Key to Unit 8.2 Practice Problems

Worksheet – Integrated Rate Laws

The dependence of the rate of a chemical reaction on the concentration of the reactants is given by the **rate law** and takes the form:

$$\textbf{rate} = k[A]^a[B]^b[C]^c$$

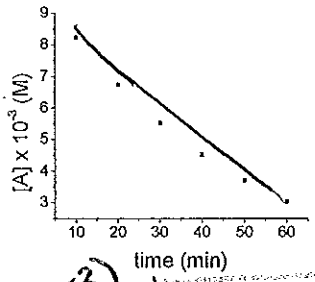
where the exponents, a,b,c, , may be zero, integers or fractions.
The sum of the exponents (a+b+c+) is the **order** of the reaction.
The expressions for the change in concentration with time are differential equations which, in some cases, can be integrated to give a different, but related, form of the rate equation. These are summarized below:

order	differential rate law	integrated rate law	½ time
zero	rate = k	$[A] = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$
first	rate = k[A]	$\ln [A] = -kt + \ln[A]_0$	$t_{1/2} = \ln 2/k$
second	rate = $k[A]^2$	$1/[A] = kt + 1/[A]_0$	$t_{1/2} = 1/k[A]_0$
or	rate = k[A][B] as long as $[A]_0 = [B]_0$ and they react in a 1:1 ratio		

These are all **linear equations** of the form y = mx +b. Graphs of [A], ln[A] or 1/[A] (y) vs time (x) will give a **straight line** when the reactions are zero, 1st or 2nd order, respectively. There are no analytical solutions for other rate laws.

1. For the reaction 2A → 2B + C, the following data were collected.

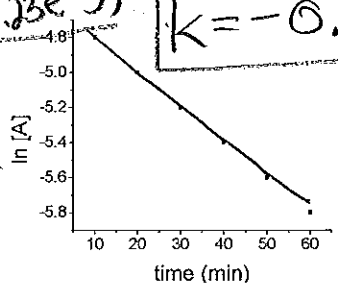
[A] (M)	t (min)
8.23×10^{-3}	10
6.74×10^{-3}	20
5.52×10^{-3}	30
4.52×10^{-3}	40
3.70×10^{-3}	50
3.03×10^{-3}	60



a. Determine the rate law Rate = k[A]

b. Calculate k for this reaction

$\ln[A] - \ln[A_0] = -kt$ $= -\dfrac{(\ln(3.03\epsilon{-3}) - \ln(8.23\epsilon{-3}))}{60-10}$ $k = -0.01998\ s^{-1}$



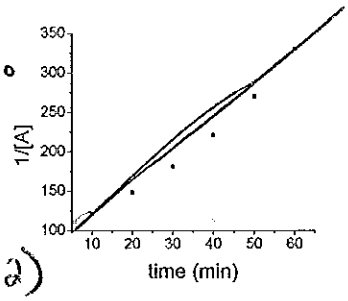
c. Calculate the half-time for this reaction

$t_{1/2} = \dfrac{0.693}{-0.01998} = 34.8$ min

d. Calculate $[A]_0$

$\ln(8.23\epsilon{-3}) = (-1.99\epsilon{-2})(10) + \ln[A]_0$

$\ln[A_0] = -4.60$ $[A_0] = 1.0\epsilon{-2}$ M



e. Calculate [A] after 70 minutes

$\ln[A_t] = (-1.99\epsilon{-2})(70) + \ln(1.0\epsilon{-2})$

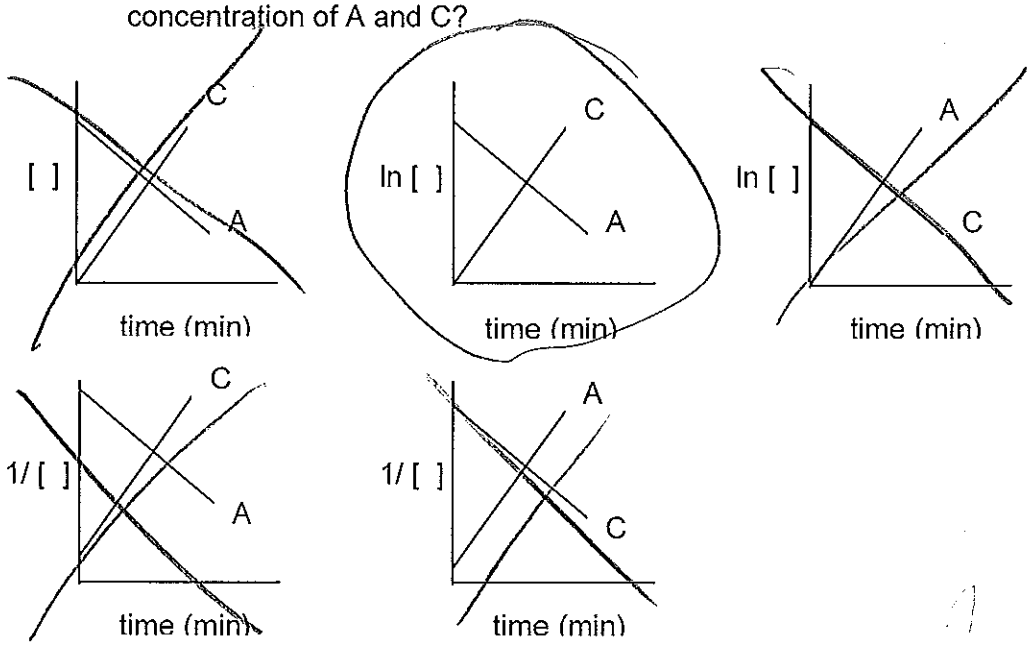
$[A] = 248\epsilon{-3}$ M

2. The reaction A → B + C is first order in A. When $[A]_0$ = 0.10 M, the reaction is 20% complete in 40.0 minutes. 100% − 20% = 80% .1 × .8 = 0.08 M

a. Calculate the rate constant, k, for this reaction, with the correct units.

$\ln(0.08) = -k(40) + \ln(.10)$ $k = 5.58E{-}3\ min^{-1}$

b. Which of the following plots best describes the changes in concentration of A and C?



3. For the reaction A → product, the first two half-times are 10 minutes and 20 minutes respectively. At the beginning of the reaction, [A] was 0.10M.

a. What is the rate law for this reaction?

b. What is the [A] at t = 80 min?

4. The half-life for ^{40}K is 1.3×10^9 years. What percent of the original remains after 3.9×10^9 years? Radioactive decay is a first order process.

$t_{1/2} = 1.3E9\ yr = \frac{0.693}{k}$ $k = 5.3E{-}10\ 1/yr$

$\ln[A]_t = -kt + \ln[A]_0$

$= -5.3E{-}10\ 1/yr\ (3.9E9\ yr) + \ln(1.0)$

$\ln[A]_t = -2.1$ $[A] = 0.127$ $0.127 \times 100\% = 12.7\%$

e^x

113.1%

More complex reactions can be studied by using **pseudo order** kinetics. The rate of reactions falls as the concentration of the reacting species fall. If all but one of the reacting species are present in **excess**, the rate of the reaction will depend solely on the changing concentration of the limiting reactant.

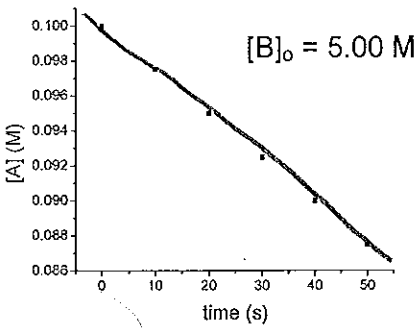
For example the reaction A + B → C can be run with $[A]_0$=0.1 M and $[B]_0$=10 M.

rate = $k[A]^a [B]^b$ but since [B] doesn't really change, this becomes

rate = $k'[A]^a$ where $k' = k[B]$

The results can then be analyzed using the integrated rate laws. Then the [B] is changed, but is still present in excess. The effect of this change will give the order of the reaction with respect to B.

[B] = 5.00 M		[B] = 10.00 M	
time (s)	**[A]**	**time (s)**	**[A]**
0	0.1000	0	0.1000
10	0.0975	10	0.0900
20	0.0950	20	0.0800
30	0.0925	30	0.0700
40	0.0900	40	0.0600
50	0.0875	50	0.0500



a. What is the order with respect to A? zero order

b. What is $[B]_{50}$ in each experiment?

5.00 − 0.0875 = 4.91 M 10 − 0.05 = 9.95 M

c. What is the apparent rate constant, k', with $[B]_0$ = 5.00 M?

d. What is the apparent rate constant, k' with $[B]_0$ = 10.00 M?

e. What is the order of the reaction with respect to B?

$$\frac{k'_{10.00}}{k'_{5.00}} = \frac{[10.00]^b}{[5.00]^b}$$

f. What is the rate law, including a value of k with units?

Worksheet – Reaction Mechanisms

The sequence of **elementary steps** that leads to the formation of products is called the **reaction mechanism**. There are three types of elementary steps:

unimolecular	A → product	rate = k[A]
bimolecular	A+A or A+B → product	rate = k[A]^2 or k[A][B]
termolecular	A+A+A or A+A+B→ product	rate = k[A]^3 or k[A]^2[B] etc.

These describe literally what is happening at the atomic scale.
The **sum** of the elementary steps must give the **overall balanced equation**.
They must also explain the experimentally determined **rate law**. The **slowest step** in the reaction mechanism will determine the overall rate of the reaction and is called the **rate determining step**.

1. The kinetics of the reaction: $2X + Y \rightarrow Z$ was studied and the results are:

Expt	$[X]_0$ (M)	$[Y]_0$(M)	Initial rate (M/s)
1	0.20	0.10	7.0×10^{-4}
2	0.20	0.20	1.4×10^{-3}
3	0.40	0.20	1.4×10^{-3}
4	0.60	0.60	4.2×10^{-3}

a. Deduce the rate law including the value of k with units

[Y] $\frac{.1}{.2} = \frac{1}{2}$ $\frac{7.0e^{-4}}{1.4e^{-3}} = \frac{1}{2}$

[X] $\frac{.2}{.4} = \frac{1}{2}$ $\frac{1.4e^{-3}}{1.4e^{-3}} = \frac{1}{1}$

$R = k[Y]$

$7.0e^{-4} = k\,[0.1]$

$k = 0.007\ 1/s$

b. The following 3 mechanism have been proposed. The species M and N are called *intermediates,* they are formed in early steps and consumed in later steps. What is the overall reaction for each mechanism? What is the molecularity of each step? What is the rate law derived from each? Which mechanism is consistent with the rate law from part a?

Mechanism I

$X + Y \rightarrow M$ (slow) – bimolecular
$X + M \rightarrow Z$ (fast) – bimolecular

$2X + Y \rightarrow Z$

$R = k[X][Y]$

Mechanism II

$Y \rightarrow M$ (slow) – unimolecular
$X + M \rightarrow Z$ (fast) – bimolecular

$X + Y \rightarrow Z$

$R = k[Y]$

Mechanism III

$Y \rightarrow M$ (slow) – uni
$M + X \rightarrow N$ (fast) – bi
$N + X \rightarrow Z$ (fast) – bi

$Y + 2X \rightarrow Z$

correct Stoichiometry

$Rate = k[Y]$

correct rate

There are often **equilibrium steps** in mechanisms. We will usually assume that they are not rate limiting. The concentration of the species involved can be determined by setting up the equilibrium expression:

$K = [product]^p / [reactant]^r$ so that, for example, $[reactant]^r = K\,[product]^p$

2. Given the following mechanism:

step 1 $2\,NO \leftrightarrows N_2O_2$
step 2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)
step 3 $N_2O + H_2 \rightarrow N_2 + H_2O$

$2NO + N_2O_2 + H_2 + N_2O + H_2$
$\downarrow$
$N_2O_2 + N_2O + H_2O$
$+ N_2 + H_2O$

a. Determine the overall reaction.

$2NO + 2H_2 \rightarrow 2H_2O + N_2$

b. Are there any intermediates in this reaction mechanism?

Yes → N_2O_2, N_2O

c. Determine the rate law. Intermediates **may not** appear in rate laws. Use the equilibrium expression to write the rate law only in terms of [reactants].

d. What is the overall order of the reactions?

e. What is the molecularity of the rate determining step?

$N_2O_2 + H_2 \rightarrow N_2O + H_2O$

bimolecular

Another common component of reaction mechanisms is a **catalyst**. These are compounds that change the reaction mechanism and provide a pathway with a lower activation energy, and correspondingly faster reaction rate. They are a **reactant** in an early step in the mechanism and a **product** in a later step. They do not appear in the overall reaction, but do appear in the rate law.

3. A reaction occurs by the following mechanism.

step 1 $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$
step 2 $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$
step 3 $Tl^{+} + Mn^{4+} \rightarrow Tl^{3+} + Mn^{2+}$

a) Write the overall reaction

$2Ce^{4+} + Tl^{+} \rightarrow 2Ce^{3+} + Tl^{3+}$

b. Identify each of the components as a reactant, product, intermediate or catalyst:

Mn^{2+} = catalyst
Mn^{3+} = intermediate
Ce^{4+} = reactant
Ce^{3+} = product
Mn^{4+} = intermediate
Tl^{+} = reactant
Tl^{3+} = product

c. Assuming that the catalyst is involved in the rate determining step, what is the rate law for this reaction?

d. Why is the **uncatalyzed** reaction so slow? (Hint: look at the molecularity)

4. Under certain conditions, the reaction:

$$2\ NO + Cl_2 \rightarrow 2\ NOCl$$

is found to be second order in NO and first order in Cl_2.

Given the following mechanism,

step 1 $NO + Cl_2 \leftrightarrows NOCl_2$
step 2 $NOCl_2 + NO \rightarrow 2\ NOCl$

what are the relative rates of the two elementary steps under these conditions?

5. The rate of the reaction shown below was studied:

$2\ NO + H_2 \rightarrow N_2O + H_2O$

It was found that the rate doubled when the $[H_2]$ was doubled. It was also found that the rate increased by a factor of four when the NO concentration was doubled. Which of the following mechanisms is/are consistent with these data?

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

X *step 1* $NO + H_2 \rightarrow N + H_2O$ (slow) $rate = k[NO][H_2]$
step 2 $N + NO \rightarrow N_2O$

step 1 $NO + NO \leftrightarrows N_2O_2$
step 2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)

$2NO + H_2 \Rightarrow N_2O + H_2O$

$Rate = k[N_2O_2][H_2]$

$\downarrow$

$Rate\ [NO]^2[H_2]$

step 1 $H_2 \leftrightarrows 2\ H$
step 2 $H + 2\ NO \rightarrow N_2O + OH$ (slow)
step 3 $OH + H \rightarrow H_2O$

$H_2 + 2NO \Rightarrow$

step 1 $NO + NO \rightarrow NO_2 + N$ (slow)
step 2 $NO_2 + H_2 \rightarrow NO + H_2O$
step 3 $N + NO \rightarrow N_2O$

Chemistry 12
Worksheet 1-3 - Reaction Mechanisms

1. It is known that compounds called ***chlorofluorocarbons*** (C.F.C.s) (eg. $CFCl_3$) will break up in the presence of ultraviolet radiation, such as found in the upper atmosphere, forming single chlorine atoms:

$$CFCl_3 \rightarrow CFCl_2 + Cl$$

The Cl atoms then react with Ozone (O_3) as outlined in the following mechanism.

Step 1: $Cl + O_3 \rightarrow ClO + O_2$

Step 2: $ClO + O \rightarrow Cl + O_2$ *(single "O" atoms occur naturally in the atmosphere.)*

a) Write the equation for the ***overall reaction***. (Using steps 1 and 2)

$O_3 + O \rightarrow 2O_2$

b) What is the ***catalyst*** in this reaction? Cl

c) Identify an ***intermediate*** in this reaction ClO

d) Explain how a *small* amount of chlorofluorocarbons can destroy a *large* amount of ozone.

When a Cl "destroys" O_3 (step 1), it is "regenerated" in step 2 to "destroy" more

e) What breaks the bond in the $CFCl_3$ and releases the free Cl atom?

a photon of UV radiation

2. Given the following mechanism, answer the questions below:

Step 1: $O_3 + NO \rightarrow NO_2 + O_2$ (slow)

Step 2: $NO_2 + O \rightarrow NO + O_2$ (fast)

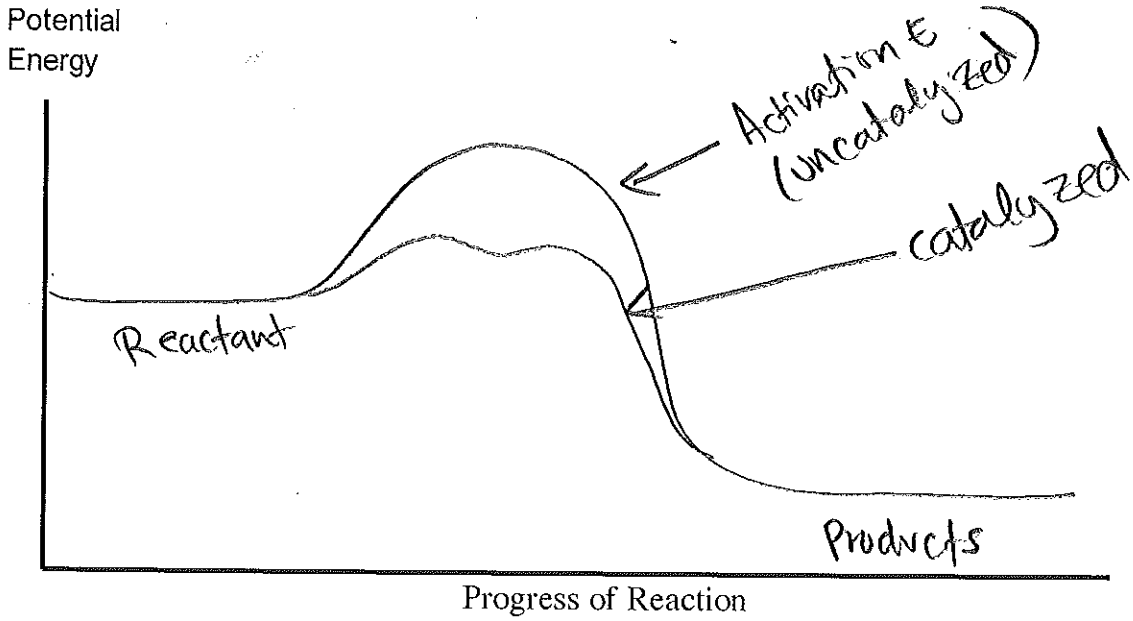
a) Give the equation for the ***overall reaction***.

$O_3 + O \rightarrow 2O_2$

b) What could the ***catalyst*** be in this mechanism? NO

c) What is an ***intermediate*** in this mechanism? NO_2

d) Given that the **uncatalyzed** overall reaction is a ***slow exothermic*** reaction, draw a *potential energy graph* which shows the possible shape of the curve for the ***uncatalyzed*** reaction. On the same graph, show a possible curve for the ***catalyzed*** reaction.



3. Consider the following mechanism:

Step 1: $H_2O_2 + \cancel{I^-} \rightarrow H_2O + \cancel{IO^-}$ *(slow)*

Step 2: $H_2O_2 + \cancel{IO^-} \rightarrow H_2O + O_2 + \cancel{I^-}$ *(fast)*

a) Give the equation for the overall reaction.

$2H_2O_2 \rightarrow 2H_2O + 1O_2$

b) What acts as a ***catalyst*** in this mechanism? I^-

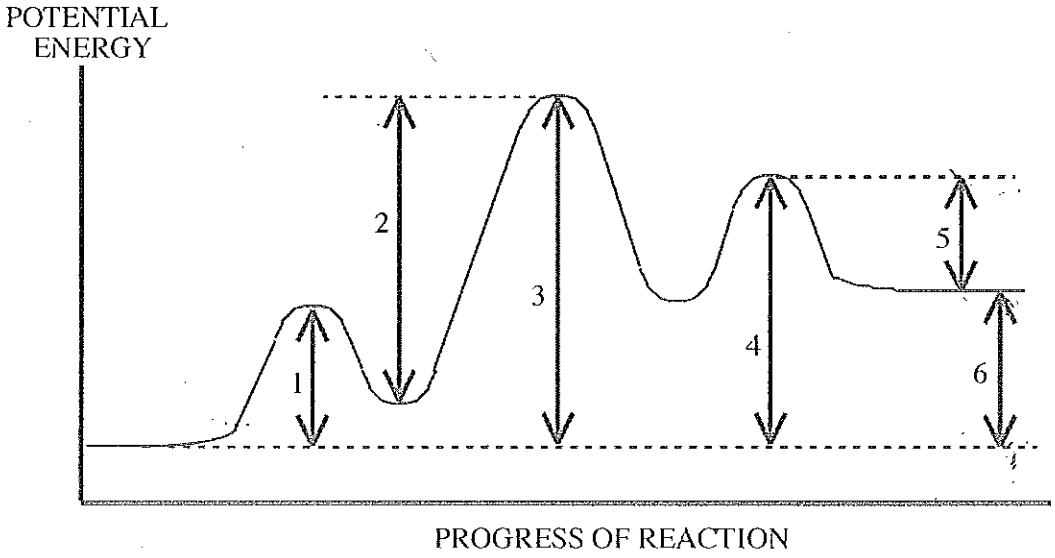
c) What acts as an ***intermediate*** in this mechanism? IO^-

4. What is meant by the ***rate determining step*** in a reaction mechanism? The slowest step

5. What is meant by a ***reaction mechanism***? Shows a series of steps (elementary processes) for a rxn

6. How are reaction mechanisms determined? experimentally

7. Given the following *Potential Energy Diagram* for a 3 step reaction, answer the questions below it:



a) Which arrow indicates the *activation energy* for the *first* step of the reverse reaction? 5

b) Which arrow indicates the *activation energy* for the *first* step of the forward reaction? 1

c) Which arrow indicates the *activation energy* for the *second* step of the forward reaction? 2

d) Which arrow indicates the *enthalpy change* (ΔH) *or* "*enthalpy change*" for the *overall* **forward** reaction? 6

e) Which arrow indicates the *enthalpy change* (ΔH) *or* "*enthalpy change*" for the *overall* **reverse** reaction? 6

f) Which arrow indicates the *activation energy* for the ***overall*** forward reaction? 3

g) Which step would be the ***rate determining step*** in the *forward* reaction? 2

h) In a dashed line or another colour sketch a possible curve that would represent the route for the ***uncatalyzed overall reaction***. Label this on the graph.

8. Given the reaction:

$$4HBr + O_2 \rightarrow 2H_2O + 2Br_2$$

a) Would you expect this reaction to take place in a single step? _____

Why or why not? _____

b) This reaction is thought to take place by means of the following mechanism:

Step 1: $HBr + O_2 \rightarrow HOOBr$ (slow)

Step 2: $HBr + HOOBr \rightarrow 2HOBr$ (fast)

Step 3: $2HBr + 2HOBr \rightarrow 2H_2O + 2Br_2$ (fast)

c) Identify the two ***intermediates*** HOOBr and 2NOBr

d) A catalyst is discovered which increases the rate of *Step 3*. How will this affect the rate of the *overall reaction*? no effect

Explain your answer. slowest step has already happened

e) A catalyst is discovered which increases the rate of *Step 1*. How will this affect the rate of the *overall reaction*? it will increase the rate

Explain your answer. when you speed up proces, the whole process speeds up

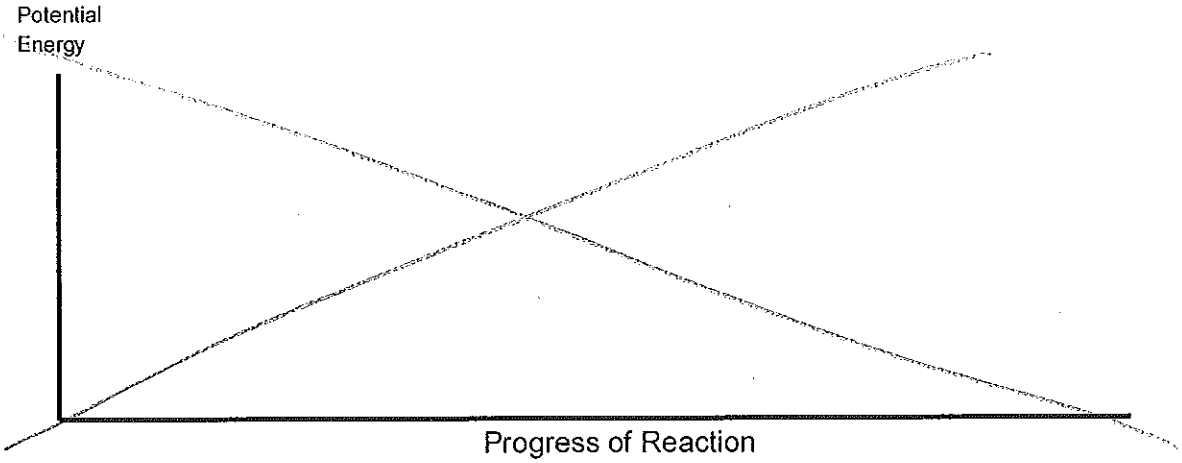
f) Which step has the greatest ***activation energy***? Step 1

g) How many "bumps" will the potential energy diagram for the reaction mechanism have? 3

h) Which step is called the ***rate determining step*** in this mechanism? Step 1

i) In order to have successful collisions, the colliding particles must have **both** the proper amount of *energy* and the proper Collision geometry/orientation

j) On the set of axes below, draw the shape of the curve you might expect for the reaction in this question. The overall reaction is *exothermic*! Make sure you get the "bumps" the correct relative sizes.



9. The equation for an ***overall*** reaction is:

$$I^- + OCl^- \rightarrow IO^- + Cl^-$$

a) The following is a proposed *mechanism* for this reaction. One of the species has been left out. ***Determine what that species is and write it in the box.*** Make sure the *charge* is correct if it has one!

Step 1: $OCl^- + H_2O \rightarrow HOCl + OH^-$ (fast)

Step 2: $I^- + HOCl \rightarrow IOH + Cl^-$ (slow)

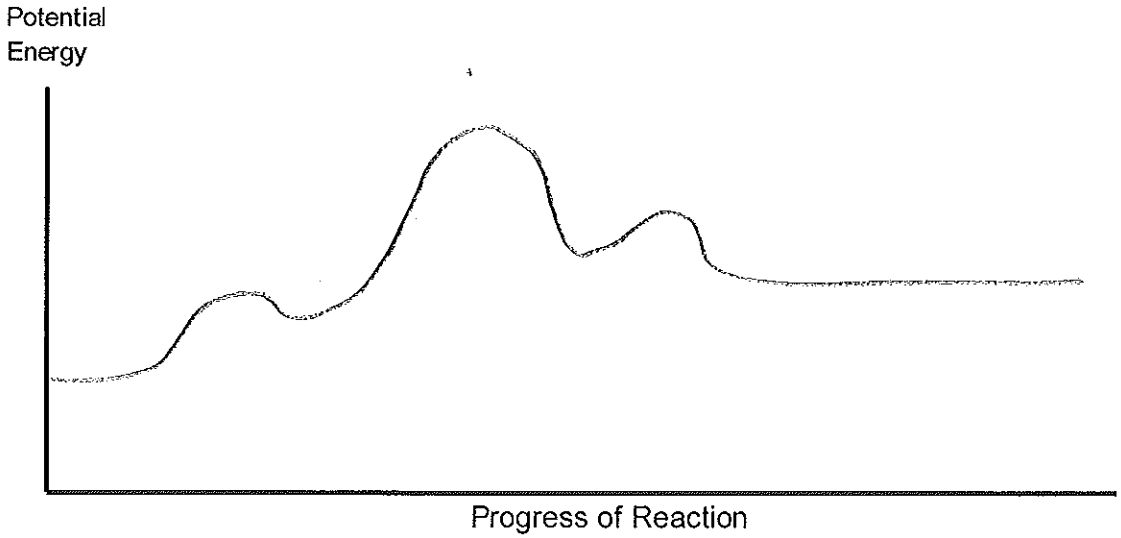
Step 3: $IOH + OH^- \rightarrow \boxed{IO^-} + H_2O$ (fast)

b) Which species in the mechanism above acts as a ***catalyst***? H_2O

c) Which three species in the mechanism above are ***intermediates***? HOCl, IOH, OH^-

d) Step 2 is the ***rate determining step.***

e) On the set of axes below, draw the shape of the curve you might expect for the reaction in this question. The overall reaction is *endothermic*! Make sure you get the "bumps" the correct relative sizes.



10. Given the following steps for a mechanism:

Step 1: $Br_2 \rightarrow 2Br$ *(fast)*

Step 2: $Br + OCl_2 \rightarrow BrOCl + Cl$ *(slow)*

Step 3: $Br + Cl \rightarrow BrCl$ *(fast)*

a) Write the equation for the ***overall reaction***.

$Br_2 + OCl_2 \rightarrow BrCl + BrOCl$

b) A substance is added that *decreases* the *activation energy* for step *1*. Will this speed up, slow down, or have no effect on the rate of the overall reaction? no effect

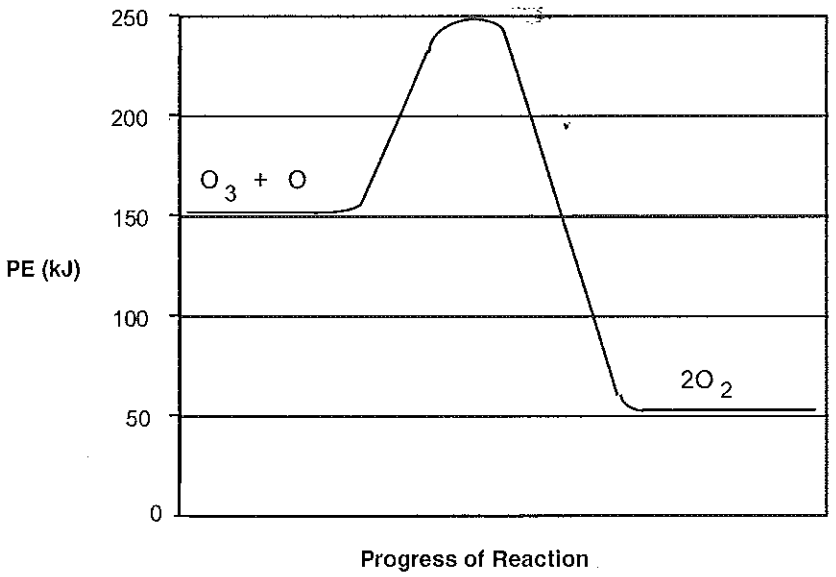
Give a reason for your answer. Step 1 is not rate determining

c) Is there a ***catalyst*** in this mechanism? NO. If so, what is it? _____

d) Is there an ***intermediate*** in this mechanism? yes. If so, what is it? Br, Cl

e) Which step is the ***rate determining step***? Step 2

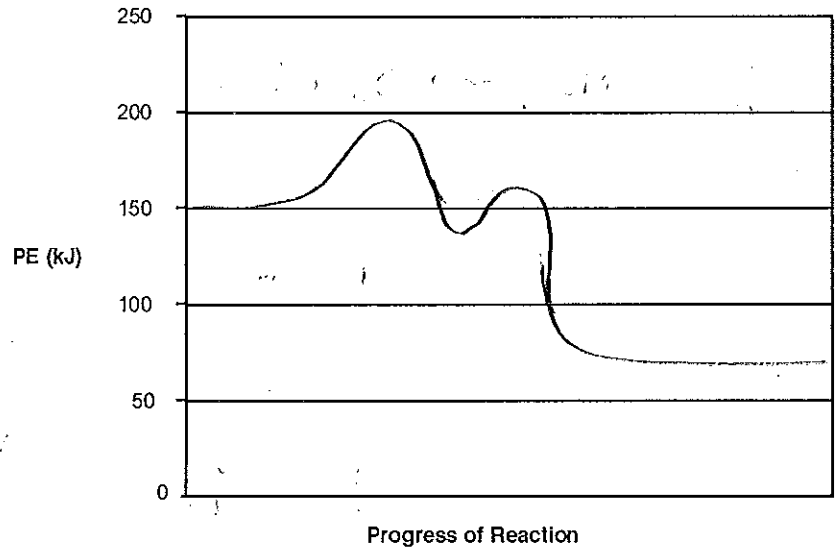
11. The following ***potential energy diagram*** refers to a very slow one-step reaction of ozone (O_3) and oxygen atoms in the upper atmosphere.



On the axis below, draw a potential energy diagram which could represent the *catalyzed mechanism* for the reaction:

Step 1: $O_3 + NO \rightarrow NO_2 + O_2$ (slow)

Step 2: $NO_2 + O \rightarrow NO + O_2$ (fast)



12. A certain chemical can provide a reaction with an alternate mechanism having a *greater* activation energy. What will happen to the *rate of the reaction* when this chemical is added?

no change

Explain your answer. The rxn will continue to take place following the original mechanism

13. The following overall reaction is *fast* at room temperature:

$$H^+ + I^- + H_2O_2 \rightarrow H_2O + HOI$$

A student proposes the following two-step mechanism for the above reaction:

Step 1 : $H^+ + H^+ + H_2O_2 \rightarrow H_4O_2^{2+}$

Step 2 : $H_4O_2^{2+} + I^- \rightarrow H_2O + HOI + H^+$

Would you *agree* or *disagree* with this proposed mechanism? disagree

Explain your answer Step 1 involves 3 particles, which would be slow and the rxn is supposed to be fast at room temp

14. Consider the following reaction:

$$CO + NO_2 \rightarrow CO_2 + NO$$

a) The *first step* in each of two proposed reaction mechanisms for the above reaction is listed below. If each proposed reaction mechanism consists of only *two* steps, ***determine the second step for each mechanism***.

Proposed Mechanism One:

Step 1: $2NO_2 \rightarrow NO_3 + NO$ (slow)

Step 2: $CO + NO_3 \rightarrow NO_2 + CO_2$ (fast)

Proposed Mechanism Two:

Step 1: $2NO_2 \rightarrow N_2O_4$ (fast)

Step 2: $N_2O_4 + CO \rightarrow NO_2 + CO_2 + NO$ (slow)

b) Experimental data show that the rate of the reaction is *not* affected by a change in the [CO]. Which of these two mechanisms would be consistent with these data? 1

Explain your answer. increasing [CO] is mech 2 would increase the rate as it is the rate determining step