Electrochemistry Problems

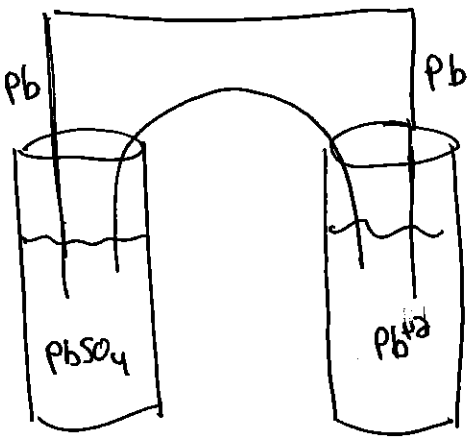
Key

20. Calculate $E°$ for the following cells: (Draw Cell Also)

(a) $Pb \mid PbSO_4 \parallel Pb^{2+} \mid Pb$

(b) $Pt \mid Cl_2, ClO_3^- \parallel O_2, H_2O \mid Pt$

a)

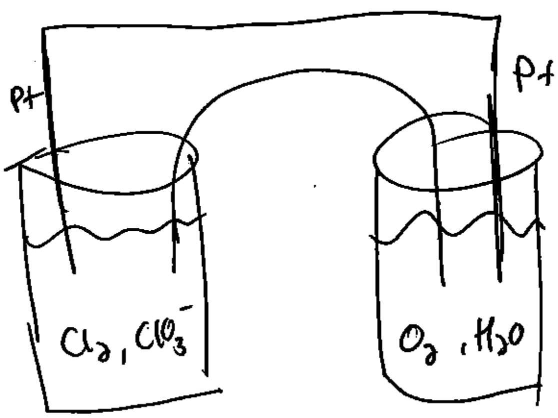


$SO_4^{-2} + Pb \xrightarrow{ox} PbSO_4 + 2e^-$ $\quad \mathcal{E}_{ox} = +.36V$

$Pb^{+2} + 2e^- \xrightarrow{red} Pb$ $\quad \mathcal{E}_{red} = -.13V$

$\boxed{\mathcal{E}_{tot} = .23V}$

b)



$\frac{1}{2}Cl_2 + 3H_2O \xrightarrow{ox} ClO_3^- + 6H^+ + 5e^-$ $\quad \mathcal{E}_{ox} = -1.47$

$4e^- + O_2 + 4H^+ \xrightarrow{red} 2H_2O$ $\quad \mathcal{E}_{red} = 1.23$

$\boxed{\mathcal{E}_{tot} = -.24V}$

34. Consider a cell reaction at 25°C where $n = 4$. Fill in the following table.

	$\Delta G°$	$E°$	K
(a)	1.60×10^4 J	.0414V	1.6×10^{-3}
(b)	−45.2 kJ	0.117 V	8.1×10^7
(c)	−5.8 kJ	.0150V	10.4

a) $\ln K = \frac{n\mathcal{E}}{.0257}$ $\quad \mathcal{E} = \frac{.0257 \ln K}{n} = \frac{.0257 \ln(1.6 \times 10^{-3})}{4} = -.0414\text{ V}$

$$\Delta G = -n\mathcal{F}\mathcal{E} = -4(96{,}500)(-.0414) = \boxed{+15{,}966\text{ J}}$$

b) $\Delta G = -n\mathcal{F}\mathcal{E}$

$\Delta G = -4(96{,}500)(.117)$

$\boxed{\Delta G = -45{,}162\text{ J}}$

$\ln K = \frac{n\mathcal{E}}{.0257} = \frac{(4)(.117)}{.0257}$

$\ln K = 18.2$

$\boxed{K = 8.1 \times 10^7}$

c) $\mathcal{E} = \frac{\Delta G}{-n\mathcal{F}} = \frac{-5{,}800\text{ J}}{-4(96{,}500)} = \boxed{.0150\text{ V}}$

$\ln K = \frac{n\mathcal{E}}{.0257} = \frac{4(.015)}{.0257} = 2.34$

$\boxed{K = 10.4}$

WEB 38. Calculate $E°$, $\Delta G°$, and K at 25°C for the reaction

$$3S^{2-} + 2NO_3^-(aq) + 4H_2O \longrightarrow 3S(s) + 2NO + 8\ OH^-(aq)$$

$3S^{2-} + 6e^- \rightarrow 3S$

$2NO_3^- + 4H_2O \rightarrow 2NO + 8OH^-$

This is in basic solution.
We don't have $\mathcal{E}°_{red}$ values

45. Consider a voltaic cell in which the following reaction takes place.

$$2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O$$

(a) Calculate $E°$.
(b) Write the Nernst equation for the cell.
(c) Calculate E under the following conditions: $[Fe^{2+}] = 0.00813\ M$, $[H_2O_2] = 0.914\ M$, $Fe^{3+} = 0.199\ M$, pH = 2.88.

$[H^+] = 10^{-2.88} = .00132$

a) $2Fe^{+2} \xrightarrow{ox} 2Fe^{+3} + 2e^-$ $\quad \mathcal{E}^\circ_{ox} = -.77V$

$H_2O_2 + 2H^+ + 2e^- \xrightarrow{red} 2H_2O$ $\quad \mathcal{E}^\circ_{red} = 1.77V$

$n=2$ $\quad \mathcal{E}^\circ_{tot} = 1.00V$

b) $$\mathcal{E} = \mathcal{E}^\circ_{tot} - \frac{.0257}{2}\left(\ln \frac{[Fe^{+3}]^2}{[Fe^{+2}]^2[H_2O_2][H^+]^2}\right)$$

c) $$\mathcal{E} = 1.00V - \frac{.0257}{2}\left(\ln \frac{(.199)^2}{(.00813)^2(.914)(.00132)^2}\right)$$

$$\boxed{\mathcal{E} = .746V}$$

49. Consider the reaction

$$2Cu^{2+}(aq) + Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2Cu^+(aq)$$

At what concentration of Cu^{2+} is the voltage zero, if all other species are at 0.200 M?

$2Cu^{+2} + 2e^- \xrightarrow{red} 2Cu^{+1}$ $\quad \mathcal{E}_{red} = .15V$

$Sn^{+2} \xrightarrow{ox} Sn^{+4} + 2e^-$ $\quad \mathcal{E}_{ox} = -.15$

$n=2$ $\quad \mathcal{E}_{tot} = 0$

$$\mathcal{E} = \mathcal{E}^\circ - \frac{.0257}{2}\left(\ln \frac{[Sn^{+4}][Cu^+]^2}{[Cu^{+2}]^2[Sn^{+2}]}\right)$$

$$0 = 0 - \frac{.0257}{2}\left(\ln \frac{\cancel{(.2)}(.2)^2}{(x)^2\cancel{(.2)}}\right)$$

in order for $\mathcal{E} = 0$, the $\ln Q$ needs to equal "0".
the $\ln 1 = 0$, so Q must $= 1$, the [react] = [prod]

$$\boxed{[Cu^{+2}] = x = .2M}$$

50. Consider the reaction

$$S(s) + 2H^+(aq) + 2Ag(s) + 2Br^-(aq) \longrightarrow 2AgBr(s) + H_2S(aq)$$ $[H_2S] = [Br^-] = 1M$

At what pH is the voltage zero if all other species are at standard concentrations?

$S + 2H^+ + 2e^- \xrightarrow{red} H_2S$ $E_{red} = .14V$

$2Ag + 2Br^- \xrightarrow{ox} 2AgBr + 2e^-$ $E_{ox} = -.07V$

$n = 2$

$E^\circ_{tot} = .07V$

$$\mathcal{E} = \mathcal{E}^\circ - \frac{.0257}{n} \ln \frac{[H_2S]}{[H^+]^2[Br^-]^2}$$

$$0 = .07 - \frac{.0257}{2}\left(\ln \frac{1}{(x)^2(1)^2}\right)$$

$$5.45 = \ln\left(\frac{1}{x^2}\right)$$

$$5.45 = \cancel{\ln 1}^{0} - \ln x^2$$

$5.45 = -2\ln x$

$\ln x = -2.72$

$x = [H^+] = .0656$

$pH = -\log[H^+] = -\log(.0656)$

$\boxed{pH = 1.18}$

54. Consider the reaction below at 25°C:

$$3SO_4^{2-}(aq) + 12H^+(aq) + 2Cr(s) \longrightarrow 3SO_2(g) + 2Cr^{3+}(aq) + 6H_2O$$

Use Table 18.1 to answer the following questions. Support your answers with calculations.

(a) Is the reaction spontaneous at standard conditions?

(b) Is the reaction spontaneous at a pH of 3.00 with all other ionic species at 0.100 *M* and gases at 1.00 atm? $[H^+] = 10^{-3}$

(c) Is the reaction spontaneous at a pH of 8.00 with all other ionic species at 0.100 *M* and gases at 1.00 atm? $[H^+] = 10^{-8}$

(d) At what pH is the reaction at equilibrium with all other ionic species at 0.100 *M* and gases at 1.00 atm?

$2Cr_{(s)} \xrightarrow{ox} 2Cr^{+3}_{(aq)} + 6e^-$

$6e^- + 3SO_4^{-2} + 12H^+ \xrightarrow{red} 3SO_2 + 6H_2O$

$n = 6$ $E_{ox} = .74V$

$E_{red} = .2V$

$E_{tot} = .94V$

a) $\mathcal{E}^\circ_{tot} = .94$, Yes it is spontaneous $\mathcal{E}^\circ_{tot} > 0$

b) $$\mathcal{E} = \mathcal{E}^\circ - \frac{.0257}{6} \ln \frac{[SO_2]^3[Cr^{+3}]^2}{[SO_4^{-2}]^3[H^+]^{12}} = .94 - \frac{.0257}{6}\ln\frac{(1)^3(.1)^2}{(.1)^3(10^{-3})^{12}}$$

$\mathcal{E} = .575$ Yes it is spontaneous.

c) $$\mathcal{E} = .94 - \frac{.0257}{6}\ln\frac{(1)^3(.1)^2}{(.1)^3(10^{-8})^{12}} = -.0167$$ No, it is not spont.

d) $$0 = .94 - \frac{.0257}{6}\ln\frac{(1)^3(.1)^2}{(.1)^3(x)^{12}}$$

$219.5 = \ln \frac{.01}{.001x^{12}}$

$219.5 = \ln(.01) - 12\ln(.001x)$

$\ln(.001x) = -18.67$

$.001x = 7.78\times10^{-9}$

$[H^+] = x = 7.78\times10^{-6}$

$\boxed{pH = 5.11}$

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