Thus

$$K_m = (\text{slope}) \times V$$
$$= (3.57 \times 10^3 \text{ s}) \times (2.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1})$$
$$= 7.14 \times 10^{-4} \text{ mol dm}^{-3}$$

(b) When $[S]_0 \gg K_m$, equation 8 reduces to

$$J_0 = V$$

where V is the limiting rate. Clearly, if K_m is small, this condition is achieved at low substrate concentration, whereas if K_m is large a high concentration of substrate is required. Hence, the Michaelis constant (K_m) governs the range of substrate concentrations over which the initial rate approaches its limiting value. If an enzyme with a small K_m were present in tissue where the concentration of substrate is high, it would *always* be working flat out such that it would be insensitive to changes in substrate concentration.

Question 4

Combining the half-reactions given in the question yields the overall cell reaction

$$Ag_2O(s) + Zn(s) = 2Ag(s) + ZnO(s) \tag{A1}$$

Taking values from the data sheet:

$$\Delta H_m^{\ominus} = \Delta H_f^{\ominus}(ZnO, s) - \Delta H_f^{\ominus}(Ag_2O, s) \quad \text{(as } \Delta H_f = 0 \text{ for the elements, Ag and Zn)}$$
$$= \{-348.3 - (-31.0)\} \text{ kJ mol}^{-1} = -317.3 \text{ kJ mol}^{-1}$$
$$\Delta S_m^{\ominus} = 2S^{\ominus}(Ag, s) + S^{\ominus}(ZnO, s) - S^{\ominus}(Ag_2O, s) - S^{\ominus}(Zn, s)$$
$$= \{2(42.6) + 43.6 - 121.3 - 41.6\} \text{ J K}^{-1} \text{ mol}^{-1}$$
$$= -34.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Assuming $\Delta H_m^{\ominus}$ and $\Delta S_m^{\ominus}$ are independent of T:

$$\Delta G_m^{\ominus}(323.15 \text{ K}) = \Delta H_m^{\ominus} - T\Delta S_m^{\ominus}$$
$$= -317.3 \text{ kJ mol}^{-1} - (323.15 \text{ K} \times -34.1 \text{ J K}^{-1} \text{ mol}^{-1})$$
$$= -317.3 \text{ kJ mol}^{-1} + 11.02 \text{ kJ mol}^{-1}$$
$$= -306.3 \text{ kJ mol}^{-1}$$
$$= -w_{el, max}$$

That is, $-\Delta G_m^{\ominus}$ is the *maximum electrical work* obtainable under standard conditions. Here, the overall cell reaction involves only solids, which can be taken to be in their standard states (that is, $a = 1$).

[It would be worth noting that the maximum work would be obtained only under reversible conditions.]

$\Delta G_m^{\ominus} < 0$, so equation A1 *is* the spontaneous cell reaction, with oxidation at the Zn/ZnO *anode* (the negative electrode) and reduction at the Ag/Ag$_2$O *cathode* (the positive electrode).

$$E^{\ominus} = -\Delta G_m^{\ominus}/nF \text{ with } n = 2 \text{ (from the half-reactions)}$$
$$= 306.3 \times 10^3 \text{ J mol}^{-1}/(2 \times 96\,485 \text{ C mol}^{-1})$$
$$= 1.59 \text{ V}$$

Because OH$^-$ does not appear in the cell reaction, the emf should be *independent of the pH of the electrolyte*.