Chemistry 192
Exam 2
Spring 2018
Solution

R =8.3144 J mol^{-1} K^{-1}

R=.0821 L atm mol^{-1} K^{-1}

R=.08314 L bar mol^{-1} K^{-1}

$N_A = 6.022 \times 10^{23}$ molecules mol^{-1}

$T = t + 273.15$

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$F = 96485$ C mol^{-1}

Name:

1. The zinc cyanide coordination complex, $Zn(CN)_4^{2-}$, has a formation constant $K_f = 1.0 \times 10^{18}$. Zinc sulfide, ZnS, is sparingly soluble in water with a solubility product constant $K_{sp} = 2.0 \times 10^{-25}$. Calculate the molar solubility of zinc sulfide in an aqueous 0.100 M CN^- solution. Approximations work for this problem.

Answer:

$$ZnS_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + S^{2-}_{(aq)} \qquad K_{sp}$$

$$Zn^{2+}_{(aq)} + 4CN^-_{(aq)} \rightleftharpoons Zn(CN)^{2-}_{4(aq)} \qquad K_f$$

$$ZnS_{(s)} + 4CN^-_{(aq)} \rightleftharpoons Zn(CN)^{2-}_{4(aq)} + S^{2-}_{(aq)} \qquad K = K_f K_{sp} = 2.0 \times 10^{-7}$$

	$[CN^-]$	$[Zn(CN)_4^{2-}]$	$[S^-]$
initial	0.100 M	0 M	0 M
change	-4s	s	s
equilibrium	(0.100-4s) M	s M	s M

$$K = 2.0 \times 10^{-7} = \frac{[Zn(CN)_4^{2-}][S^{2-}]}{[CN^-]^4}$$

$$= \frac{s^2}{(0.100 - 4s)^4} \approx \frac{s^2}{0.100^4} \qquad s = 4.5 \times 10^{-6}\ \text{M}$$

Name:

2. At a total pressure of 2.00 bar, the equilibrium degree of dissociation, α, for the gas-phase dissociation reaction

$$\mathrm{ClF}_{3(g)} \rightleftharpoons \frac{1}{2}\mathrm{Cl}_{2(g)} + \frac{3}{2}\mathrm{F}_{2(g)}$$

is $\alpha = 6.17 \times 10^{-6}$ at 500. K and $\alpha = 0.112$ at 1000. K. Calculate $\Delta_{r,m}H^\circ, \Delta_{r,m}G^\circ$ and $\Delta_{r,m}S^\circ$ at 1000. K for the reaction.

Answer:

	n_{ClF_3}	n_{Cl_2}	n_{F_2}
initial	n_0	0	0
change	-αn_0	$\alpha n_0/2$	$3\alpha n_0/2$
equilibrium	$n_0(1-\alpha)$	$\alpha n_0/2$	$3\alpha n_0/2$

$$n_{tot} = n_0(1+\alpha)$$

$$K_P = \frac{P_{Cl_2}^{1/2} P_{F_2}^{3/2}}{P_{ClF_3}} = \frac{\left(\frac{\alpha/2}{(1+\alpha)}P\right)^{1/2} \left(\frac{3\alpha/2}{(1+\alpha)}P\right)^{3/2}}{\frac{1-\alpha}{1+\alpha}P}$$

$$K_P(500) = 9.90 \times 10^{-11} \qquad K_P(1000) = 0.0330$$

$$\ln\frac{K_P(T_2)}{K_P(T_1)} = \frac{\Delta_{r,m}H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{0.0330}{9.90 \times 10^{-11}} = \frac{\Delta_{r,m}H^\circ}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{500 \text{ K}} - \frac{1}{1000 \text{ K}}\right) \qquad \Delta_{r,m}H^\circ = 163000 \text{ J mol}^{-1}$$

$$\Delta_{r,m}G^\circ = -RT\ln K_P = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(1000 \text{ K})\ln(0.0330) = 28400 \text{ J mol}^{-1}$$

$$\Delta_{r,m}S^\circ = \frac{\Delta_{r,m}H^\circ - \Delta_{r,m}G^\circ}{T} = 135 \text{ J mol}^{-1}\text{K}^{-1}$$

Name:

3. Consider the electrochemical cell at 298K

$$\text{Pt}_{(s)}|\text{Cl}_{2(g)}(P = 2.53\text{ bar})|\text{Cl}^-_{(aq)}(1.23 \times 10^{-3}\text{ M})||\text{Br}^-_{(aq)}(3.77 \times 10^{-4}\text{ M})|\text{PbBr}_{2(s)}|\text{Pb}_{(s)}$$

Given $E^\circ_{Pt/Cl_2/Cl^-} = 1.35827$ V and $E^\circ_{Br^-/PbBr_2/Pb} = -0.284$ V, calculate the EMF of the cell. Indicate which electrode is the cathode and which is the anode under the specific cell conditions.

Answer:

$$\text{Right : PbBr}_{2(s)} + 2e^- \longrightarrow \text{Pb}_{(s)} + 2\text{Br}^-_{(aq)}$$

$$\text{Left : } \underline{\text{Cl}_{2(g)} + 2e^- \longrightarrow 2\text{Cl}^-_{(aq)}}$$

$$\text{Overall : PbBr}_{2(s)} + 2\text{Cl}^-_{(aq)} \longrightarrow \text{Pb}_{(s)} + 2\text{Br}^-_{(aq)} + \text{Cl}_{2(g)}$$

$$Q_p = \frac{[\text{Br}^-]^2 P_{Cl_2}}{[\text{Cl}^-]^2}$$

$$E^\circ = E^\circ_R - E^\circ_L = -1.642\text{ V}$$

$$E = E^\circ - \frac{RT}{nF}\ln Q_P = -1.642\text{ V} - \frac{(8.3144\text{ J mol}^{-1}\text{K}^{-1})(298\text{ K})}{2(96485\text{ C mol}^{-1})}\ln\frac{(3.77 \times 10^{-4})^2(2.53)}{(1.23 \times 10^{-3})^2}$$

$$= -1.623\text{ V}$$

The chlorine/chloride electrode is the cathode and the lead bromide electrode is the anode.

Name:

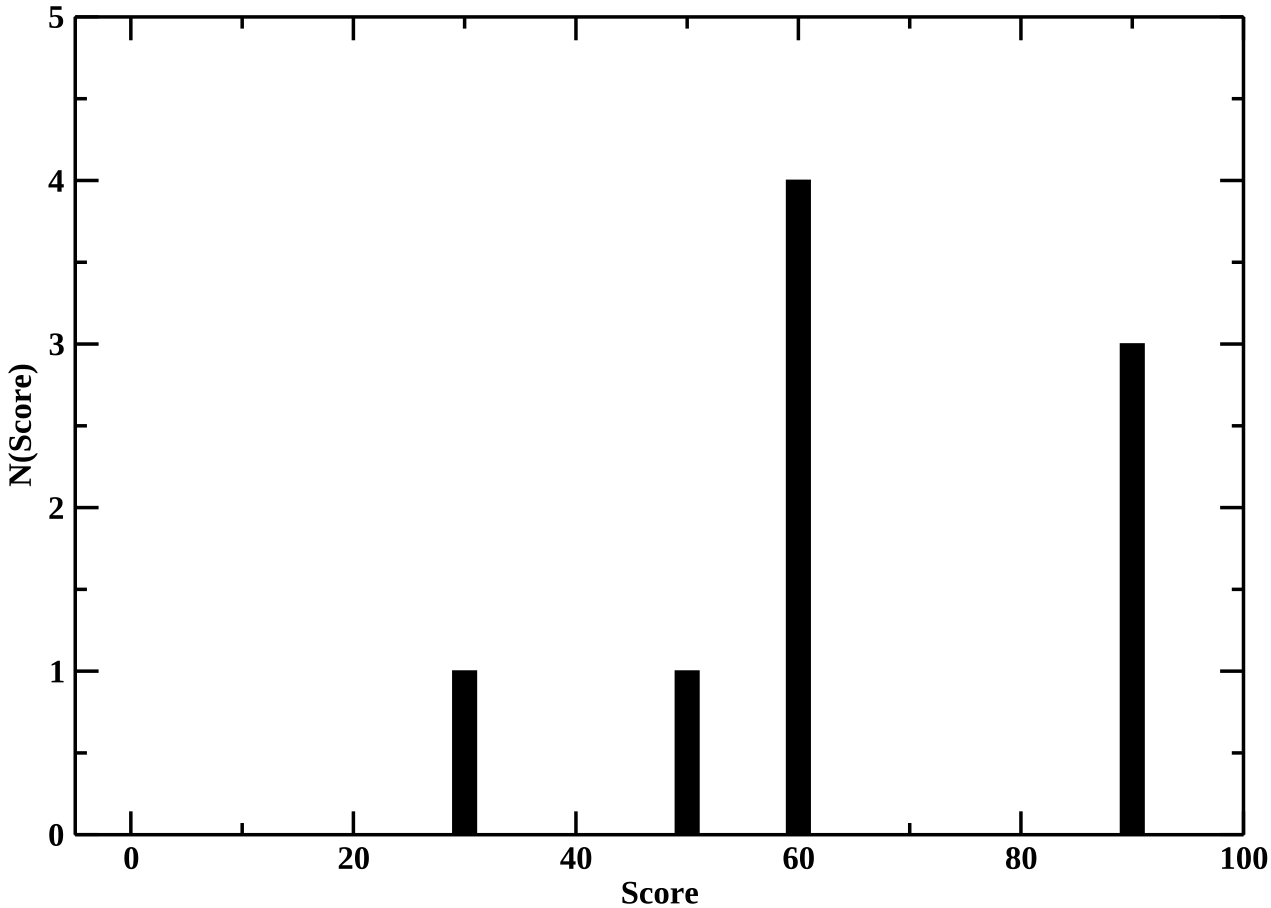

Figure 1: **High = 100, Median = 66, Mean = 71**