The data show that cyanide has a drastic effect on the rate of the reaction. A total variation of about 10,000-fold in k is observed. Small amounts diminish the rate; a minimum at less than 1% of the initial value of k is observed at a $(\Sigma CN^-)/(\Sigma Tl(III))$ ratio of 3.5; subsequently the rate rises about as the third power of (CN^-). A similar effect has been observed[6] with chloride in the Tl(I)–Tl(III) reaction, except that in this case the minimum occurs at a $(\Sigma Cl^-)/(\Sigma Tl(III))$ ratio of 1.5, is less deep, and the subsequent rise is a little less than second order in chloride.

We believe the decrease in rate caused by small amounts of cyanide can best be explained by the formation of thallium–cyanide complexes which are inert to the exchange reaction; indeed, no other plausible interpretation has occurred to us. On this view, the kinetic data furnish strong evidence for the existence of stable complexes $TlCN^{++}$ and $Tl(CN)^+$, and permit an estimate of the relative magnitude of the equilibrium constants for their formation. The initial effect is attributed to the formation of these species because: (1) there is evidence[16] for the existence of $Tl(CN)_4^-$ in aqueous solution; (2) stepwise association of Tl(III) with chloride and bromide, leading to very stable species, has been demonstrated[17]; (3) a self-consistent analysis of the data based on this assumption can be made, and (4) in general thallous ions forms only weakly associated complexes with simple anions.[18]

Consider the stepwise association reactions

$$A + X = AX, \text{ and } AX + X = AX_2$$

with the equilibrium constants

$$K_1 = \frac{(AX)}{(A)(X)} \text{ and } K_2 = \frac{(AX_2)}{(AX)(X)}$$

If K_1 and K_2 are each sufficiently large that the fraction of uncomplexed X is very small, mass balance leads to the expression

$$\frac{K_2}{K_1} = y\frac{\alpha - 1 + y}{(2 - \alpha - 2y)^2}$$

where α is the ratio of the formal concentration of X to that of A and y is the ratio of the concentration of uncomplexed A to the formal concentration of A. If one assumes that neither AX nor AX_2 react, and that higher complexes may be neglected for α less than 2, then $k/k_0 = y$, where k is the observed second-order rate constant, and k_0 is its value in the absence of the complexing agent X. Thus, the ratio of equilibrium constants can be calculated from the observed values of k. For the four runs in which α ranged from 0.7 to 1.7 the mean value of K_2/K_1 was found to be 0.15, with an average deviation of 0.05. The foregoing expression was solved for y, and evaluated at the values of α corresponding to the measurements in the range $0 < \alpha < 2$.

The concordance of the experimental data with this analysis is shown by the last column in Table I under the heading $k_{\text{predicted}}$. The average deviation between calculated and observed k's is 7% as k ranges from 0.735 to 0.011 mole^{-1} l. hr.$^{-1}$.

We ascribe the increase in rate at higher cyanide concentrations to the formation of other thallium-cyanide complexes. In view of the strong tendence of Tl(III) to complex with Cl^- and Br^-,[17] the generally strong complexing tendency of CN^-, and the fact that Tl(I) forms only weakly associated complex ions, it is most reasonable to infer that $Tl(CN)_3$ or $Tl(CN)_4^-$, reacting with Tl^+, are responsible for the increase near the minimum.

The continued subsequent increase may well be due to the equilibrium formation of still other thallium–cyanide species which participate more readily in the exchange reaction than the species which they replace. From analogy with the corresponding chloride system we are inclined to suppose that these are thallous complexes such as TlCN, $Tl(CN)_2^-$, or $Tl(CN)_3^=$. Equilibrium studies would aid in clarifying this point.

The acidity of the system would be expected to have a strong effect on equilibria involving cyanide and hence on the rates of reactions involving products of these equilibria. The hydrogen ion concentration would also appear in the rate expression if the reacting complex ions were themselves weak acids or the anions of weak acids, particularly if hydrogen atom transfer,[10,19] were important in the rate-determining step. That such effects occur is evident from the data in Table I, *e.g.*, in the results at total cyanide 0.193 and 0.200 *f*. The system in which cyanide was present largely as the free ion has a second-order rate constant at least 200 times greater than that in which it was present largely as HCN.

It would be of considerable interest to determine equilibrium constants for the formation of the various complexes of Tl(I) and Tl(III) with cyanide, and to relate these to the exchange kinetics. More extensive exchange measurements, at various temperatures and acidities, might then be profitably undertaken and the results related to the growing body of information about the rates of oxidation–reduction exchanges.

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The Polarographic Reduction of Ferric Ion in Fluoride Media

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West and Dean[1,2] have reported that the ferric ion in 1 *M* sodium fluoride exhibits no polarographic reduction wave to potentials as negative as *ca.* − 2 volts. Presumably, their medium would have a *p*H

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[1] P. W. West and J. F. Dean, *Anal. Chem.*, **17**, 686 (1945).

[2] P. W. West J. F. Dean and E. J. Breda, *Collection Czechoslov. Chem. Communs.*, **13**, 1 (1948).

of *ca.* 5 ± 1. Stackelberg and Freyhold[3] have reported that ferric iron reduces with an $E_{1/2}$ of -1.36 volt in 0.04 to 0.8 *M* potassium fluoride. Shoemaker[4] has recently reported the irreversible reduction of FeF^{++} at a rotating platinum microelectrode. Recent study in this Laboratory clarifies some of these discordant reports.

At 25° and within a *p*H range of about 5 to 6.5, a small reduction wave is observed with the dropping mercury electrode at -1.36 volt *vs.* S.C.E. in 0.3 to 1.0 *M* potassium fluoride. However this wave is found with or without ferric ion present, and is apparently due to hydrogen discharge or other phenomena. At a *p*H of 5.8 a reversible (based on slope if $n = 1$) ferric to ferrous reduction wave does occur with an $E_{1/2}$ of -0.49 volt *vs.* S.C.E. in 1.0 *M* fluoride. The wave is observed within a very limited range of *p*H, however. Only about one-third of the diffusion current remains on lowering the *p*H to 5.4 or on raising it to 6.2.

The $E_{1/2}$ of this wave is not appreciably *p*H dependent.

At a *p*H of 5.8 the relation of $E_{1/2}$ to log $[F^-]$, for $[F^-] = 0.3$ to 1.0 *M*, fits the conclusion that one (or, one *additional*) fluoride ion is being complexed. A plot of these data is shown in Fig. 1.

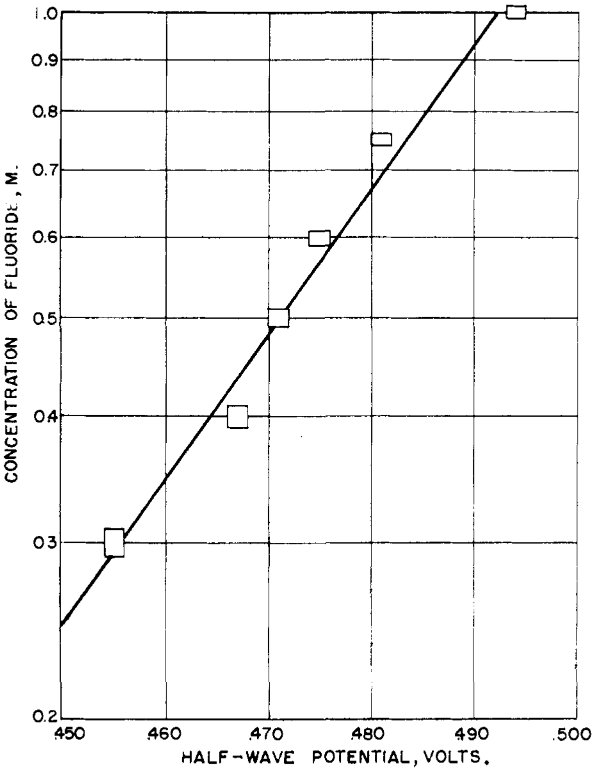

Fig. 1.—Variation of half-wave potential of ferric ion with fluoride concentration.

At 25° in 1 *M* KF and at a *p*H of 5.8, the diffusion coefficient of the ferric fluoride complex is estimated as being 5.8×10^{-6} cm.^{2} sec.$^{-1}$. The capillary characteristics were $t = 2.35$ sec. and $m = 3.48$ mg. sec.$^{-1}$ at -0.47 volt.[5]

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[3] M. von Stackelberg and H. von Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

[4] C. E. Shoemaker, paper presented at American Chemical Society Meeting, Kansas City, March, 1954.

[5] This work was performed under Contract No. AF 18(600)-379 with the Air Research and Development Command, Wright Air Development Center.

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The Heats of Combustion and Formation of Boron Carbide

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There appear to be no published data for the heat and free energy of formation of boron carbide, B_4C, a compound of considerable technical interest as a possible refractory and neutron absorber. We decided to measure the heat of combustion of boron carbide since we are interested in the thermochemistry of boron compounds and had developed methods for their combustion and analysis. Although a more direct measurement of heat of formation would be desirable, it is possible to derive a reasonably reliable value from the heat of combustion.

Experimental

Boron Carbide.—A sample of high purity boron carbide together with its analysis was supplied to us through the courtesy of Dr. G. R. Finlay of Norton Company, Research and Development Department. The analysis showed B = 77.81%, C = 21.63%, corresponding to 3.99 boron atoms per carbon atom, or within experimental error to the stoichiometric composition B_4C. There was apparently no free boron or carbon in the sample. However, because of the small heat of formation of B_4C, traces of the free elements would cause negligible errors. The sample contained 0.16% iron. Calculation showed that if the iron impurity were present as either free iron or cementite, Fe_3C, and burned to Fe_2O_3 an error no greater than 0.03% would be introduced, while if the iron were already partially or completely converted to oxide the error would be smaller. Therefore, we have made no allowance for the presence of iron impurity in the absence of exact knowledge about its fate.

The following atomic weights were used: B, 10.82; C, 12.110; O, 16.000.

Apparatus.—Heat of combustion measurements were made in a Parr oxygen bomb calorimeter, modified as described by Dworkin, Sasmor and Van Artsdalen.[2] The bomb itself, a double valve type, constructed of illium, has a volume of about 360 cc. A smaller weight of water than in our previous work was used in the calorimeter during the present study; the standard amount was 1990.0 g. and corrections were applied for slight deviations from this amount from run to run. Three different types of crucibles were used to contain the charge of boron carbide: namely, stainless steel, platinum and quartz, of which quartz was most satisfactory and least attacked, though it seemed to hinder combustion somewhat. Available stainless steel and platinum crucibles were light weight and ruptured in most combustions. The calorimeter was calibrated by combustion of N.B.S. benzoic acid, standard sample 39g, according to Bureau of Standards recommendations at 30 atm. of oxygen when there was one ml. of water in the bomb and the pelleted benzoic acid was contained in a stainless steel crucible. A series of five calibrations made during the course of work with boron carbide gave 2437.7 ± 1.7 cal./deg. for the thermal equivalent of the calorimeter containing 1990.0 g. of water. The temperature rise in calibration was comparable with that in B_4C experiments. Appro-

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[1] Consultant and summer employee, Oak Ridge National Laboratory.

[2] A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, *J. Chem. Phys.*, **22**, 837 (1954).