

Chemistry 192
Practice Exam 2
Spring 2018
Solutions

$$R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$$

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

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

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

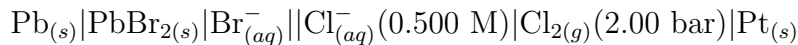
$$T = t + 273.15$$

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

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

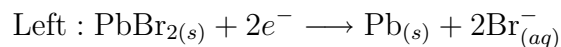
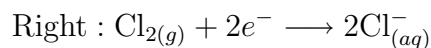
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1. The electrochemical cell



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 $E^{\circ}_{\text{Cl}^{-}/\text{Cl}_2/\text{Pt}} = 1.35827\text{ V}$, $E^{\circ}_{\text{Pb}/\text{PbBr}_2/\text{Br}^{-}} = -0.284\text{ V}$ and the solubility product of lead bromide is $K_{sp} = 4.00 \times 10^{-5}$. Calculate the EMF of the cell.

Answer:



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

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

$$E^{\circ} = E^{\circ}_R - E^{\circ}_L = 1.35827\text{ V} - (-0.284\text{ V}) = 1.642\text{ V}$$

$$E = E^{\circ} - \frac{RT}{nF} \ln Q_P \quad Q_P = \frac{[\text{Cl}^{-}]^2}{[\text{Br}^{-}]^2 P_{\text{Cl}_2}}$$

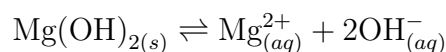
$$E = 1.642\text{ V} - \frac{(8.3144\text{ J mol}^{-1}\text{K}^{-1})(298\text{ K})}{2(96485\text{ C mol}^{-1})} \ln \frac{0.500^2}{(4.4 \times 10^{-2})^2(2.00)} = 1.59\text{ V}$$

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

Substance	$\Delta H_{f,m}^\circ$ (kJ mol ⁻¹)	$\Delta G_{f,m}^\circ$ (kJ mol ⁻¹)	S_m° (J mol ⁻¹ K ⁻¹)
$\text{Mg}(\text{OH})_{2(s)}$	-924.5	-833.5	63.18
$\text{Mg}_{(aq)}^{2+}$	-466.9	-454.8	-138.1
$\text{OH}_{(aq)}^-$	-230.0	-157.2	-10.75

Answer:



$$\Delta G_{r,m}^\circ = \Delta G_{f,m}^\circ(\text{Mg}_{(aq)}^{2+}) + 2\Delta G_{f,m}^\circ(\text{OH}_{(aq)}^-) - \Delta G_{f,m}^\circ(\text{Mg}(\text{OH})_{2(s)})$$

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

$$\Delta H_{r,m}^\circ = \Delta H_{f,m}^\circ(\text{Mg}_{(aq)}^{2+}) + 2\Delta H_{f,m}^\circ(\text{OH}_{(aq)}^-) - \Delta H_{f,m}^\circ(\text{Mg}(\text{OH})_{2(s)})$$

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

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

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

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

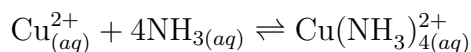
	$[\text{Mg}^{2+}]$	$[\text{OH}^-]$
initial	0 M	0 M
change	s M	$2s$ M
equilibrium	s M	$2s$ M

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

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

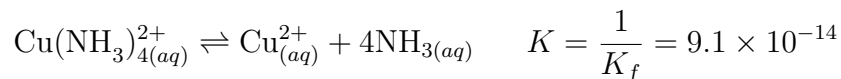
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3. Copper II ions form a strong coordination complex with ammonia



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

Answer:



Assume initially

$$[\text{Cu}(\text{NH}_3)_4^{2+}] = \frac{0.010 \text{ mol}}{0.10 \text{ L}} = 0.10 \text{ M} \quad [\text{NH}_3] = \frac{(0.50 \text{ mol L}^{-1})(0.10 \text{ L}) - 4(0.010 \text{ mol})}{0.10 \text{ L}} = 0.10 \text{ M}$$

	$[\text{Cu}(\text{NH}_3)_4^{2+}]$	$[\text{Cu}^{2+}]$	$[\text{NH}_3]$
initial	0.10 M	0 M	0.10 M
change	$-y$	y	$4y$
equilibrium	$(0.10 - y) \text{ M}$	$y \text{ M}$	$(0.10 + 4y) \text{ M}$

$$9.1 \times 10^{-14} = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}]} = \frac{y(0.10 + 4y)^4}{0.10 - y} \approx \frac{y(0.10)^4}{0.10}$$

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

Name: