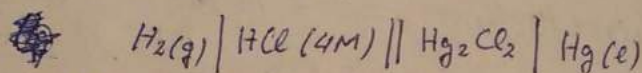


OPQS CATALUNYA
PROBLEMA 1995-2.2
Química

A 25°C el coeficiente de actividad iónica media de una disolución acuosa 4M de ácido clorhídrico es 1,762 y la presión parcial del cloruro de hidrógeno en el vapor en equilibrio con la disolución es $0,2395 \cdot 10^{-4}$ atm. Si el potencial estándar de reducción del electrodo:



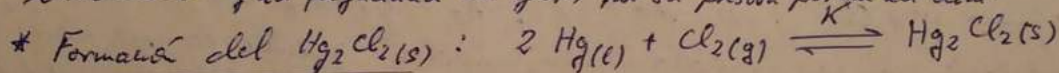
vale 0,268V a 25°C, calcular la energía estándar de formación del H_2Cl_2 a esta temperatura.

Datos: Constante de los gases: $R = 8,31 \text{ J K}^{-1} \text{ mol}^{-1}$

Constante de Faraday: $F = 96500 \text{ C mol}^{-1}$

Energía estándar de formación del $\text{HCl}(\text{g})$: $\Delta G_f^\circ = -92299 \text{ J mol}^{-1}$

Solución: Aproximaremos actividades de sólidos y líquidos con la unidad, y la fugacidad de gases por su presión parcial en atm.

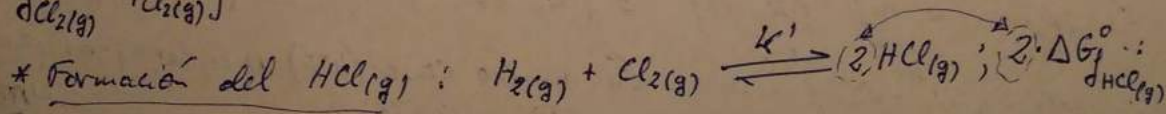


$$\Delta G_f^\circ = -RT \ln K$$

$$K = \frac{a_{\text{Hg}_2\text{Cl}_2(\text{s})}}{a_{\text{Hg}(\text{e})}^2 \cdot f_{\text{Cl}_2(\text{g})}} \approx \frac{1}{f_{\text{Cl}_2(\text{g})}}$$

$$\Delta G_f^\circ \approx -RT \ln \frac{1}{f_{\text{Cl}_2(\text{g})}} = RT \ln f_{\text{Cl}_2(\text{g})} \quad [1]$$

$$\left. \begin{array}{l} a_{\text{Hg}(\text{e})} \approx 1 \\ f_{\text{Cl}_2(\text{g})} \approx P_{\text{Cl}_2(\text{g})} \end{array} \right\}$$



$$\therefore 2 \cdot \Delta G_f^\circ_{\text{HCl}(\text{g})} = -RT \ln K'$$

$$K' = \frac{f_{\text{HCl}(\text{g})}^2}{f_{\text{H}_2(\text{g})} \cdot f_{\text{Cl}_2(\text{g})}} \quad ; \quad K' \approx \frac{P_{\text{HCl}(\text{g})}^2}{P_{\text{H}_2(\text{g})} \cdot P_{\text{Cl}_2(\text{g})}}$$

$$2 \cdot \Delta G_f^\circ_{\text{HCl}(\text{g})} \approx -RT \cdot \ln \frac{P_{\text{HCl}(\text{g})}^2}{P_{\text{H}_2(\text{g})} \cdot P_{\text{Cl}_2(\text{g})}} \quad [2]$$

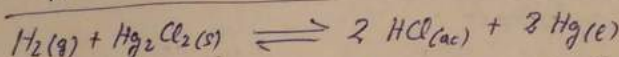
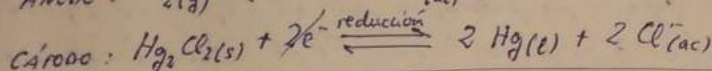
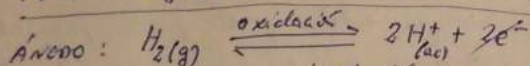
$$f_{\text{HCl}(\text{g})} \approx P_{\text{HCl}(\text{g})}; f_{\text{H}_2(\text{g})} \approx P_{\text{H}_2(\text{g})}; f_{\text{Cl}_2(\text{g})} \approx P_{\text{Cl}_2(\text{g})}$$

Despejamos $RT \ln P_{\text{Cl}_2(\text{g})}$ en [2] y sustituimos en [1]:

$$2 \cdot \Delta G_f^\circ_{\text{HCl}(\text{g})} = RT \ln \frac{P_{\text{H}_2(\text{g})}}{P_{\text{HCl}(\text{g})}^2} + RT \ln P_{\text{Cl}_2(\text{g})} \quad \therefore RT \ln P_{\text{Cl}_2(\text{g})} = 2 \cdot \Delta G_f^\circ_{\text{HCl}(\text{g})} + RT \ln \frac{P_{\text{HCl}(\text{g})}^2}{P_{\text{H}_2(\text{g})}}$$

Sustituyendo en [1]: $\Delta G_f^\circ = 2 \cdot \Delta G_f^\circ \text{HCl(g)} + RT \ln \frac{P_{\text{HCl(g)}}^2}{P_{\text{H}_2(\text{g})}}$ [2]

* Pila: $\text{Hg(g)} | \text{HCl (4M)} || \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg(l)}$:



En el equilibrio: $E_{\text{pila}} = 0 = E_{\text{pila}}^\circ - \frac{RT}{nF} \ln \frac{a_{\text{HCl(ac)}}^2 \cdot a_{\text{Hg(l)}}^2}{a_{\text{Hg}_2\text{Cl}_2(\text{s})} \cdot P_{\text{H}_2(\text{g})}}$

$a_{\text{Hg(l)}} \approx 1 \approx a_{\text{Hg}_2\text{Cl}_2(\text{s})}$; $P_{\text{H}_2(\text{g})} \approx P_{\text{H}_2(\text{g})}$; $a_{\text{HCl}} = \gamma_{\pm} \cdot m$

Además la actividad iónica media se define como: $a_{\pm} = a_{\pm}^\nu = (\gamma_{\pm} \cdot m_{\pm})^\nu$ } $\left. \begin{array}{l} \text{coeficiente} \\ \text{de actividad} \end{array} \right\}$ $\left. \begin{array}{l} \text{molalidad} \end{array} \right\}$

Para un electrolito en general: $C_{\nu} A_{\nu} \rightleftharpoons \nu_+ C^{\nu_+} + \nu_- A^{\nu_-}$ siendo ν , el número total de iones: $\nu = \nu_+ + \nu_-$ en nuestro caso:

$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$; $\nu = 1 + 1 = 2$; $\gamma_{\pm} = 1,762$; como las cantidades iónicas medias son media geométrica de las cantidades iónicas individuales, podemos calcular la molalidad iónica media, m_{\pm} , en función de la molalidad individual del anión, m_- , y del catión, m_+ $\Rightarrow m_{\pm}^\nu = m_+^{\nu_+} \cdot m_-^{\nu_-}$

De la fórmula del electrolito $C_{\nu} A_{\nu}$ $\left. \begin{array}{l} m_+ = \nu_+ \cdot m \\ m_- = \nu_- \cdot m \end{array} \right\} \therefore$

$\therefore m_{\pm}^\nu = (\nu_+ m)^{\nu_+} (\nu_- m)^{\nu_-} = (\nu_+^{\nu_+} \cdot \nu_-^{\nu_-}) m^{(\nu_+ + \nu_-)} = (\nu_+^{\nu_+} \cdot \nu_-^{\nu_-}) \cdot m^\nu$

$\therefore m_{\pm} = (\nu_+^{\nu_+} \cdot \nu_-^{\nu_-})^{1/\nu} \cdot m$. En nuestro caso (HCl) $\Rightarrow \nu_+ = \nu_- = 1 \Rightarrow m_{\pm} = m = 4 \text{ molal}$

Por lo tanto: $a_{\text{HCl}} = (\gamma_{\pm} \cdot m_{\pm})^2 = (\gamma_{\pm} \cdot m)^2$. Sustituyendo en la ecuación de Nernst: $E_{\text{pila}}^\circ = \frac{RT}{nF} \ln \frac{a_{\text{HCl(ac)}}^2}{P_{\text{H}_2(\text{g})}} = \frac{RT}{nF} \ln \frac{(\gamma_{\pm} \cdot m)^4}{P_{\text{H}_2(\text{g})}}$

$\therefore n F E_{\text{pila}}^\circ = RT \ln (\gamma_{\pm} \cdot m)^4 + RT \ln P_{\text{H}_2(\text{g})} = 4RT \ln (\gamma_{\pm} \cdot m) + RT \ln P_{\text{H}_2(\text{g})}$

$\therefore RT \ln P_{\text{H}_2(\text{g})} = n F E_{\text{pila}}^\circ - 4RT \ln (\gamma_{\pm} \cdot m)$ [4]

* De la ecuación [3]: ~~$\Delta G_f^\circ = 2 \cdot \Delta G_f^\circ \text{HCl(g)} + RT \ln \frac{P_{\text{HCl(g)}}^2}{P_{\text{H}_2(\text{g})}}$~~

$\Delta G_f^\circ = 2 \cdot \Delta G_f^\circ \text{HCl(g)} + RT \ln \frac{P_{\text{HCl(g)}}^2}{P_{\text{H}_2(\text{g})}} - (RT \ln P_{\text{H}_2(\text{g})})$. Sustituyendo [4]:

$\Delta G_f^\circ = 2 \cdot \Delta G_f^\circ \text{HCl(g)} + 2RT \ln P_{\text{HCl(g)}} - n F E_{\text{pila}}^\circ + 4RT \ln (\gamma_{\pm} \cdot m)$

- 2 -

$$\therefore \Delta G_f^\circ = 2 \cdot \Delta G_{\text{HCl(g)}}^\circ - n F E_{\text{pila}}^\circ + 2 R T \left[\ln p_{\text{HCl(g)}} + 2 \ln (\gamma_{\pm} \cdot m) \right]$$

Acabamos finalmente sustituyendo los datos:

$$\Delta G_{\text{HCl(g)}}^\circ = -92299 \text{ J} \cdot \text{mol}^{-1} ; n = 2 e^- \text{ intercambiados en la pila ;}$$

$$F = 96500 \text{ C} \cdot \text{mol}^{-1} ; E_{\text{pila}}^\circ = 0,268 \text{ V} ; R = 8,31 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} ; T = 298,15 \text{ K} \text{ (25}^\circ\text{C)}$$

$$p_{\text{HCl(g)}} = 0,2395 \cdot 10^{-4} \text{ atm} ; \gamma_{\pm} = 1,762 ; m = 4 \text{ molal}$$

$$\Delta G_{\text{Hg}_2\text{Cl}_2(\text{s})}^\circ = 2 \cdot (-92299) - 2 \cdot 96500 \cdot 0,268 + 2 \cdot 8,31 \cdot 298,15 \cdot \left[\ln(0,2395 \cdot 10^{-4}) + 2 \cdot \ln(1,762 \cdot 4) \right] \Rightarrow \Delta G_{\text{Hg}_2\text{Cl}_2(\text{s})}^\circ = -269691 \text{ J} \cdot \text{mol}^{-1}$$

Mirando cifras significativas: $\Delta G_{\text{Hg}_2\text{Cl}_2(\text{s})}^\circ = -270 \text{ kJ} \cdot \text{mol}^{-1}$