

Chapter 12 problems - Chemical Kinetics

①

30, 36, 37, 38, 39, 40, 42, 45, 46, 49, 50,
52, 61, 66, 67, 70, 72, 75, 79, 82, 86, 106, 117

30 - M/s or $M^{-1}sec^{-1}$ or $\frac{mol}{L \cdot sec}$

36 - (a) $-\frac{\Delta[H_2]}{\Delta t} = -3 \frac{\Delta[N_2]}{\Delta t}$. The rate that the H_2 is used up is 3X faster.

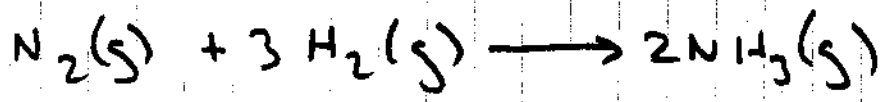
(b) $\frac{\Delta[NH_3]}{\Delta t} = -2 \frac{\Delta[N_2]}{\Delta t}$. The rate of formation of NH_3 is 2X faster.

37 - (a) $-\frac{\Delta[O_2]}{\Delta t} = -\frac{5}{4} \frac{\Delta[NH_3]}{\Delta t}$. The rate of consumption of O_2 is 1.25 X faster.

(b) $\frac{\Delta[NO]}{\Delta t} = -\frac{\Delta[NH_3]}{\Delta t}$. The rate of formation is equal to the rate of consumption of the ammonia.

$\frac{\Delta[H_2O]}{\Delta t} = -\frac{6}{4} \frac{\Delta[NH_3]}{\Delta t}$. The rate of formation of H_2O is 1.5X faster.

38-



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

39-

(a)
$$\frac{-\Delta[I^-]}{\Delta t} = -3 \frac{\Delta[S_2O_8^{2-}]}{\Delta t} = 3(1.5 \times 10^{-3} M/s) = 4.5 \times 10^{-3} M/s$$

(b)
$$\frac{\Delta[SO_4^{2-}]}{\Delta t} = -2 \frac{\Delta[S_2O_8^{2-}]}{\Delta t} = 2(1.5 \times 10^{-3} M/s) = 3.0 \times 10^{-3} M/s$$

40-

$$r = k [NO]^2 [Br_2]$$

The order w.r. respect to: [NO] is 2nd order
[Br₂] is 1st order
overall is 3rd order

42-

$$r = k [H_2] [Ice];$$
 + The units are $M^{-1} sec^{-1}$ for k.

45-

(3)

$$(a) \quad r = k [\text{Br}^-] [\text{BrO}_3^-] [\text{H}^+]^2$$

$$(b) \quad \text{The overall order is } 1 + 1 + 2 = 4^{\text{th}}$$

(c) Since the rxn. is 2nd order in H^+ , if $[\text{H}^+]$ conc. is tripled, the rate will increase by a factor of $3^2 = 9$.

(d) Since the rxn. is 1st order in both $[\text{Br}^-]$ & $[\text{BrO}_3^-]$ if both are cut in half, the rate will decrease by a factor of 4 ($1/2 \times 1/2$) = $1/4$

$$6 - \quad r = k [\text{CH}_3\text{COCH}_3]^x$$

$$7.8 \times 10^{-5} = k [9.0 \times 10^{-3}]^x \quad \textcircled{2}$$

$$5.2 \times 10^{-5} = k [6.0 \times 10^{-3}]^x \quad \textcircled{1}$$

$$1.5 = 1.5^x \quad \therefore x = 1 \quad \text{The rate law would be:}$$

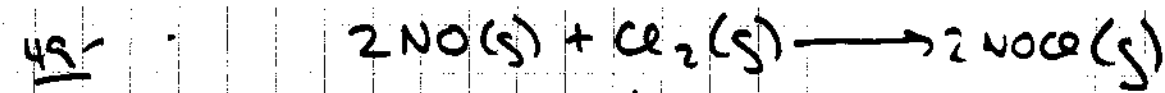
$$r = k [\text{CH}_3\text{COCH}_3]$$

(b) using ①

$$5.2 \times 10^{-5} \text{ M/s} = k [6.0 \times 10^{-3}]^1$$

$$k = 8.7 \times 10^{-3} \text{ sec}^{-1}$$

$$c) \quad r = (8.7 \times 10^{-3} \text{ sec}^{-1})(1.8 \times 10^{-3} \text{ M}) = 1.6 \times 10^{-5} \text{ M/s}$$



$$r = k [\text{NO}]^x [\text{Cl}_2]^y$$

to find NO order. $\textcircled{2}/\textcircled{1}$

$$\frac{4 \times 10^{-2}}{1 \times 10^{-2}} = \frac{k [0.26]^x [0.2]^y}{k [0.13]^x [0.2]^y}$$

$$4 = 2^x \therefore x = 2$$

now to find y (Cl_2) using $\textcircled{1}/\textcircled{3}$

$$\frac{1 \times 10^{-2}}{5 \times 10^{-3}} = \frac{k [0.13]^x (0.2)^y}{k [0.13]^x (0.1)^y}$$

$$2 = 2^y \therefore y = 1$$

$$r = k [\text{NO}]^2 [\text{Cl}_2]$$

$$\text{(5)} \quad \text{using } \textcircled{1} \quad 1.0 \times 10^{-2} \text{ M/sec} = k [0.13]^2 [0.20]$$

$$1.0 \times 10^{-2} \text{ M/sec} = k \cdot 0.00338 \text{ M}^3$$

$$k = \underline{3.0 \text{ M}^{-2} \text{ sec}^{-1}}$$

$$\text{(c)} \quad r \Rightarrow (3.0 \text{ M}^{-2} \text{ sec}^{-1}) (0.12 \text{ M})^2 (0.12 \text{ M}) =$$

$$5.2 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$$

50-

(5)

$$\ln \frac{[C_3H_6]}{[C_3H_6]_0} = -kt \quad ; \quad k = 6.7 \times 10^{-4} \text{ sec}^{-1}$$

(a) $t = 30 \text{ min} \rightarrow 1800 \text{ sec.}$

$$\ln [C_3H_6] = -kt + \ln [C_3H_6]_0 =$$

$$(-6.7 \times 10^{-4} \text{ sec}^{-1})(1800 \text{ sec}) + \ln(0.050) = -4.202$$

$$[C_3H_6] = e^{-4.202} = 0.015 \text{ M}$$

(b) $t = \frac{\ln [C_3H_6] / [C_3H_6]_0}{-k} = \frac{\ln \left(\frac{0.0100}{0.0500} \right)}{-(6.7 \times 10^{-4} \text{ sec}^{-1})} = 2402 \text{ sec}$

$$t = 2402 \text{ sec} \approx \underline{40 \text{ min}}$$

(c) $[C_3H_6]_0 = 0.050 \text{ M}$; if 25% C_3H_6 reacts then 75% is left.

$$[C_3H_6] = (0.75)(0.050) = 0.0375 \text{ M}$$

$$t = \frac{\ln [C_3H_6] / [C_3H_6]_0}{-k} = \frac{\ln (0.0375 / 0.050)}{-(6.7 \times 10^{-4} \text{ sec}^{-1})} = 429 \text{ sec or } 7.2 \text{ min}$$

S2-

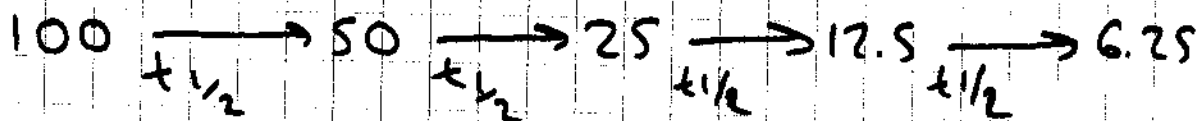
(c)

$$t_{1/2} = 0.693 / k = 0.693 / 6.7 \times 10^{-4} \text{ sec}^{-1} = 1034 \text{ sec or } 17 \text{ min}$$

$$t = \frac{\ln \left[\frac{[C_3H_6]}{[C_3H_6]_0} \right]}{-k} = \frac{\ln \left(\frac{0.0625}{0.0500} \right)}{-6.7 \times 10^{-4} \text{ sec}^{-1}} = 4140 \text{ sec.}$$

t = 4140 sec or 69 min.

This is 4 half-lives



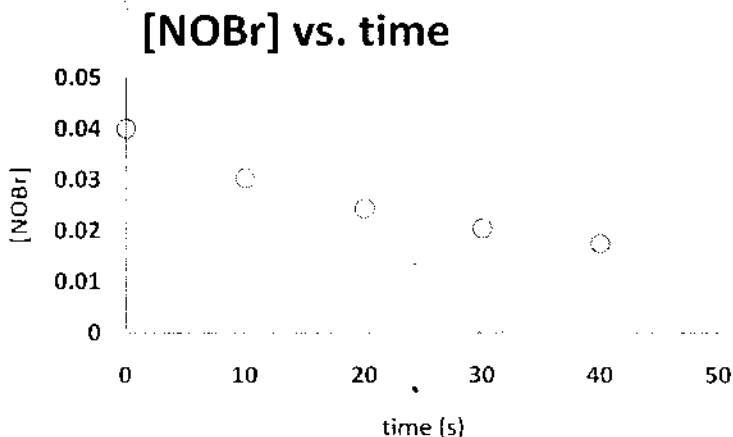
G1 The data needs to be graphed to answer this question.

time (s)	[NOBr]	ln [NOBr]	1/[NOBr]
0	0.04	-3.219	25
10	0.0303	-3.497	33.0033
20	0.0244	-3.713	40.98361
30	0.0204	-3.892	49.01961
40	0.0175	-4.046	57.14286

$$\ln [NOBr] = \ln [NOBr]_0 - kt \quad \text{1st order}$$

$$\frac{1}{[NOBr]} = \frac{1}{[NOBr]_0} + kt \quad \text{2nd order}$$

Since both of these integrated rate eqs. are linear, the data directly plotted does not provide info. to determine the order

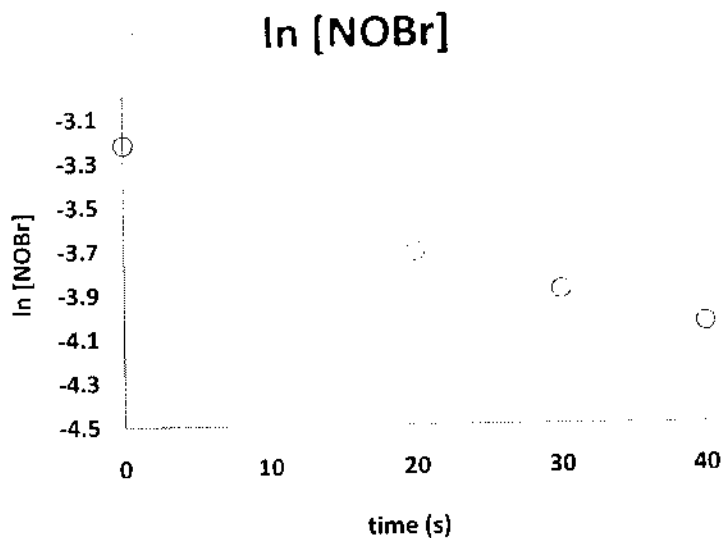


Non-linear

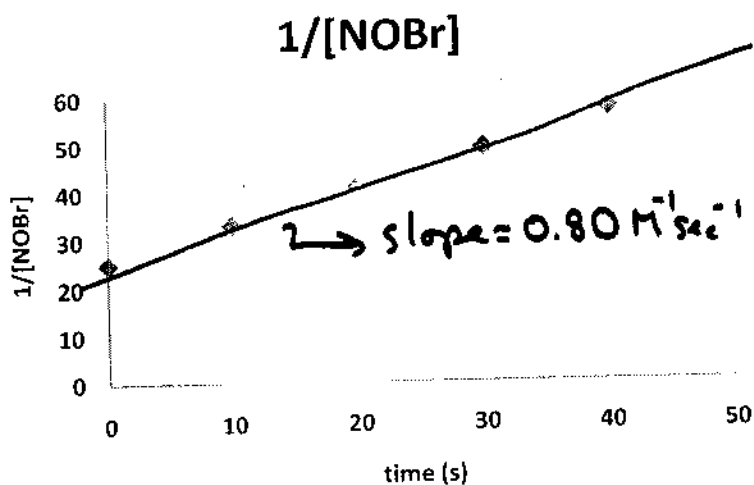
(NXT. PG)

Q1 - cont.

6a



If the order was 1st - then this plot of $\ln[\text{NOBr}]$ vs time would be linear
← BUT it is clear that the line is curved.
∴ NOT 1st order



This plot of $\frac{1}{[\text{NOBr}]}$ vs time is linear!
Therefore -
Order is 2nd

The slope of the line is the value of the k (the rate constant)

$$\text{since } \frac{1}{[\text{NOBr}]} = \frac{1}{[\text{NOBr}]_0} + kt$$

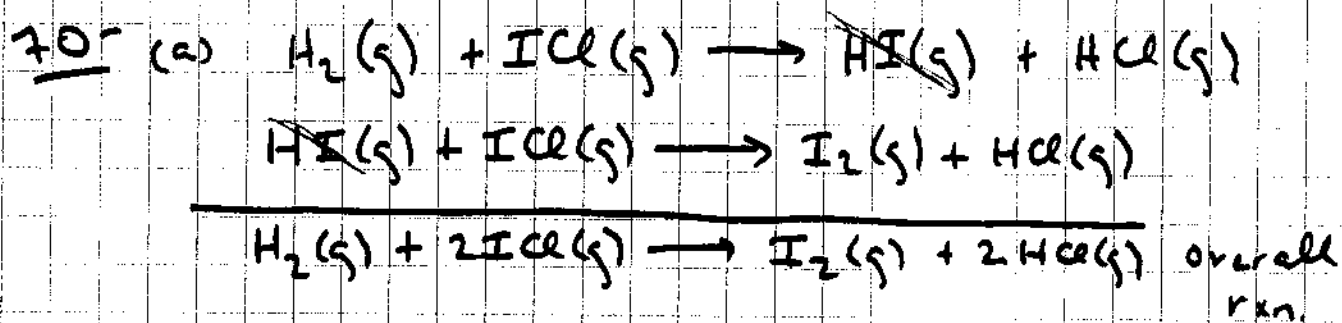
\uparrow \uparrow \uparrow

$$y = b + mx$$

66- An elementary rxn. is an individual molecular event that involves breaking + or making bonds. An overall rxn. describes only the stoichiometry of the overall process, but provides no info. about how the rxn. occurs. (7)

67. Molecularity is the number of reactant molecules or atoms for an elementary rxn.

Reaction order is the sum of the exponents of the conc. terms in the rate law.

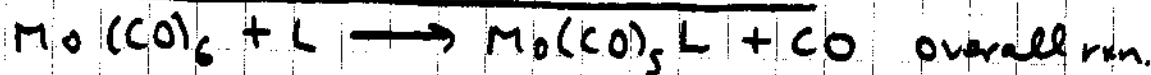
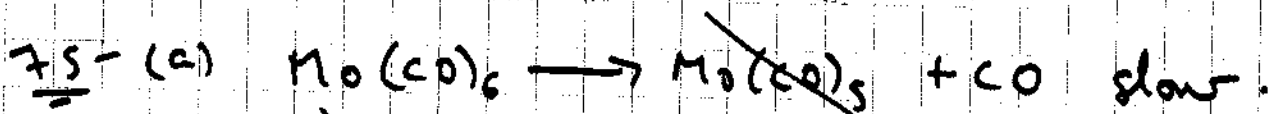


(b) Since $\text{HI}(\text{g})$ is produced in the first rxn. + used up in the second, it is a rxn. intermediate.

(c) Each elementary rxn is bimolecular, since they each involve 2 reactants.

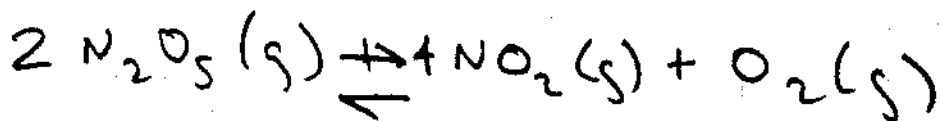
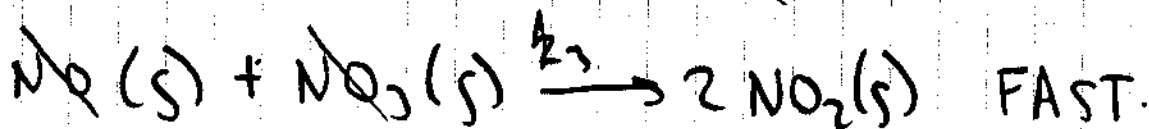
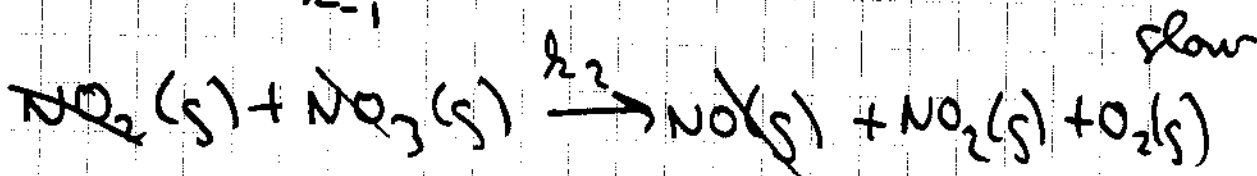
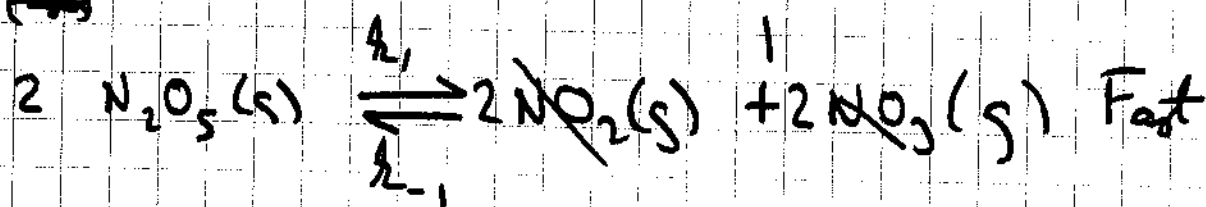
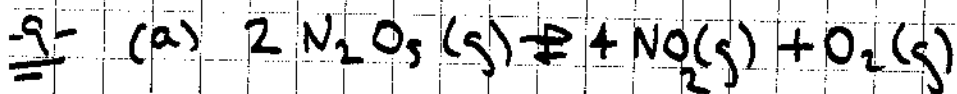
72-

- (a) bimolecular, $r = k[\text{O}_3][\text{Ce}]$
- (b) unimolecular, $r = k[\text{NO}_2]$
- (c) bimolecular, $r = k[\text{CeO}][\text{CO}]$
- (d) termolecular, $r = k[\text{Ce}]^2[\text{N}_2]$



(b) 1. unimolecular ; 2. bimolecular.

(c) $r = k[\text{Mo}(\text{CO})_6]$



(cont. N&T. PG)

Problem 79 cont.

(8a)

(b) An intermediate is formed in rxn 1. & used up in the next step.

NO_2 is an intermediate and a product.

NO_2 & NO are intermediates

$$(c) r_{\text{forward}} = k_1 [\text{N}_2\text{O}_5]$$

$$r_{\text{reverse}} = k_{-1} [\text{NO}_2][\text{NO}_3]$$

Because this example is equilibrium - Rate forward = Rate reverse

$$\therefore k_1 [\text{N}_2\text{O}_5] = k_{-1} [\text{NO}_2][\text{NO}_3]$$

$$\frac{k_1}{k_{-1}} [\text{N}_2\text{O}_5] = [\text{NO}_2][\text{NO}_3]$$

The rate law for the rate determining step is \Rightarrow

$$r = k_2 [\text{NO}_2][\text{NO}_3], \text{ so we can subs.}$$

for $[\text{NO}_2][\text{NO}_3]$

$$r = k_2 \frac{k_1}{k_{-1}} [\text{N}_2\text{O}_5]$$

$$(d) k = \frac{k_2 k_1}{k_{-1}}$$

82 - Graphing is again necessary to answer this question 9

If the rate constant for a particular rxn. is measured as a function of temperature, the activation energy may be determined.

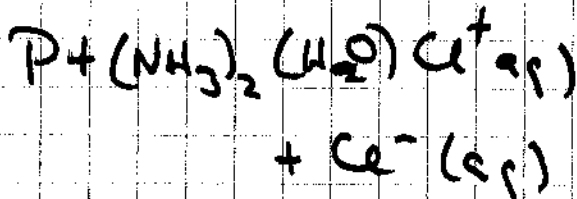
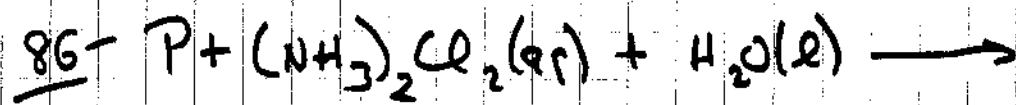
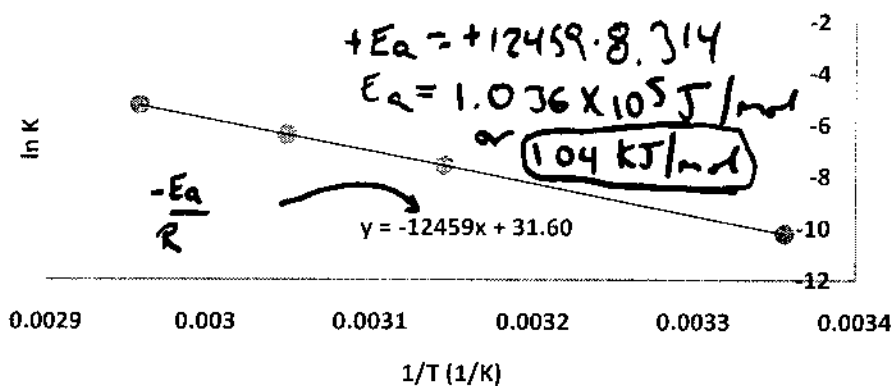
Temperature (K)	1/T	k (sec ⁻¹)	ln k
298	0.003355705	3.70E-05	-10.2046
318	0.003144654	5.10E-04	-7.5811
328	0.00304878	1.70E-03	-6.37713
338	0.00295858	5.20E-03	-5.2591

Since $k = A e^{-E_a/RT}$

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$

\uparrow \uparrow \uparrow
 $y = b - m \cdot x$

Arrhenius Plot



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

if $k_1 = 1.0 \text{ M}^{-1} \text{ sec}^{-1}$ 298K
 $k_2 = 15 \text{ M}^{-1} \text{ sec}^{-1}$ 323K

$$E_a = \frac{[\ln k_2 - \ln k_1] R}{\left(\frac{1}{T_2} - \frac{1}{T_1} \right)} = \frac{(\ln(15) - \ln(1)) 8.314 \text{ J/mol}}{\left(\frac{1}{323\text{K}} - \frac{1}{298\text{K}} \right)}$$

$= 87,000 \text{ J/mol}$ or 87 kJ/mol



$$r = k [\text{C}_2\text{H}_4\text{Br}_2]^x [\text{I}^-]^y$$

+ to find x; $\frac{(2)}{(1)}$

$$\frac{1.74 \times 10^{-4}}{6.45 \times 10^{-5}} = \frac{k (0.343)^x (0.102)^y}{k (0.127)^x (0.102)^y}$$

$$2.69 = 2.69^x ; x = 1.$$

+ for + to find y; $\frac{(3)}{(2)}$

$$\frac{1.26 \times 10^{-4}}{1.74 \times 10^{-4}} = \frac{k (0.203)^1 (0.125)^y}{k (0.343)^1 (0.102)^y}$$

$$0.724 = 0.59 (1.225)^y$$

$$0.724 = 0.724^y \therefore y = 1.$$

$$r = k [\text{C}_2\text{H}_4\text{Br}_2] [\text{I}^-]$$

b) using eq. (1) $\rightarrow 6.45 \times 10^{-5} \text{ M sec}^{-1} = k (0.127)(0.102)$

$$6.45 \times 10^{-5} \text{ M sec}^{-1} = k (0.012954)$$

$$k = 4.979 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$$

$$(c) r = (4.979 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}) (0.150)(0.150) = 1.12 \times 10^{-4} \text{ M/sec}$$

107-

(11)



Using the Provided Data - & the Arrhenius Eq.
The E_a (activation energy) can be determined.

$$r = k [\text{N}_2\text{O}_4] ; k = \frac{r}{[\text{N}_2\text{O}_4]}$$

$$\text{at } 25^\circ\text{C} \quad k_1 = \frac{5.0 \times 10^{-3} \text{ M/s}}{0.10 \text{ M}} = 5.0 \times 10^{-4} \text{ sec}^{-1}$$

$$\text{at } 40^\circ\text{C} \quad k_2 = \frac{2.3 \times 10^{-1} \text{ M/s}}{0.150 \text{ M}} = 1.5 \times 10^{-3} \text{ sec}^{-1}$$

$$25^\circ\text{C} = 298 \text{ K} ; 40^\circ\text{C} = 313 \text{ K}$$

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

$$E_a = \frac{(\ln(1.5 \times 10^{-3}) - \ln(5.0 \times 10^{-4})) (8.314 \text{ J/mol}\cdot\text{K})}{\left(\frac{1}{313} - \frac{1}{298}\right)} =$$

$$56,800 \text{ J/mol} \Rightarrow \underline{56.8 \text{ kJ/mol}}$$