

CHG 8191L

Assignment#1

Electrochemical Thermodynamics

Application to fuel cells

Assignment + solutions

General

If no other indication is given, consider the following numerical data when solving problems in Module 1 :

| | ΔH_f° kJ / mol | S° J / mol K | C_p° J / mol K |
|----------------------|--------------------------------|------------------------|--------------------------|
| C | 0 | 5.73 | 8.52 |
| H ₂ | 0 | 130.5 | 28.8 |
| O ₂ | 0 | 204.8 | 29.3 |
| CH ₄ | -74.6 | 186.3 | 35.3 |
| CO | -110.5 | 197.7 | 29.1 |
| H ₂ O (l) | -285.8 | 69.9 | 75.2 |
| H ₂ O (g) | -241.8 | 188.8 | 33.5 |

Standard (1 atm, 298 K) equilibrium potential : $E_{eq}^\circ = 1.229V$

valid for $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(l)$

Consider : 1 atm \approx 1 bar

Water vapor pressure (at $40^\circ C \leq T \leq 60^\circ C$) : $p_{H_2O}(mbar) = 1.286 \times 10^{-5} e^{0.04966T(K)}$

Problem 1 : Solution

$$\text{General : } \Delta G_T^\circ = \Delta H_T^\circ - T \cdot \Delta S_T^\circ$$

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \Delta C_p^\circ (T - 298)$$

$$\Delta S_T^\circ = \Delta S_{298}^\circ + \Delta C_p^\circ \ln(T/298)$$

$$\Delta H_{298}^\circ = \Delta H_{f, \text{H}_2\text{O}(l)}^\circ = -285.8 \text{ kJ/mol}$$

$$\Delta S_{298}^\circ = S_{\text{H}_2\text{O}(l)}^\circ - S_{\text{H}_2}^\circ - \frac{1}{2} S_{\text{O}_2}^\circ = 69.9 - 130.5 - 204.8/2 = -163.0 \text{ J/mol K}$$

$$\Delta C_p^\circ = C_{p, \text{H}_2\text{O}(l)}^\circ - C_{p, \text{H}_2}^\circ - \frac{1}{2} C_{p, \text{O}_2}^\circ = 75.2 - 28.8 - 29.3/2 = 31.75 \text{ J/mol K}$$

$$\Delta H_{353}^\circ = -285.8 + 31.75 \cdot (353 - 298)/1000 = -284.1 \text{ kJ/mol}$$

$$\Delta S_{353}^\circ = -163.0 + 31.75 \cdot \ln(353/298) = -157.6 \text{ J/mol K}$$

$$\Delta G_{353}^\circ = -284.1 + 353 \cdot 157.6/1000 = -228.5 \text{ kJ/mol}$$

Problem 1: Solution

$$E_{\text{eq}}^{\circ}(80) = -\Delta G^{\circ}(80)/2F$$

$$E_{\text{eq}}^{\circ}(80) = - (228.5 \times 10^3) / (2 \times 96\,485) = 1.184 \text{ V}$$

$$E_{\text{cell}} = 0.6 \times 1.184 = 0.7104 \text{ V}$$

$$E_{\text{stack}} = \# \text{ cells} \times E_{\text{cell}} = 10 * 0.7104 = \underline{7.104 \text{ V}}$$

$$I = P / E_{\text{stack}} = 6 \times 10^3 \text{ W} / 7.104 \text{ V} = \underline{844.6 \text{ A}}$$

Problem 2: Solution

$$\Delta G_T^\circ = \Delta H_T^\circ - T \cdot \Delta S_T^\circ$$

where $T = 348 \text{ K}$

And (from Question 1) we know:

$$\Delta H_{298}^\circ = -285.8 \text{ kJ/mol}, \Delta S_{298}^\circ = -163.0 \text{ J/mol.K}$$

$$\text{And, } \Delta C_p^\circ = 31.75 \text{ J/mol.K}$$

Then we will use:

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \Delta C_p^\circ (T - 298)$$

$$\Delta S_T^\circ = \Delta S_{298}^\circ + \Delta C_p^\circ \ln(T/298)$$

$$\text{To find: } \Delta H_{T \text{ at } 348}^\circ = -284.2 \text{ kJ/mol}$$

$$\Delta S_{T \text{ at } 348}^\circ = 158.07 \text{ J/mol.K}$$

$$\Delta G_{T \text{ at } 348}^\circ = -229.2 \text{ kJ/mol}$$

Problem 2: Solution

Now we will find E_{eq}^0 at 75 °C

$$E_{eq}^0(75) = -\Delta G^0(75)/2F$$

$$E_{eq}^0(75) = - (229.2 \times 10^3) / (2 \times 96\,485) = 1.1877 \text{ V}$$

Please note that it is **PURE** hydrogen so $P_{H_2} = 1.0$

And Air is fed, so $P_{O_2} = 0.2$

$$E_{eq}^0 \text{ at } (75 \text{ °C or } 348 \text{ K}) = 1.1877 + [(8.3 * 348)/(2 * 96485) \ln \frac{1.0 * 0.2^{0.5}}{1.0}]$$

$$E_{eq}^0 = \mathbf{1.176 \text{ Volts}}$$

Now: using these formulas: $E_{cell} = \eta_{el} \times E_{eq}(75)$

$$E_{stack} = 20 \times E_{cell}$$

$$I = P / E_{stack}$$

Problem 2 : Solution

$$E_{\text{cell}} = 0.65 \times 1.176 = 0.7644 \text{ V}$$

$$E_{\text{stack}} = 20 \times 0.7644 = 15.288 \text{ V}$$

$$I = 1 \times 10^3 / 15.228 = 65.7 \text{ A}$$

$$\dot{n}_{\text{H}_2} = \frac{1}{\eta_{\text{conv}}} \cdot 20 \cdot \frac{I}{2F} = \frac{1}{0.5} \cdot 20 \cdot \frac{65.7}{2 \cdot 96485} \cdot 3600 = \underline{\underline{49.03 \text{ mol/h}}}$$

Problem 3 : Solution

$$\left. \begin{array}{l} \text{PEM : H}_2\text{O(l)} \\ p_{\text{H}_2} = p_{\text{O}_2} = 1 \text{ bar} \end{array} \right\} \begin{array}{l} E_{\text{eq},298} = E_{\text{eq},298}^{\circ} = 1.229 \text{ V} \\ \eta_{\text{th}} = 0.83 \quad \eta_{\text{c}} = 1 \end{array}$$

$$\eta_{\text{el}} = 0.75/1.229 = 0.61 \text{ V}$$

$$P_{\text{el,max}} = P_{\text{el}}/\eta_{\text{el}} \quad P_{\text{tot}} = P_{\text{el,max}}/\eta_{\text{th}} \quad P_{\text{el}} = 500 \text{ W}$$

$$P_{\text{Q}} = P_{\text{tot}} - P_{\text{el}} = P_{\text{el}} \cdot \left[\frac{1}{\eta_{\text{el}} \cdot \eta_{\text{th}}} - 1 \right] = 487.5 \text{ W}$$

$$Q = P_{\text{Q}} \times t = 487.56 \times 2 \times 3600 = \underline{3.5 \times 10^6 \text{ J}}$$

Problem 4 : Solution

$$\eta_{\text{el}}^{\text{EZ}} = E_{\text{eq}}/E_{\text{EL}} = 1.229/2.7$$

$$\eta_{\text{el}}^{\text{FC}} = E_{\text{FC}}/E_{\text{eq}} = 0.7/1.229$$

$$\eta_{\text{el}}^{\text{tot}} = \eta_{\text{el}}^{\text{EZ}} \cdot \eta_{\text{el}}^{\text{FC}} = 0.7/2.7 = \underline{\underline{0.26}}$$