Potassium permanganate is a powerful oxidising agent, whose reduction in an acid solution proceeds as:

\[ \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}. \]

Sulphuric acid is the most suitable acid, as it has no action upon permanganate in dilute solution; with hydrochloric acid there is the likelihood of the reaction

\[ 2\text{KMnO}_4 + 16\text{HCl} = 2\text{KCl} + 2\text{MnCl}_2 + 5\text{Cl}_2 + 8\text{H}_2\text{O} \]

taking place and some permanganate may be consumed in the formation of chlorine, which is a powerful oxidising agent capable of oxidising red phosphorus drastically, especially when suspended in solution, and hence an hydrochloric acid medium can normally interfere with the P-KMnO_4 reaction.

Numerous oxidation studies with potassium permanganate led the above authors to investigate the possibility of using it for the oxidation of red phosphorus to phosphoric acid. Even though Slater suggested the use of yellow phosphorus as a reductant in the reduction of permanganate to manganese dioxide and Rosenstein observed that solutions of permanganates are reduced to manganous salts by a few minutes boiling with red phosphorus, the available information in the literature about the quantitative oxidation of red phosphorus by permanganate is meagre.
The addition of acidified potassium permanganate solution to red phosphorus leads to its gradual disappearance accompanied with a simultaneous fading of the pink colour of the permanganate. The rate of the above change is measurably slow at ordinary temperatures and with excess of permanganate, complete oxidation of red phosphorus could be effected.

The present work was therefore undertaken to study the factors affecting this reaction and to determine its applicability to the determination of elementary phosphorus.

**Experimental**

Red phosphorus of B.D.H. laboratory reagent grade quality was purified by Buehner and Schurps method and subsequently by the copper phosphide process. Its purity was checked by the bromate procedure. An accurately weighed quantity (0.02–0.03 gm.) of the sample of red P was introduced in a ground glass stoppered Erlenmeyer flask to which a known excess of standard potassium permanganate solution (75 ml. N/6) was added, followed by the required quantity of dilute sulphuric acid (25 ml. 4N), so as to maintain the overall acidity of the system at or about 1N sulphuric acid. The flask containing the red P and permanganate and sulphuric acid solutions was maintained at a desired constant temperature for nearly 30 minutes before commencing the reaction, as also during the course of subsequent observations in an electrically heated thermostat fitted with an accurately calibrated automatic thermostater or in an ice-cooled bath, for low temperatures. The contents of the flask were swirled from time to time and an aliquot portion (2 ml.) of the clear supernatent solution was pipetted out carefully at different time intervals into known excess of ferrous ammonium sulphate solution (10 ml. 0.05 N) to arrest the reaction and the ferrous ammonium sulphate left over was titrated against standard potassium permanganate. Series of experiments were carried out at different temperatures, viz., 0, 10, 20, 30 and 40°C using the same concentrations and also by varying the concentrations of potassium permanganate and red P over a fairly wide range.

**Results and Discussion**

The concentrations of potassium permanganate as determined and represented in terms of number of ml. of ferrous ammonium sulphate solution in the experimental results, have been made use of, in calculating the order of the reaction by the integration method from the initial titre value of permanganate and that obtained at various time intervals during the course of the oxidation. Under the given operative conditions the value of K was found to be constant and within limits of experimental error according to the following equation:

\[
K = \frac{2.303}{t} \log_{10} \frac{T_i (T_o - T_x)}{T_o (T_i - T_x)}
\]

where \( T_o \) initial concentration of permanganate, \( T_i \) concentration of permanganate at time \( t \), \( T_x \) concentration of permanganate at time \( x \), and \( t \) time in minutes.