1. Use the following data to determine the ***rate law***, the ***rate constant*** and the ***overall order*** for the following reaction:

$$A + 2\,B \rightarrow C$$

The following data were taken at 25°C.

| $[A]_0$ (mol $L^{-1}$) | $[B]_0$ (mol $L^{-1}$) | Initial rate (mol $L^{-1}$ $s^{-1}$) |
|---|---|---|
| 0.0010 | 0.0010 | $1.35\times10^{-4}$ |
| 0.0020 | 0.0010 | $1.08\times10^{-3}$ |
| 0.0020 | 0.0030 | $1.87\times10^{-3}$ |

$$\frac{R_2}{R_1} = \frac{1.08\times10^{-3}}{1.35\times10^{-4}} = 8 = \frac{\cancel{k}[A]_2^m\,\cancel{[B]_2^n}}{\cancel{k}[A]_1^m\,\cancel{[B]_1^n}} = \left(\frac{0.0020}{0.0010}\right)^m = 2^m$$

$$\log 8 = \log 2^m = m \log 2$$

$$m = \frac{\log 8}{\log 2} = 3$$

$$\frac{R_3}{R_2} = \frac{1.87\times10^{-3}}{1.08\times10^{-3}} = 1.73148 = \frac{\cancel{k}\cancel{[A]_3^m}\,[B]_3^n}{\cancel{k}\cancel{[A]_2^m}\,[B]_2^n} = \left(\frac{0.0030}{0.0010}\right)^m = 3^m$$

$$\log 1.73148 = \log 3^m = m \log 3$$

$$m = \frac{\log 1.73148}{\log 3} = 0.50$$

$$Rate = k[A]^3[B]^{0.50} \Rightarrow k = \frac{Rate}{[A]^3[B]^{0.50}} = \frac{1.35\times10^{-4}\ \text{M s}^{-1}}{(0.0010\ \text{M})^3(0.0010\ \text{M})^{0.50}}$$

$$= 4.27\times10^{6}\ \text{M}^{-2.5}\ \text{s}^{-1}$$

Overall order = 3.5

2. (20 pts) ***Name*** the following compounds.

a. $Al_2[Fe(en)(C_2O_4)_2]_3$

aluminum (ethylenediamine)dioxalatoferrate(II)

b. $[Ni(H_2O)_3(NH_3)_3]SO_4$

triamminetriaquanickel(II) sulfate

3. ***Complete*** the following nuclear equations.

a. ${}_{0}^{1}n + {}_{92}^{238}U \rightarrow {}_{53}^{127}I + {}_{39}^{108}Y + 4\,{}_{0}^{1}n$

b. ${}_{2}^{3}He + {}_{1}^{1}H \rightarrow {}_{2}^{4}He + {}_{1}^{0}e$

c. Beta decay of Berkelium-248

${}_{97}^{248}Bk \rightarrow {}_{-1}^{0}e + {}_{98}^{248}Cf$

d. Positron emission of Copper-65

${}_{29}^{65}Cu \rightarrow {}_{1}^{0}e + {}_{28}^{65}Ni$

4. Calculate the amount of ***energy, in MJ***, released when 15.0 g or Uranium-238 undergoes alpha decay. U-238 = 238.05078 amu, Th-234 = 234.03660 amu, He-4 = 4.00260 amu.

${}_{92}^{238}U \rightarrow {}_{2}^{4}He + {}_{90}^{234}Th$

$$\Delta m = (4.00260\text{ amu} + 234.03660\text{ amu}) - 238.05078\text{ amu} = -0.01158\text{ amu}$$

$$= -1.922949 \times 10^{-29}\text{ kg}$$

$$E = mc^2 = (1.922949 \times 10^{-29}\text{ kg})(2.998 \times 10^{8}\text{ m s}^{-1})^2$$

$$= -1.072834 \times 10^{-12}\text{ J/nucleus}$$

$$15.0\text{ g U} \times \frac{1\text{ mol U}}{238.05078\text{ g}} \times \frac{6.022 \times 10^{23}\text{ nuclei}}{1\text{ mol U}} \times \frac{-1.072834 \times 10^{-12}\text{ J}}{\text{nucleus}} \times \frac{1\text{ MJ}}{10^{6}\text{ J}}$$

$$= -6.56 \times 10^{4}\text{ MJ}$$

5. A second order reaction:

$$2\ A \rightarrow B + C$$

has a half-life of 53.67 s when the initial concentration of A is 0.3453 M. What is the ***rate constant*** for this reaction?

$$\lambda = \frac{1}{k[A]_0} \Rightarrow k = \frac{1}{\lambda [A]_0} = \frac{1}{(53.67\ \text{s})(0.3453\ \text{M})} = 0.05396\ \text{M}^{-1}\text{s}^{-1}$$

How ***many seconds*** will it take for the concentration of A to drop to 0.0023 M if the initial concentration is 0.0103 M?

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt \Rightarrow t = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{k} = \frac{\frac{1}{0.0023\ \text{M}} - \frac{1}{0.0103\ \text{M}}}{0.05396\ \text{M}^{-1}\ \text{s}^{-1}}$$

$$= 6.26 \times 10^3\ \text{s}$$

6. Calculate the ***equilibrium constant*** for a cell comprised of the $Cd^{2+}/Cd$ and the $MnO_4^-/Mn^{2+}$ half-cells if the initial concentrations are $[Cd^{2+}] = 0.15$ M, $[H^+] = 0.0050$ M, $[MnO_4^-] = 0.30$ M, and $[Mn^{2+}] = 0.10$ M.

| | | |
|---|---|---|
| $Cd^{2+} + 2e^- \rightarrow Cd$ | E° = -0.403 V | anode |
| $MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ | E° = +1.679 V | cathode |

$$E^\circ = +1.679 \text{ V} - (-0.403 \text{ V}) = 2.082 \text{ V}$$

$$K = e^{\frac{nFE^\circ}{RT}} = e^{\frac{(10)(96485)(2.082)}{(8.314)(298.15)}} = 10^{352}$$

Write the ***cell notation*** for this cell.

$Cd|Cd^{2+}||MnO_4^-, Mn^{2+}|Pt$

Calculate the ***actual cell voltage***.

$$2MnO_4^- + 5\,Cd + 16\,H^+ \rightarrow 2\,Mn^{2+} + 5\,Cd^{2+} + 8\,H_2O$$

$$E = E^\circ_{cell} - \frac{RT}{nF}\ln Q = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[Cd^{2+}]^5[Mn^{2+}]^2}{[MnO_4^-]^2[H^+]^{16}}$$

$$= 2.082 \text{ V} - \frac{(8.314 \text{ J mol}^{-1}\text{ K}^{-1})(298.15 \text{ K})}{(10 \text{ mol e}^- \text{ mol}^{-1})(96485 \text{ C }(\text{mol e}^-)^{-1})}\ln\frac{[0.15]^5[0.10]^2}{[0.30]^2[0.50]^{16}}$$

$$= 2.084 \text{ V}$$

7. ***Write formulas*** for the following.

a. Tris(ethylenediamine)cobalt(III) Nitrate

$[Co(en)_3](NO_3)_3$

b. Calcium Triaquatrichloromanganate(I)

$Ca_2\ [MnCl_3(H_2O)_3]$

8. Carbon reacts with steam to produce Carbon Monoxide and Hydrogen gas. If a 250.0 L vessel contains 15.00 moles of steam at 300°C and a large amount of solid carbon, what will be the ***equilibrium mixture composition*** when this system comes to equilibrium?

$$C_{(s)} + H_2O_{(g)} \leftrightharpoons CO_{(g)} + H_{2\,(g)}$$

$$\Delta H = \left(-110.525 \text{ kJ mol}^{-1}\right) - \left(-241.818 \text{ kJ mol}^{-1}\right) = 131.293 \text{ kJ mol}^{-1}$$

$$\Delta S = \left[\left(130.684 \text{ J mol}^{-1}\text{ K}^{-1}\right) + \left(197.674 \text{ J mol}^{-1}\text{ K}^{-1}\right)\right] - \left[\left(188.825 \text{ J mol}^{-1}\text{ K}^{-1}\right) + \left(5.74 \text{ J mol}^{-1}\text{ K}^{-1}\right)\right]$$

$$= 133.793 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = \left(131.293\times10^{3} \text{ J mol}^{-1}\right) - \left(573 \text{ K}\right)\left(133.793 \text{ J mol}^{-1}\text{ K}^{-1}\right) = 54629.611 \text{ J mol}^{-1}$$

$$K = e^{-\Delta G/RT} = e^{-\left(54629.611 \text{ J mol}^{-1}\right)/\left(8.314 \text{ J mol}^{-1}\text{ K}^{-1}\right)\left(573 \text{ K}\right)} = 1.05\times10^{-5} = K_p$$

$$P_{H_2O,i} = \frac{nRT}{V} = \frac{\left(15.00 \text{ mol}\right)\left(0.08206 \text{ L atm mol}^{-1}\text{ K}^{-1}\right)\left(573 \text{ K}\right)}{250.0 \text{ L}} = 2.8212 \text{ atm}$$

| | $H_2O$ | CO | $H_2$ |
|---|---|---|---|
| I | 2.8212 | 0 | 0 |
| C | -x | +x | +x |
| E | 2.8212-x | x | x |

$$K_p = \frac{P_{CO}P_{H_2}}{P_{H_2O}} = 1.05\times10^{-5} = \frac{(x)(x)}{(2.8212 - x)}$$

$$x^2 = 2.9622\times10^{-5} - 1.05\times10^{-5}x$$

$$x^2 + 1.05\times10^{-5}x - 2.9622\times10^{-5} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-\left(1.05\times10^{-5}\right) \pm \sqrt{\left(1.05\times10^{-5}\right)^2 - 4(1)\left(-2.9622\times10^{-5}\right)}}{2(1)}$$

$$= 5.43\times10^{-3}, -5.43\times10^{-3}$$

$$x = 5.43\times10^{-3} \text{ atm} = P_{CO} = P_{H_2}$$

$$P_{H_2O} = 2.8212 - 5.43\times10^{-3} = 2.816 \text{ atm}$$

9. A solution contains $4.87\times10^{-2}$ M Manganese(II) ions and $7.45\times10^{-2}$ M Cadmium ions. What ***range of carbonate ion concentration*** is required to precipitate one ion and not the other? ***Which ion will precipitate first*** as we increase the carbonate ion concentration?

$$K_{sp} = \left[Mn^{2+}\right]\left[CO_3^{2-}\right] = 2.2\times10^{-11}$$

$$\left[CO_3^{2-}\right] = \frac{K_{sp}}{\left[Mn^{2+}\right]} = \frac{2.2\times10^{-11}}{4.87\times10^{-2}} = 4.5\times10^{-10}$$

$$K_{sp} = \left[Cd^{2+}\right]\left[CO_3^{2-}\right] = 6.2\times10^{-12}$$

$$\left[CO_3^{2-}\right] = \frac{K_{sp}}{\left[Cd^{2+}\right]} = \frac{6.2\times10^{-12}}{7.45\times10^{-2}} = 8.3\times10^{-11}$$

The carbonate ion concentration range is from $8.3\times10^{-11}$ M to $4.5\times10^{-10}$ M.

The cadmium will precipitate first because it requires a lower concentration of carbonate to precipitate.

10. An electrode is prepared by dipping an Silver strip into a saturated solution of Silver Chromate containing 0.0500 M $CrO_4^{2-}$. Using the $K_{sp}$ in the chart determine the ***cell voltage*** for this electrode paired with a Standard Hydrogen Electrode.

$$K_{sp} = \left[Ag^+\right]^2\left[CrO_4^{2-}\right]$$

$$\left[Ag^+\right] = \sqrt{\frac{K_{sp}}{\left[CrO_4^{2-}\right]}} = \sqrt{\frac{2.0\times10^{-12}}{0.0500}} = 6.32\times10^{-6}\ \text{M}$$

$Ag^+ + e^- \rightarrow Ag$ E°=+0.7996 V cathode

$2H^+ + 2\,e^- \rightarrow H_2$ E° = 0.00 V anode

Overall equation:

$H_2 + 2\,Ag^+ \rightarrow 2\,H^+ + Ag$ E° = 0.7996 V

$$E = E^\circ_{cell} - \frac{RT}{nF}\ln Q = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{\left[H^+\right]^2}{P_{H_2}\left[Ag^+\right]^2}$$

$$= 0.7996\text{ V} - \frac{\left(8.314\text{ J mol}^{-1}\text{ K}^{-1}\right)\left(298.15\text{ K}\right)}{\left(\frac{2\text{ mol e}^-}{\text{mol}}\right)\left(\frac{96485\text{ C}}{\text{mol e}^-}\right)}\ln\frac{\left[1.00\right]^2}{\left[1.00\right]\left[6.32\times10^{-5}\right]^2}$$

$$= 0.5512\text{ V}$$

11. A rock is found outside of a volcano. It is found to have 3.56 mg of Lead and 6.57 mg of Uranium-238. The half-life of U-238 is $4.5\times10^9$ years. How many ***years*** old is the rock?

$$n_{Pb} = 3.56 \text{ mg Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} = 1.718\times10^{-2} \text{ mmol Pb}$$

$$n_U = 6.57 \text{ mg U} \times \frac{1 \text{ mol U}}{238.03 \text{ g U}} = 2.670\times10^{-2} \text{ mmol U}$$

$$n_{U,Orig} = n_{Pb} + n_U = 4.478\times10^{-2} \text{ mmol U}$$

$$\lambda = \frac{\ln 2}{k} \Rightarrow k = \frac{\ln 2}{\lambda} = \frac{\ln 2}{4.5\times10^9 \text{ yr}} = 1.540\times10^{-10} \text{ yr}^{-1}$$

$$\ln\frac{N_t}{N_0} = -kt$$

$$t = -\frac{\ln\frac{N_t}{N_0}}{k} = -\frac{\ln\frac{2.670\times10^{-2}}{4.478\times10^{-2}}}{1.540\times10^{-10} \text{ yr}^{-1}} = 3.36\times10^9 \text{ yr}$$