Kinetics **Ch. 14 Problem Set**

1. Explain the effect of increasing the temperature on the reaction rate at the molecular level.

2. The reaction of $(CH_3)_3CBr$ with hydroxide ion proceeds with the formation of $(CH_3)_3COH$.

$$(CH_3)_3CBr(aq) + OH^-(aq) \rightarrow (CH_3)_3COH(aq) + Br^-(aq)$$

The following data were obtained at 55°C.

Expt.	$[(CH_3)_3CBr]_0$ (M)	$[OH^-]_0$ (M)	Initial Rate (M/s)
1	0.10	0.10	1.0×10^{-3}
2	0.20	0.10	2.0×10^{-3}
3	0.10	0.20	1.0×10^{-3}

(a) What is the reaction order with respect to $(CH_3)_3CBr$?

(b) What is the reaction order with respect to OH^-?

(c) What is the rate law for this reaction? (d) Calculate the rate constant (include units!)?

(e) A fourth experiment is performed with $[(CH_3)_3CBr]_0 = 0.30$ M and $[OH^-]_0 = 0.20$ M. What would be the initial rate (in M/s) for this experiment?

3. The following questions refer to the gas-phase decomposition of ethylene chloride.

$$C_2H_5Cl \rightarrow \text{products}$$

Experiment shows that the decomposition is first order. The following information was obtained for this reaction:

Time (s)	ln (C_2H_5Cl) (M)
1.0	−1.625
2.0	−1.735
3.0	−1.845

(a) What is the rate constant for this decomposition?

(b) What was the initial concentration of the ethylene chloride?

(c) What would the concentration be after 5.0 seconds?

(d) Determine the half-life ($t_{1/2}$) in seconds?

(e) Does the half-life of this reaction change as the reaction proceeds? Explain.

4. Consider the following overall balanced reaction and experimental data:

$$2\,H_2O_2(aq) + 3\,I^-(aq) \rightarrow I_3^-(aq) + 2\,H_2O(l) + O_2(g)$$

Expt	$[H_2O_2]_0$, M	$[I^-]_0$, M	Initial rate, M/s
1	0.100	0.100	1.15×10^{-4}
2	0.100	0.200	2.30×10^{-4}
3	0.200	0.100	2.30×10^{-4}
4	0.200	0.200	4.60×10^{-4}

What is the reaction order with respect to...

(a) H_2O_2?

(b) I^-?

(c) What is the rate law for the overall reaction?

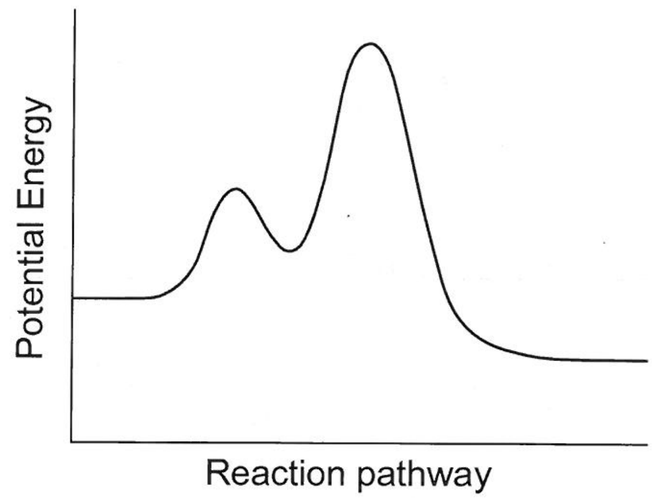
(d) What is the rate constant for this reaction, including units?

5. A commonly used "rule of thumb" in chemistry is that a reaction rate will increase by about a factor of two for every 10 °C increase in temperature. Use equation 14.21 to calculate the activation energy implied by this rule, assuming that the rate exactly doubles when the temperature is raised from 20 °C to 30 °C.

6. The rate law for the reaction of NO_2 with CO to produce NO and CO_2 is second order with respect to NO_2. What will happen to the rate of the reaction if $[NO_2]$ changes by a factor of…

(a) 2?	(b) 0.25?

7. Consider the following reaction energy profile. Briefly explain each of your answers.



(a) How many intermediates are formed in the reaction? Label them on the graph.

(b) How many activated complexes (i.e. transition states) are there? Label them on the graph.

(c) How many elementary steps are in the reaction mechanism?

(d) Which step would be rate-determining? Explain your answer.

(e) Is the overall reaction endothermic or exothermic? Explain your answer and label ΔH on the graph.

8. The reaction of hydrogen with iodine produces hydrogen iodide according to the following reaction: $H_2(g) + I_2(g) \rightarrow 2\,HI(g)$
Three mechanisms have been proposed to rationalize this transformation. Write the rate law for each proposed mechanism.

(a) Mechanism A $H_2(g) + I_2(g) \xrightarrow{k_1} 2\,HI(g)$	**(b) Mechanism B** $I_2(g) \xrightarrow{k_1} 2\,I(g)$ (slow) $H_2(g) + 2\,I(g) \xrightarrow{k_2} 2\,HI(g)$ (fast)
(c) Mechanism C $I_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,I(g)$ (fast) $H_2(g) + 2I(g) \xrightarrow{k_2} 2\,HI(g)$ (slow)	**(d)** The experimentally determined rate law is found to be first order with respect to H_2 and first order with respect to I_2. Write the experimentally determined rate law. **(e)** Which of the mechanisms is consistent with this rate law? **Mechanism: A B C**

9. The dimerization of tetrafluoroethylene at 403 K proceeds according to the rate law:

$$\text{rate} = 1.6 \times 10^{-3}\ M^{-1}s^{-1}(C_2F_4)^2$$

(a) What is the concentration of C_2F_4 after 1.0 hr if 0.80 mole of C_2F_4 is injected into a 1.0-L reaction vessel?

(b) What is the first half-life of the reaction based on the conditions in (a)?

CHEM 1252 Problem Set 2 **Spring 2016**

1. Explain the effect of increasing the temperature on the reaction rate at the molecular level.

Increasing the temperature increases the speed and kinetic energy of the reactant molecules. This increased energy causes an increase in the number of effective collisions, which increases the reaction rate.

2. The reaction of $(CH_3)_3CBr$ with hydroxide ion proceeds with the formation of $(CH_3)_3COH$.

$$(CH_3)_3CBr(aq) + OH^-(aq) \rightarrow (CH_3)_3COH(aq) + Br^-(aq)$$

The following data were obtained at 55°C.

Expt.	$[(CH_3)_3CBr]_0$ (M)	$[OH^-]_0$ (M)	Initial Rate (M/s)
1	0.10	0.10	1.0×10^{-3}
2	0.20	0.10	2.0×10^{-3}
3	0.10	0.20	1.0×10^{-3}

(a) What is the reaction order with respect to $(CH_3)_3CBr$?

$$\left(\frac{[(CH_3)_3CBr]_2}{[(CH_3)_3CBr]_1}\right)^X = \frac{rate_2}{rate_1} \qquad \left(\frac{0.20}{0.10}\right)^X = \left(\frac{2.0\times10^{-3}}{1.0\times10^{-3}}\right)$$

$$2^X = 2 \qquad X = 1 \qquad \boxed{1}$$

(b) What is the reaction order with respect to OH^-?

$$\left(\frac{[OH^-]_3}{[OH^-]_1}\right)^Y = \frac{rate_3}{rate_1} \qquad \left(\frac{0.20}{0.10}\right)^Y = \left(\frac{1.0\times10^{-3}}{1.0\times10^{-3}}\right)$$

$$2^Y = 1 \qquad Y = \emptyset \qquad \boxed{\emptyset}$$

(c) What is the rate law for this reaction?

$$rate = k[(CH_3)_3CBr]^1$$

(d) Calculate the rate constant (include units!)?

$$k = \frac{rate}{[(CH_3)_3CBr]} = \frac{2.0\times10^{-3}\,\cancel{M}/s}{0.20\,\cancel{M}} = \boxed{1.0\times10^{-2}\,s^{-1}}$$

(e) A fourth experiment is performed with $[(CH_3)_3CBr]_0 = 0.30$ M and $[OH^-]_0 = 0.20$ M. What would be the initial rate (in M/s) for this experiment?

$$rate = k[(CH_3)_3CBr] = (1.0\times10^{-2}\,s^{-1})(0.30\,M)$$

$$= \boxed{3.0\times10^{-3}\,M/s}$$

3. The following questions refer to the gas-phase decomposition of ethylene chloride.

$C_2H_5Cl \rightarrow$ products

Experiment shows that the decomposition is first order. The following information was obtained for this reaction:

Time (s)	ln [C_2H_5Cl] (M)
1.0	−1.625
2.0	−1.735
3.0	−1.845

note!

$$\text{Slope} = \frac{Y_2 - Y_1}{X_2 - X_1} = \frac{\ln A_2 - \ln A_1}{t_2 - t_1} \Rightarrow \frac{\ln \frac{A_2 (M)}{A_1 (M)}}{s}$$

t_2 (s), t_1 (s); units cancel

(a) What is the rate constant for this decomposition?

$\ln[A] = -k t + \ln[A_0]$

$-k$ = slope

$$-k = \frac{-1.735 - (-1.625)}{2.0s - 1.0s} = -0.11 s^{-1}$$

$\boxed{k = 0.11 s^{-1}}$

(b) What was the initial concentration of the ethylene chloride?

$\ln[A] = -kt + \ln[A_0]$

$-1.735 = (-0.11 s^{-1})(2.0 s) + \ln[A_0]$

$\ln[A_0] = -1.735 - (-0.22) = -1.515$

$[A_0] = e^{-1.515}$

$= 0.2198 M$

$\boxed{[A_0] = 0.22 M}$

(c) What would the concentration be after 5.0 seconds?

$\ln[A] = -kt + \ln[A_0]$

$= (-0.11 s^{-1})(5.0 s) + (-1.515)$

$= -0.55 - 1.515 = -2.065$

$[A] = e^{-2.065}$

$= 0.1268 M$

$\boxed{[A] = 0.13 M}$

(d) Determine the half-life ($t_{1/2}$) in seconds?

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{0.11 s^{-1}} = 6.3013 s$$

$\boxed{t_{1/2} = 6.3 s}$

(e) Does the half-life of this reaction change as the reaction proceeds? Explain.

The half-life does NOT depend on the initial concentration for a first order reaction, only on the rate constant k, which is a constant for the rxn. Thus, $t_{1/2}$ does not change as the rxn proceeds.

4. Consider the following overall balanced reaction and experimental data:

$$2\,H_2O_2(aq) + 3\,I^-(aq) \rightarrow I_3^-(aq) + 2\,H_2O(l) + O_2(g)$$

Expt	$[H_2O_2]_0$, M	$[I^-]_0$, M	Initial rate, M/s
1	0.100	0.100	1.15×10^{-4}
2	0.100	0.200	2.30×10^{-4}
3	0.200	0.100	2.30×10^{-4}
4	0.200	0.200	4.60×10^{-4}

or

What is the reaction order with respect to…

(a) H_2O_2?

$$\left(\frac{[H_2O_2]_3}{[H_2O_2]_1}\right)^X = \frac{\text{rate}_3}{\text{rate}_1}$$

$$\left(\frac{0.200}{0.100}\right)^X = \frac{2.30\times10^{-4}}{1.15\times10^{-4}}$$

$2^X = 2$ $\boxed{X = 1 \text{ 1st order}}$

(b) I^-?

$$\left(\frac{[I^-]_2}{[I^-]_1}\right)^Y = \frac{\text{rate}_2}{\text{rate}_1}$$

$$\left(\frac{0.200}{0.100}\right)^Y = \frac{2.30\times10^{-4}}{1.15\times10^{-4}}$$

$2^Y = 2$ $\boxed{Y = 1 \text{ first order}}$

(c) What is the rate law for the overall reaction?

$\text{rate} = k[H_2O_2]^1[I^-]^1$

(d) What is the rate constant for this reaction, including units?

$$k = \frac{\text{rate}}{[H_2O_2][I^-]} = \frac{2.30\times10^{-4}\ M/s}{(0.100\ M)(0.200\ M)} = 0.01150\ M^{-1}s^{-1}$$

$\boxed{k = 0.0115\ M^{-1}s^{-1}}$

5. A commonly used "rule of thumb" in chemistry is that a reaction rate will increase by about a factor of two for every 10 °C increase in temperature. Use equation 14.21 to calculate the (typo) activation energy implied by this rule, assuming that the rate exactly doubles when the temperature is raised from 20 °C to 30 °C.

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{1}{2} = \frac{E_a}{8.314\ J/mol\cdot K}\left(\frac{1}{303.15} - \frac{1}{293.15}\right)$$

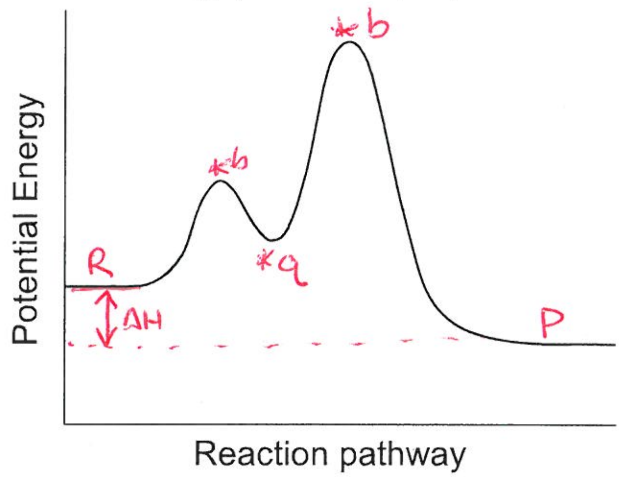
$$\frac{(-0.69315)(8.314\ J/mol\cdot K)}{-1.12526e^{-4}\ K^{-1}} = E_a = +51213.5\ J/mol$$

$\boxed{E_a = 5.12\times10^4\ J/mol}$

6. The rate law for the reaction of NO_2 with CO to produce NO and CO_2 is second order with respect to NO_2. What will happen to the rate of the reaction if $[NO_2]$ changes by a factor of…

(a) 2? rate $\propto [NO_2]^2$ rate $\propto (2)^2 = 4$ $\boxed{\text{quadruples}}$	(b) 0.25? rate $\propto (\overset{\frac{1}{4}}{0.25}[NO_2])^2$ $\frac{1}{16}$th or $\boxed{\text{0.0625 of original}}$

7. Consider the following reaction energy profile. Briefly explain each of your answers.



(a) How many intermediates are formed in the reaction? Label them on the graph.

1 (*a)

(b) How many activated complexes (i.e. transition states) are there? Label them on the graph.

2 (*b)

(c) How many elementary steps are in the reaction mechanism?

2

(d) Which step would be rate-determining? Explain your answer.

Step 2 has the largest E_a ∴ smaller k + slower rate
Slowest step is the rate determining step

(e) Is the overall reaction endothermic or exothermic? Explain your answer and label ΔH on the graph.

products are of lower H than reactants therefore $\Delta H = -$
$\boxed{\text{exothermic}}$

8. The reaction of hydrogen with iodine produces hydrogen iodide according to the following reaction: $H_2(g) + I_2(g) \rightarrow 2\ HI(g)$

Three mechanisms have been proposed to rationalize this transformation. Write the rate law for each proposed mechanism. All steps are elementary.

(a) Mechanism A $H_2(g) + I_2(g) \xrightarrow{k_1} 2\ HI(g)$ rate $= k_1[H_2][I_2]$	**(b) Mechanism B** $I_2(g) \xrightarrow{k_1} 2\ I(g)$ (slow) $H_2(g) + 2\ I(g) \xrightarrow{k_2} 2\ HI(g)$ (fast) rate $= k_1[I_2]$
(c) Mechanism C $I_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ I(g)$ (fast) $\boxed{H_2(g) + 2I(g) \xrightarrow{k_2} 2\ HI(g) \quad \text{(slow)}}$ rate $= k_2[H_2][I]^2$	**(d)** The experimentally determined rate law is found to be first order with respect to H_2 and first order with respect to I_2. Write the experimentally determined rate law. rate $= k[H_2][I_2]$ **(e)** Which of the mechanisms is consistent with this rate law? **Mechanism:** **A** **B** **C**

9. The dimerization of tetrafluoroethylene at 403 K proceeds according to the rate law:

$$\text{rate} = 1.6 \times 10^{-3}\ M^{-1}s^{-1}[C_2F_4]^2$$ – Second order rxn

(a) What is the concentration of C_2F_4 after 1.0 hr if 0.80 mole of C_2F_4 is injected into a 1.0-L reaction vessel?

$A_0 = \frac{0.80\ mol}{1.0\ L} = 0.80\ M$ $\qquad \frac{1}{[A]_t} = kt + \frac{1}{[A_0]} =$

~~kt~~ $(1.6\times10^{-3}\ mol^{-1}s^{-1})(1.0\ hr)\left(\frac{60\ min}{hr}\right)\left(\frac{60\ sec}{min}\right) + \frac{1}{0.80M} = 7.01\ M^{-1}$

$[A]_{1hr} = \frac{1}{7.01\ M^{-1}} = 0.143\ M = \boxed{0.14M}$

(b) What is the first half-life of the reaction based on the conditions in (a)?

$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(0.80M)(1.6\times10^{-3}\ M^{-1}s^{-1})} = \frac{1}{0.00128\ s^{-1}} = 781.25\ s$

$\boxed{t_{1/2} = 780\ s}$ = 13 min