Ch. 16 ~~7~~, ~~11~~, ~~15~~, ~~17~~, ~~24~~, ~~35~~, (37), ~~38~~, ~~41~~, ~~43~~, ~~44~~, ~~52~~, ~~62~~, ~~64~~, ~~73~~, ~~78~~, ~~76~~, ~~82~~, ~~86~~, ~~88~~, ~~92~~, ~~95~~, ~~98~~, ~~100~~, 103a, ~~110~~, ~~112~~, ~~116~~, 125

④ G + S (large) vs (small)   * more surface area = more rxn sites = faster reaction

⑪ ⓐ average rate = $\dfrac{[c]_0 - [c]_{end}}{\Delta t_{entire\ rxn}}$ (neg of slope = rate)

ⓑ rate at x = slope of tangent line at x ← (neg of slope = rate)

ⓒ initial rate = slope of tangent line at time = 0

ⓓ would values be different if plotted [D]
   ↳ signs would be opposite = no need to take neg of sl

⑮ $D \rightarrow \dfrac{3}{2}E + \dfrac{5}{2}F$

rate = $-\dfrac{[D]}{\Delta t} = +\dfrac{\partial[E]}{3\,\Delta t} = +\dfrac{\partial[F]}{5\,\Delta t}$

[E] increasing at 0.25 mol/L·s , how fast is [F] increasing

$\dfrac{2(0.25)}{3} = \dfrac{\partial[F]}{5}$

[F] = 0.417 mol/L·s

⑰ $2D + 3E + F \rightarrow 2G + H$

$\dfrac{-1[D]}{2\Delta t} = \dfrac{-1[E]}{3\,\Delta t} = \dfrac{-1[F]}{1\,\Delta t} = +\dfrac{1[G]}{2\Delta t} = +\dfrac{1[H]}{\Delta t}$

$\dfrac{0.1}{2} = [H]$ [H] = 0.05 mol/L·s

(24) $A_2 (g) + B_2 (g) \rightarrow 2 AB (g)$

(a) graph $[A_2]$ vs time, take neg slope of tangent at time $= \emptyset$ to obtain initial rate

(b) reaction order — run series of exp. & use method of initial rates to determine order w/ respect to A & to B

(c) rate constant — once you know rate law, use [values] of A & B to determine rate constant

(35) to determine order of A

$$\frac{Exp\ 2}{Exp\ 1} \qquad \frac{1.25 \times 10^{-2}}{6.25 \times 10^{-3}} = \left(\frac{0.1}{0.05}\right)^m \qquad 2 = 2^m \qquad \text{1st order w/ A}$$
$$m = 1$$

to determine order of B

$$\frac{Exp\ 3}{Exp\ 2} \qquad \frac{5 \times 10^{-2}}{1.25 \times 10^{-2}} = \left(\frac{0.1}{0.05}\right)^n \qquad 4 = 2^n \qquad \text{2nd order w/ B}$$
$$n = 2$$

to determine order of C

$$\frac{Exp\ 4}{Exp\ 1} \qquad \frac{6.25 \times 10^{-3}}{6.25 \times 10^{-3}} = \left(\frac{0.02}{0.01}\right)^x \qquad 1 = 2^x \qquad \emptyset \text{ order w/ C}$$
$$x = \emptyset$$

<u>rate law</u> $rate = k [A][B]^2$

rate constant using Exp #1

$$\frac{mol/L \cdot s}{(mol/L)^3}$$

$$6.25 \times 10^{-3} = k (0.05)(0.05)^2$$
$$k = 50.0 \, L^2/mol^2 \cdot s$$

(37) what is overall order given following rate constants

(a) $k = \dfrac{mol}{L \cdot s}$

$rate = k[A]$

$mol/L \cdot s = mol/L \cdot s \, [mol/L)$

$\downarrow$ same units
as rate so $\emptyset$ order

1st order

$k = L/mol \cdot s$

(b) $k = yr^{-1}$

if rate measured in years instead of second

$mol//L \cdot yr = \dfrac{1}{yr} \cdot \dfrac{mol}{L}$ solve for K $k = yr^{-1}$

$rate = k[A]$

so 1st order

(c) $k = \left(\dfrac{mol}{L}\right)^{1/2} s^{-1}$

$\dfrac{mol}{L \cdot s} = \dfrac{\left(\dfrac{mol}{L}\right)^{1/2} s^{-1} \left(\dfrac{mol}{L}\right)^{x}}{\left(\dfrac{mol}{L}\right)^{1/2} s^{-1} = \left(\dfrac{mol}{L}\right)^{x}}$

$\tfrac{1}{2}$ order

(d) $k = \left(\dfrac{mol}{L}\right)^{-5/2} \cdot min^{-1}$

answer $\dfrac{7}{2}$ order

☆ C + D not likely on the test

(38) $CO_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)}$

determine order of CO

$$\frac{Exp\ 2}{Exp\ 1} = \frac{1.33 \times 10^{-30}}{1.29 \times 10^{-29}} = \left(\frac{0.1}{1}\right)^m \qquad 0.10 = 0.1^m \qquad \text{1st order}$$
$$m = 1 \qquad \text{in CO}$$

determine order of Cl_2

$$\frac{Exp\ 4}{Exp\ 3} \qquad \frac{1.32 \times 10^{-31}}{1.30 \times 10^{-29}} = \left(\frac{0.01}{1}\right)^n \qquad 0.01 = 0.01^n \qquad \text{1st order}$$
$$n = 1 \qquad \text{in } Cl_2$$

rate law: rate $= k\,[CO]\,[Cl_2]$

average value of k

Exp #1 $1.29 \times 10^{-29} = k\,(1)(0.1)$
$$K = 1.29 \times 10^{-28}\ L/mol \cdot s$$

Exp #2 $1.33 \times 10^{-30} = k\,(0.1)(0.1)$
$$k = 1.33 \times 10^{-28}\ L/mol \cdot s$$

Exp #3 $1.30 \times 10^{-29} = k\,(0.1)(1)$
$$k = 1.3 \times 10^{-28}\ L/mol \cdot s$$

Exp #4 $1.32 \times 10^{-31} = k\,(0.1)(0.01)$
$$k = 1.32 \times 10^{-28}\ L/mol \cdot s$$

$$\boxed{\text{average } k = 1.31 \times 10^{-28}\ L/mol \cdot s}$$

(41) $AB \rightarrow A + B$ rate $= k [AB]^2$ $k = 0.2$ L/mol·s
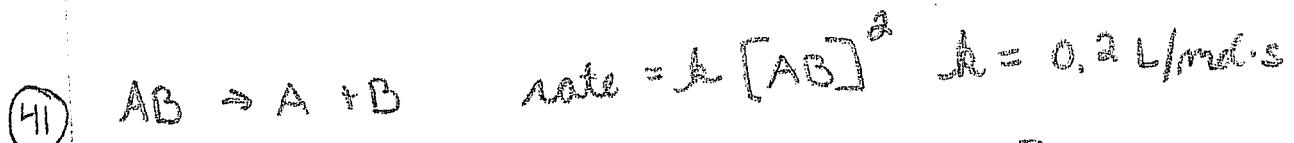
How long for $[AB]$ to reach $\frac{1}{3}$ of $[AB]_0$ of $1.50 M$?

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{0.5} = 0.2(t) + \frac{1}{1.50}$$

$$t = 6.67 s$$

(43) 1st order, 50% decomposes in 10.5 min
 (a) What is rate constant? $t_{1/2} = \frac{\ln 2}{k}$ $10.5 = \frac{\ln 2}{k}$ $k = 0.066$
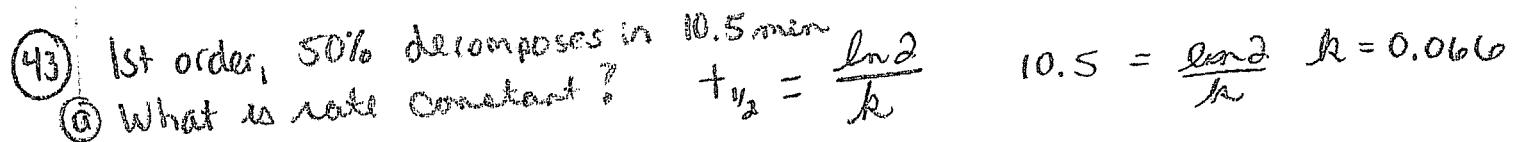
(b) time for 75% to decompose? 21 minutes

✓ 1st order

(44) decomposition reaction $k = 0.0012$ yr^{-1} $\frac{mol}{L \cdot yr} = \frac{1}{yr} \frac{mol}{L}$
 (a) What is half life?
    First order based on units of k so $\frac{1}{2}$ life is $= \frac{\ln 2}{k}$
 $$t_{1/2} = \frac{0.693}{0.0012} = 577.6 \text{ yr.}$$
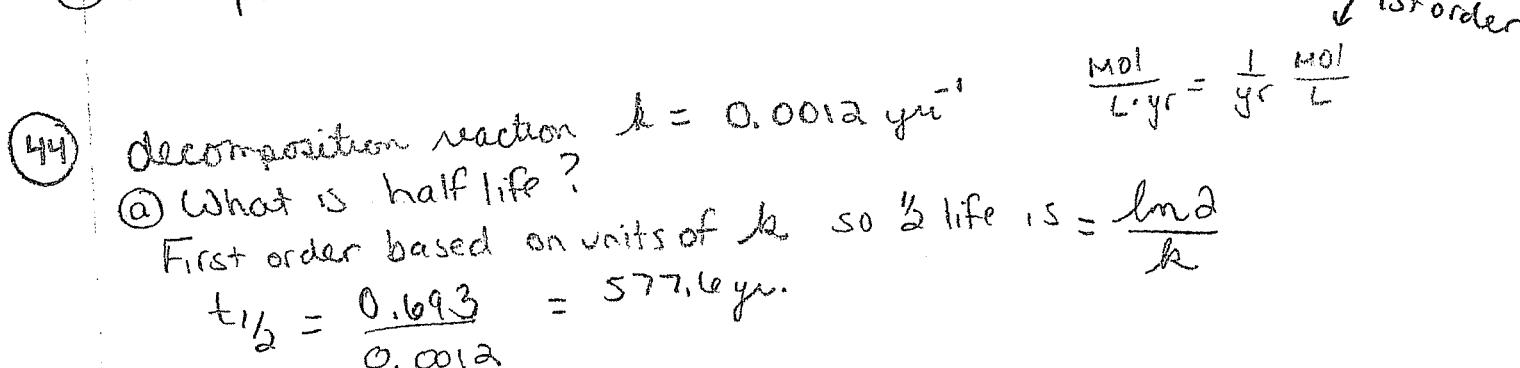
(b) How long to get to 12.5% of original value?
    $100 \searrow t$
    $50 \searrow t$ 3 $\frac{1}{2}$ lives $577.6(3) = 1.73 \times 10^3$ yrs.
    $25 \searrow t$
    12.5

(52) (a) E_a what happens to rate if we ↑T then rate ↑

(b) If ↓E_a ↑rate of reaction, easier to get over energy hill

(62) $A_2 + B_2 \rightarrow 2AB$ $E_{a\,for} = 125\,KJ/MOl$

$E_{a\,rev} = 85\,KJ/MOl$

$125 - 85 = 40$

$\Delta H_{rxn} = 40\,KJ/MOl$

2AB

$A_2 + B_2$ 125

(64) $NO + Cl_2 \rightarrow NOCl + Cl$ $\Delta H = 83\,KJ$ $E_{a\,for} = 86\,KJ/MOl$

NOCl + Cl

$E_{a\,rev} = 3\,KJ/MOl$

NO + Cl₂   86 KJ   83 KJ ΔH

(c) do not have to do this

(73)

$ClO^- + \cancel{H_2O} \rightleftharpoons \cancel{HClO} + \cancel{OH^-}$ fast

$I^- + HClO \rightarrow \cancel{H_2O} + Cl^-$ slow

$\cancel{OH^-} + \cancel{H_2O} \rightleftharpoons \cancel{H_2O} + IO^-$ fast

(a) Overall rxn $ClO^- + I^- \rightarrow Cl^- + IO^-$

(b) intermediates $HClO, OH^-, HIO$

(c) bimolecular $rate = k\,[ClO^-][H_2O]$

bimolecular $rate = k\,[I^-][HClO]$

bimolecular $rate = k\,[OH^-][HIO]$
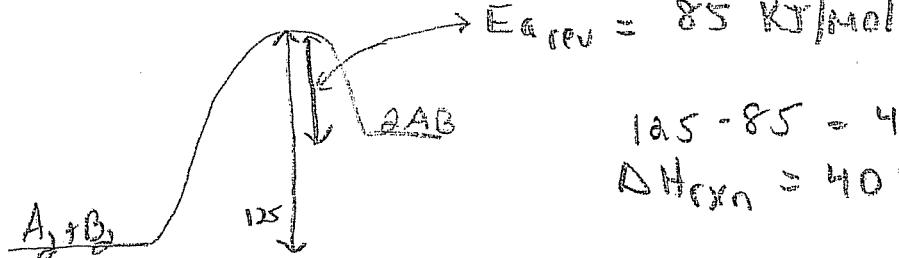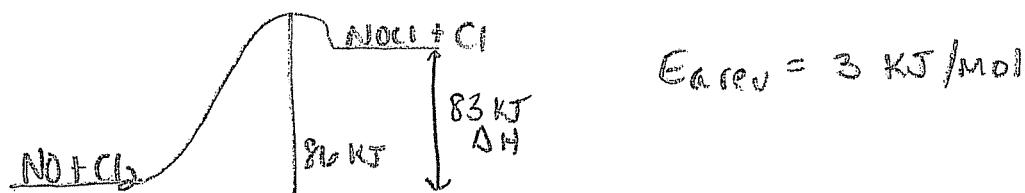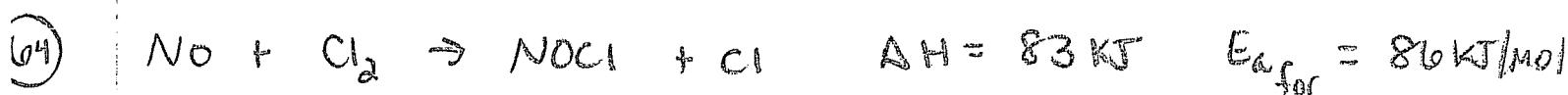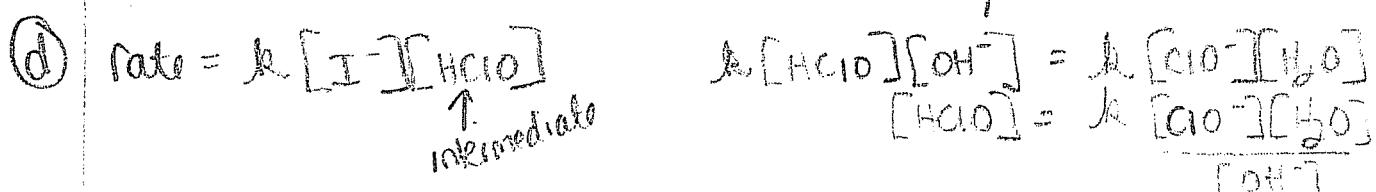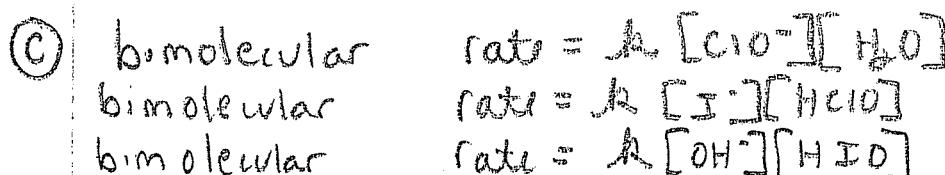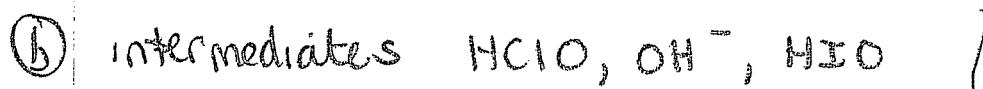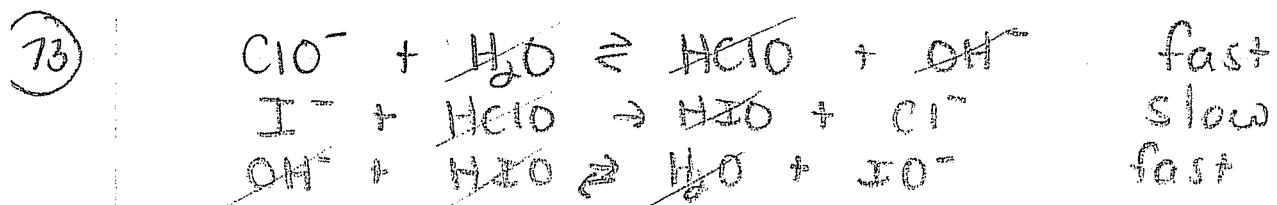
(d) $rate = k\,[I^-][HClO]$
               ↑
          intermediate

$k\,[HClO][OH^-] = k\,[ClO^-][H_2O]$

$[HClO] = k\,\dfrac{[ClO^-][H_2O]}{[OH^-]}$

$$\text{rate} = k\,[I^-][HClO]$$

$$\text{rate} = k\,\frac{[I^-][ClO^-][H_2O]}{[OH^-]}$$

does not match proposed rate law

(15) $2\,NO + O_2 \rightarrow 2\,NO_2$

$$\text{rate} = k\,[NO]^2[O_2]$$

from pg. 709

I $NO + O_2 \rightleftharpoons NO_3$ fast
II $NO_3 + NO \rightarrow 2\,NO_2$ slow
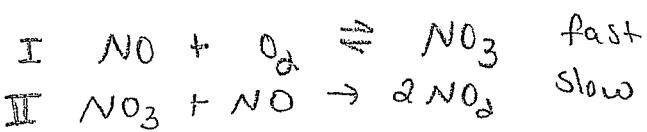
$$\text{rate} = k\,[NO_3][NO]$$
$$\frac{k\,[NO][O_2]}{k} = \frac{k\,[NO_3]}{k}$$
$$[NO_3] = [NO][O_2]$$

$$\text{rate} = k\,[NO]^2[O_2]$$
possible Mechanism

also bimol.

I⁻ $2\,NO + O_2 \rightarrow 2\,NO_2$

$$\text{rate} = k\,[NO]^2[O_2]$$

possible mechanism
termolecular

All 4 Mechanisms can work

I $2\,NO \rightleftharpoons N_2O_2$ fast
II $N_2O_2 + O_2 \rightleftharpoons 2\,NO_2$ slow

disfavored because 3 molecules
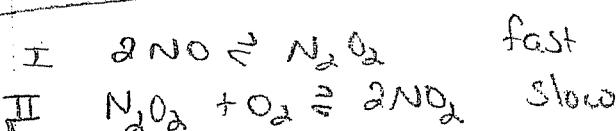
$$\text{rate} = k\,[N_2O_2][O_2]$$

$$\frac{k\,[NO]^2}{k} = \frac{k\,[N_2O_2]}{k}$$
$$[N_2O_2] = k\,[NO]^2$$

$$\text{rate} = k\,[NO]^2[O_2]$$

possible Mechanism
bimolecular

I $2\,NO \rightleftharpoons N_2 + O_2$ fast
II $N_2 + 2\,O_2 \rightarrow 2\,NO_2$ slow
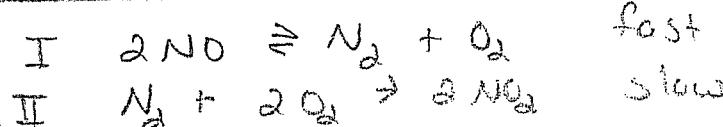
$$\text{rate} = k\,[N_2][O_2]^2$$

$$\frac{k\,[NO]^2}{k\,[O_2]} = \frac{k\,[N_2][O_2]}{k\,[O_2]}$$

$$\text{rate} = k\,\frac{[NO]^2[O_2]^2}{[O_2]}$$

$$\text{rate} = k\,[NO]^2[O_2]$$ termolecular
possible mechanism

(76) $N_2O \rightarrow N_2 + \frac{1}{2}O_2$

(a) Au is a heterogeneous catalyst (solid)

(b)

uncatalyzed
w/ catalyst

or

uncatalyzed
catalyzed

depends on ΔH of rxn

(82)
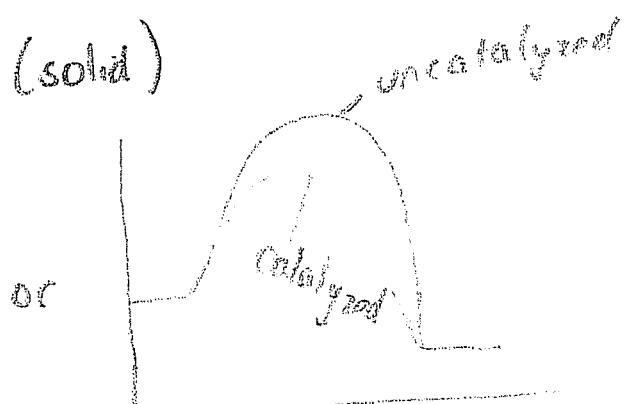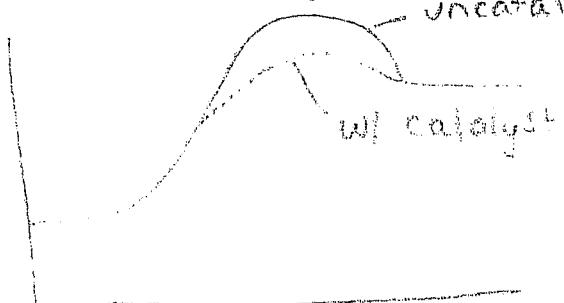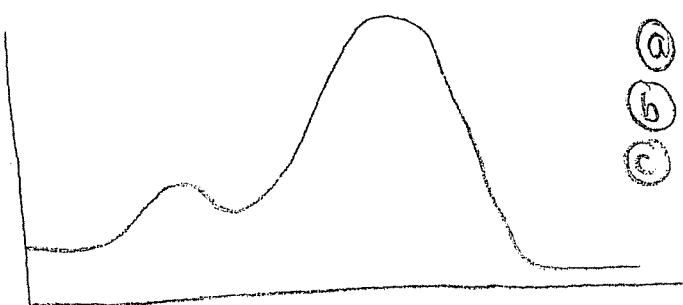
(a) Two elementary steps
(b) Step 2 is rate limiting
(c) over $= \Delta H = \ominus$ exothermic

* higher hill = rate limiting

(83) overall $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + H^+ + Br^-$
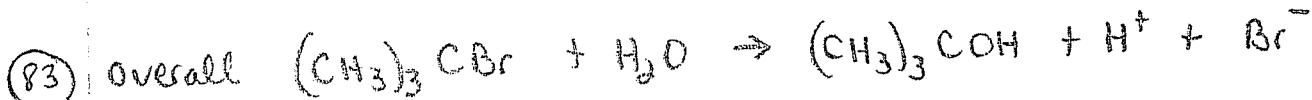
exp. rate law $\quad$ rate $= k\left[(CH_3)_3CBr\right]$

rate from accepted mechanism $\quad$ rate $= k\left[(CH_3)_3CBr\right]$

(a) no H_2O, only acts as solvent
(b) step #1 $\quad$ rate $= k\left[(CH_3)_3CBr\right]$
   step #2 $\quad$ rate $= k\left[(CH_3)_3C^+\right]$
   step #3 $\quad$ rate $= k\left[(CH_3)_3C-OH_2^+\right]$

(c) reaction intermediates $(CH_3)_3C^+$ and $(CH_3)_3C-OH_2^+$

(d) rate law from slow step $\quad$ rate $= k\left[(CH_3)_3CBr\right]$ matches exp rate law

(88) $2A + 2B + C \rightarrow D + 3E$
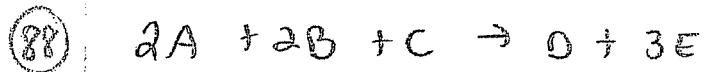
order of A

$$\frac{Exp\ 2}{Exp\ 1} \qquad \frac{9.6 \times 10^{-5}}{6.0 \times 10^{-6}} = \left(\frac{0.096}{0.024}\right)^x \qquad 16 = 4^x \quad x = 2 \quad \text{2nd order in } A$$

order of B

$$\frac{Exp\ 4}{Exp\ 2} \qquad \frac{1.5 \times 10^{-6}}{9.6 \times 10^{-5}} = \left(\frac{0.012}{0.096}\right)^2 \left(\frac{0.170}{0.085}\right)^x \qquad \text{Zero order in } B$$

$$0.0156 = 0.0156 \,(2)^x$$
$$1 = 2^x$$
$$X = 0$$

order of C

$$\frac{Exp\ 4}{Exp\ 3} \qquad \frac{1.5 \times 10^{-6}}{1.5 \times 10^{-5}} = \left(\frac{0.012}{0.024}\right)^2 \left(\frac{0.170}{0.034}\right)^0 \left(\frac{0.032}{0.080}\right)^x \qquad \text{1st order in } C$$

$$0.1 = 0.25\,(1)(0.4)^x$$
$$0.4 = 0.4^x$$
$$X = 1$$

ⓐ/ⓒ rate $= k[A]^2[C]$

ⓑ k using Exp #1 $6.0 \times 10^{-6} = k\,(0.024)^2(0.032)$
$$k = 0.33 \; L^2/{M^2 \cdot S}$$

ⓓ $\dfrac{-1[A]}{2\,\Delta t} = \dfrac{-1[B]}{2\,\Delta t} = \dfrac{-[C]}{\Delta t} = \dfrac{+[D]}{\Delta t} = \dfrac{+1[E]}{3\,\Delta t}$

(92) $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

$rate = k[CHCl_3][Cl_2]^{1/2}$

using mechanism
$rate = k[Cl][CHCl_3]$

↑
rxn
intermediate

$\sqrt{k[Cl_2]} = \sqrt{k[Cl]^2}$

$[Cl_2]^{1/2} = [Cl]$ and substitute in for $[Cl]$

So $rate = k[Cl_2]^{1/2}[CHCl_3]$

(95) $A + B \rightarrow AB$ $rate = 0.20 \, mol/L \cdot s$ $[A]_0 = [B]_0 = 1.0 \, mol/L$

$rate = k[A]^2[B]$ what is rate when $[A]_0 = 2.0 \, mol/L$

$[B]_0 = 3.0 \, mol/L$
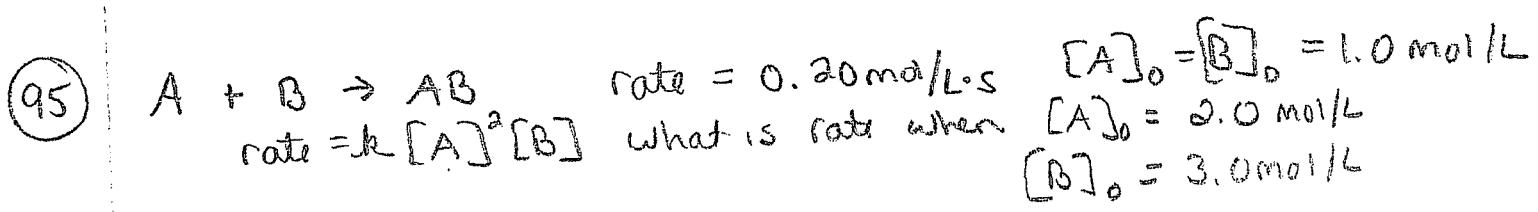
solve for k first

$0.20 = k(1)^2(1)$

$0.20 = k$

$rate = 0.20(2)^2(3)$

$rate = 2.4 \, mol/L \cdot s$

98 (a) False – same average KE
(b) False – less pressure = less collisions = slower rate
(c) true
(d) false – depends on E_a (biological catalysts degrade w/ heat)
(e) False – need correct orientation
(f) false – E_a depends on mechanism of rxn
(g) false – typically decreases
(h) false – depends on mechanism
(i) false – lowers E_a
(j) false – Kinetics are not related to thermodynamics
(k) false – temp is part of frequency factor ✷ do not need to calc.
(l) true
(m) false ΔH does not change w/ E_a
(n) true single atoms easy to orient for rxn
(o) true
(p) false no relationship between molecularity and rate
(q) false not related

(100) $H_2 + I_2 \rightarrow 2HI$ rate $= k[H_2][I_2]$

from slow step   rate $= k[H_2I][I]$
↑ intermediate   ↓ intermediate

from fast step $k[H_2][I] = k[H_2I]$
so replacing $[H_2I]$

   rate $= k[H_2][I]^2$

from other fast step $k[I_2] = k[I]^2$
so replacing $[I]$
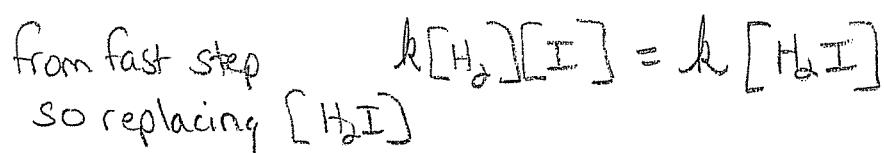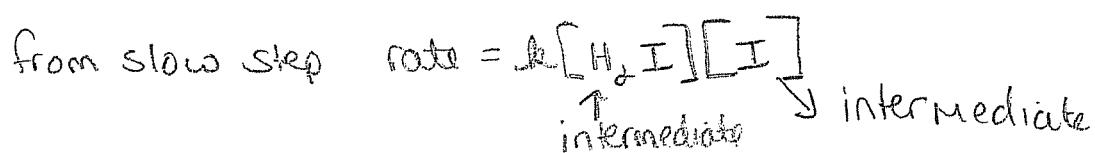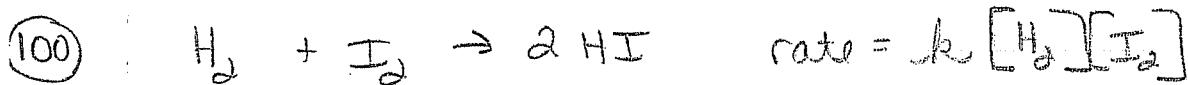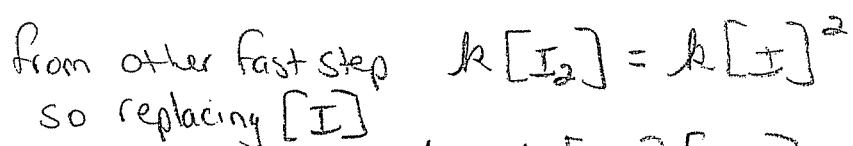
   rate $= k[H_2][I_2]$ which is consistent
w/ rate law

(103a) 1st order decomposition

@ 2 tablets   0.60g
   after 30min reach max [ ] = 2 mg/100mL
   ½ life is 90min
   what is [ ] after 2.5hr after max concentration

$$t_{1/2} = \frac{\ln 2}{k}$$

first order

$$\ln [A]_t = -k\,t + \ln [A]_0$$

$$90 = \frac{\ln 2}{k}$$

$$\ln(x) = -0.0077(150) + \ln(2/100)$$

$$\ln(x) = -1.155 + (-3.912)$$

$$\ln x = -5.067$$

$$90k = 0.693$$

$$x = 0.0063 \text{mg} = \boxed{0.63 \text{mg}/100\text{mL}}$$

$$k = 0.0077$$

$$\frac{}{1\text{mL}}$$

---

(110) $2 N_2O_5 \rightarrow 4 NO_2 + O_2$ rate $= k[N_2O_5]$

I   rate $= k[N_2O_5]^2$ not valid
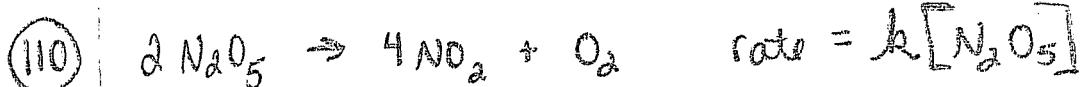
II   rate $= k[N_2O_5]^2$ not valid

III rate $= [NO_2][N_2O_5]$
                intermediate
     $k[N_2O_5] = k[NO_3][NO_2]$
     so... $\boxed{[NO_2]}$ $\boxed{[NO_3]}$
     rate $= k\,[N_2O_5]\dfrac{[N_2O_5]}{[NO_3]}$

        not valid

IV   rate $= k[N_2O_3][O]$

$$k[N_2O_5]^2 = k[NO_2]^2[N_2O_3][O]^3$$

$$\text{rate} = \frac{k[N_2O_5]^2}{[NO_2]^2[O]^2}$$

does not match

V   rate $= k[N_2O_5]^2$

     does not match

(13) $CS_2 \rightarrow C + S$

determine order CS_2

$$\frac{2.2 \times 10^{-7}}{2.7 \times 10^{-7}} = \left(\frac{0.08}{0.1}\right)^x$$

$0.815 = 0.8^x$ $x = 1$ first order   rate $= k[CS_2]$

calculate
average k

$2.7 \times 10^{-7} = k(0.1)$
$k = 2.7 \times 10^{-6}$

$2.2 \times 10^{-7} = k(0.08)$
$k = 2.75 \times 10^{-6}$

$1.5 \times 10^{-7} = k(0.055)$
$k = 2.73 \times 10^{-6}$

$1.2 \times 10^{-7} = k(0.044)$
$k = 2.73 \times 10^{-6}$

$$\boxed{\text{average } k = 2.73 \times 10^{-6} \, s^{-1}}$$

$mol/L \cdot s = k (mol/L)$

(116) cyclopropene → propene   1st order

$\boxed{@ \; t_{1/2} = 30 \text{ minutes}}$

$t = 0$ 12 molecules
$t = 20$ 8 molecules
$t = 60$ 3 molecules

1 half life ⟨ 12 cyclo
             6
2nd half life ⟨ 3

$$t_{1/2} = \frac{0.693}{k}$$

$$30 = \frac{0.693}{k}$$

$$k = 0.0231 \, min^{-1}$$

(125)   acetone → methane + Ketene   @ 600°C
                                       $k = 8.7 \times 10^{-3} s^{-1}$

@ what is half-life
$$t_{1/2} = \frac{0.693}{8.7 \times 10^{-3}}$$
$$t_{1/2} = 79.7 s$$

(b) how long for 40% of sample to decompose?
    integrated rate law 1st order reaction
    $$\ln[A]_t = -kt + \ln[A]_0$$

100
50 → ? 40%
25

$$\ln \frac{[A]_0}{[A]_t} = kt$$

$$\boxed{t = 58.7 s}$$

either form of integrated rate law works

or $\ln[A]_t = -kt + \ln[A]_0$
$$\ln(60) = -8.7 \times 10^{-3}(t) + \ln(100)$$
$$4.09 = -8.7 \times 10^{-3}(t) + 4.61$$
$$\boxed{t = 59.8 s}$$

Ⓒ 90% decompaed

$$\ln\left(\frac{100}{10}\right) = 8.7 \times 10^{-3}(t)$$

$$\boxed{t = 264.7s}$$