Thursday July 7, 2016
Chem 104 – PLI 26
Chapter 14 (kinetics)

1. Please identify the following statements as either true or false:

a) T Adding solute to a pure solvent widens the temperature range at which the solution is liquid. ↓FP , ↑BP

b) F The units of the rate constant, k, are the same for all order reactions. $\frac{0}{M/s}$ $\frac{1^{st}}{1/s}$ $\frac{2^{nd}}{1/s\cdot M}$

c) F The graph of reactant concentration vs. time is linear for all order reactions. ↳ only for 0 order rxns

d) T Radioactive decay is always a first-order process.

e) T For first-order reactions, the reaction half-life is always $t_{1/2} = \frac{\ln 2}{k}$.

f) F The order of a reaction with respect to a particular reactant is always that reactant's stoichiometric coefficient as written in the reaction.

g) F The concentration of a catalyst can never appear in the rate equation.

h) T A catalyst can increase the rate at which reactants are converted to products.

i) F A catalyst can make a reaction more product favored. ⟶ catalysts don't influence rxn equilibrium

2. For the following reaction at 856 °C: $2\ NH_3 \longrightarrow N_2 + 3\ H_2$
the average rate of disappearance of $NH_3$ over the time period from t = 0 s to t = 4186 s is found to be $1.50\times10^{-6}$ M $s^{-1}$. The average rate of formation of $H_2$ over the same time period is:

avg rxn rate $= -\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2]}{\Delta t}$

$\frac{\Delta[NH_3]}{\Delta t} = -1.50\times10^{-6}\frac{M}{s}$ $-\frac{1}{2}(-1.50\times10^{-6} M/s) = \frac{1}{3}\frac{\Delta[H_2]}{\Delta t}$

$\frac{\Delta[H_2]}{\Delta t} = \boxed{2.25\times10^{-6}\frac{M}{s}}$

3. Write an expression for the reaction rate law and calculate the value of the rate constant, *k* based on the following data. What is the overall order of the reaction?

$$2\ NO_{2\ (g)} + F_{2\ (g)} \longrightarrow 2\ NO_2F_{\ (g)}$$

| [NO2] (M) | [F2] (M) | Initial Rate (M/s) |
|---|---|---|
| 0.100 | 0.100 | 0.026 |
| 0.200 | 0.100 | 0.051 |
| 0.200 | 0.200 | 0.103 |
| 0.400 | 0.400 | 0.411 |

first order for $NO_2$ x2

x2 x2 first order for $F_2$

$\ast$ rxn rate $= k[NO_2][F_2]$

$\ast$ $k = \frac{\text{rxn rate}}{[NO_2][F_2]} = \frac{0.026\ M/s}{[0.100M][0.100M]} = \boxed{2.6\ \frac{1}{M\cdot s}}$

Second order rxn!

have to ask yourself for which values would the graph be linear? In this case 1/[NOBr] vs. t is linear, so this is a second order rxn

4. Please use the table below to determine the order of NOBr decomposition and the value of k:

| Time (s) | [NOBr] (M) | ln[NOBr] | 1/[NOBr] |
|---|---|---|---|
| 10 | 0.50 | −0.693 | 2.0 |
| 20 | 0.33 | −1.11 | 3.0 |
| 30 | 0.25 | −1.39 | 4.0 |
| 40 | 0.20 | −1.60 | 5.0 |

For second order rxn, k = slope, b/c

$\frac{1}{[NOBr]_t} = kt + \frac{1}{[NOBr]_0}$ ; $y = mx + b$

slope $= \frac{rise}{run} = \frac{5.0-4.0}{40-30} = \frac{1}{10}$, so $k = 0.10\ M^{-1} \cdot s^{-1}$

5. The decomposition of XY is second order in XY and has a rate constant of $7.02 \times 10^{-3}$ 1/M•s at a certain temperature:

a) How long will it take for the concentration of XY to decrease to 12.5% of its initial concentration when the initial concentration is 0.100 M?

$\frac{1}{[xy]_t} = kt + \frac{1}{[xy]_0}$

$[xy]_0 = .100\ M$

$[xy]_t = 0.100\ M \times .125 = 0.0125$

$k = 0.00702\ M^{-1}s^{-1}$

$\frac{1}{[xy]_t} - \frac{1}{[xy]_0} = kt$

$\frac{1}{0.0125} - \frac{1}{0.100} = 0.00702\,t$

$70 = 0.00702\,t$

$t = 9.97 \times 10^3$ seconds

b) How long will it take for the concentration of XY to decrease to 12.5% of its initial concentration when the initial concentration is 0.200 M?

$\frac{1}{[xy]_t} - \frac{1}{[xy]_0} = kt$

$[xy]_0 = 0.200\ M$

$[xy]_t = 0.200 \times 0.125 = 0.0250\ M$

$k = 0.00702\ M^{-1}s^{-1}$

$\frac{1}{0.0250} - \frac{1}{0.200} = 0.00702\,t$

$35 = 0.00702\,t$

$t = 4.99 \times 10^3$ sec

c) If this were a first order reaction, how would your calculations differ? Please explain briefly. If it were first order, the initial concentrations would not have mattered - it would have taken the same amount of time to reach 12.5% of the initial amount.

d) If the initial concentration of XY is 0.052 M, what is the concentration of XY after 64 s?

$\frac{1}{[xy]_t} = kt + \frac{1}{[xy]_0}$

$\frac{1}{[XY]_t} = (0.00702\ M^{-1}s^{-1})(64\ s) + \frac{1}{0.052\ M}$

$\frac{1}{[XY]_t} = 19.7$

$[xy]_t = 0.051\ M$