

6.12. Answers:

Given the constant p ,

$$\begin{aligned}\Delta_r H_m &= Q = \Delta_r S_m \\ \Delta_r S_m &= - \left(\frac{\partial \Delta_r G_m}{\partial T} \right)_p \\ \Delta_r G_m &= -RT \ln K \\ \Rightarrow \Delta_r H_m &= RT \ln K + RT^2 \left(\frac{\partial \ln K}{\partial T} \right)_p\end{aligned}\quad (1)$$

For H_2 ,

$$\begin{aligned}H_2(g) &\rightleftharpoons H_2(aq) \\ \Rightarrow K &= \frac{a_{H_2(aq)}}{a_{H_2(g)}} = \frac{s_{H_2} \times p^\ominus / c^\ominus}{P_{H_2} / p^\ominus} = s_{H_2} \times p^\ominus / c^\ominus\end{aligned}\quad (2)$$

According to the equation of the solubility $\lg s_{H_2} = -5.39 - \frac{768}{T/K}$, and change the

unit of s_{H_2} from $\text{mol cm}^{-3} \text{ bar}^{-1}$ to $\text{mol dm}^{-3} \text{ bar}^{-1}$, we can get:

$$\ln K = -19.32 - \frac{1768.39}{T/K} \quad (3)$$

Replace the " $\ln K$ " in the Equation (1) by the Equation (3), then

$$\Delta_r H_m = -19.32RT \quad (4)$$

Given $T=570K$, from the Equation (4), we can get the enthalpy of the solution of hydrogen is: $\Delta_r H_m(H_2) = -91.56 \text{ kJ/mol}$.

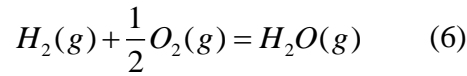
For CO , similarly we can get the enthalpy of the solution is:

$$\Delta_r H_m = -20.68RT \quad (5)$$

So the enthalpy is: $\Delta_r H_m(CO) = -97.99 \text{ kJ/mol}$.

6.14. Answers:

For a fuel cell composed by hydrogen and oxygen, the total reaction is:



Based on the thermodynamic data, the reaction Gibbs energy is:

$$\Delta_r G_m = \sum_B (\nu_B \Delta_f G_{m,B}) = -zEF \quad (7)$$

To the Equation (6), $z=2$, and $\Delta_f G_{m,H_2O} = -237.13 \text{ kJ/mol}$, we can get:

$$E = 1.229 \text{ V}$$

So the cell potential for the hydrogen-oxygen fuel cell is **1.229V**;

For a fuel cell composed of butane, similarly, we can get the total reaction is:



According to the Equation (8), $z=42$, and $\Delta_f G_{m,C_4H_{10}} = -17.03 \text{ kJ/mol}$, and

$\Delta_f G_{m,CO_2} = -394.36 \text{ kJ/mol}$, use the data to replace the Equation (7) and then we can

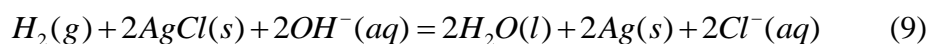
get: $E = 1.355 \text{ V}$.

So the cell potential for the butane fuel cell is 1.355V.

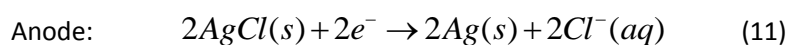
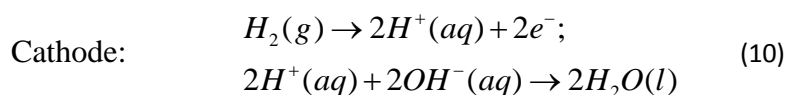
6.18. Answers:

(1) If the E^\ominus is considered as a constant:

the total cell reaction is:



and the total reaction can be divided into two half reactions on the electrodes:



According to Nernst Equation, we can get:

for the half reaction (10),

$$\phi_{cathode} = \phi_{cathode}^\ominus - \frac{RT}{2F} \ln \frac{a_{H_2(g)}}{a_{H^+(aq)}^2} = \phi_{cathode}^\ominus - \frac{RT}{F} \ln \frac{[OH^-(aq)]}{K_w} \quad (12)$$

for the half reaction (11),

$$\phi_{anode} = \phi_{anode}^\ominus - \frac{RT}{F} \ln a_{Cl^-(aq)} = \phi_{anode}^\ominus - \frac{RT}{F} \ln [Cl^-(aq)] \quad (13)$$

So the total cell potential is:

$$E = \phi_{anode} - \phi_{cathode} = E^\ominus - \frac{RT}{F} \ln \frac{[Cl^-(aq)] K_w}{[OH^-(aq)]} \quad (14)$$

the Equation (14) can be rewritten as the following:

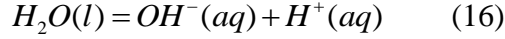
$$pK_w = 0.4343 \times \left(\ln \frac{[Cl^-(aq)]}{[OH^-(aq)]} \right) + \frac{F}{RT} (E - E^\ominus) \quad (15)$$

E^\ominus is considered as equal as $E^\ominus(298K)$ and keeps constant, so

$$E^\ominus = \phi_{anode}^\ominus(298K) = 0.2224$$

and finally we get the values of pK_w at these temperature: **14.2482 (20°C), 14.0253 (25°C), 13.8076 (30°C).**

As for water, there exists an equilibrium shown in Equation (16):



so the equilibrium constant is expressed as the following:

$$K = \frac{[H^+_{(aq)}][OH^-_{(aq)}]}{H_2O(l)} = [H^+_{(aq)}][OH^-_{(aq)}] = K_w \quad (17)$$

According to the Equation (1), (15) and (17), we can get:

$$\Delta_r S_m = F \left(\frac{\partial E^\ominus}{\partial T} - \frac{\partial E}{\partial T} \right)_p - R \ln \frac{[Cl^-_{(aq)}]}{[OH^-_{(aq)}]} \quad (18)$$

$$\Delta_r H_m = \Delta_r G_m + T \Delta_r S_m = -RT \ln K_w + T \Delta_r S_m$$

because E^\ominus is a constant, we can get:

$$\Delta_r S_m = -F \left(\frac{\partial E}{\partial T} \right)_p - R \ln \frac{[Cl^-_{(aq)}]}{[OH^-_{(aq)}]} \quad (19)$$

$$\Delta_r H_m = \Delta_r G_m + T \Delta_r S_m = -RT \ln K_w + T \Delta_r S_m$$

At 298K, the enthalpy and entropy of the autoprotolysis of water are **74.89 kJ/mol** and **-17.19 J/(mol K)** respectively.

(2) If the E^\ominus is considered as a variable of temperature:

the thermodynamic data (298K) is listed in the following table 1:

	$H_2(g)$	$H^+(aq)$	$AgCl(s)$	$Ag(s)$	$Cl^-(aq)$
$S_m^\ominus (J/mol \cdot K)$	130.684	0	96.2	42.55	56.5
$\Delta_f H_m^\ominus (kJ/mol)$	0	0	-127.07	0	-167.16

According to the Equation (20) and Nernst Equation, the basic thermodynamic data can be used to calculate the E^\ominus , considering the S_m^\ominus and $\Delta_f H_m^\ominus$ won't change with the temperature.

$$E^\ominus = -\frac{\Delta_r G_m^\ominus}{zF} = -\frac{\Delta_r H_m^\ominus - T \Delta_r S_m^\ominus}{zF}$$

$$H_2(g) + 2AgCl(s) = 2H^+(aq) + 2Ag(s) + 2Cl^-(aq) \quad (20)$$

$$\Delta_r H_m^\ominus = -80.18 kJ/mol, \Delta_r S_m^\ominus = -125.084 J/(mol \cdot K)$$

so we can get table 2:

Temperature/K	293	298	303
E^{\ominus}/V	0.2256	0.2223	0.2191

Then we can use the similar way to calculate the pK_w and enthalpy and entropy. the results are shown in the following table 3:

Temperature/K	293	298	303
pK_w	14.1932	14.0270	13.8625

with Equation (18), we get the enthalpy and entropy of the autoprotolysis of water:

$$\Delta_r H_m = 56.20 \text{ kJ/mol}, \quad \Delta_r S_m = -79.90 \text{ J/(mol K)}$$