

38, 39, 42, 45, 49, 50, 52, 59, 76, 78, 81, 85, 88, ~~110~~, ~~106~~, ~~107~~

38 - (a) $-\frac{\Delta[\text{H}_2]}{\Delta t} = -3 \frac{\Delta[\text{N}_2]}{\Delta t}$ The rate that H_2 is used up is 3X faster.

(b) $\frac{\Delta[\text{NH}_3]}{\Delta t} = -2 \frac{\Delta[\text{N}_2]}{\Delta t}$ The rate of formation of NH_3 is 2X faster.

39 -

(a) $-\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{5}{4} \frac{\Delta[\text{NH}_3]}{\Delta t}$ The rate of consumption of O_2 is 1.25 X faster.

(b) $\frac{\Delta[\text{NO}]}{\Delta t} = -\frac{\Delta[\text{NH}_3]}{\Delta t}$ The rate of formation is equal to the rate of consumption of the ammonia.

$\frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = \frac{6}{4} \frac{\Delta[\text{NH}_3]}{\Delta t}$ The rate of formation of H_2O is 1.5X faster.

42 -

$v = k[\text{H}_2][\text{I}_2]$; + The units are $\text{M}^{-1} \text{sec}^{-1}$ for k .

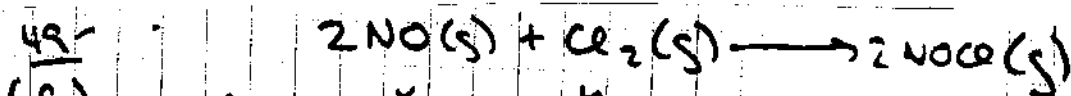
$$(c) \text{Rate} = k [\text{Br}^-] [\text{BrO}_3^-] [\text{H}^+]^2$$

(2)

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

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



(a) $\text{Rate} = k [\text{NO}]^x [\text{Cl}_2]^y$
to find NO order. (2)/(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 (1)/(3)

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

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

cont \rightarrow next pg.

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

(b) using ① $1.0 \times 10^{-2} \text{ M/sec} = k [0.13]^2 [0.20]$
 $1.0 \times 10^{-2} \text{ M/sec} = k \cdot 0.00338 \text{ M}^3$
 $k = \underline{3.0 \text{ M}^{-2} \text{ sec}^{-1}}$

(c) $r \Rightarrow (3.0 \text{ M}^{-2} \text{ sec}^{-1}) (0.12 \text{ M})^2 (0.12 \text{ M}) =$
 $5.2 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$

50-

$$\ln \frac{[\text{C}_3\text{H}_6]}{[\text{C}_3\text{H}_6]_0} = -kt \quad ; \quad k = 6.7 \times 10^{-4} \text{ sec}^{-1}$$

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

$$\ln [\text{C}_3\text{H}_6] = -kt + \ln [\text{C}_3\text{H}_6]_0 =$$

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

-4.202

$$[\text{C}_3\text{H}_6] = e^{-4.202} = 0.015 \text{ M}$$

(b) $t = \frac{\ln [\text{C}_3\text{H}_6] / [\text{C}_3\text{H}_6]_0}{-k} = \frac{\ln \left(\frac{0.0100}{0.0500} \right)}{-(6.7 \times 10^{-4} \text{ sec}^{-1})} = 2402 \text{ sec}$

cont. next pg.

50 cont. \Rightarrow

4

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

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

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

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

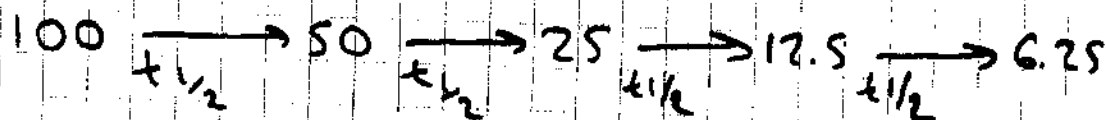
S2-

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

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

$$t = 4140 \text{ sec or } 69 \text{ min.}$$

This is 4 half-lives

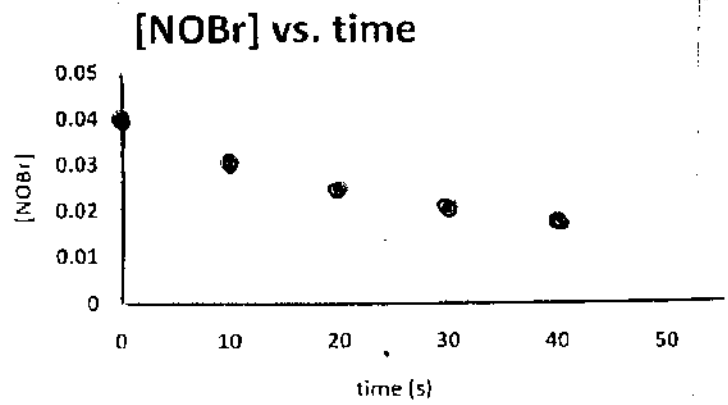


The data needs to be graphed to answer this question.

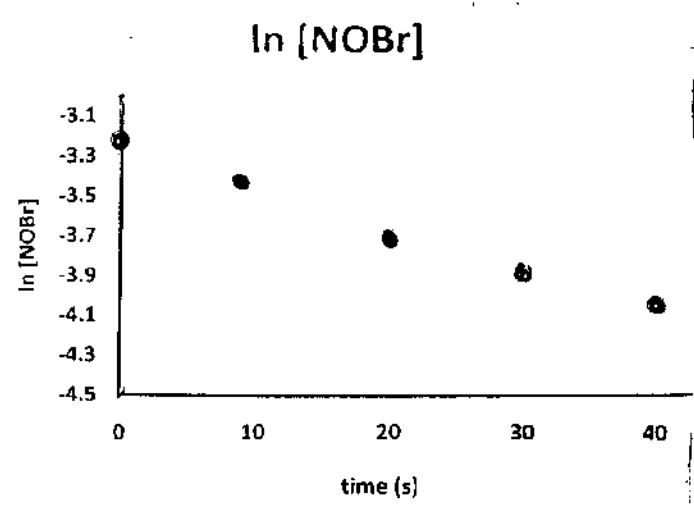
time (s)	[NOBr]	ln [NOBr]	1/[NOBr]
0	0.04	-3.219	25
10	0.0303	-3.497	33.0033
20	0.0244	-3.713	40.98361
30	0.0204	-3.892	49.01961
40	0.0175	-4.046	57.14286

$\ln[\text{NOBr}] = \ln[\text{NOBr}]_0 - kt$ 1st order
 $\frac{1}{[\text{NOBr}]} = \frac{1}{[\text{NOBr}]_0} + kt$ 2nd order.

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

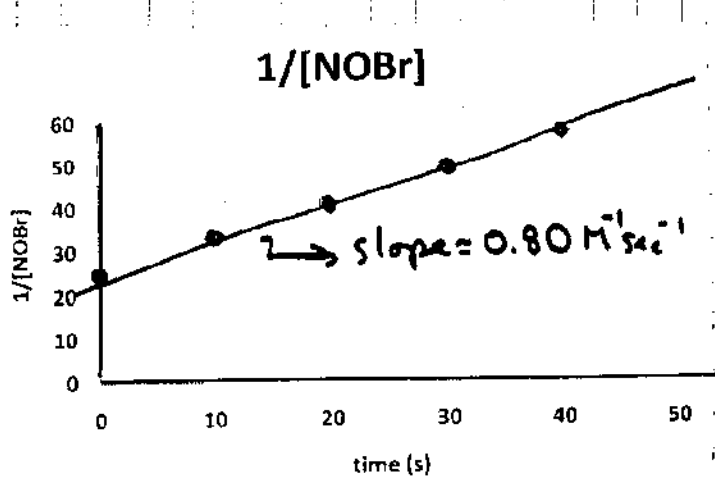


← Non-linear



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.
 \therefore NOT 1st order

Cont. Next Pg =>



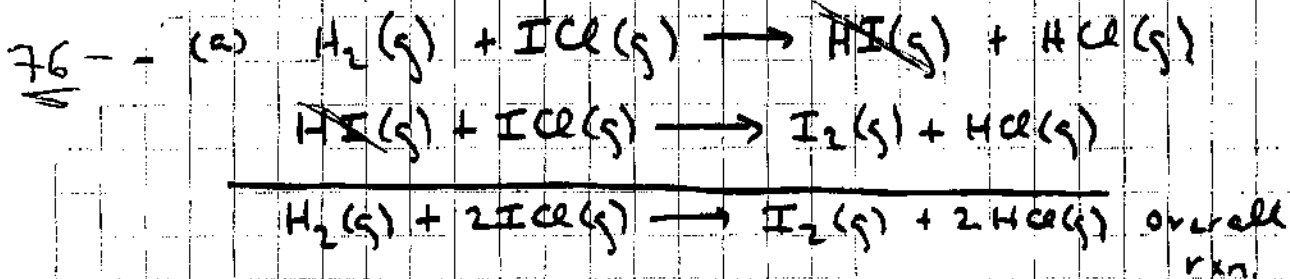
This plot of $\frac{1}{[\text{NOBr}]}$ vs time is linear! therefore -
Order is 2nd

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

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

\uparrow \uparrow \uparrow
 y b m x

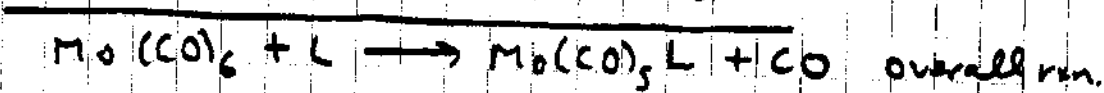
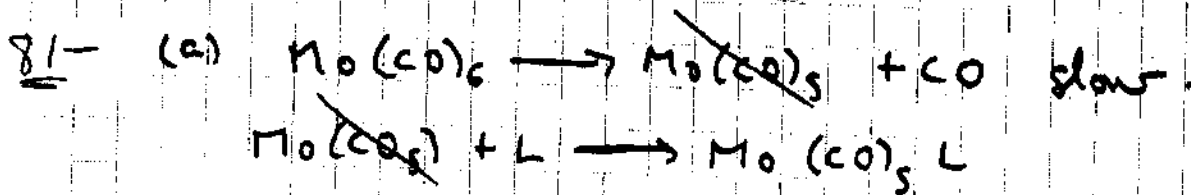
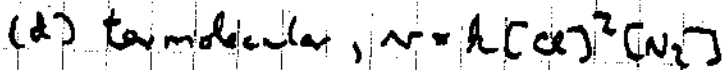
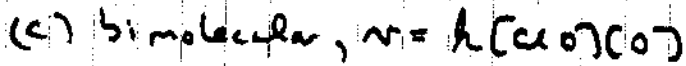
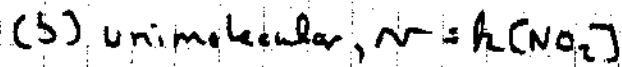
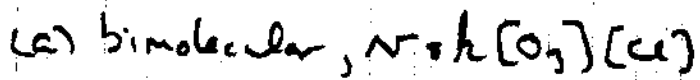
$y = b + mx$



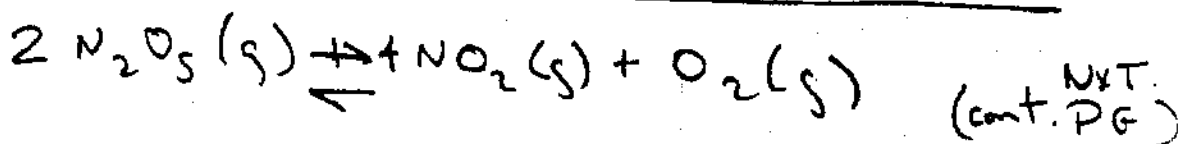
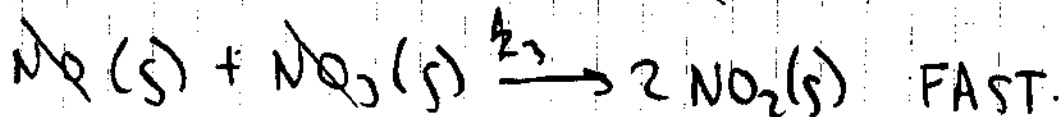
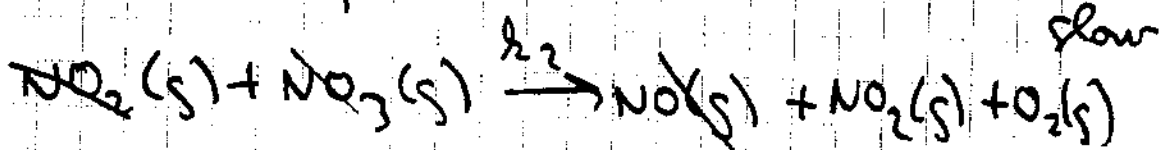
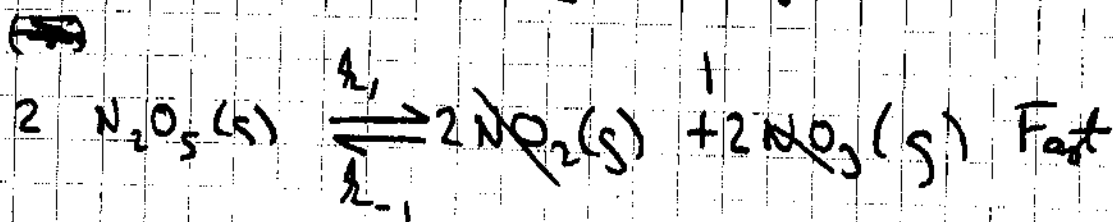
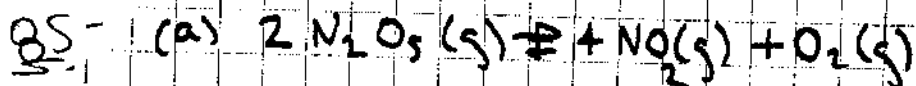
(b) Since $\text{HI}(\text{g})$ is produced in the first rxn. & used up in the second, it is a rxn. intermediate.

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

78-



(b) 1. unimolecular } 2. bimolecular



85 cont =>

8

(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

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

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

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

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

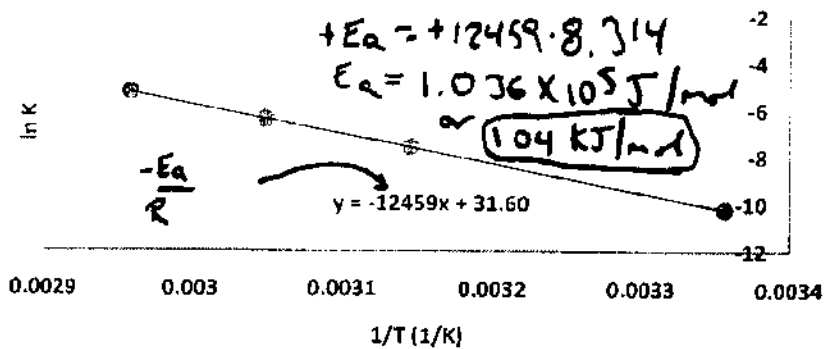
88- Graphing is again Necessary to answer this Question 9

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

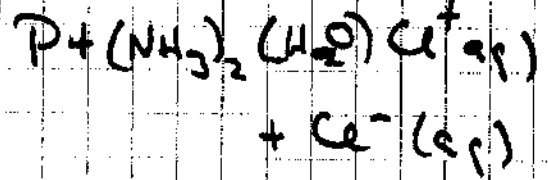
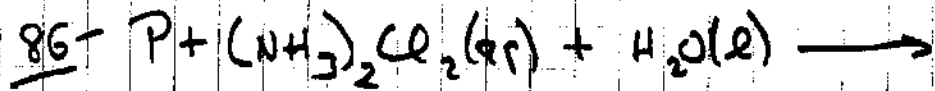
Since Δ Activ. Energy \rightarrow
 $k = Ae^{-E_a/RT}$

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

Arrhenius Plot



$\ln k = \ln A - \frac{E_a}{RT}$
 $\uparrow \quad \uparrow \quad \uparrow$
 $y = b - m \cdot x$



$\ln \left(\frac{k_2}{k_1} \right) = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ if $k_1 = 1.0 M^{-1} sec^{-1}$ 298K
 $k_2 = 15 M^{-1} sec^{-1}$ 323K

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

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



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

+ o find x ; $\textcircled{2}/\textcircled{1}$

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

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

+ find y ; $\textcircled{3}/\textcircled{2}$

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

$$0.724 = 0.59 \cdot 1.225^y$$

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

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

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

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

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

$$\textcircled{11} \quad r = (4.979 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}) (0.150)(0.150) = 1.12 \times 10^{-4} \text{ M/sec}$$