

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



The following data were taken at 25°C.

[A] <sub>0</sub> (mol L <sup>-1</sup> )	[B] <sub>0</sub> (mol L <sup>-1</sup> )	Initial rate (mol L <sup>-1</sup> s <sup>-1</sup> )
0.0010	0.0010	1.35×10 <sup>-4</sup>
0.0020	0.0010	1.08×10 <sup>-3</sup>
0.0020	0.0030	1.87×10 <sup>-3</sup>

$$\frac{R_2}{R_1} = \frac{1.08 \times 10^{-3}}{1.35 \times 10^{-4}} = 8 = \frac{\cancel{k} [A]_2^m \cancel{[B]_2^n}}{\cancel{k} [A]_1^m \cancel{[B]_1^n}} = \left( \frac{0.0020}{0.0010} \right)^m = 2^m$$

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

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

$$\frac{R_3}{R_2} = \frac{1.87 \times 10^{-3}}{1.08 \times 10^{-3}} = 1.73148 = \frac{\cancel{k} \cancel{[A]_3^m} [B]_3^n}{\cancel{k} \cancel{[A]_2^m} [B]_2^n} = \left( \frac{0.0030}{0.0010} \right)^n = 3^n$$

$$\log 1.73148 = \log 3^n = n \log 3$$

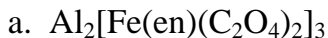
$$n = \frac{\log 1.73148}{\log 3} = 0.50$$

$$\text{Rate} = k [A]^3 [B]^{0.50} \Rightarrow k = \frac{\text{Rate}}{[A]^3 [B]^{0.50}} = \frac{1.35 \times 10^{-4} \text{ M s}^{-1}}{(0.0010 \text{ M})^3 (0.0010 \text{ M})^{0.50}}$$

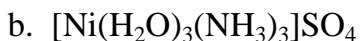
$$= 4.27 \times 10^6 \text{ M}^{-2.5} \text{ s}^{-1}$$

Overall order = 3.5

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

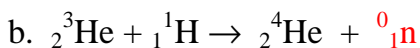
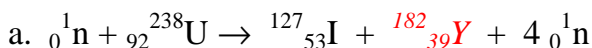


Aluminum DioxalatoEthylenediammineferrate(II)

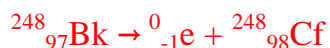


Triamminetriaquanickel(II) sulfate

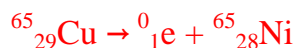
3. *Complete* the following nuclear equations.



c. Beta decay of Berkelium-248



d. Positron emission of Copper-65



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



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

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

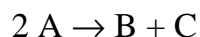
$$E = mc^2 = (1.922949 \times 10^{-29} \text{ kg})(2.998 \times 10^8 \text{ m s}^{-1})^2$$

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

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

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

5. A second order reaction:



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?

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

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?

$$\begin{aligned} \frac{1}{[\text{A}]_t} &= \frac{1}{[\text{A}]_0} + kt \Rightarrow t = \frac{\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0}}{k} = \frac{\frac{1}{0.0023 \text{ M}} - \frac{1}{0.0103 \text{ M}}}{0.05396 \text{ M}^{-1} \text{ s}^{-1}} \\ &= 6.26 \times 10^3 \text{ s} \end{aligned}$$

6. Calculate the *equilibrium constant* for a cell comprised of the  $\text{Cd}^{2+}/\text{Cd}$  and the  $\text{MnO}_4^-/\text{Mn}^{2+}$  half-cells if the initial concentrations are  $[\text{Cd}^{2+}] = 0.15 \text{ M}$ ,  $[\text{H}^+] = 0.0050 \text{ M}$ ,  $[\text{MnO}_4^-] = 0.30 \text{ M}$ , and  $[\text{Mn}^{2+}] = 0.10 \text{ M}$ .



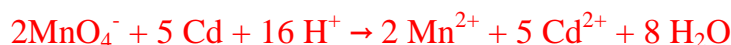
$$E^\circ = +1.679 \text{ V} - (-0.403 \text{ V}) = 2.082 \text{ V}$$

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

Write the *cell notation* for this cell.



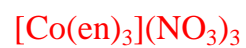
Calculate the *actual cell voltage*.



$$\begin{aligned} E &= E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \frac{[\text{Cd}^{2+}]^5 [\text{Mn}^{2+}]^2}{[\text{MnO}_4^-]^2 [\text{H}^+]^{16}} \\ &= 2.082 \text{ V} - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(10 \text{ mol e}^- \text{ mol}^{-1})(96485 \text{ C (mol e}^-)^{-1})} \ln \frac{[0.15]^5 [0.10]^2}{[0.30]^2 [0.50]^{16}} \\ &= 2.084 \text{ V} \end{aligned}$$

7. *Write formulas* for the following.

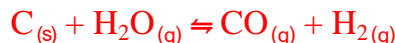
a. Tris(ethylenediamine)cobalt(III) Nitrate



b. Calcium Triaquatrichloromanganate(VI)



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?



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

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

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

$$\Delta G = \Delta H - T\Delta S = (131.293 \times 10^3 \text{ J mol}^{-1}) - (573 \text{ K})(133.793 \text{ J mol}^{-1} \text{ K}^{-1}) = 54629.611 \text{ J mol}^{-1}$$

$$K = e^{-\Delta G/RT} = e^{-\frac{(54629.611 \text{ J mol}^{-1})}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(573 \text{ K})}} = 1.05 \times 10^{-5} = K_p$$

$$P_{\text{H}_2\text{O},i} = \frac{nRT}{V} = \frac{(15.00 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(573 \text{ K})}{250.0 \text{ L}} = 2.8212 \text{ atm}$$

	H <sub>2</sub> O	CO	H <sub>2</sub>
I	2.8212	0	0
C	-x	+x	+x
E	2.8212-x	x	x

$$K_p = \frac{P_{\text{CO}}P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = 1.05 \times 10^{-5} = \frac{(x)(x)}{(2.8212 - x)}$$

$$x^2 = 2.9622 \times 10^{-5} - 1.05 \times 10^{-5} x$$

$$x^2 + 1.05 \times 10^{-5} x - 2.9622 \times 10^{-5} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(1.05 \times 10^{-5}) \pm \sqrt{(1.05 \times 10^{-5})^2 - 4(1)(-2.9622 \times 10^{-5})}}{2(1)}$$

$$= 5.43 \times 10^{-3}, -5.43 \times 10^{-3}$$

$$x = 5.43 \times 10^{-3} \text{ atm} = P_{\text{CO}} = P_{\text{H}_2}$$

$$P_{\text{H}_2\text{O}} = 2.8212 - 5.43 \times 10^{-3} = 2.816 \text{ atm}$$

9. A solution contains  $4.87 \times 10^{-2}$  M Manganese(II) ions and  $7.45 \times 10^{-2}$  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?

$$K_{sp} = [Mn^{2+}][CO_3^{2-}] = 2.2 \times 10^{-11}$$

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

$$K_{sp} = [Cd^{2+}][CO_3^{2-}] = 6.2 \times 10^{-12}$$

$$[CO_3^{2-}] = \frac{K_{sp}}{[Cd^{2+}]} = \frac{6.2 \times 10^{-12}}{7.45 \times 10^{-2}} = 8.3 \times 10^{-11}$$

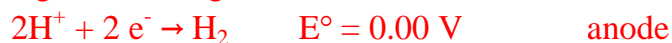
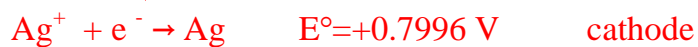
The carbonate ion concentration range is from  $8.3 \times 10^{-11}$  M to  $4.5 \times 10^{-10}$  M.

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  $\text{CrO}_4^{2-}$ . Using the  $K_{sp}$  in the chart determine the **cell voltage** for this electrode paired with a Standard Hydrogen Electrode.

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$[\text{Ag}^+] = \sqrt{\frac{K_{sp}}{[\text{CrO}_4^{2-}]}} = \sqrt{\frac{2.0 \times 10^{-12}}{0.0500}} = 6.32 \times 10^{-6} \text{ M}$$



Overall equation:



$$\begin{aligned} E &= E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \frac{[\text{H}^+]^2}{P_{\text{H}_2} [\text{Ag}^+]^2} \\ &= 0.7996 \text{ V} - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{\left(\frac{2 \text{ mol e}^-}{\text{mol}}\right) \left(\frac{96485 \text{ C}}{\text{mol e}^-}\right)} \ln \frac{[1.00]^2}{[1.00][6.32 \times 10^{-5}]^2} \\ &= 0.5512 \text{ V} \end{aligned}$$

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  $4.5 \times 10^9$  years. How many *years* old is the rock?

$$n_{Pb} = 3.56 \text{ mg Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} = 1.718 \times 10^{-2} \text{ mmol Pb}$$

$$n_U = 6.57 \text{ mg U} \times \frac{1 \text{ mol U}}{238.03 \text{ g U}} = 2.670 \times 10^{-2} \text{ mmol U}$$

$$n_{U, \text{Orig}} = n_{Pb} + n_U = 4.478 \times 10^{-2} \text{ mmol U}$$

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

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

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