Question 5
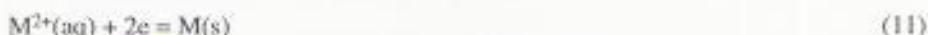
(a) The required value of i_c is obtained by reading off from Figure 2 the value of $\log |i|/A\,m^{-2}|$ at which the Tafel plot for the process

$$M^{2+}(aq) + 2e = M(s) \tag{11}$$

intersects the horizontal line at $V = -0.8$ V (relative to the S.H.E.). In this case, $\log |i|/A\,m^{-2}| = -8$, so $i_c = 10^{-8}\,A\,m^{-2}$.

This value of the exchange current density is a measure of the rate of the oxidation $(M \rightarrow M^{2+})$ and reduction $(M^{2+} \rightarrow M)$ reactions at equilibrium, *under the experimental conditions in Figure 2* – that is, at 298.15 K with a metal M electrode dipping into a solution of a particular pH, and containing unit concentration (1 mol dm^{-3}) of M^{2+} ions.

(b) At 0.0 V, neither of the reduction curves has been reached – that is, oxidation is tending to occur. Thus, metal M would tend to corrode $(M \rightarrow M^{2+})$ and H_2 (if there is any present in the solution) would be oxidized to H^+.

At -0.18 V, the 'H' curve is reached. H^+ ions will be reduced, with H_2 gas being liberated at the metal surface; metal M would still be undergoing corrosion.

At -0.80 V, both processes can occur, but the rate of H_2 liberation will exceed the rate of production of M. The current efficiency for production of M will be low $(< 50\%)$.

This situation would continue until the potential becomes more negative than -1.1 V. Thereafter, the rate of production of M will exceed the rate of liberation of H_2, and the current efficiency for the production of M will increase.

Question 6

(i) From the stoichiometry of reaction 12,

$$2CH_3OH(g) = C_2H_4(g) + 2H_2O(g) \tag{12}$$

the expression for $K^{\ominus}$ is

$$K^{\ominus} = \frac{a(C_2H_4)\{a(H_2O)\}^2}{\{a(CH_3OH)\}^2}$$

where a represents the activity of each species. The expression for K_p is

$$K_p = \frac{p(C_2H_4)\{p(H_2O)\}^2}{\{p(CH_3OH)\}^2}$$

where p represents the partial pressure of each species.

Assuming ideal behaviour for each gas, $a = p/p^{\ominus}$, where $p^{\ominus}$ is a standard pressure $(= 1$ bar). So

$$K^{\ominus} = \frac{\{p(C_2H_4)/p^{\ominus}\}\{p(H_2O)/p^{\ominus}\}^2}{\{p(CH_3OH)/p^{\ominus}\}^2}$$

$$= \frac{p(C_2H_4)\{p(H_2O)\}^2}{\{p(CH_3OH)\}^2} \times \frac{(p^{\ominus})^2}{p^{\ominus}(p^{\ominus})^2}$$

$$= K_p/p^{\ominus}$$

The temperature-dependence of $K^{\ominus}$ is determined by the sign of $\Delta H_m^{\ominus}$; $K^{\ominus}$ will increase with increasing T if $\Delta H_m^{\ominus}$ is positive, and decrease if $\Delta H_m^{\ominus}$ is negative. Taking information from the data sheet, for reaction 12:

$$\Delta H_m^{\ominus} = \Delta H_f^{\ominus}(C_2H_4, g) + 2\,\Delta H_f^{\ominus}(H_2O, g) - 2\,\Delta H_f^{\ominus}(CH_3OH, g)$$

$$= \{52.3 + 2(-241.8) - 2(-200.7)\}\,kJ\,mol^{-1}$$

$$= -29.9\,kJ\,mol^{-1}$$

Since $\Delta H_m^{\ominus} < 0$, $K^{\ominus}$ will decrease with increasing T.