539. *The Equilibrium between Iron*(II) *and Titanium*(IV) *in Sulphuric Acid*

By M. L. Reynolds

Solutions of iron(II) and titanium(IV) in sulphuric acid are brown. Beukenkamp and Herrington [1] report that spectrophotometric investigations showed the absorbing species to contain iron and titanium in the molar ratios of 2 : 1, and ion-exchange experiments indicated that the formation constant of the reaction was very small.

Preliminary experiments showed that the interaction between iron(II) and titanium(IV) occurred in perchloric acid as well as in sulphuric acid. At constant iron and titanium concentrations the degree of complex formation depends on the sulphuric acid concentration, increasing rapidly up to about 1M-acid, then more gradually up to an acidity of 9M, after which there is a gradual decrease. Job's plots at two different total metal ion concentrations (Figure 1) suggest that species containing iron and titanium in the molar ratios 1 : 1 and 2 : 1 are formed.* Solid complexes of varying composition have been isolated (preceding Note).

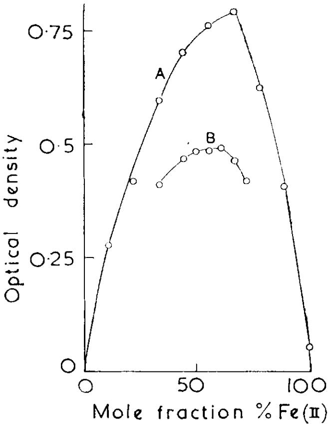

Figure 1. Job's plots at two different total metal ion concentrations for the interaction of iron(II) and titanium(IV) in sulphuric acid

A, 0·279M Fe in 1·80M H_2SO_4
B, 0·159M Fe in 1·48M H_2SO_4

A more detailed investigation of the system was then made in 1·85M-sulphuric acid. It was assumed that the complexes formed do not themselves polymerise, that only one each of the iron and titanium species interact with each other, and that, since the sulphuric acid concentration was at least five times greater than the combined iron and titanium concentrations in all experiments, activity coefficients were effectively constant. It was assumed further that when the titanium concentration is much greater than the iron concentration only a 1 : 1 species, represented as X, is formed. The system is then defined by the equations:

$$T_{\mathrm{Ti}} = [S_{\mathrm{Ti}}]\mathrm{f}(\mathrm{H}) + [\mathrm{X}] \qquad (1)$$

$$T_{\mathrm{Fe}} = S_{\mathrm{Fe}}\mathrm{g}(\mathrm{H}) + [\mathrm{X}] \qquad (2)$$

$$K_1 = [\mathrm{X}]/[S_{\mathrm{Ti}}][S_{\mathrm{Fe}}] \qquad (3)$$

$$D = E_1[\mathrm{X}] \qquad (4)$$

* At higher total ferrous concentrations the formation of a 2 : 1 species is favoured, whereas the 1:1 species tends to predominate at lower total ferrous concentrations.

[1] J. Beukenkamp and K. D. Herrington, *J. Amer. Chem. Soc.*, 1960, **82**, 3025.

T_{Ti} and T_{Fe} represent the total analytical concentrations of titanium and iron in the solutions, S_{Ti} and S_{Fe} represent the species chosen to interact with each other, f(H) and g(H) are functions relating the concentration terms S_{Ti} and S_{Fe} to all the other iron and titanium species in the solution and are dependent only on the acidity and formation constants of these species, D is the optical density of the solution, and E_1 the extinction coefficient of X. The experimental conditions chosen were such that $T_{\mathrm{Ti}} \gg T_{\mathrm{Fe}}$, so that $T_{\mathrm{Ti}} - \mathrm{X}$ may be replaced by T_{Ti}. Combining equations (1)—(4) and writing k_1 for $K_1/\mathrm{f(H)}\,.\,\mathrm{g(H)}$ for conditions of constant acidity gives:

$$D(1/T_{\mathrm{Ti}} + k_1) = k_1 E_1 T_{\mathrm{Fe}} \qquad (5)$$

A plot of $1/T_{\mathrm{Ti}}$ *versus* $1/D$ at constant T_{Fe} should give a straight line of slope $k_1E_1T_{\mathrm{Fe}}$ and intercept $-k_1$. For constant T_{Ti} a plot of D *versus* T_{Fe} gives a straight line of slope $k_1E_1/(1/T_{\mathrm{Ti}} + k_1)$ which should confirm the above values.

The experimental results are plotted in Figures 2 and 3. Optical densities were measured in 2-cm. cells, so that E_1 refers to a path length of 2 cm. The values derived from Figure 2 for k_1 and E_1 are 8·5 and 17·5, respectively. Substitution of these values in equation (5) gives a calculated slope of 11·0 for the plot of D *versus* T_{Fe} (Figure 3) compared with an observed slope of 11·3. Confirmation of the E_1 value as 17·5 l. mole^{-1} cm.$^{-1}$, was obtained by increasing the titanium concentration in solutions of fixed iron concentration until a maximum value for the optical density was observed. This occurred when the titanium : iron molar ratio was of the order of 25 : 1.

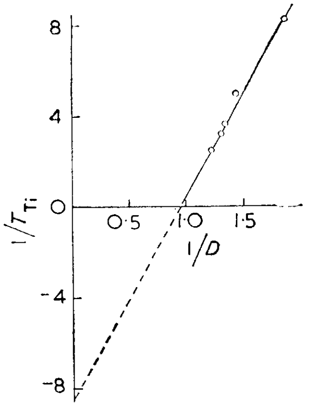

FIGURE 2. Variation of optical density (D) with total titanium(IV) concentration (T_{Ti}); $T_{\mathrm{Fe}} = 0{\cdot}06\mathrm{M}$, $\mathrm{H_2SO_4} = 1{\cdot}85\mathrm{M}$

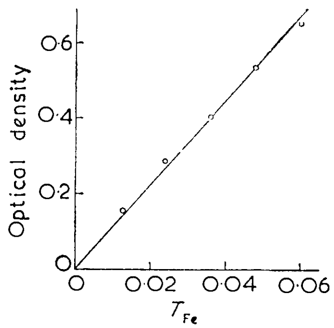

FIGURE 3. Variation of optical density (D) with total iron(II) concentration (T_{Fe}); $T_{\mathrm{Ti}} = 0{\cdot}20\mathrm{M}$, $\mathrm{H_2SO_4} = 1{\cdot}85\mathrm{M}$

The continuous-variation experiments show, however, that when the iron concentration is greater than the titanium concentration a species containing iron and titanium in the molar ratio of 2 : 1 is formed. By an argument similar to that used above, the equation for a system in which iron is present in sufficient excess for its concentration to be assumed constant is:

$$T_{\mathrm{Ti}}[E_2K_1K_2T_{\mathrm{Fe}}^2 + E_1K_1T_{\mathrm{Fe}}\mathrm{g(H)}] = D[K_1T_{\mathrm{Fe}}\mathrm{g(H)} + \mathrm{f(H)g^2(H)} + K_1K_2T_{\mathrm{Fe}}^2] \qquad (6)$$

where K_2 is the formation constant and E_2 the extinction coefficient of the 2 : 1 iron : titanium species.

K_2 cannot be evaluated since the functions f(H) and g(H) are unknown. A value for E_2 of 12 l. mole^{-1} cm.$^{-1}$ was obtained by increasing the iron concentration at constant titanium concentration in a series of titanium solutions until maximum optical density was observed.

Experimental.—Titanium(IV) sulphate solutions were prepared from titanyl sulphate dihydrate. Ferrous sulphate solutions were prepared by dissolving AnalaR ferrous sulphate in 2N-sulphuric acid with a little iron wire. Optical densities were measured in a Spekker absorptiometer at 4047 Å; in this way uncertainties which would have arisen in setting a variable-wavelength spectrophotometer to an arbitrary wavelength on the side of the steep absorption curve were avoided.

BRITISH TITAN PRODUCTS LIMITED, BILLINGHAM, CO. DURHAM.
[Present address: 6 NOTTINGHAM ROAD, BRISTOL 7.]

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