Relative H–D Exchange Rates.—The B^{11} resonance of a solution of 1.7 mmoles of $Na_2B_{12}H_{12} \cdot H_2O$ in 3 ml. of 3.8% DCl in D_2O was followed with time. As H–D exchange occurred, the initial B–H doublet became less intense as the singlet resonance of B–D began to appear midway between the two B–H peaks. In 19.25 hr., the B–D peak height was approximately equal to the height of the B–H doublet, and the signal had become an essentially flat topped plateau. At the same DCl and anion molarity, the low-field doublet of $B_{10}H_{10}^{-2}$ (apical BH) had disappeared before a measurement could be made, and it required only 17 min. for the high-field doublet to reach the end point. For comparison of the relative exchange rates of apical to equatorial BH in $B_{10}H_{10}^{-2}$, a solution of 600 mg. of $(NH_4)_2B_{10}H_{10}$ in 4 ml. of D_2O containing 1 drop of 38% DCl in D_2O was examined. The high-field doublet became flat in 3.25 hr., and the low-field doublet in 40 min. Thus, the relative rates of deuteration are $B_{12}H_{12}^{-2} = 1$, equatorial $B_{10}H_{10}^{-2} = 68$, apical $B_{10}H_{10}^{-2} = 330$.

Spectral Characterization.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet and visible spectra were examined with a Cary Model 14 spectrometer. Nuclear magnetic resonance was observed on a Varian Model V4300 spectrometer. Double irradiation was effected with an NMR Specialities Model SD 60 spin decoupler (B^{11} saturation by 19.2 Mc. irradiation while observing H^1 at 60 Mc., and H^1 saturation by 60 Mc. irradiation while examining B^{11} at 19.2 Mc.).

Polarography.—$Na_2B_{12}H_{12}$ and $[(CH_3)_4N]_2B_{10}H_{10}$ were examined with a dropping Hg electrode *vs.* a saturated calomel electrode over the maximum usable potential range in the following aqueous media: (1) 0.1 M LiClO$_4$ (+0.3 to −1.8 v.); (2) 0.1 M LiClO$_4$ and 0.002 M HClO$_4$ (+0.4 to −1.3 v.); and (3) 0.05 M NaOH (−0.1 to −1.8 v.). There was no evidence of either reduction or oxidation of the anions within these potential limits.

To extend the study beyond the oxidation potential of mercury (+0.4 v. in acid solution) the oxidation of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ was examined using a graphite–Nujol paste electrode *vs.* a saturated calomel electrode by which a potential up to about +1.4 v. can be attained.

$B_{12}H_{12}^{-2}$ (3.3 × 10^{-4} and 10^{-5} M $Na_2B_{12}H_{12}$) was not oxidized in 0.1 M aqueous KH_2PO_4 up to +1.4 v. $B_{10}H_{10}^{-2}$ (4.6 × 10^{-5} M $[(CH_3)_4N]_2B_{10}H_{10}$) oxidized at a potential of +0.85 v., in Britton–Robinson standard buffer solutions ranging in pH from 2.4 to 9.7. The peak current was a linear function of concentration within the reproducibility of the measurement. The temperature coefficient of the peak current was about 1.5% deg.$^{-1}$, indicating the process to be diffusion controlled. The peak current was insensitive to pH over the range 2.4 to 8.0, indicating that the compound is relatively stable to hydrolysis over this pH region. The peak current divided by concentration gave a value of 329 compared to 10.7 for $K_4Fe(CN)_6$, establishing a multi-electron change, probably due to gross degradation.

Notes

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Vapor Pressures of Zirconium Tetrachloride above Sodium Chloride and Sodium Hexachlorozirconate(IV)

BY B. G. KORSHUNOV[1] AND N. W. GREGORY

The system NaCl–ZrCl$_4$ has been studied by a number of investigators. Morozov and Korshunov[2] and Korshunov, Reznik, and Morozov[3] have published phase information which demonstrates the existence of the compound Na_2ZrCl_6. Cooling curve stops at 377 and 341° led them to suggest that Na_2ZrCl_6 may undergo polymorphic transitions. Howell, Sommer, and Kellogg[4] have confirmed the general features of the phase diagram but observe stops at 381, 373, and 362° and suggest that other intermediate compounds may exist in the system. A simple eutectic behavior

between NaCl and Na_2ZrCl_6 with no evidence of solid solution was observed by both groups of workers.

We have made a study of decomposition pressures of ZrCl$_4$ above solid mixtures of NaCl and Na_2ZrCl_6 between 300 and 525°, which includes the range in which transitions were reported. Similar data between 425 and 660° have been reported earlier by Morozov and Sun.[5]

Experimental

A transpiration method was used with (1) argon flowing over mixtures of NaCl and Na_2ZrCl_6 and (2) argon with ZrCl$_4$ flowing over initially pure NaCl. The apparatus was essentially the same as described in previous work from this laboratory.[6] For (1) solid samples of 50–50 mole % NaCl and Na_2ZrCl_6 were prepared by melting together in a Pyrex ampoule weighed amounts of NaCl (Mallinckrodt, analytical grade) and ZrCl$_4$ (Fairmount Chemical, analysis provided: Al, 330 p.p.m.; Fe, 860 p.p.m.; Si, 110 p.p.m.; Ti, 50 p.p.m.; oxychloride, 1.7%, insolubles, <0.1%; Hf, 2–3%. This material was resublimed in a current of chlorine). All samples were handled under high vacuum or in a drybox. The solidified melt was ground, and fresh samples of 4–5 g. were used for each series (*ca.* five runs) of transpiration experiments.

The transported chloride condensate, a white film collected at the edge of the reaction furnace, was washed out with water and the zirconium content determined colorimetrically (with a Beckman DU spectrophotometer) as a zirconium alizarin sulfonate lake.[7]

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(2) I. S. Morozov and B. G. Korshunov, *Zh. Neorgan. Khim.*, **1**, 145 (1956).

(3) B. G. Korshunov, A. M. Reznik, and I. S. Morozov, *Tr. Moscov Inst. Tonkoi Khim. Technol. im. M. V. Lomonosova*, **7**, 127 (1958).

(4) L. J. Howell, R. C. Sommer, and H. H. Kellogg, *J. Metals*, **209**, 193 (1957).

(5) I. S. Morozov and I. Sun, *Zh. Neorgan. Khim.*, **4**, 2551 (1959).

(6) N. W. Gregory and co-workers, *J. Phys. Chem.*, **59**, 110 (1955); *ibid.*, **62**, 433 (1958); *J. Am. Chem. Soc.*, **82**, 93 (1960).

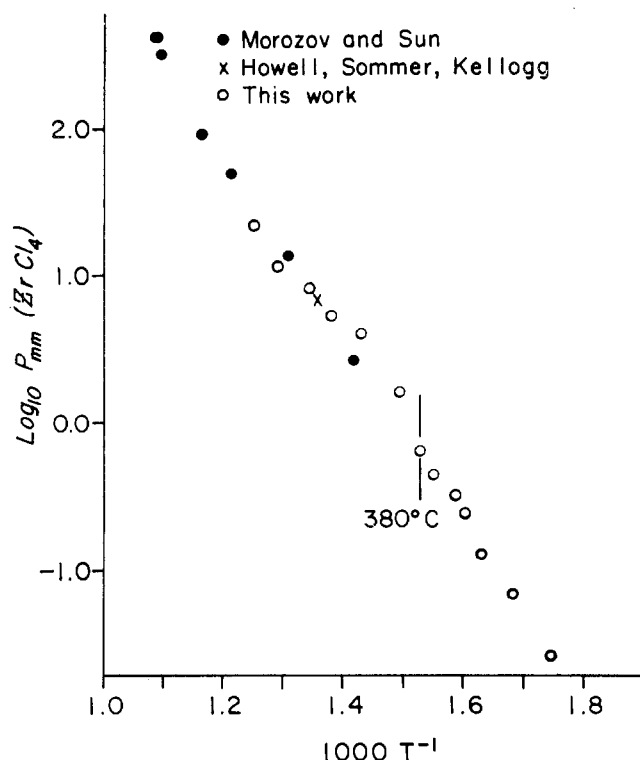(7) D. E. Green, *Anal. Chem.*, **20**, 370 (1948).

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.

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

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

$$Na_2ZrCl_6(s) = 2NaCl(s) + ZrCl_4(g)$$
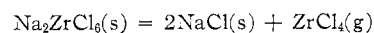
The mean entropy change $\Delta S°$ (atm.) is 28 e.u. In view of the general consistency of the data the enthalpy and entropy changes associated with any transitions in this range are expected to be small.

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			

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

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-