01918	0.02022
10,000	0.02145	0.02018	0.02143
20,000	0.02254	0.02096	0.02243
30,000	0.02338	0.02164	0.02324
40,000	0.02402	0.02222	0.02386
50,000	0.02447	0.02260	0.02435
60,000	0.02484	0.02280	0.02473
70,000	0.02514	0.02310	0.02500

TABLE II

PRESSURE DEPENDENCE OF THE SPECIFIC CONDUCTANCE OF AQUEOUS $FeCl_3$–HCl, $Fe(ClO_4)_3$–$HClO_4$, AND $Fe(NO_3)_3$–HNO_3 SOLUTIONS

Specific conductance in ohm^{-1} $cm.^{-1}$ at 25.03 ± 0.05°

Pressure, p.s.i.	0.05 *M* $FeCl_3$ 0.05 *M* HCl	0.05 *M* $Fe(ClO_4)_3$ 0.05 *M* $HClO_4$	0.05 *M* $Fe(NO_3)_3$ 0.05 *M* HNO_3
15	0.03040	0.03108	0.03071
10,000	0.03293	0.03215	0.03204
20,000	0.03462	0.03288	0.03305
30,000	0.03585	0.03322	0.03364
40,000	0.03671	0.03344	0.03401
50,000	0.03726	0.03352	0.03423
60,000	0.03761	0.03351	0.03427
70,000	0.03771	0.03338	0.03420
80,000	0.03773	...	...
90,000	0.03732	...	...

The conductive contribution of the salt, ΔK_a^-, may be estimated by subtracting the conductance of the acid alone (Table I) from that of the salt–acid solution (Table II), and values thus obtained are given in Table III.

TABLE III

CONDUCTIVE CONTRIBUTIONS OF THE SALTS

Pressure, p.s.i.	ΔK_{Cl^-}, ohm^{-1} $cm.^{-1}$	$\Delta K_{ClO_4^-}$, ohm^{-1} $cm.^{-1}$	$\Delta K_{NO_3^-}$, ohm^{-1} $cm.^{-1}$
15	0.00924	0.01190	0.01049
10,000	0.01148	0.01197	0.01061
20,000	0.01208	0.01192	0.01062
30,000	0.01247	0.01158	0.01040
40,000	0.01269	0.01122	0.01015
50,000	0.01279	0.01092	0.00988
60,000	0.01277	0.01071	0.00954
70,000	0.01261	0.01028	0.00920

The conductive contribution of $Fe(ClO_4)_3$ and $Fe(NO_3)_3$ both at first increase with increasing pressure, go through a maximum at about 10,000 to 15,000 p.s.i., the same pressure range in which the viscosity of water is a minimum,[5] and then decrease with roughly equal slopes. In contrast, the conductive contribution of $FeCl_3$, while starting below both of the former curves, increases rapidly with pressure and does not reach its maximum until about 53,000 p.s.i., behavior characteristic of a weak electrolyte. From these observations the qualitative conclusion may be drawn that the dissociation of iron(III) monochloride complex ion increases with increasing pressure.

Reliable association constants can be calculated from conductance data only in the case of relatively dilute solutions of 1:1 electrolytes. However, if we assume that ferric ion does not complex with perchlorate ion,[6] if we ignore the formation of higher complexes, polynuclear species, and hydrolysis products, and if we assume that the term $\Delta K/\Sigma\Lambda^0$, where $\Sigma\Lambda^0$ is the sum of the 1-atm. limiting conductances of all of the system's major ionic species, has the same value for all three salts and is independent of pressure, then a semiquantitative estimation of the pressure dependence of the equilibria constants can be made. Using the limiting equivalent conductivities of 67 (average value for trivalent cations) 76, 67, 71, and 53 (value for the larger divalent cations) for Fe^{+3}, Cl^- ClO_4^-, NO_3^-, and $FeCl^{+2}$, respectively,[7] one obtains 4.45×10^{-5} equiv./cm.^{3} for $\Delta K/\Sigma\Lambda^0$. If we let X be the fraction of Fe(III) in the form of the complex $FeCl^{+2}$, we can write

$$\frac{K_{Cl^-}}{(1 - X)67 + (3 - X)(76) + X53} = 4.45 \times 10^{-5} \text{ (at 1 atm.)} \quad (1)$$

from which it follows that the value of X is 0.97. Now

$$(Cl^-) = 3(FeCl_3)_i + (HCl)_i - (FeCl^{+2}) = 0.15 \quad (2)$$

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[2] S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworths Scientific Publications, London, 1957, pp. 129–131, 149–156.

[3] A. H. Ewald and S. D. Hamann, *Australian J. Chem.*, **9**, 54 (1956).

[4] R. A. Horne and G. R. Frysinger, *J. Geophys. Res.*, **68**, 1967 (1963).

[5] R. Cohen, *Ann. Phys.*, **45**, 666 (1892).

[6] M. M. Jones, E. A. Jones, D. F. Harmon, and R. T. Semmes, *J. Am. Chem. Soc.*, **83**, 2038 (1961); see also F. Klanberg, J. P. Hunt, and H. W. Dodgen, *Inorg. Chem.*, **2**, 139 (1963).

[7] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths Scientific Publications, London, 1959, p. 463.

and at 1 atm. and 25° it follows that $K_{\mathrm{FeCl^{+2}}}$ is 21 M^{-1}. This value is in agreement with Bray and Hershey[8] and Badoz-Lambling[9] but is higher than the values reported by other investigators. Similar analysis for the $\mathrm{Fe(NO_3)_3}$–$\mathrm{HNO_3}$ solutions using a value of 50 for $\Lambda^0_{\mathrm{FeNO_3^{+2}}}$ yields a $K_{\mathrm{FeNO_3^{+2}}}$ of 5.7 M^{-1}, which is in reasonable agreement with the results of Sykes[10] but again higher than the value reported by some other investigators. Repeating these calculations at the higher pressures we find that the formation constant of $\mathrm{FeCl^{+2}}$ decreases 20-fold from 21 to 0.4 M^{-1} in going from 15 to 30,000 p.s.i., whereas the formation constant of $\mathrm{FeNO_3^{+2}}$ decreases only from 5.7 to 4.6 M^{-1} in going from 15 to 70,000 p.s.i.

One might expect that the effect of pressure on ion-pair formation should be less than upon true complex ion formation inasmuch as the former requires fewer alterations in solvation and, hence, does not entail large volume changes. Such being the case, the present results suggest that $\mathrm{FeCl^{+2}}$ is a complex ion, but that $\mathrm{FeNO_3^{+2}}$ is an ion pair, that is to say, the composition of the innermost hydration spheres of the participants is unchanged.

Acknowledgments.—We wish to acknowledge the valuable assistance of Professor R. M. Fuoss of Yale University and Dr. M. L. Vidale.

(8) W. C. Bray and A. V. Hershey, *J. Am. Chem. Soc.*, **56**, 1889 (1934).
(9) J. Badoz-Lambling, *Bull. Soc. Chim. France*, 552 (1950).
(10) K. W. Sykes, *J. Chem. Soc.*, 124 (1952).

Contribution from the Chemical Technology Division,
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Hydrolysis of Neutron-Irradiated Uranium Monocarbide[1]

By M. J. Bradley, J. H. Goode, L. M. Ferris,
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Received December 5, 1963

The reaction of neutron-irradiated uranium monocarbide with water at 80° is markedly different from that of unirradiated uranium monocarbide.[2] After irradiation to 6000 and 16,000 Mwatt-days/metric ton of total uranium (0.6 and 1.6 atom % burnup), uranium monocarbide specimens were nearly inert to water at 80 and 100°. In contrast, 4-g. specimens of unirradiated monocarbide reacted completely with 80° water within 3 hr. Hydrolysis of specimens that had been irradiated to the relatively low level of 600 Mwatt-days/metric ton of total uranium (0.06 atom % U burnup) yielded 96 ml. (STP) of gas per g. of carbide, consisting of 67 volume % methane, 28% hydrogen, and small quantities of higher hydrocarbons (Table I). In contrast, the gaseous products from the hydrolysis of unirradiated specimens from the same batch of carbide as the irradiated specimens contained much more methane (88 volume %) and less hydrogen (9%).[3] Only 86% of the original carbide carbon was found in the gaseous products from the slightly irradiated specimen, *vs.* essentially all of the carbon from the unirradiated specimens. In both cases the nonvolatile hydrolysis residue dissolved completely in 6 N HCl yielding a solution of tetravalent uranium (and fission products, if irradiated). Heating unirradiated specimens in a niobium capsule for 3 weeks (the length of the irradiation period) at 800° (the approximate temperature of the carbide during irradiation) had no effect on the hydrolysis behavior, indicating that the effect observed with the irradiated specimens was not thermally induced.

Table I
Effect of Neutron-Irradiation Level on the Hydrolysis of Uranium Monocarbide at 80°

Specimen burnup, Mwatt-days/metric ton of uranium	0	0[a]	600	6000	16,000
Vol. of gas evolved, ml./g. at STP	90.4	89.7	96.2	No reaction in 24-hr. tests	
Gaseous products, vol. %					
Hydrogen	8.9	8.5	28		
Methane	88	88	67		
Ethane	1.88	2.33	3.01		
Propane	0.44	0.43	0.52		
Butane	0.23	0.20	0.34		
C_5–C_8 alkanes	0.09	. . .	0.10		
Alkenes	0.20	0.08	0.48		
Alkynes	. . .	0.01	0.08		
Unidentified	0.01	0.09	0.26		
Carbon in gas, % of total	98	97	86		
Reaction time, hr.	3	3	>6		

[a] Specimen heated for 3 weeks at 800° in a niobium capsule.

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] M. J. Bradley and L. M. Ferris, *Inorg. Chem.*, **1**, 683 (1962).

[3] M. J. Bradley, L. M. Ferris, T. Hikido, and J. W. Ullmann, U. S. Atomic Energy Commission Report ORNL-3403 (March 19, 1963).

Contribution from the McPherson Chemistry
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The Compounds $(B_5H_8)_2CH_2$ and $B_5H_8CH_2BCl_2$

By E. R. Altwicker, G. E. Ryschkewitsch,[1]
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In a recent paper[2] we presented evidence that alkylation of pentaborane-9, B_5H_9, with olefins and alkyl halides in the presence of aluminum chloride is a general reaction of B_5H_9 and leads to substitution on the apex

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[1] Department of Chemistry, University of Florida, Gainesville, Florida.

[2] G. E. Ryschkewitsch, S. W. Harris, E. J. Mezey, H. H. Sisler, E. W. Weilmuenster, and A. B. Garrett, *Inorg. Chem.*, **2**, 890 (1963).