PART II

Attempt any **THREE** *of the following* **FIVE** *questions. You are advised to spend about* **35 minutes** *on* **each** *of the three questions. Each question carries 20 per cent of the total marks for this examination.*

Question 7

A metal M forms a sparingly soluble hydroxide, $M(OH)_2$. At 298.15 K, $K_{sp}^{\ominus}(M(OH)_2) = 5.48 \times 10^{-15}$.

For the $M^{2+}|M$ couple:

$$M^{2+}(aq) + 2e = M(s); \quad E^{\ominus}(298.15\ K) = -0.40\ V$$

(a) (5 marks) Use the information above to calculate the standard electrode potential at 298.15 K of the following couple:

$$M(OH)_2(s) + 2e = M(s) + 2OH^-(aq) \qquad (13)$$

(b) (8 marks) Taking any further information you need from the data sheet, confirm that the metal M has a thermodynamic tendency to corrode in contact with aerated water that is slightly acidic (pH 5). Explain your reasoning and state any assumptions involved in your answer.

(c) (7 marks) Suppose that the metal M corrodes by differential aeration corrosion. Describe an experiment designed to illustrate the principle of this type of corrosion, and outline, giving examples, the sort of situation in which it is likely to occur in practice.

Question 8

The oxidation of thiosulfate ion, $S_2O_3^{2-}$, by iodate ion, IO_3^-, in acidic solution has the following time-independent stoichiometry:

$$6S_2O_3^{2-}(aq) + IO_3^-(aq) + 6H^+(aq) = I^-(aq) + 3S_4O_6^{2-}(aq) + 3H_2O(l) \qquad (14)$$

(a) (8 marks) Describe in full, *but without giving experimental detail*, how the method of initial rates may be used to establish the experimental rate equation for this reaction. What is the main reason for using this method in kinetic studies?

(b) (12 marks) For an experiment at 300 K with the initial concentration of hydrogen ions, $[H^+]_0$, equal to 1.0×10^{-4} mol dm^{-3}, and the initial concentrations of thiosulfate ions and iodate ions both in large excess, the experimental rate equation was found to be:

$$J = k_R[H^+]^2$$

After 0.5 s of reaction, the concentration of iodide ions, $[I^-]$, was found to be 2.5×10^{-6} mol dm^{-3}.

(i) What is the concentration of hydrogen ions, $[H^+]$, after 0.5 s of reaction?

(ii) What is the value of the pseudo-second-order rate constant, k_R?

(iii) If all of the experimental conditions are kept the same, except that the temperature is increased to 308 K, then the value of the pseudo-second-order rate constant, k_R, is found to double. What is the activation energy for reaction 14?