Chemistry 192
Practice Exam 2
Spring 2018
Solutions

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}

$T = t + 273.15$

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

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

Name: ________________________

1.The electrochemical cell

$$\mathrm{Pb}_{(s)}|\mathrm{PbBr}_{2(s)}|\mathrm{Br}^-_{(aq)}||\mathrm{Cl}^-_{(aq)}(0.500\ \mathrm{M})|\mathrm{Cl}_{2(g)}(2.00\ \mathrm{bar})|\mathrm{Pt}_{(s)}$$

is made by immersing the lead bromide electrode on the left in water to produce a saturated lead bromide solution. The standard reduction potentials for the cell at 298 K are $E^\circ_{Cl^-/Cl_2/Pt}$=1.35827 V, $E^\circ_{Pb/PbBr_2/Br^-}$=-0.284 V and the solubility product of lead bromide is $K_{sp} = 4.00 \times 10^{-5}$. Calculate the EMF of the cell.

Answer:

$$\mathrm{Right} : \mathrm{Cl}_{2(g)} + 2e^- \longrightarrow 2\mathrm{Cl}^-_{(aq)}$$

$$\mathrm{Left} : \underline{\mathrm{PbBr}_{2(s)} + 2e^- \longrightarrow \mathrm{Pb}_{(s)} + 2\mathrm{Br}^-_{(aq)}}$$

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

	$[\mathrm{Pb}^{2+}]$	$[\mathrm{Br}^-]$
initial	0 M	0 M
change	s M	$2s$ M
equilibrium	s M	$2s$ M

$$4.0 \times 10^{-5} = [\mathrm{Pb}^{2+}][\mathrm{Br}^-]^2 = 4s^3 \qquad s = 2.2 \times 10^{-2}\ \mathrm{M} \qquad [\mathrm{Br}^-] = 2s = 4.4 \times 10^{-2}\ \mathrm{M}$$

$$E^\circ = E^\circ_R - E^\circ_L = 1.35827\ \mathrm{V} - (-0.284\ \mathrm{V}) = 1.642\ \mathrm{V}$$

$$E = E^\circ - \frac{RT}{nF}\ln Q_P \qquad Q_P = \frac{[\mathrm{Cl}^-]^2}{[\mathrm{Br}^-]^2 P_{Cl_2}}$$

$$E = 1.642\ \mathrm{V} - \frac{(8.3144\ \mathrm{J\ mol^{-1}K^{-1}})(298\ \mathrm{K})}{2(96485\ \mathrm{C\ mol^{-1}})}\ln\frac{0.500^2}{(4.4 \times 10^{-2})^2(2.00)} = 1.59\ \mathrm{V}$$

Name:

2. Use the table of thermodynamic data valid at 298 K given below to calculate the pOH of a saturated $Mg(OH)_2$ aqueous solution at 323 K.

Substance	$\Delta H^\circ_{f,m}$ (kJ mol^{-1})	$\Delta G^\circ_{f,m}$ (kJ mol^{-1})	S°_m (J mol^{-1}K^{-1})
$Mg(OH)_{2(s)}$	-924.5	-833.5	63.18
$Mg^{2+}_{(aq)}$	-466.9	-454.8	-138.1
$OH^-_{(aq)}$	-230.0	-157.2	-10.75

Answer:

$$\mathrm{Mg(OH)}_{2(s)} \rightleftharpoons \mathrm{Mg}^{2+}_{(aq)} + 2\mathrm{OH}^-_{(aq)}$$

$$\Delta G^\circ_{r,m} = \Delta G^\circ_{f,m}(\mathrm{Mg}^+_{(aq)}) + 2\Delta G^\circ_{f,m}(\mathrm{OH}^-_{(aq)}) - \Delta G^\circ_{f,m}(\mathrm{Mg(OH)}_{2(s)})$$

$$= -454.8 \text{ kJ mol}^{-1} + 2(-157.2 \text{ kJ mol}^{-1}) - (-833.5 \text{ kJ mol}^{-1}) = 64.3 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{r,m} = \Delta H^\circ_{f,m}(\mathrm{Mg}^+_{(aq)}) + 2\Delta H^\circ_{f,m}(\mathrm{OH}^-_{(aq)}) - \Delta H^\circ_{f,m}(\mathrm{Mg(OH)}_{2(s)})$$

$$= -466.9 \text{ kJ mol}^{-1} + 2(-230.0 \text{ kJ mol}^{-1}) - (-924.5 \text{ kJ mol}^{-1}) = -2.4 \text{ kJ mol}^{-1}$$

$$K_{sp}(298) = \exp\left(-\frac{\Delta G^\circ_{r,m}}{RT}\right) = \exp\left(-\frac{64300 \text{ J mol}^{-1}}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}\right) = 5.36 \times 10^{-12}$$

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{\Delta H^\circ_{r,m}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{K(323)}{5.36 \times 10^{-12}} = \frac{-2400 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{298 \text{ K}} - \frac{1}{323 \text{ K}}\right) \qquad K_{sp}(323) = 5.0 \times 10^{-12}$$

	$[Mg^{2+}]$	$[OH^-]$
initial	0 M	0 M
change	s M	$2s$ M
equilibrium	s M	$2s$ M

$$5.0 \times 10^{-12} = [\mathrm{Mg}^{2+}][\mathrm{OH}^-]^2 = s(2s)^2 = 4s^3 \qquad s = 1.1 \times 10^{-4} \text{ M}$$

$$[\mathrm{OH}^-] = 2s = 2.2 \times 10^{-4} \text{ M} \qquad \mathrm{pOH} = -\log_{10}(2.2 \times 10^{-4}) = 3.66$$

Name:

3. Copper II ions form a strong coordination complex with ammonia

$$\mathrm{Cu}^{2+}_{(aq)} + 4\mathrm{NH}_{3(aq)} \rightleftharpoons \mathrm{Cu(NH_3)}^{2+}_{4(aq)}$$

with formation constant $K_f = 1.1 \times 10^{13}$. Calculate the concentration of free copper ions, $[\mathrm{Cu}^{2+}]$, when 0.010 moles of Cu^{2+} are added to 0.10 L of 0.50 M aqueous $\mathrm{NH_3}$. Approximations work for this problem.

Answer:

$$\mathrm{Cu(NH_3)}^{2+}_{4(aq)} \rightleftharpoons \mathrm{Cu}^{2+}_{(aq)} + 4\mathrm{NH}_{3(aq)} \qquad K = \frac{1}{K_f} = 9.1 \times 10^{-14}$$

Assume initially

$$[\mathrm{Cu(NH_3)}_4^{2+}] = \frac{0.010\ \mathrm{mol}}{0.10\ \mathrm{L}} = 0.10\ \mathrm{M} \quad [\mathrm{NH_3}] = \frac{(0.50\ \mathrm{mol\ L^{-1}})(0.10\ \mathrm{L}) - 4(0.010\ \mathrm{mol})}{0.10\ \mathrm{L}} = 0.10\ \mathrm{M}$$

	$[\mathrm{Cu(NH_3)}_4^{2+}]$	$[\mathrm{Cu}^{2+}]$	$[\mathrm{NH_3}]$
initial	0.10 M	0 M	0.10 M
change	$-y$	y	$4y$
equilibrium	$(0.10 - y)$ M	y M	$(0.10 + 4y)$ M

$$9.1 \times 10^{-14} = \frac{[\mathrm{Cu}^{2+}][\mathrm{NH_3}]^4}{[\mathrm{Cu(NH_3)}_4^{2+}]} = \frac{y(0.10+4y)^4}{0.10-y} \approx \frac{y(0.10)^4}{0.10}$$

$$y = [\mathrm{Cu}^{2+}] = 9.1 \times 10^{-11}\ \mathrm{M}$$

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