

CHEM1612 Answers to Problem Sheet 8

1.	species	name	stereoisomerism of complex
(a)	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	<b>pentamminechloridocobalt(III) chloride</b>	<b>none</b>
(a)	$[\text{FeBr}_2(\text{OH}_2)_4]$	<b>tetraaquadibromidoiron(II)</b>	<p style="text-align: center;"><b>geometric isomers:</b></p> <p style="text-align: center;"><i>trans</i>                      <i>cis</i></p>
(a)	$\text{K}[\text{Ag}(\text{CN})_2]$	<b>potassium dicyanidoargenate</b>	<b>none</b>

2.  $1.0 \text{ g of Au corresponds to } \frac{\text{mass}}{\text{atomic mass}} = \frac{1.0 \text{ g}}{196.97 \text{ g mol}^{-1}} = 0.0051 \text{ mol.}$

Reduction to  $\text{Au}^{3+}$  requires  $3\text{e}^-$ ,  $\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$ . Production of  $0.051 \text{ mol}$  of Au therefore requires  $(3 \times 0.0051) = 0.015 \text{ mol}$  of electrons =  $n$ .

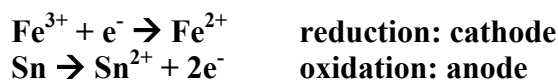
The number of electrons delivered by a current  $I$  in a time  $t$  is given by:

$$\text{number of moles of electrons} = \frac{I \times t}{F} \text{ where } F \text{ is Faraday's constant} = 96485 \text{ C mol}^{-1}$$

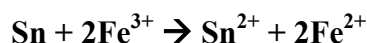
Therefore,

$$t = \frac{F \times n}{I} = \frac{(96485 \text{ C mol}^{-1}) \times (0.015 \text{ mol})}{(2.0 \text{ Cs}^{-1})} = 730 \text{ s} = 12 \text{ minutes}$$

3. (a) Reduction always occurs at the cathode. Oxidation always occurs at the anode. As  $\text{Sn}^{2+}$  has the less positive reduction potential, it is reversed so the two half cell reactions are:



- (b) The two half cells combine:



- (c) The cell potential is given by:

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = ((0.77) - (-0.13) \text{ V}) = 0.90 \text{ V}$$

- (d) The equilibrium constant for this  $2e^-$  process can be calculated using  $E_{\text{cell}}^\circ$   
 $= \frac{RT}{nF} \ln K$  :

$$\ln K = \frac{(2) \times (96485 \text{ C mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \times (0.90 \text{ V}) = 70$$

$$K = e^{70} = 2.8 \times 10^{30}$$

The cell potential of 0.90 V corresponds to a highly favourable cell reaction.

- (e) Using  $\Delta G^\circ = -nFE^\circ$  or  $\Delta G^\circ = -RT \ln K$ :

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ = -(2) \times (96485 \text{ C mol}^{-1}) \times (0.90 \text{ V}) = 170000 \text{ J mol}^{-1} \\ &= 170 \text{ kJ mol}^{-1} \end{aligned}$$

or

$$\begin{aligned} \Delta G^\circ &= -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(2.8 \times 10^{30}) \\ &= 170 \text{ kJ mol}^{-1} \end{aligned}$$

- (f) When equilibrium is reached, the cell is exhausted and  $E = 0 \text{ V}$ .

- (g) The reaction quotient  $Q$  is given by:

$$Q = \frac{[\text{Sn}^{2+}][\text{Fe}^{3+}]^2}{[\text{Fe}^{2+}]^2}$$

The cell potential when  $[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = 1 \text{ M}$  and  $[\text{Sn}^{2+}] = 0.001 \text{ M}$  can be calculated using the Nernst equation,

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \ln Q \\ &= (0.90 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(2) \times (96485 \text{ C mol}^{-1})} \ln \left[ \frac{(0.001)(1)^2}{(1)^2} \right] = 0.99 \text{ V} \end{aligned}$$

4. The reaction quotient is given by  $Q = \frac{[\text{NAD}^+][\text{H}^+]^2}{[\text{NADH}][\text{H}^+]} = [\text{H}^+]$

as NADH and  $\text{NAD}^+$  are at standard, 1 M concentrations.

As  $\text{pH} = -\log_{10}([\text{H}^+])$ , the biological standard state corresponds to  $[\text{H}^+] = 10^{-7.0} \text{ M}$ .

The cell potential for this  $2e^-$  process with  $[\text{H}^+] = 10^{-7.0} \text{ M}$  can be calculated using the Nernst equation,

$$E^\circ' = E^\circ - \frac{RT}{nF} \ln Q = (0.527) - \frac{(8.314) \times (298)}{(2) \times (96485)} \ln(10^{-7.0}) = 0.73 \text{ V}$$

5. (a) Combining the half cell for oxidation of NADH with the half cell for reduction of the  $\text{Py}^-$  ion gives the overall cell reaction as:



or



(b)  $E^{\circ'} = -0.185 + 0.73 = 0.55 \text{ V}$

- (c) The equilibrium constant for this  $2e^-$  process can be calculated using  $E_{\text{cell}}^{\circ}$   
 $= \frac{RT}{nF} \ln K$  :

$$\ln K = \frac{(2) \times (96485 \text{ C mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \times (0.55) = 42.8$$

$$K = e^{42.8} = 3.7 \times 10^{18}$$

- (d) Using  $\Delta G^{\circ} = -nFE^{\circ}$  or  $\Delta G^{\circ} = -RT \ln K$ :

$$\Delta G^{\circ} = -nFE^{\circ} = -(2) \times (96485 \text{ C mol}^{-1}) \times (0.55 \text{ V})$$

$$= -110000 \text{ J mol}^{-1} = -110 \text{ kJ mol}^{-1}$$

or

$$\Delta G^{\circ} = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(3.7 \times 10^{18})$$

$$= -110 \text{ kJ mol}^{-1}$$

- (e) (i) If the pH is reduced to 6.0,  $[\text{H}^+] = 10^{-6.0}$ . This will decrease  $E$  for the oxidation of NADH and hence increase the overall cell potential:

$$E(\text{NADH}/\text{NAD}^+) = E^{\circ} - \frac{RT}{nF} \ln Q$$

$$= (0.527 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(2) \times (96485 \text{ C mol}^{-1})} \ln(10^{-6.0})$$

$$= 0.70 \text{ V}$$

Hence,  $E_{\text{overall}} = (-0.185 + 0.70) \text{ V} = 0.52 \text{ V}$

- (ii) If NADH is at the non-standard concentration of 0.1 M, the reaction quotient for the NADH/ $\text{NAD}^+$  cell becomes

$$Q = \frac{[\text{NAD}^+][\text{H}^+]^2}{[\text{NADH}][\text{H}^+]} = \frac{[\text{H}^+]}{[\text{NADH}]} = \frac{(10^{-7.0})}{(0.1)} = 10^{-6}$$

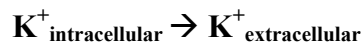
As in part (i), this decreases  $E(\text{NADH}/\text{NAD}^+)$  to 0.70 V and hence decreases  $E_{\text{overall}}$  to 0.52 V.

- (iii) The Nernst equation gives the half cell potentials as:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

The effect of changing the temperature is not just due to the value of T in this equation. Changing the temperature will also affect the equilibrium constant and hence  $E^{\circ}$ . The standard potential is *not* defined as being at 298 K and a different value must be used for each temperature.

6. Assuming that the cell membrane has a much higher permeability to  $K^{+}$  than for all other ions, the intracellular  $\rightarrow$  extracellular process corresponds to the reaction and reaction quotient below:



$$Q = [K^{+}]_{\text{extracellular}} / [K^{+}]_{\text{intracellular}} = 4/140 = 0.029$$

The temperature of healthy human is around 37 °C, or (37 + 273) K = 310 K.

The *standard* cell potential,  $E^{\circ}$ , is zero as if all concentrations are 1 M, there is no overall process. Hence, the potential difference arises from the concentration difference only and is given by the Nernst equation (z is the valence of the ion diffusing, i.e. +1 for  $K^{+}$ ):

$$E = \frac{RT}{zF} \ln Q = [(8.314 \times 310)/96500] \ln(0.029) = -0.095 \text{ V}$$