

The Relative Stability of Ferric Iron Complexes

DONNA D. THOMS and E. ST. CLAIR GANTZ, Purdue University

Ferric iron is a strong complex former and usually exists as a complex ion in solution. Each ferric complex has a characteristic hue which is shown by a spectral transmittancy curve. The change in this curve on the addition of other anions was used to establish the stability of the complex.

The transmittancy measurements were made with the Coleman Universal Spectrophotometer, Model 11. They were determined in the 350 to 750 mu. range, using 1.31 cm. absorption cells. Redistilled water was used in the reference cell. The measurements were made in 10 mu. intervals using a deep purple filter in the 350-400 range, a purple filter in the 400-650 range, and a red filter in the 650-750 range. There is a break in the curve when the filter is changed at 400 mu. which is seen in the figures.

It was assumed that the ferric ion has a coordination number of six so all the solutions were prepared on this basis. A standard solution of approximately 0.1 *M* ferric chloride was prepared by dissolving ferric chloride hexahydrate in redistilled water that was 0.3 *M* in hydrochloric acid. The exact molarity of the ferric ion was determined by titration with a standard potassium dichromate solution using sodium diphenylaminesulfonate as an internal indicator. Eighty-seven hundredths ml. of this standard solution, diluted to 100 ml. gave a solution 0.001 *M* in ferric ion. The stock solutions of the anions were prepared so that 1 ml. of the solution, diluted to 100 ml. was 0.006 *N* in the desired anion. The potassium or sodium salt of the anion was used.

The effect of each anion was measured in the presence of the chloride ion and the transmittancy curve compared to the curve for ferric chloride. These curves were used as a standard for that particular ferric complex.

There was no difference in the type of curve formed when the reagents were added in a different order.

Each anion was measured in the presence of every other anion and from the total results the stability list was established. The curve for the ferric cyanide complex was not changed by the presence of any other anion so the ferric cyanide complex was assumed to be the most stable. The nitrate ion had no effect on any of the curves for the other complexes so it was assumed to be the least stable. Since the phosphate ion formed a turbid solution with the acetate, tetraborate, sulfate, and tartrate complexes its position was obtained only by indirect evidence.

In figures 1,2,3, and 4 it is shown how the stability was established. These figures show only one or two of the curves for a certain anion but each position determined has been confirmed from the curves with the other anions.

In each figure the ordinate is the percent transmittancy and the abscissa is the wave length in μ .

The stability was established by comparing the curve for the mixture of two ions with the original curve for each complex. The curve of the complex that the mixture more closely resembled was the curve of the more stable complex.

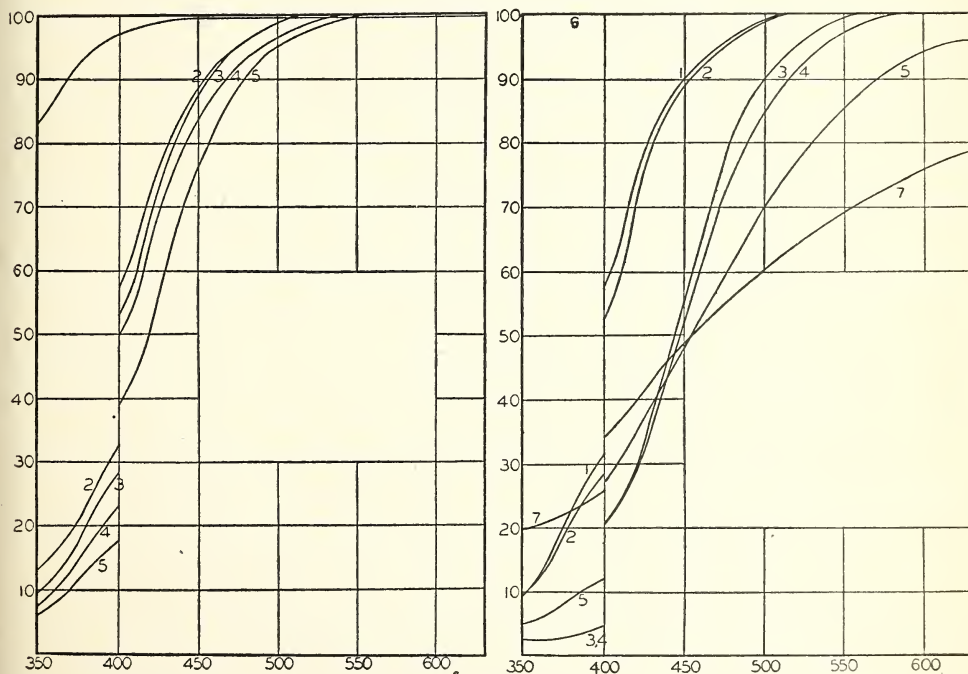


Fig. 1. Transmittancy curves for the Ferric complexes of: 1) Phosphate ion; 2) Phosphate and Oxalate ions; 3) Oxalate ion; 4) Citrate ion; 5) Citrate and Oxalate ions.

Fig. 2. Transmittancy curves for the Ferric complexes of: 1) Oxalate and Tartrate ions; 2) Oxalate ion; 3) Tartrate ion; 4) Tartrate and Acetate ions; 5) Acetate ion; 6) Fluoride ion; 7) Fluoride and Acetate ions.

In figure one it is seen that the citrate complex is more stable than the oxalate complex which is more stable than the phosphate complex.

In figure two it is seen that the oxalate complex is more stable than the tartrate complex which is more stable than the acetate complex. The fluoride complex is less stable than the acetate complex.

In figure three it is seen that the phosphate complex is more stable than the fluoride complex which is more stable than the thiocyanate complex.

In figure four it is seen that the thiocyanate complex is more stable than both the tetraborate and the sulfate complexes. The tetraborate

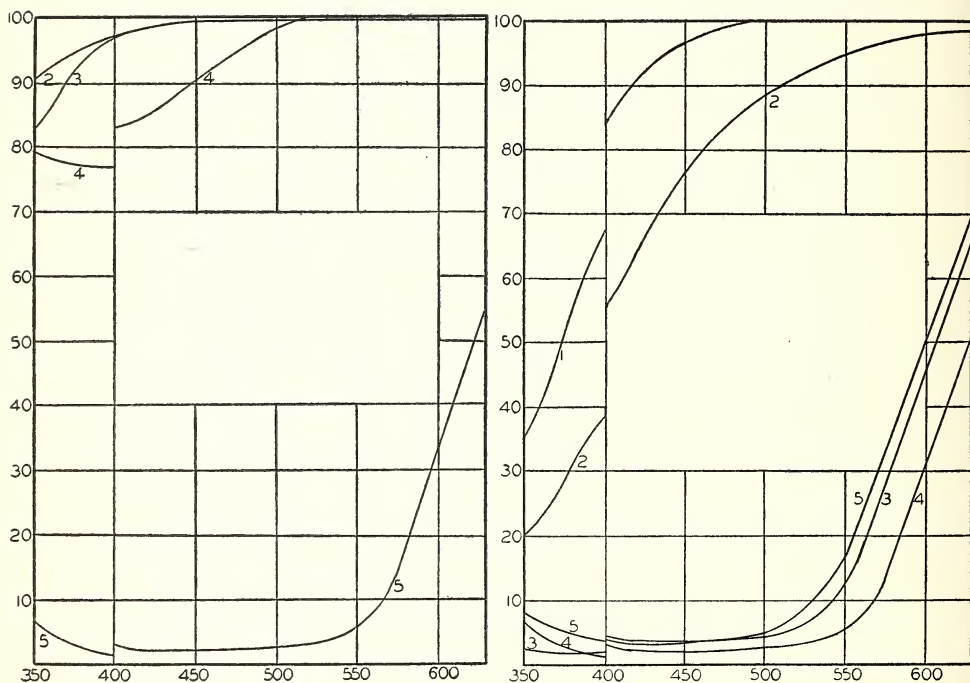


Fig. 3. Transmittancy curves for the Ferric complexes of: 1) Fluoride ion; 2) Fluoride and Phosphate ions; 3) Phosphate ion; 4) Fluoride and Thiocyanate ions; 5) Thiocyanate ion.

Fig. 4. Transmittancy curves for the Ferric complexes of: 1) Sulfate ion; 2) Tetraborate ion; 3) Tetraborate and Thiocyanate ions; 4) Thiocyanate ion; 5) Sulfate and Thiocyanate ions.

complex with the sulfate ion formed a turbid solution so the tetraborate complex was placed above the sulfate complex on the evidence that it changed the curves for the acetate, citrate, fluoride, and oxalate complexes while the sulfate ion had no effect on these curves.

The bromide ion had a small effect only on the curve for the sulfate complex.

The relative stability observed for the complexes, the most stable being listed first, is as follows:

Cyanide
Citrate
Oxalate
Tartrate
Acetate
Phosphate
Fluoride
Thiocyanate
Tetraborate
Sulfate
Chloride
Bromide
Nitrate

Literature Cited

1. Bobtelsky and Simchen, *Compt. rend.*, **208**:1646-7 (1937).
2. Gladstone, *Chem. News*, **67**:1 (1893).
Phil. Trans., 179 (1855).
3. Paulenc-Ferrand, *Compt. rend.*, **210**:54 (1940).
4. Vernon, *Chem. News*, **66**:177, 191, 202, 214 (1892).