CHEM 132
Problem Set Ch.13

Key begins on Page 3.

1. If ΔH = -138 kJ for a certain process, then:

a) it occurs rapidly
b) it does not need a catalyst
c) it does need a catalyst
d) it is exothermic
e) it is endothermic

2. The reaction

$$2\ H_{2(g)} + 2\ NO_{(g)} \longrightarrow 2\ H_2O_{(g)} + N_{2(g)}$$

is first order in H_2 and second order in NO. Write out the **Rate Law** for this reaction.

3. Nitrosyl chloride is produced from the reaction of nitrogen(II)oxide and chlorine.

$$2\ NO_{(g)} + Cl_{2(g)} \longrightarrow 2\ NOCl(g)$$

The following initial rates at a given temperature were obtained for the concentrations given below:

Experiment	Rate (mol/L.hr)	NO (mol/L)	Cl_2 (mol/L)
1	2.21	0.25	0.25
2	8.83	0.50	0.25
3	17.5	0.50	0.50

What is the **experimental Rate Law**?

4. At a given temperature, a first-order reaction has a rate constant of 2.5 x 10^{-3} s^{-1}. Calculate the **time** required (in seconds) for the reaction to be 75% complete.

__________________sec

5. A first-order reaction is observed to have a rate constant of 35 min^{-1}. Calculate the corresponding **half-life** for the reaction.

$t_{1/2}$ = _____________min.

6. ^{64}Co decays by a first-order process via the emission of a beta particle. The ^{64}Co isotope has a half-life of 7.8 min. How long (in min) will it take for 31/32 of the cobalt to undergo decay?

________________min

7. A first-order reaction has a half-life of 11.6 minutes. Calculate the **rate constant** for this reaction in sec^{-1}.

k = ______________s^{-1}

8.Given the following reaction

$$\frac{1}{2}\ N_2O_{4(g)} \longrightarrow NO_{2(g)} \qquad \Delta H = 28.6\ kJ$$

at 30°C, k = 5.1×10^6 s^{-1}, and the activation energy is 54.0 kJ.

a) What is the **rate constant** of the same reaction at 45°C?

b) What is the **activation energy** for the reverse reaction?

9. A suggested mechanism for the decomposition of ozone is

$$O_3 \longrightarrow O_2 + O \qquad \text{(fast, equilibrium)}$$

$$O + O_3 \longrightarrow 2\,O_2 \qquad \text{(slow)}$$

write out a **rate law** that is consistent with this mechanism.

10. Briefly explain why the half-life of a second-order reaction increases as the reaction proceeds.

KEY.

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1. If $\Delta H = -138$ kJ for a certain process, then:

a) it occurs rapidly
b) it does not need a catalyst
c) it does need a catalyst
d) it is exothermic
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2. The reaction

$$2\ H_{2(g)} + 2\ NO_{(g)} \longrightarrow 2\ H_2O_{(g)} + N_{2(g)}$$

is first order in H_2 and second order in NO. Write out the **Rate Law** for this reaction.

RATE = $k[H_2][NO]^2$

3. Nitrosyl chloride is produced from the reaction of nitrogen(II)oxide and chlorine.

$$2\ NO_{(g)} + Cl_{2(g)} \longrightarrow 2\ NOCl(g)$$

The following initial rates at a given temperature were obtained for the concentrations given below:

Experiment	Rate (mol/L.hr)	NO (mol/L)	Cl_2 (mol/L)
1	2.21	0.25	0.25
2	8.83 (x4)	0.50 (x2)	0.25
3	17.5 (x2)	0.50	0.50 (x2)

What is the **experimental Rate Law**?

RATE = $k[NO]^2[Cl_2]$

4. At a given temperature, a first-order reaction has a rate constant of 2.5×10^{-3} s^{-1}. Calculate the **time** required (in seconds) for the reaction to be 75% complete.

IF RXN IS 75% COMPLETE THEN $\frac{[A_t]}{[A_0]} = 0.25$

SO $\log(0.25) = \frac{-(2.5\times10^{-3}s^{-1})t}{2.303}$ OR $t = \frac{2.303 \log(0.25)}{-2.5\times10^{-3}s^{-1}}$ = 555 sec

5. A first-order reaction is observed to have a rate constant of 35 min^{-1}. Calculate the corresponding **half-life** for the reaction.

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{35\ min^{-1}} = 1.98\times10^{-2}$ $t_{1/2}$ = 1.98×10^{-2} min.

6. ^{60}Co decays by a first-order process via the emission of a beta particle. The ^{60}Co isotope has a half-life of 7.8 min. How long (in min) will it take for 31/32 of the cobalt to undergo decay?

IF ONLY 1/32 OF THE COBALT REMAINS... THEN 5 HALF LIVES HAVE PASSED

$1 \rightarrow \frac{1}{2} \rightarrow \frac{1}{4} \rightarrow \frac{1}{8} \rightarrow \frac{1}{16} \rightarrow \frac{1}{32}$ $\quad 5 \times 7.8 = 39$ min

$t_{1/2}$ $\quad 2t_{1/2}$ $\quad 3t_{1/2}$ $\quad 4t_{1/2}$ $\quad 5t_{1/2}$

39 min

7. A first-order reaction has a half-life of 11.6 minutes. Calculate the **rate constant** for this reaction in sec^{-1}.

SINCE $t_{1/2} = \frac{0.693}{k}$ $\quad$ ↳ 696 sec

THEN $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{696 \text{ sec}} = 9.96 \times 10^{-4}$ sec^{-1} $\quad$ k = 9.96×10^{-4} s^{-1}

8. Given the following reaction

$$\frac{1}{2}\ N_2O_{4(g)} \longrightarrow NO_{2(g)} \qquad \Delta H = 28.6 \text{ kJ}$$

at 30°C, $k = 5.1 \times 10^6\ s^{-1}$, and the activation energy is 54.0 kJ/mol. — OOPS...SHOULD BE JUST kJ

a) What is the **rate constant** of the same reaction at 45°C? FROM $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

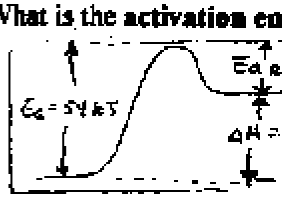
$\log k_2 = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \log k_1$

$\log k_2 = \frac{54000 \text{ J}}{(2.303)(8.31 \text{ J/mol K})}\left(\frac{1}{303K} - \frac{1}{318K}\right) + \log(5.1 \times 10^6)$ → SO $\log k_2 = 7.1468$

$k_2 = \text{ANTILOG}(7.1468)$

$k_2 = 1.40 \times 10^7\ sec^{-1}$

b) What is the **activation energy** for the reverse reaction?



$E_{a\,rev} = E_{a(forward)} - \Delta H = 54.0 \text{ kJ} - 28.6 \text{ kJ}$

$= 25.4$ kJ

9. A suggested mechanism for the decomposition of ozone is

$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ $\qquad$ (fast, equilibrium)

$O + O_3 \xrightarrow{k_2} 2O_2$ $\qquad$ (slow)

$k_1[O_3] = k_{-1}[O_2][O]$

SOLVING FOR [O] WE GET

$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$

write out a **rate law** that is consistent with this mechanism.

FROM THE RATE DETERM. STEP (RXN 2) WE GET

RATE $= k_2[O][O_3]$ BUT TO GET RID OF [O], WE SUBSTITUTE .... SO

RATE $= \frac{k_2 k_1 [O_3]^2}{k_{-1} [O_2]}$

OR

RATE $=$ "k" $[O_3]^2[O_2]^{-1}$

10. Briefly explain why the half-life of a second-order reaction increases as the reaction proceeds.

SINCE $t_{1/2} = \frac{1}{k[A_0]}$ AFTER ONE HALF LIFE HAS PASSED, YOU NOW HAVE LESS "A" TO USE AS YOUR NEW STARTING POINT FOR THE NEXT HALF-LIFE. AS "A" CONTINUES TO DECREASE, $t_{1/2}$ INCREASES

A CLOSE EXAMINATION SHOWS THAT THE SECOND HALF LIFE WOULD BE TWICE AS LONG AS THE FIRST .... THE THIRD HALF-LIFE WOULD BE FOUR TIMES AS LONG AS THE FIRST.... etc.