Determination of Iron in Ore by Redox Titration

Oxidation-reduction reactions are suitable for titration reactions if they are rapid and quantitative. The end point can be seen by indicators or by instrumental methods such as potentiometry.

Potentiometric Titration of Ferrous Ion

The reaction of ferrous ion with ceric ion meets the above requirements.

The course of the titration may be followed potentiometrically with a platinum electrode. The following cell may be used:

Pt | Titration mixture of Fe3+, Fe3+, Ce4+, Ce3+ | SCE

The potential of the Pt electrode must obey the Nernst equation since the half reactions between Fe³⁺ and Fe²⁺ and between Ce⁴⁺ and Ce³⁺ are nearly reversible.

$$E_{p_1} = E^0(\text{Fe}^{3+}, \text{Fe}^{3+}) + 0.5916 \log \left[\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right] = E^0(\text{Ce}^{4+}, \text{Ce}^{3+}) + 0.05916 \log \left[\frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \right]$$
(2)

Equation 2 states that the Pt electrode can have only one potential, and the ratios of [Fe³⁺]/[Fe²⁺] and [Ce⁴⁺]/[Ce³⁺] must be such that the Nernst equation is satisfied for both half reactions. Reaction 1 will occur spontaneously to such an extent that equation 2 will be true. The ratios [Fe³⁺]/[Fe²⁺] and [Ce⁴⁺]/[Ce³⁺] change greatly at the equivalence point. The equivalence point is determined from the break in the titration curve.

Indicator Titration of Ferrous Ion

Specific indicators and true exidation-reduction indicators are available for redex titrations. Specific indicators are substances that react with one or more of the participants in a titration to produce a color change. A classic example is starch that forms a dark blue complex with I₂. In redex titrations with I₂ as the titrant, blue color develops to mark the end point of the reaction when I₂ begins to accumulate in the solution. Thiocyanate is an indicator that forms a red complex with Fe³⁺ but not with Fe²⁺, and thus can be used to indicate the formation or disappearance of Fe³⁺. Sometimes a redex reagent itself is deeply colored and can be used to indicate the end point. For example, MnO₄ is a purple ion often used as an exidizing agent. The first trace of purple color indicates that the MnO₄ is no longer being reduced by the titration reaction.

A true oxidation-reduction indicator is a substance that has different colors when in different oxidation states.

$$\ln_{ex} + n e - \ln_{ret}$$
 (3)

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Kaurav M. S.

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