AP Chemistry Review Name ~~Key~~
Chapter ~~13~~: Chemical Kinetics
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Solve the following problems showing all work.

→ Can't use this to tell zero order b/c it's the rate not (k).

1. In the reaction: $H_2O_2(aq) \rightarrow H_2O(l) + \frac{1}{2} O_2(g)$, the initial concentration of H_2O_2 is 0.2546 *M*, and the initial rate of reaction is 9.32×10^{-4} $M\ s^{-1}$. What will be the $[H_2O_2]$ after 35 s?

$$R = -\frac{\Delta[H_2O_2]}{\Delta t} = \frac{-(x - .2546)M}{35 s} = 9.32 \times 10^{-4} M s^{-1}$$

$x =$ **.2220 M**

$-(x - .2546) = .03262$

$-x + .2546 = .03262$

$-x = -.22198$

$x = .2220\ M$

2. The rate of the following reaction in aqueous solution is monitored by measuring the rate of formation of I_3^-. The data obtained are listed in the table.

$$S_2O_8^{2-} + 3\ I^- \rightarrow 2\ Cl^- + 2\ SO_4^{2-} + I_3^-$$

Experiment	$[S_2O_8^{2-}]$, *M*	$[I^-]$, *M*	Initial Rate, $M\ s^{-1}$
1	0.038	0.060	1.4×10^{-5}
2	0.076	0.060	2.8×10^{-5}
3	0.076	0.120	5.6×10^{-5}

a. Determine the order of the reaction with respect to $S_2O_8^{2-}$, with respect to I^- and overall.
b. What is the value of the rate constant *k*?
c. What would be the initial rate of reaction if $[S_2O_8^{2-}] = 0.025$ *M* and $[I^-] =$ 0.045 *M*?

$$\frac{R_2}{R_1} = \frac{k_2[S_2O_8^{2-}]_2^n}{k_1[S_2O_8^{2-}]_1^n} = \frac{2.8 \times 10^{-5}}{1.4 \times 10^{-5}} = \left(\frac{.076}{.038}\right)^n \Rightarrow 2 = 2^n$$

n = 1

$$\frac{R_3}{R_2} = \frac{5.6 \times 10^{-5}}{2.8 \times 10^{-5}} = \left(\frac{.120}{.06}\right)^m \Rightarrow 2 = 2^m$$

m = 1

$R = k[S_2O_8^{2-}][I^-]$ **2nd overall**

b) $k = \frac{R}{[S_2O_8^{2-}][I^-]} = \frac{1.4 \times 10^{-5} M s^{-1}}{(.038 M)(.060 M)} =$ **$6.1\cancel{8} \times 10^{-3} M^{-1} s^{-1}$**

c) $R = (6.1 \times 10^{-3} M^{-1} s^{-1})(.025 M)(.045 M) =$ **$6.9 \times 10^{-6}\ M s^{-1}$**

.25

6.9×10^{-5}?

3. The half-life for the first-order decomposition of sulfuryl chloride at 320 °C is 8.75 h.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

$\ln[A] = -kt + \ln[A]_0$

a. What is the value of the rate constant k?
b. What is the pressure of sulfuryl chloride 3.00 h after the start of the reaction, if its initial pressure is 722 mmHg?
c. How long after the start of the reaction will it be before the pressure of sulfuryl chloride becomes 125 mmHg?

1st order: $t_{\frac{1}{2}} = \frac{.693}{K} \Rightarrow K = \frac{.693}{8.75\ h} = \boxed{.0792\ h^{-1}} \Rightarrow \boxed{2.2\times10^{-5}\ s^{-1}}$

b) $\ln\left(\frac{P_t}{P_0}\right) = -kt \Rightarrow \ln\left(\frac{x}{722}\right) = -(.0792\ h^{-1})(3.00\ h)$

integrated rate law

$\frac{x}{722} = .7885 \Rightarrow x = \boxed{569\ mm\ Hg}$

c) $\ln\left(\frac{125}{722}\right) = -(.0792)t \Rightarrow t = \boxed{22.1\ h}$

4. In the zero-order decomposition of ammonia on a tungsten surface at 1100°C,

$$NH_3(g) \rightarrow \tfrac{1}{2} N_2(g) + \tfrac{3}{2} H_2(g)$$

The rate is $3.40 \times 10^{-6}\ M\,s^{-1}$. What is the half-life in hours for the reaction in which $[NH_3] = 0.0452\ M$?

$R = K = 3.40\times10^{-6}\ M s^{-1}$

Zero order: $t_{\frac{1}{2}} = \frac{[NH_3]_0}{2k} = \frac{.0452\ M}{2(3.40\times10^{-6}\ M s^{-1})} = 6647\ s \cdot \frac{h}{3600\ s}$

$= \boxed{1.85\ h}$

5. The rate constant for the second-order decomposition of hydrogen iodide at 700 K is $k = 1.2\text{x}10^{-3}\ M^{-1}\ s^{-1}$. In a reaction in which $[HI]_0 = 0.56\ M$, at what time will $[HI] = 0.28\ M$?

2nd order: $R = k[HI]^2$

$\frac{1}{[HI]_t} = kt + \frac{1}{[HI]_0} \Rightarrow \frac{1}{.28\ M} = (1.2\times10^{-3}\ M^{-1}s^{-1})t + \frac{1}{.56}$

$\Rightarrow 3.571 = 1.2\times10^{-3}\,t + 1.786$

$t = \boxed{1488\ s} \cdot \frac{1\ min}{60\ s} = 24.8\ min \sim \boxed{25\ min}$

$\sim \boxed{.41\ h}$

6. The first-order decomposition of di-*tert*-butyl peroxide (DTBP) has a half-life of 320 min at 135°C and 100 min at 145°C. Calculate E_a for this reaction.

$$\underset{\text{DTBP}}{C_8H_{18}O_2\,(g)} \rightarrow \underset{\text{acetone}}{2\,(CH_3)_2CO(g)} + \underset{\text{ethane}}{C_2H_6(g)}$$

$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

1st order: $t_{\frac{1}{2}} = \frac{.693}{k}$ ⇒ $k_1 = \frac{.693}{320\,min} = 2.17 \times 10^{-3}\ min^{-1}$

$k_2 = \frac{.693}{100\,min} = 6.93 \times 10^{-3}\ min^{-1}$

$\ln\left(\frac{6.93\times10^{-3}}{2.17\times10^{-3}}\right) = \frac{E_a}{(8.3145\,J/mol\,K)}\left(\frac{1}{408K} - \frac{1}{418K}\right)$

$9.654\ \frac{J}{mol\cdot K} = E_a(5.864\times10^{-5})K \Rightarrow E_a = \boxed{165\ kJ/mol}$

6) ~~10~~. Is the following mechanism a plausible mechanism for the reaction: Explain.

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ Below 600 K, $R = k[NO_2]^2$.

Fast: $2\,NO_2 \leftrightarrow N_2O_4$

Slow: $N_2O_4 + 2\,CO \rightarrow 2\,NO + 2\,CO_2$

$R_{slow} = k[N_2O_4][CO]^2$

$R_{f_1} = k_f[NO_2]^2 = k_r[N_2O_4] = R_r \Rightarrow [N_2O_4] = \frac{k_f}{k_r}[NO_2]^2 = k'[NO_2]^2$

$\rightarrow R_s = k'[NO_2]^2[CO]^2$

NOT plausible
does not agree w/ given rate law

7) ~~8~~.