

Chemistry 12

Unit I - Kinetics

KEY

Chemistry 11 Review

I) Mass to Moles

You have 16.7g of NaOH; convert it to moles NaOH.

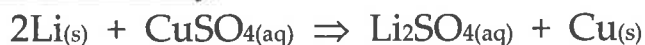
$$\frac{16.7 \text{ g NaOH}}{40.0 \text{ g NaOH}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol NaOH}} = 0.418 \text{ mol NaOH}$$

II) Moles to Mass

You have 0.756 moles of HCN; what mass of HCN is present?

$$0.756 \text{ mol HCN} \times \frac{27.0 \text{ g HCN}}{1 \text{ mol HCN}} = 20.4 \text{ g HCN}$$

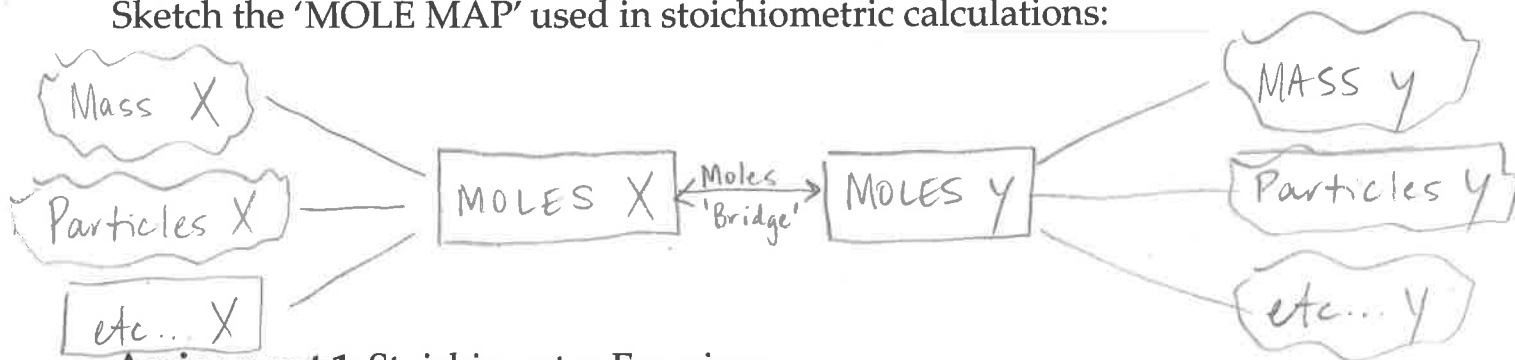
III) Stoichiometry:



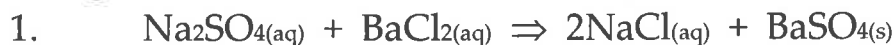
What mass of Cu metal is produced if 14.5g of Li metal reacts with an excess of CuSO₄(aq)?

$$\frac{14.5 \text{ g Li}}{6.9 \text{ g Li}} \times \frac{1 \text{ mol Li}}{2 \text{ mol Li}} \times \frac{1 \text{ mol Cu}}{1 \text{ mol Cu}} \times \frac{63.5 \text{ g Cu}}{1 \text{ mol Cu}} = 67 \text{ g Cu}$$

Sketch the 'MOLE MAP' used in stoichiometric calculations:



Assignment 1: Stoichiometry Exercises



a) How many grams of NaCl would be produced from 80.0g of BaCl₂?

$$\frac{80.0 \text{ g BaCl}_2}{208.3 \text{ g BaCl}_2} \times \frac{1 \text{ mol BaCl}_2}{1 \text{ mol BaCl}_2} \times \frac{2 \text{ mol NaCl}}{1 \text{ mol BaCl}_2} \times \frac{58.5 \text{ g NaCl}}{1 \text{ mol NaCl}} = 44.9 \text{ g NaCl}$$

b) How many grams of BaCl₂ would be required to produce 65.5g of NaCl?

$$\frac{65.5 \text{ g NaCl}}{58.5 \text{ g NaCl}} \times \frac{1 \text{ mol NaCl}}{2 \text{ mol NaCl}} \times \frac{1 \text{ mol BaCl}_2}{1 \text{ mol BaCl}_2} \times \frac{208.3 \text{ g BaCl}_2}{1 \text{ mol BaCl}_2} = 117 \text{ g BaCl}_2$$

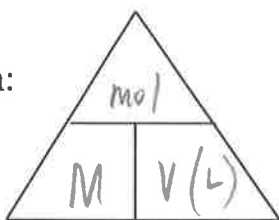
2. When iron reacts with copper II chloride, solid copper and iron III chloride are formed. What mass of copper is produced if 0.594 moles of Fe react? $2\text{Fe} + 3\text{CuCl}_2 \rightarrow 3\text{Cu} + 2\text{FeCl}_3$

$$\frac{0.594 \text{ Fe} \mid 3 \text{ mol Cu} \mid 63.5 \text{ g Cu}}{2 \text{ mol Fe} \mid 1 \text{ mol Cu}} = \boxed{56.6 \text{ g Cu}}$$

IV) Molarity

$$\text{Molarity (M)} = \frac{\text{mol}}{V} = \frac{\text{mol}}{L} \quad \left(m M = \frac{\text{mol}}{\text{mL}} \right)$$

Triangle form:



What is molarity a measure of?

concentration; solution strength

What do square brackets mean? i.e. $[\text{NO}_3^-]$ = "concentration of nitrate"

Assignment 2: Molarity Exercises

1. What is the molarity of a solution made by dissolving 2.45 mol of potassium nitrate in 1.50 L of solution?

$$M = \frac{\text{mol}}{L} = \frac{2.45 \text{ mol}}{1.50 \text{ L}} = \boxed{1.63 \text{ M KNO}_3}$$

2. How many moles of NaCl must be dissolved in 400.0 mL of solution in order to make a 0.25 M solution?

$$\text{mol} = MV = (0.25 \text{ M})(0.4000 \text{ L}) = \boxed{0.10 \text{ mol NaCl}}$$

3. What is the volume if 0.555 mol of MgS makes a 2.00 M solution?

$$V = \frac{\text{mol}}{M} = \frac{0.555 \text{ mol}}{2.00 \text{ M}} = \boxed{0.278 \text{ L} = 278 \text{ mL}}$$

4. Find $[\text{NaOH}]$ when 0.32 mol NaOH is dissolved in 5.00×10^2 mL of solution?

$$[\text{NaOH}] = \frac{\text{mol}}{L} = \frac{0.32 \text{ mol}}{0.500 \text{ L}} = \boxed{0.64 \text{ M NaOH}}$$

V) Dilution

When diluting, most of the time you are simply adding more water to a solution. In this context, the moles of solute are not affected. That said, the final volume will INCREASE (relative to the initial volume) and the final concentration (molarity) will DECREASE (relative to the initial molarity).

$$M_i V_i = M_f V_f \quad \text{where 'i' is initial and 'f' is final}$$

$$\text{OR } M_1 V_1 = M_2 V_2$$

OR

$$M_c V_c = M_d V_d$$

Assignment 3: Dilution Exercises

1. If 350 mL of water is added to 100.0 mL of a 0.60 M solution of HCl, what would be the final [HCl]?

$$[\text{HCl}]_f = \frac{M_i V_i}{V_f} = \frac{(0.60 \text{ M})(0.1000 \text{ L})}{0.45 \text{ L}} = \boxed{0.13 \text{ M HCl}}$$

2. How much water must be added to 100.0 mL of a 0.50 M KCl solution in order to dilute it to a 0.30 M solution? *Careful with SigFigs!

$$V_f = \frac{M_i V_i}{M_f} = \frac{(0.50 \text{ M})(0.1000 \text{ L})}{(0.30 \text{ M})} = 0.166667 \text{ L}$$

$V = 0.07 \text{ L} = 70 \text{ mL}$

$$V = V_f - V_i = 0.166667 - 0.1000 \text{ L}$$

3. If 40.0 mL of 0.80 M HBr is diluted to a total volume of 100.0 mL, what is the concentration of the final solution?

$$M_f = \frac{M_i V_i}{V_f} = \frac{(0.80 \text{ M})(0.0400 \text{ L})}{0.1000 \text{ L}} = \boxed{0.32 \text{ M HBr}}$$

4. What volume of water must be added to 300.0 mL of 0.700 M NaOH in order to dilute it to 0.200 M?

$$V_f = \frac{M_i V_i}{M_f} = \frac{(0.700 \text{ M})(0.3000 \text{ L})}{0.200 \text{ M}} = 1.05 \text{ L}$$

$$V = V_f - V_i = 1.05 \text{ L} - 0.3000 \text{ L} = \boxed{0.75 \text{ L} = 750 \text{ mL}}$$

KINETICS

Rate Calculations

Rate: change in a specific quantity over a unit TIME, or written mathematically: $\text{rate} = \frac{\Delta \text{quantity}}{\Delta \text{TIME}}$

The quantity can be mass, volume (gas), concentration, pressure, pH, pOH, temperature, colour intensity etc...

Depending on how long a particular reaction takes, time units could be:

s, min, h, ms, etc...

Therefore, possible rate units are: $\frac{g}{s}, \frac{g}{min}, \frac{mg}{s}, \frac{mL}{s}, \frac{L}{s}, \frac{M}{s}, \frac{^{\circ}C}{s}, \frac{\Delta pH}{s},$
etc...

Rate may be measured in two different themes: the consumption of a REACTANT or production of a PRODUCT, using any of the above quantities.

How can we monitor the rate of the following reaction in the laboratory?

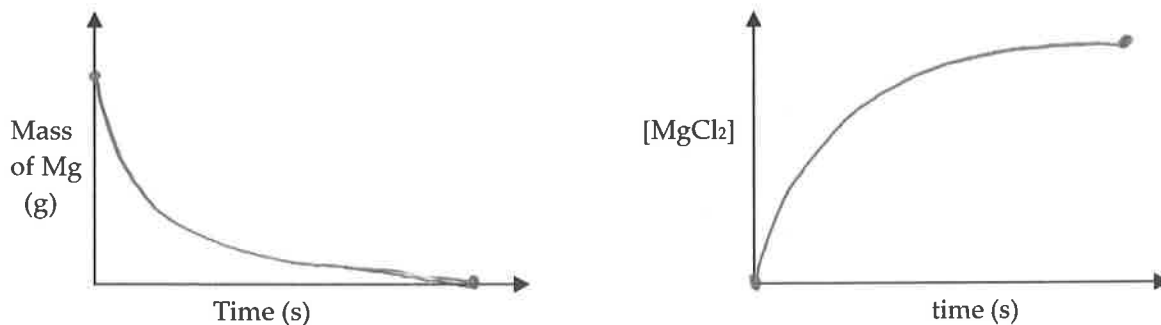


Before we begin...NOTE: CLOSED reaction systems do NOT lose mass (Law of Conservation of Mass); Open reaction systems do lose mass if GAS is produced. Do NOT ever consider utilizing an open system if at least one of the reactants is a gas!

OK, back to the original question: Possible rate equations to monitor the above reaction include:

only if OPEN system! $\frac{\Delta \text{mass of system}}{s}, \frac{\Delta \text{mass Mg}}{s}, \frac{\Delta \text{Volume H}_2}{s}, \frac{\Delta [\text{MgCl}_2]}{s}, \frac{\Delta \text{temp.}}{s}, \frac{\Delta \text{pH}}{s}$

If we choose to calculate our rate by observing the mass loss of Mg (consumption of a reactant) per unit time, then draw a graph of Mg loss vs. time. If we also then choose to calculate rate by observing the increase in the $[MgCl_2]$, then graph the concentration increase of magnesium chloride (production of a product) vs. time.



Comparing only the time-zero point and the time-completion point, write the units for the slope of each of the previous two graphs.

Recall: Slope = rise/run = $\Delta y/\Delta x$.

Graph i) $\frac{\Delta \text{mass Mg}}{\Delta \text{time}}$

Graph ii) $\frac{\Delta [MgCl_2]}{\Delta \text{time}}$

Compare with your rate equations on the last page.

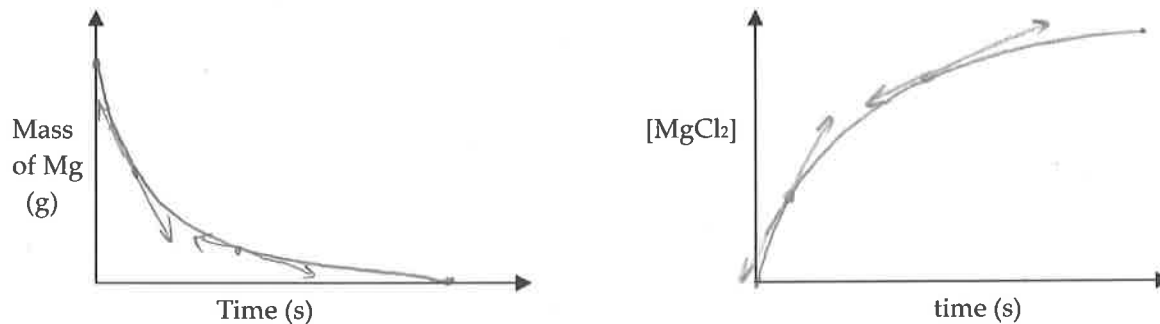
Conclusion?

Rate and slope units are the same!

Note: An AVERAGE rate refers to the rate of a reaction between *two different times* (ie. the slope of the line joining any two points on the graph). The OVERALL rate = the average rate from time-zero to time-completion.

An INSTANTANEOUS rate refers to the rate of a reaction at one discrete point on a curve. It can be calculated by finding the slope of the tangent line to that particular point on the curve (requires Calculus skills).

What do you notice about the magnitude (ie. absolute value) of the slope as your reaction proceeds?



Answer: The magnitude of the slope DECREASES
(applies to both average and instantaneous slopes).

Answer the following:

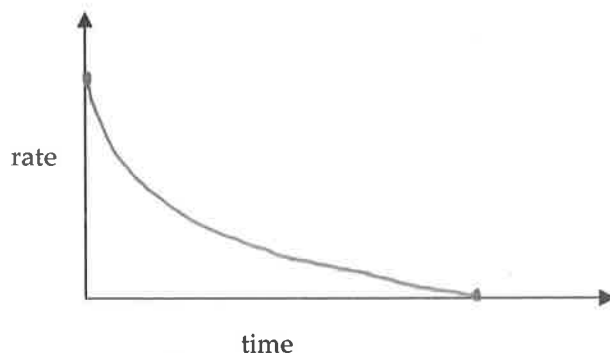
1. What happens to the [reactants] as the reaction proceeds?

DECREASE

2. What effect would this have on the reaction rate?

DECREASE

Draw a graph of *rate* vs. time for a reaction such as the one above.



AS A REACTION PROCEEDS, THE RATE IS ALWAYS DECREASING

Assignment 4:

Complete exercises #1-5 on p. 2 of Hebden

Complete exercise #17 on p. 10 and #19 on p. 11 of Hebden

Assignment 5: Rate Calculation Problems

1)

Time (s)	Mass of Pb (g)
0	65
15	52
30	41
45	32
60	25

* SigFigs and TIME when data given in a table: Find the number with the *most* amount of sigfigs in your particular calculation and that will be your amount of sigfigs for time.

The above is data for a reaction in which Pb is a reactant.

a) Calculate the overall rate of the reaction.

$$\frac{\Delta \text{mass}}{\Delta \text{time}} = \frac{65 - 25 \text{ g}}{0 - 60 \text{ s}} = \frac{40 \text{ g}}{-60 \text{ s}} = -0.67 \text{ g Pb/s} = \boxed{0.67 \text{ g Pb used/s}}$$

** interpret as the consumption of a reactant.*

b) Calculate the rate from 0-30s and from 30-60s.

$$\text{i) } \frac{65 - 41 \text{ g}}{0 - 30 \text{ s}} = \frac{24 \text{ g}}{-30 \text{ s}} = \boxed{0.80 \text{ g Pb used/s}} \quad \text{ii) } \frac{41 - 25 \text{ g}}{30 - 60 \text{ s}} = \frac{16 \text{ g}}{-30 \text{ s}} = \boxed{0.53 \text{ g Pb used/s}}$$

c) Explain why the 30-60s rate is lower than the 0-30s rate.

Later in rxn; less reactants. (or, state that: as a rxn proceeds, rate is always decreasing).

2) If 24.3g of HCl are used up after reacting with Zn for 12 minutes, what is the rate of the reaction?

$$\text{Rate} = \frac{\Delta \text{mass}}{\Delta \text{time}} = \frac{24.3 \text{ g HCl}}{12 \text{ min.}} = \boxed{2.0 \text{ g HCl used/min.}}$$

3) When CaCO_3 reacts with HCl, $\text{CO}_2(\text{g})$ is produced. If we have an open system, and the mass of the system decreases by 12.3 g in 55 seconds, what is the rate of this reaction? You may not use mass of the system as a quantity in your answer!

$$\frac{12.3 \text{ g CO}_2 \text{ produced}}{55 \text{ s}} = \boxed{0.22 \text{ g CO}_2 \text{ produced/s}}$$

4) A 5.0g sample of Mg reacts completely with HCl in 120s. What is the average rate of this reaction?

$$\frac{5.0 \text{ g}}{120 \text{ s}} = \boxed{0.042 \text{ g Mg used / s}}$$

5) How long will it take (in seconds) for 45.0g of Mg to react with HCl, if the average rate of the reaction is 2.30g Mg/min?

$$\frac{2.30 \text{ g Mg}}{\text{min}} \left| \frac{1 \text{ min}}{60 \text{ s}} \right| = 0.038333 \text{ g Mg / s}$$

$$\text{Rate} = \frac{\Delta \text{mass}}{\Delta \text{time}}$$

$$\Delta \text{time} = \frac{\Delta \text{mass}}{\text{rate}}$$

$$= \frac{45.0 \text{ g}}{0.038333 \text{ g/s}} = \boxed{1170 \text{ s}}$$

6) Electrolysis of H₂O will produce H₂ gas at an average rate of 28.5mL/min. What volume of H₂ can be produced in 6.0 min?

$$\frac{28.5 \text{ mL}}{\text{min}} \cdot 6.0 \text{ min} = \boxed{1.7 \times 10^2 \text{ mL}}$$

7) Given the reaction: $\text{H}_{2(g)} + \text{Cl}_{2(g)} \Rightarrow 2\text{HCl}_{(g)}$

a) If 2.32g of HCl are produced in 4.0 min, what is the rate of reaction in mol HCl/second?

$$\frac{2.32 \text{ g HCl}}{4.0 \text{ min}} \left| \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right| \left| \frac{1 \text{ min}}{60 \text{ s}} \right| = \boxed{2.6 \times 10^{-4} \text{ mol HCl / s}}$$

b) If H₂ is used up at a rate of 30.0 mol/s, at what rate is HCl produced in g/min?

$$\frac{30.0 \text{ mol H}_2}{\text{s}} \left| \frac{60 \text{ s}}{1 \text{ min}} \right| \left| \frac{2 \text{ mol HCl}}{1 \text{ mol H}_2} \right| \left| \frac{36.5 \text{ g HCl}}{1 \text{ mol HCl}} \right| = \boxed{1.31 \times 10^5 \text{ g HCl / min}}$$

8) $\text{C}_5\text{H}_{12(g)} + 8\text{O}_{2(g)} \Rightarrow 5\text{CO}_{2(g)} + 6\text{H}_2\text{O}_{(g)}$

If 17.6g of C₅H₁₂ is burned in one second, calculate the rate of the reaction in moles of H₂O per second.

$$\frac{17.6 \text{ g C}_5\text{H}_{12}}{\text{s}} \left| \frac{1 \text{ mol C}_5\text{H}_{12}}{72.0 \text{ g C}_5\text{H}_{12}} \right| \left| \frac{6 \text{ mol H}_2\text{O}}{1 \text{ mol C}_5\text{H}_{12}} \right| = \boxed{1.47 \text{ mol H}_2\text{O / s}}$$

Collision Theory

In a chemical reaction, what must occur in order for reactants to form products?

Reactant particles must COLLIDE in a successful manner in order to form products. \rightarrow reactant bonds break

Molecules are always moving - they always possess kinetic energy (KE) (unless the temperature = -273°C ABSOLUTE ZERO). KE is the energy of 'movement' and includes translational, rotational, and vibrating movements.

Solids tend to only vibrate and rotate - they have a low amount of KE. Liquid molecules have a 'medium' amount of KE (all three types) - they slide past one another. Gases have a large amount of KE and move around very quickly.

It is due to KE, and therefore movement that molecules are always colliding with one another.

Two factors that must be considered with respect to a atomic/molecular collision:

i. Is there sufficient KE (THRESHOLD Energy) possessed by the colliding molecules in order to break reactant bonds?

ii. Do the colliding molecules align properly in a geometric context?

There exist, therefore, four possible collision outcomes:

1. Molecules collide with insufficient KE and improper geometric alignment;
2. Molecules collide with insufficient KE and proper geometric alignment;
3. Molecules collide with sufficient KE and improper geometric alignment;
4. Molecules collide with sufficient KE and proper geometric alignment.

In outcomes 1-3, molecules simply BOUNCE off of one another and an INEFFECTIVE collision results (no reaction).
(UNSUCCESSFUL)

Outcome 4 represents the only collision-type that results in an EFFECTIVE collision (reaction occurs).

Due to the apparent limitless orientations that a two or three-dimensional molecule can possess, the majority of collisions are actually INEFFECTIVE. Only a very small percentage of collisions are actually *effective*, even when considering a reaction that occurs very quickly on a macroscopic level.

In the following set of diagrams, assume that Threshold Energy (TE) has been attained in each collision:

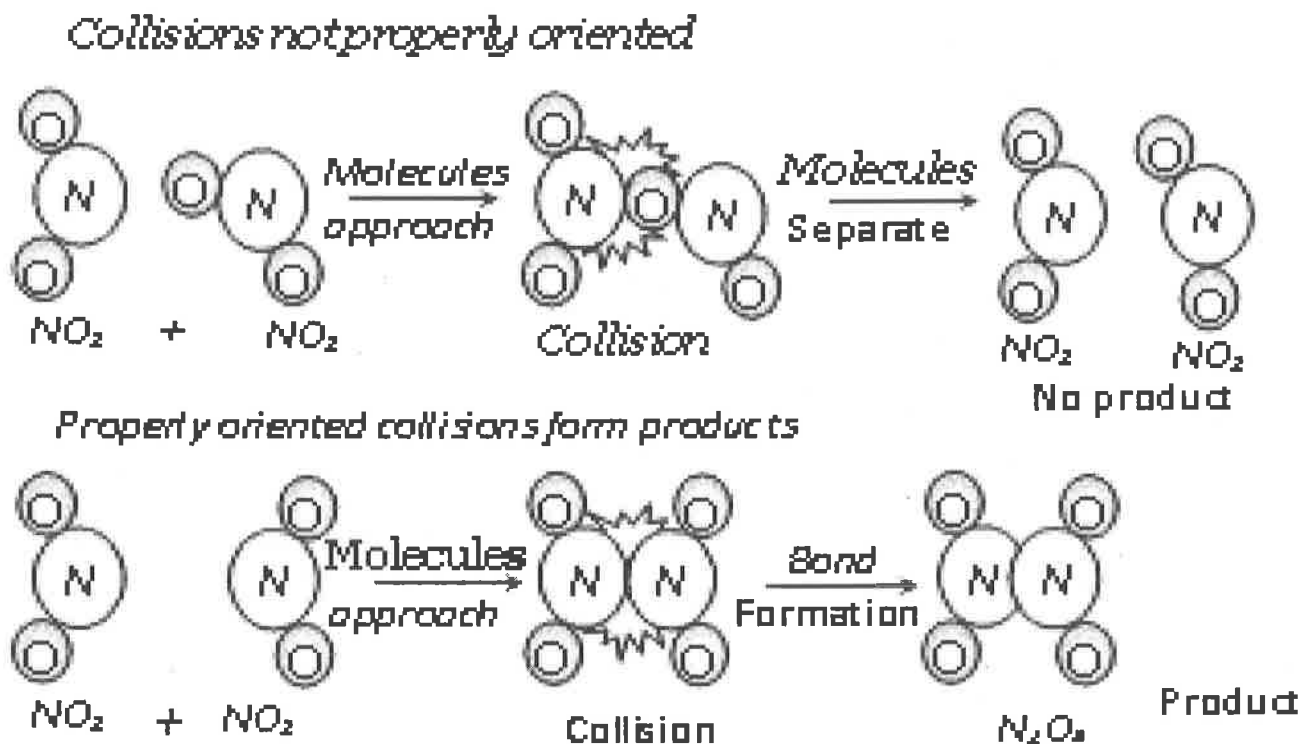


Fig. 11.1

Reaction rate depends on the *amount* of effective collisions per unit time.

Factors Affecting Reaction Rates **Part of Quizzes 1 and 2!!!

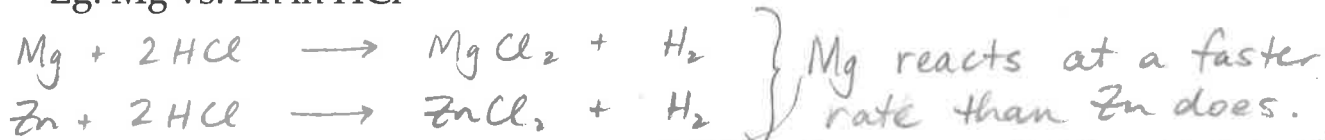
In the context of Collision Theory, there are three possible ways that a reaction rate can be increased:

- i. Increase the # of OVERALL collisions;
- ii. Increase the % of collisions that are effective;
(∴ no ↑ in overall)
- iii. Both i and ii

When considering chemical reactions, different factors may be manipulated in order to affect reaction rate. The following outlines said factors: *keep in mind that the manipulation of the following factors implies that ALL other factors/variables are held constant!

1. Nature of Reactants:

- ie. Comparing the 'reactivity' of different reactants.
- some substances may have stronger intramolecular bonds than others, requiring greater amounts of ENERGY for reactant bonds to break
- some substances may have differences in their ionization energies or their electronegativities, which would lead to differences in reaction rates.
- Some substances may achieve proper alignment more easily than others.
- Eg: Mg vs. Zn in HCl



Why? ← Ionization Energy:
Mg: 1451 kJ/mol
Zn: 1733 kJ/mol

∴ Mg and HCl collide with a higher % of effectiveness (# ii above)

- Nature of Reactants affects reaction rate by changing the % of collisions that are effective (factor ii).

* overall collisions the same!

2. Reactant Concentration:

- with respect to solids/liquids, *concentration* refers to DENSITY, which we will generalize to be *unchanging* in Chemistry 12.
- with respect to gases, *concentration* refers to PRESSURE.
- with respect to solutions (aq phase), *concentration* refers to MOLARITY (mol/L)
- in general, the greater the concentration of a reactant, the more reactant there is per unit space, the more OVERALL collisions there are between reactant molecules, leading to more effective collisions and a faster reaction rate.
- Concentration affects reaction rate by altering the # of overall collisions (factor i).

3. Surface Area of Reactants:

- whether a reaction is homogeneous (where reactants are in the SAME PHASE) or heterogeneous (where reactants are in DIFFERENT PHASES), an increase in a particular reactant's surface area will lead to an increase in reaction rate as the greater the amounts of reactant molecules exposed, the more overall collisions between reactants, the more **effective collisions**.
- eg. kindling burns faster than blocks of wood due to increased S.A.
- solutions are mixtures that display MAXIMIZED surface area (everything is mixed together 'as much as possible' (ie. Spread out as evenly as possible)) *see p. 8 in Hebden.
- Surface Area affects reaction rate by changing the # of OVERALL collisions (factor i).

4. Temperature:

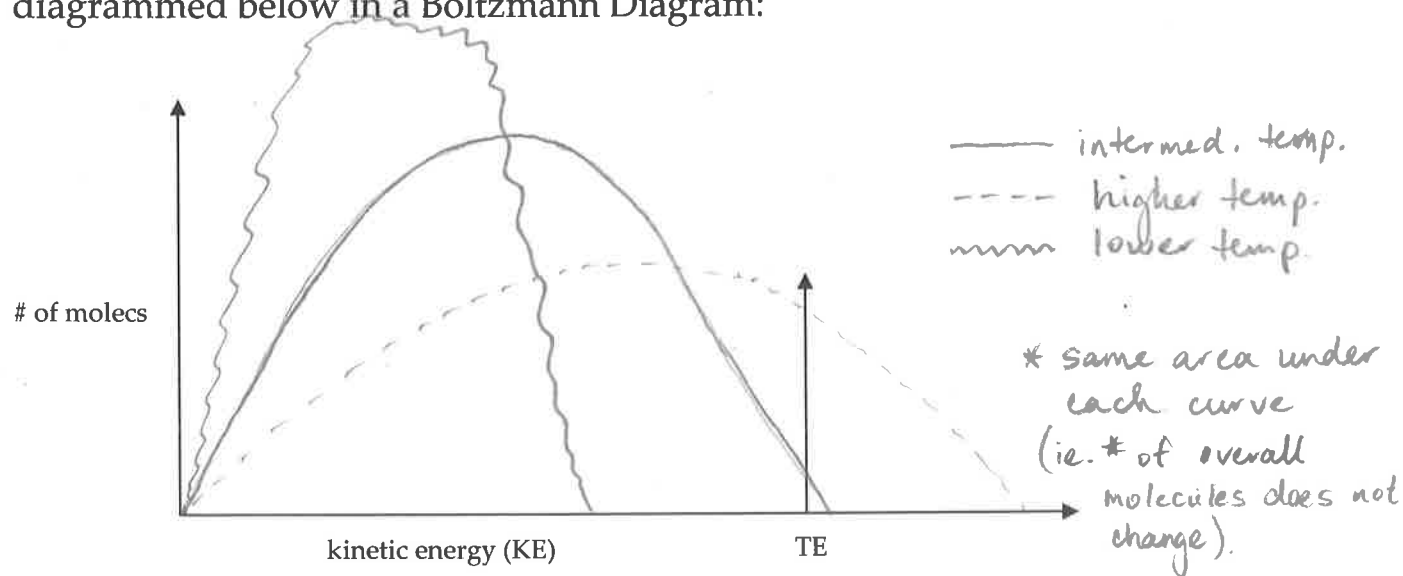
- it is generally accepted that for the most part, an increase in temperature will INCREASE the rate of a reaction.
- the higher the reactant temperature, the FASTER the reactant molecules move, meaning the more KINETIC energy they possess.

- when reactants' KE increase, the results are **twofold**:

- ↑ in the number of overall collisions, therefore more effective collisions.
- Molecules collide 'harder', ∴ ↑ in the % of collisions that are effective.

- a general chemistry rule is that for 'slow' reactions (reactions that are not INSTANTANEOUS), every 10° C increase in temperature DOUBLES the reaction rate (or, for every 10° C *decrease* in temperature – rxn rate is HALVED).

- a temperature increase will increase the amount of reactant particles that possess enough KE to react (Threshold Energy (TE)), as can be diagrammed below in a Boltzmann Diagram:



- only the molecules to the right of the vertical TE line possess sufficient KE to cause reactant bond breakage - those on the left will experience unsuccessful collisions.
- on the same graph above, draw a curve for a higher temp. and a lower temp.

- Temperature affects reaction rate by changing the # of overall collisions and the % of collisions that are effective (factor iii).

5. Catalysts and Inhibitors:

- catalysts increase reaction rate, not by producing more overall collisions, but by increasing the percentage of effective collisions (factor ii).

- They are able to do so by lowering a reaction's T. E. (threshold energy)

- Catalysts remain unchanged at the end of a reaction (ie. they are RECYCLED).

- There are two classes of catalysts:

i. Homogeneous Catalysts

ii. Heterogeneous Catalysts

- Homogeneous Catalyst – a catalyst that is in the SAME PHASE as the reactants. Most reactions involving homogeneous catalysts take place in solution (within the 'arena' of water).

o Reactions involving homogeneous catalysts proceed via an *intermediate species* formed from a reactant and the catalyst, which then reacts further and regenerates the catalyst. The TE required to form the intermediate species is LESS than the TE required for the non-catalyzed reaction to occur, thus increasing the % of collisions that are effective.

* the # of overall collisions does not change.

- Heterogeneous Catalyst – a catalyst that is in a DIFFERENT PHASE than the reactants. The catalyst is usually a SOLID and the reaction takes place on its surface.

o At least one of the reactants gets *adsorbed* onto the surface of the catalyst (ie. forms bonds to the atoms in the solid surface).

o This adsorption increases the % of effective collisions in a couple different ways:

- It may weaken some of the bonds in the reactant molecule;
- It may position the reactant molecule in a more favourable orientation for reaction.

- Inhibitors DECREASE reaction rate by inhibiting correct geometry and may or may not remain unchanged upon completion of the reaction.

6. Phase of reactants:

- rate: **FASTEST** aqueous > gases > liquids > solids **SLOWEST**
- due to proximity and/or KE of particles and/or surface area.

Assignment 6: Factors Affecting Rate Exercises

1. If 1.0g pieces of copper are placed into beakers of 0.5M, 1.0M, and 1.5M nitric acid, explain using collision theory which reaction will proceed at the highest rate and why.

The 1.5 M will exhibit the highest rate since it has the highest $[HNO_3]$ \Rightarrow more overall collisions \rightarrow more effective collisions.

2. If 1.0g pieces of copper are placed into beakers of 0.5M and 1.0M nitric acid, and 1.0g of powdered copper samples are placed into beakers of 0.5M and 1.0M nitric acid, which reaction will be the fastest? slowest?

FASTEST: 1.0g powdered Cu w/ 1.0M HNO_3
 * highest S.A. + highest $[HNO_3]$ \Rightarrow most OVERALL collisions.

SLOWEST: 1.0g pieces Cu w/ 0.5M HNO_3 .
 * lowest S.A. + lowest $[HNO_3]$ \Rightarrow least OVERALL collisions

3. If the rate of a slow reaction at $20^\circ C$ is 0.040 mol/s, what is the rate at $40^\circ C$? $80^\circ C$? $10^\circ C$?

$$40^\circ C: 0.040 \text{ mol/s} \times 2 \times 2 = \boxed{0.16 \text{ mol/s}}$$

(ie. $\times 2^2$)

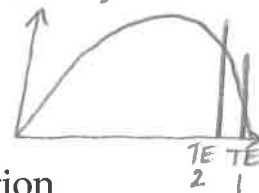
$$80^\circ C: 0.040 \text{ mol/s} \times 2^6 = \boxed{2.6 \text{ mol/s}}$$

$$10: 0.040 \text{ mol/s} \times 2^{-1} = 0.040 \text{ mol/s} \times \frac{1}{2} = \boxed{0.020 \text{ mol/s}}$$

4. Suppose two reactions are taking place in separate systems, but each have the same amount of reactant particles. Reaction 1 has a reactant triple bond that must break, whereas reaction 2 has a reactant double bond. What would be different about their KE/TE distribution graphs? Assume identical conditions (temp./pressure). Which of the six factors that affect reaction rate is at play here?

Rxn. 1's TE would be higher than rxn 2's. The size and shape of the curve for each would be the same!

** Nature of Reactants is at play.*

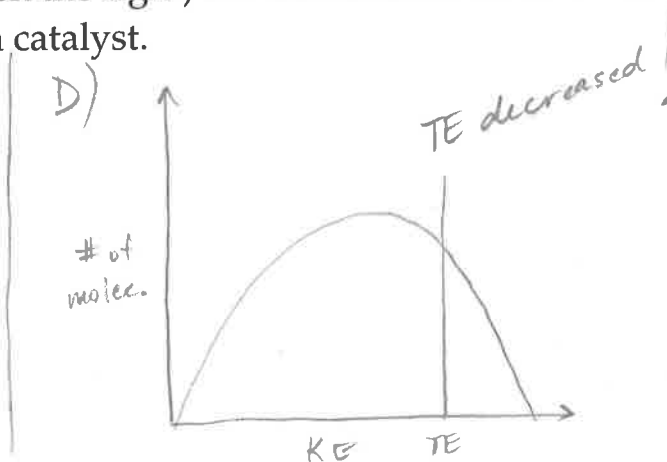
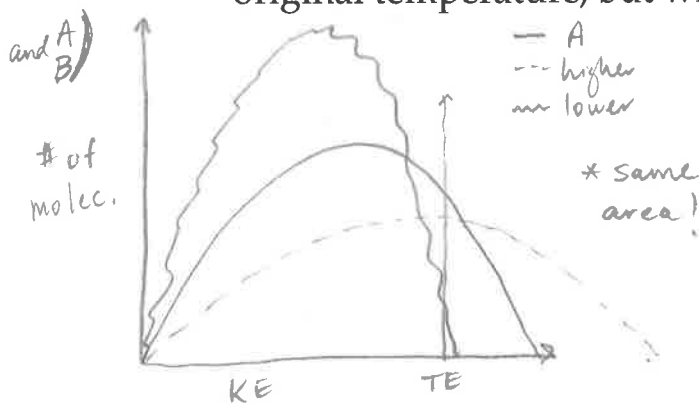


5. A) In the space below (on the left), sketch a typical KE distribution curve. KE should be on the x axis, # of molecules on the y axis, and draw a vertical line for the threshold energy.

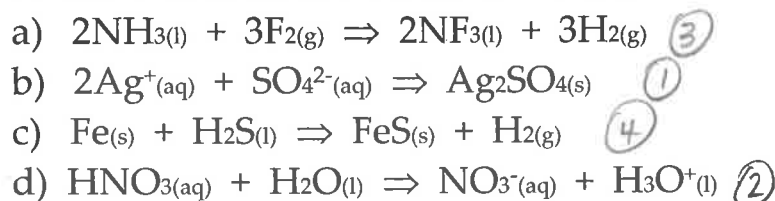
B) Sketch a distribution curve for a higher temperature system and a lower temperature system on the same axes.

C) Will the threshold energy change for any of the three curves? Why or why not? *NO. Δ temp. affects # and force of collisions but not the TE.*

D) Sketch a distribution curve (on the right) for the same reaction at the original temperature, but with a catalyst.



6. Rank each reaction from fastest (1) to slowest (4).



7. Consider the following reaction:



Identify four ways to increase the rate of the reaction.

- ① Increase SA of CaCO_3
- ② \uparrow temp.
- ③ \uparrow $[\text{HCl}]$
- ④ Add a catalyst

8. Explain, using collision theory, why a 2.0g ball of Mg metal will not react as fast as 2.0g of Mg shavings in HCl.

Shavings have greater SA \Rightarrow more overall collisions

9. Using collision theory, explain how a heterogeneous catalyst is able to increase reaction rate.

Absorbs reactant(s) onto surface and either helps to partially break bonds or helps align properly (or both).
Either way, \uparrow % of collisions that are effective.

Assignment 7: Hebden p. 8 #13, p. 9 #16 & p. 12 #21

QUIZ 1

Energy Changes in Reactions

In order for a chemical reaction to occur, energy is required to break reactant bonds (ie. energy is required to create a more UNSTABLE situation). Simultaneous to reactant bonds breaking, product bonds form. When chemical bonds form, energy gets released (ie. energy is released as a more STABLE situation is created).

Reactant molecules must collide with sufficient KE in order to for reactant bonds to break. However, as molecules approach each other, their respective KEs begin to decrease due to repulsion from ELECTRONS. Since energy cannot be destroyed, the KE is transformed to POTENTIAL energy (PE).

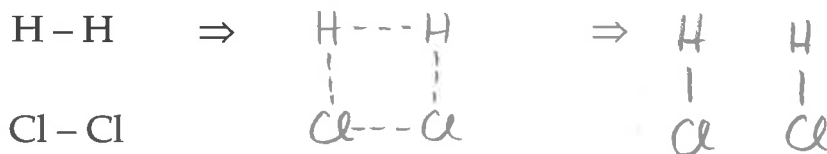
The transformation is directly proportional, in that 1J of KE creates 1J of PE, thus:

$$\text{KE} + \text{PE} = \text{total energy of system}$$

$$\text{As KE} \uparrow, \text{PE} \downarrow \quad \& \quad \text{as KE} \downarrow, \text{PE} \uparrow$$

At impact, the KE is momentarily at its lowest (KE is never zero (unless temperature is ABSOLUTE ZERO) because molecules will still be vibrating and/or rotating) and PE is at its highest. When the particles move away from one another after the collision, the KE begins to increase again, and the PE decreases.

During an effective collision, PE is used to break the reactant bonds, simultaneously forming product bonds. This structure with bonds breaking and forming simultaneously is called the ACTIVATED COMPLEX and has very high potential energy (relative to reactants and products), is very short-lived, and is relatively unstable.



activated complex

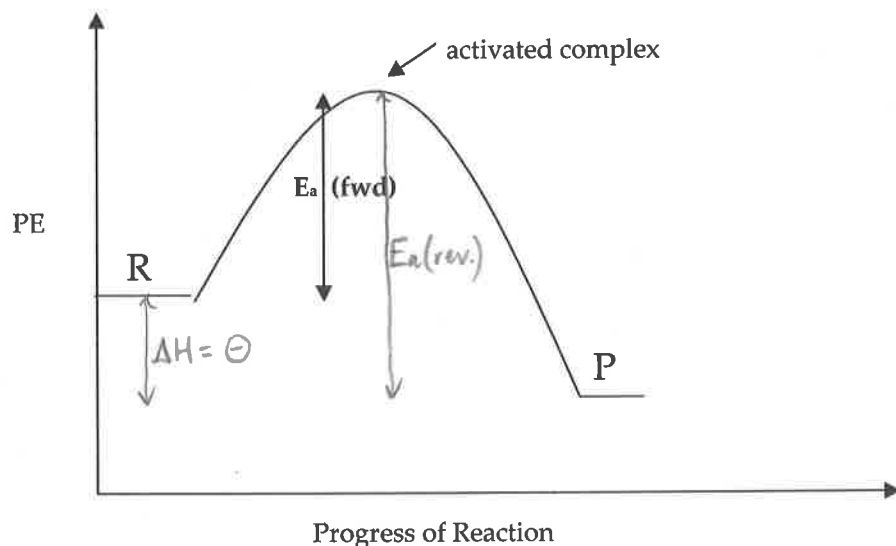


The term *threshold energy* (TE) is used to define the minimum amount of KE required for a successful collision to occur. With respect to PE (the actual energy 'currency' used for reactant bond breakage), there must exist equal to or greater PE than the ACTIVATION energy (E_a).

Definition: **Activation energy**- the minimum PE required to convert reactants into an activated complex (and henceforth into products).

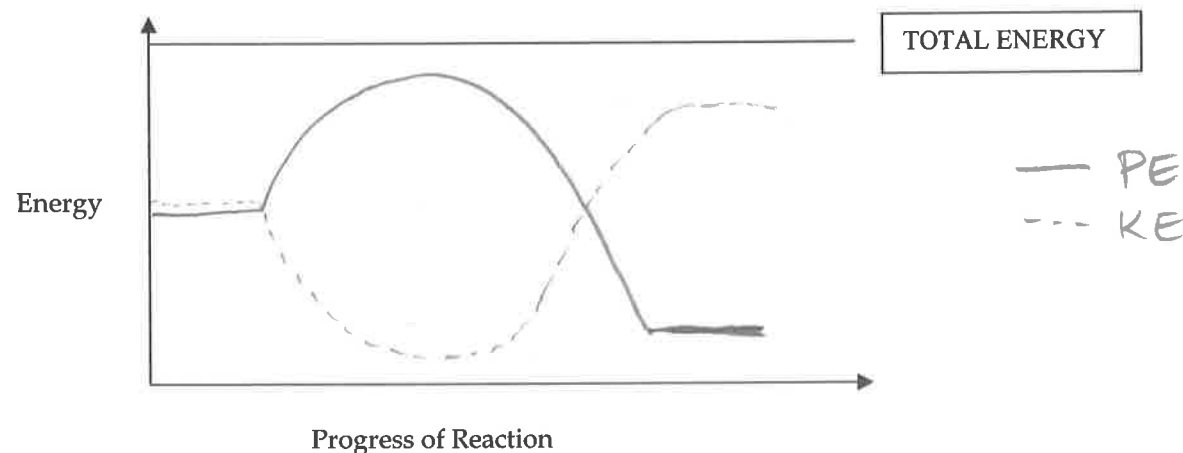
ie. $PE_{\text{ACTIVATED COMPLEX}} - PE_{\text{REACTANTS}}$

Below is a typical PE curve with both the activation energy and activated complex labeled:

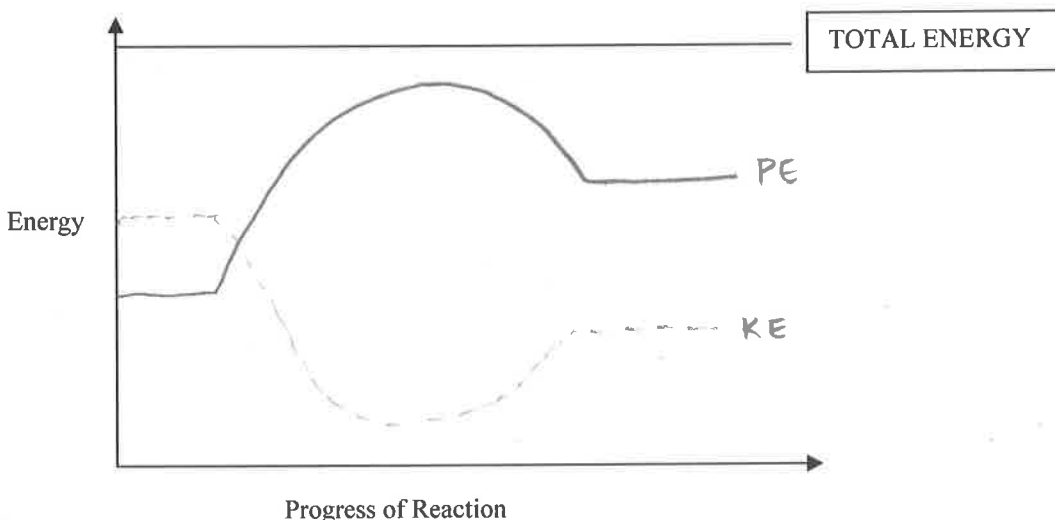


* Also: Label $E_a(\text{rev})$ and ΔH

Diagram below how the PE changes throughout an effective collision compared to the KE in an EXOTHERMIC reaction:



Draw a similar diagram for an ENDOTHERMIC reaction:



Assignment 8: Read pp.20-22, do Qs 33-39

Heats of Reaction (ΔH) (Δ Enthalpy)

An exothermic reaction releases energy as HEAT to the surroundings, therefore, products are more *stable* than reactants.

Eg. Burning a match.

How is the released energy produced?

In terms of net PE, the released energy manifests from PRODUCT BOND FORMATION. The PE that was required to break reactant bonds was less than the PE that was created (then released) when product bonds formed. This excess PE that is created is released in the form of HEAT.

An endothermic reaction absorbs energy as HEAT from the surroundings, therefore, products are less *stable* (more unstable) than reactants.

Eg. A first aid 'ice' pack.

What is the absorbed energy used for?

In terms of net PE, the absorbed energy is required to BREAK REACTANT BONDS. The PE that was required to break reactant bonds was more than the PE that was created (then released) when product bonds formed. This excess PE that is absorbed is taken from the surroundings in the form of HEAT, making the surroundings cooler.

Enthalpy (H) is a measure of the heat energy content of a system. It is usually measured in Joules (J) or Kilojoules (kJ). ΔH is the measure of how the energy changes throughout a chemical reaction, as discussed above.

$$\Delta H = H_{\text{PROD.}} - H_{\text{REAC.}} = PE_{\text{products}} - PE_{\text{reactants}}$$

ΔH can result in either a positive or negative value. If ΔH is negative, the $PE_{\text{reactants}} > PE_{\text{products}}$. Therefore, leftover energy will be released as heat, and an exothermic reaction will result. If ΔH is positive, the reaction is endothermic, since $PE_{\text{reactants}} < PE_{\text{products}}$, and heat is absorbed from the surroundings.

There are three ways to deduce whether a written or graphical reaction equation is exothermic or endothermic:

If **exothermic**:

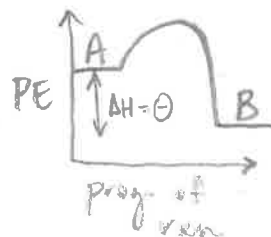
i. the energy term will be written as a product in the equation;



ii. ΔH will be negative;



iii. the products will be lower than the reactants on the PE curve.



If **endothermic**:

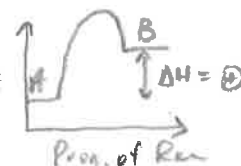
i. the energy term will be written as a reactant in the equation;



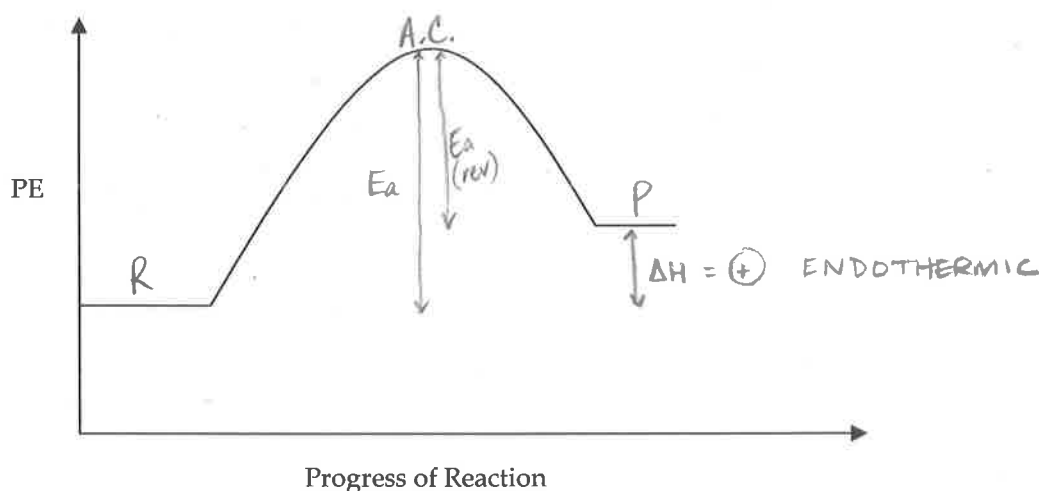
ii. ΔH will be positive;



iii. the products will be higher than the reactants on the PE curve. PE

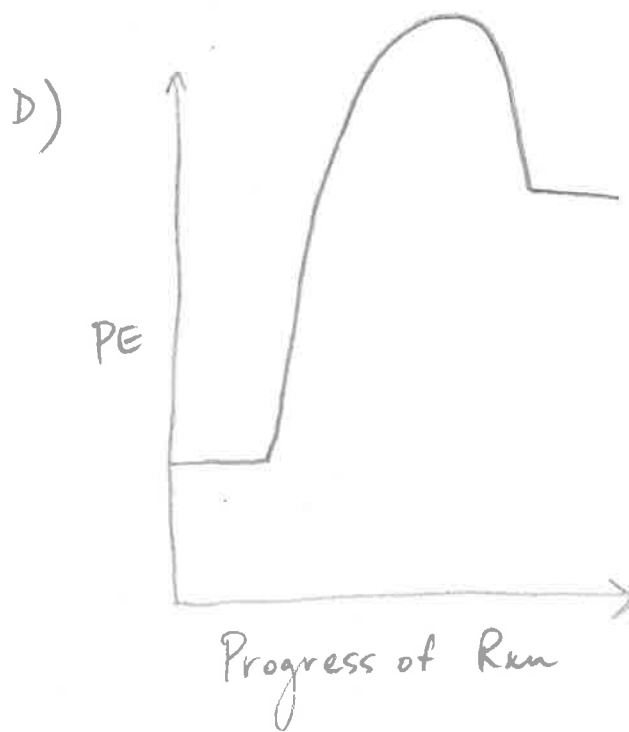
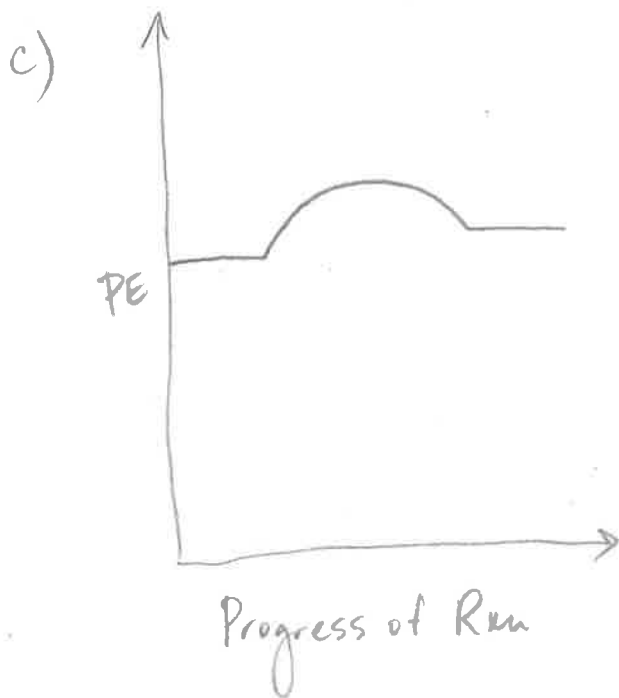
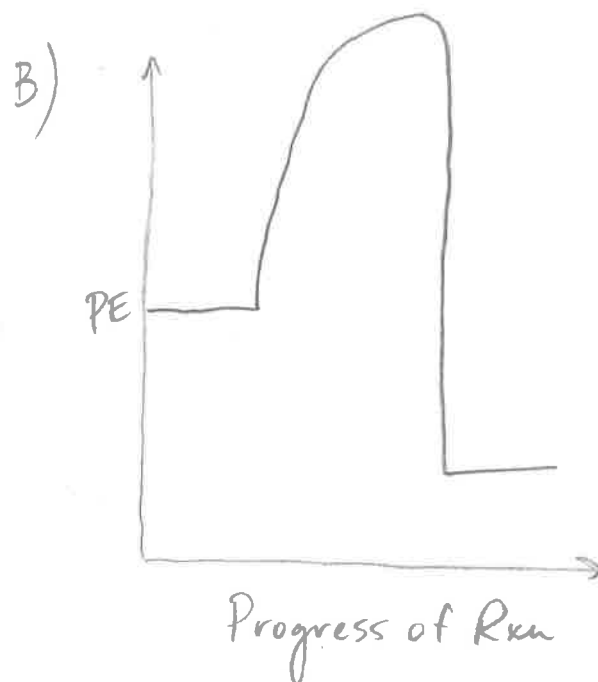
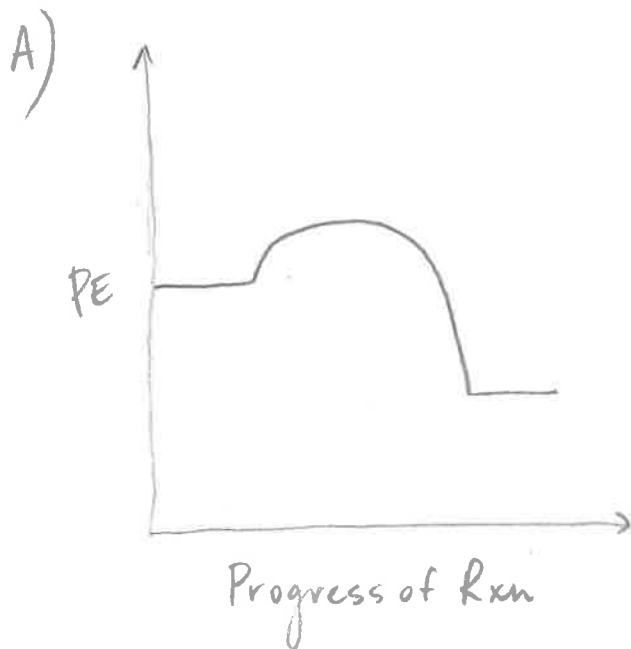


On the following curve, label E_a (fwd), E_a (rev), the location of the activated complex, reactants, products, ΔH , state whether ΔH is positive or negative, and if the reaction is endothermic or exothermic.



Observe the shape of PE curves. For a reaction to proceed, an energy hill must first be ascended (reactant bond breakage). This uphill is the activation energy, which predicts reaction spontaneity. A *small* activation energy corresponds to a more spontaneous reaction as the reactant bonds are not relatively difficult to break, whereas a *large* activation energy corresponds to more non-spontaneous reaction. Draw PE curves (label all axes, reactants, products, E_a , and ΔH) that represent the following four cases:

A) spontaneous & exothermic B) non-spontaneous & exothermic
C) spontaneous & endothermic D) non-spontaneous & endothermic

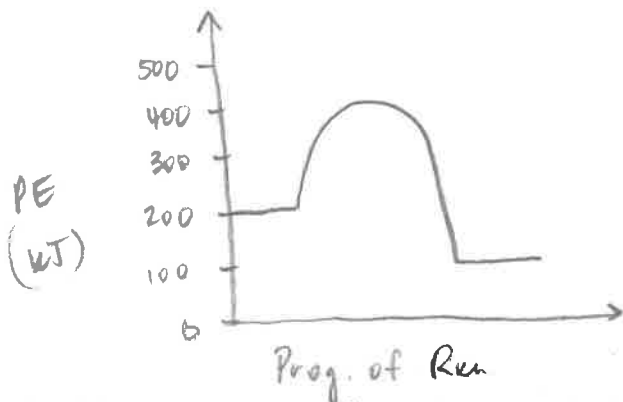


Assignment 9: PE Curve Exercises

Tip: When drawing PE curves, realize that neither reactants nor products may ever possess 0 kJ Potential Energy.

Tip2: If you are provided with E_a and no description as to whether it's forward or reverse, assume E_a (fwd) is the default.

1. Draw a PE curve with labeled axes that has a 200kJ E_a and a ΔH of -100kJ. On the y axis, make a scale from 0kJ to 500kJ.



- A) Is this reaction exothermic or endothermic?

EXOTHERMIC

- B) Are the products more stable or less stable than the reactants?

MORE STABLE

- C) Find the potential energy of the activated complex.

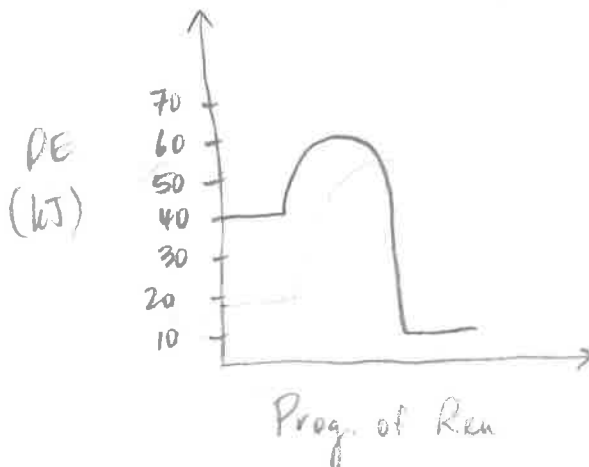
400 kJ (in this case...)

2. Sketch a PE diagram for the following reaction:



$$E_a = 20\text{kJ}$$

$$E(\text{products}) = 10\text{kJ}$$



3. Explain in terms of energy changes (kinetic and potential) what occurs when two molecules approach each other, collide, and move away as products. Be very specific and use correct vocabulary.

Approach: $KE \downarrow$; $PE \uparrow$

Collision: KE @ lowest (not zero) ; PE @ highest

Move Away: $KE \uparrow$; $PE \downarrow$

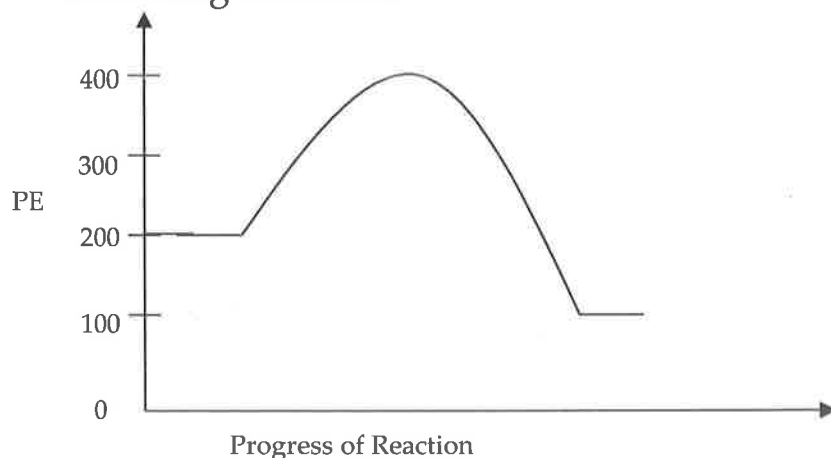
4. Does reaction rate depend on activation energy? Why or why not?

Yes! The lower the E_a , the greater the % of effective collisions, \therefore the greater the rxn. rate.

5. Does reaction rate depend on ΔH ? Why or why not?

No. Reaction rate depends solely upon E_a .
eg: An endothermic rxn may still be spontaneous.

6. Read p. 24-25 in Hebden regarding using curves to deduce information about *reverse* reactions, then answer the questions below using the following PE curve.



a) Find the E_a of the forward reaction. 200 kJ

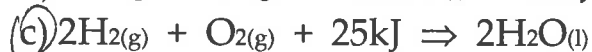
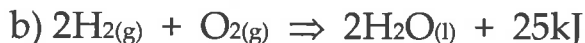
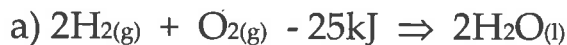
b) Find the E_a of the reverse reaction. 300 kJ

c) Find ΔH for the fwd. reaction. Endo or exo? -100 kJ exo-

d) Find ΔH for the rev. reaction. Endo or exo? 100 kJ endo-

e) What would happen to the activation energy if the temperature is increased? Nothing.

7. Which of the following is *endothermic*?



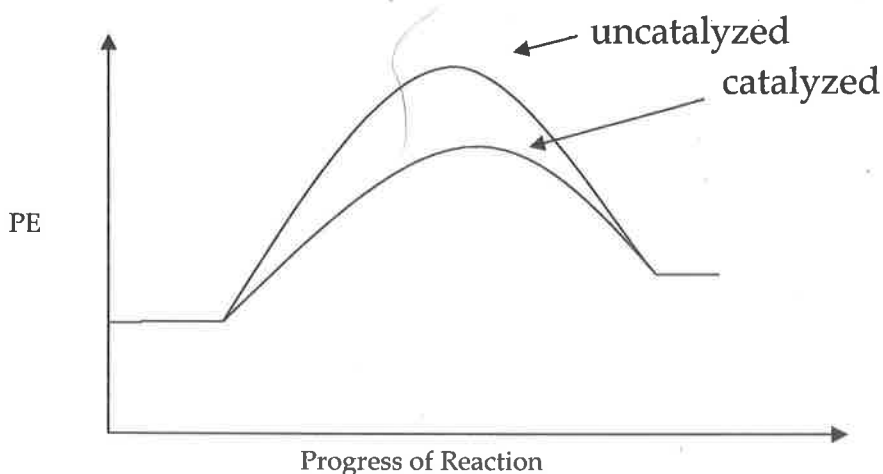
8. Provide the formula for and draw a picture of the activated complex for the following reaction: $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \Rightarrow 2\text{HBr}(\text{g}) \quad \Delta\text{H} = -125\text{kJ}$



Assignment 10: Hebden p. 25 #41-45

Catalysts

Every type of reaction follows a specific and consistent pathway with a unique activated complex. When a *catalyst* is introduced to the reaction, the reaction pathway is altered such that a different activated complex (possessing the catalyst in its structure) forms possessing a lower E_a (usually when the catalyst is homogeneous). Thus, a higher percentage of collisions will be effective, thereby increasing the reaction rate.



Catalysts are involved in creating a different, lower-energy activated complex, but are regenerated in a subsequent step. Therefore, it is noted that catalysts are never consumed in a reaction, nor do they change form; they are, in fact, recycled.

An *inhibitor*, on the other hand, forms a new activated complex that has a higher activation energy, thereby decreasing reaction rate.

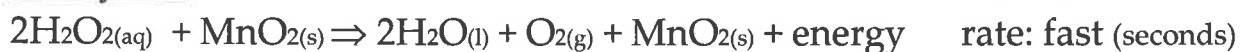
It is important to note that catalysts lower the activation energy, thereby increasing the reaction rate, but **catalysts do NOT alter ΔH in any way**; this is true because in order for a catalyst to be considered effective, it must not alter the products of the reaction.

Demo: Decomposition of hydrogen peroxide (with and without a catalyst)

Uncatalyzed:



Catalyzed:

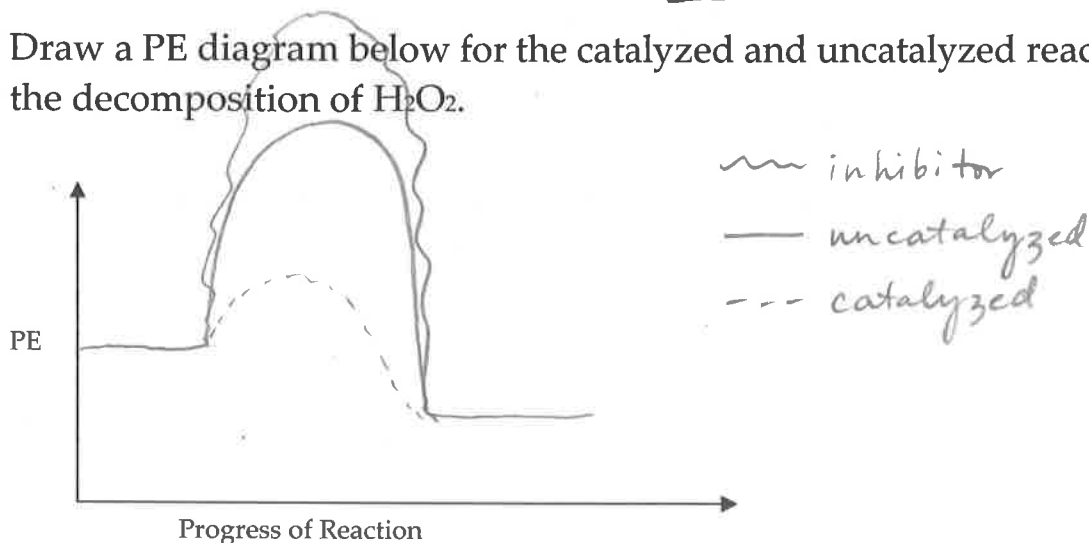


Is MnO_2 a homogeneous or a heterogeneous catalyst? **HETEROGENEUS**

How can you recognize a catalyst in a reaction equation?

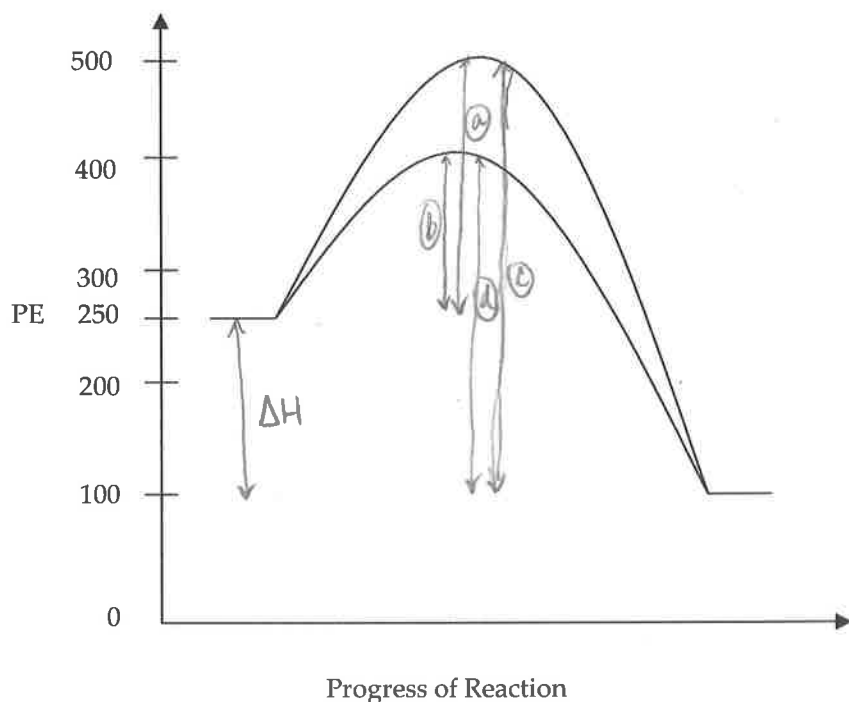
SHOWS UP ON REACTANT AND PRODUCT SIDE

Draw a PE diagram below for the catalyzed and uncatalyzed reaction of the decomposition of H_2O_2 .



Now use a different colour/type of line in the graph above to indicate the addition of an inhibitor.

Assignment 11: Catalyst Exercises



- Label and calculate the activation energy for the:
 - uncatalyzed forward reaction. 250 kJ
 - catalyzed forward reaction 150 kJ
 - uncatalyzed reverse reaction 400 kJ
 - catalyzed reverse reaction 300 kJ
- Calculate the potential energy of the:
 - uncatalyzed activated complex 500 kJ
 - catalyzed activated complex 400 kJ
- Calculate the difference in activation energy for the uncatalyzed reaction and the catalyzed reaction. 100 kJ
- Label and find the ΔH for the:
 - uncatalyzed forward reaction -150 kJ
 - catalyzed forward reaction -150 kJ
 - What do you notice about the two? *no difference*

5. Can a catalyst cause an endothermic reaction to become exothermic?
Why or why not?

No; a catalyst has no effect on ΔH . (only E_a)

6. Briefly summarize how a catalyst increases reaction rate. Be specific and use proper vocabulary.

A catalyst lowers E_a thereby increasing the % of collisions that are effective.

QUIZ 2

Reaction Mechanisms

A reaction equation outlines the original reactants and the final products of a chemical reaction, but it provides very little information about the actual process that occurs to move from reactants to products. An equation implies a one-step process, which in reality is seldom the case. Most reactions involve a series of steps in order to proceed from reactants to products.

Define **Mechanism**:

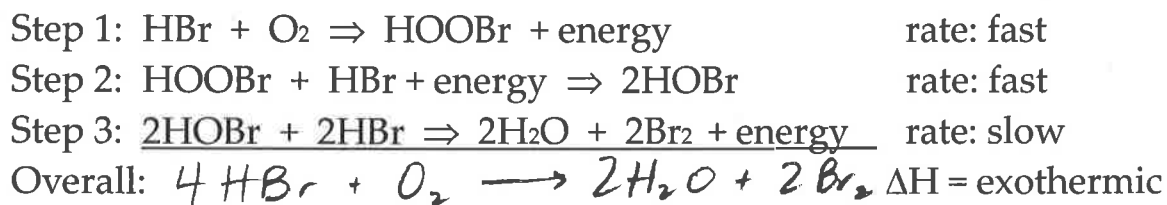
The sequence of steps (intermediate reactions) that comprise an overall reaction.

Example: $4\text{HBr} + \text{O}_2 \Rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2$

This reaction does not occur in one step. Why not?

Very low probability that 5 molecules (4 HBr + 1 O₂) collide at the same time with enough KE/PE and with the correct orientation to form an activated complex.

The above reaction is actually a three-step mechanism:



Each individual step is referred to as an ELEMENTARY PROCESS or an INTERMEDIATE REACTION.

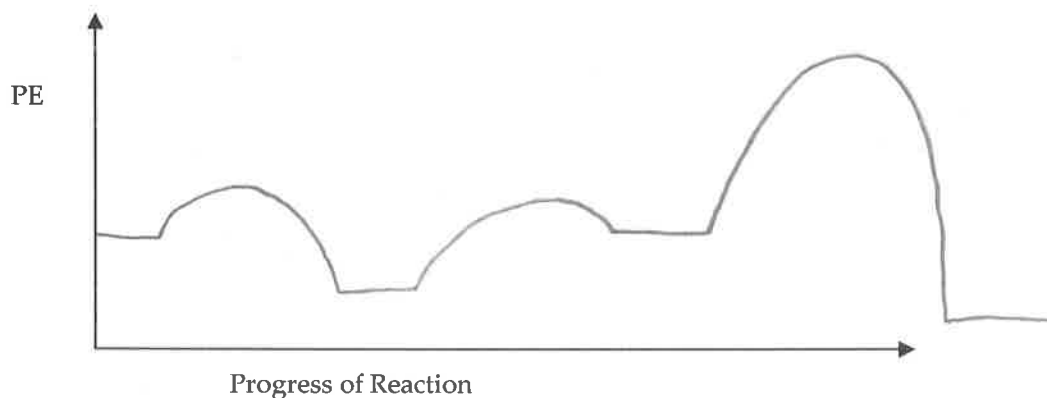
a) Which step is the rate-determining (or rate-limited) step and why?

Step 3 \Rightarrow it is the slowest

b) Why are HOBr and HBr not written in the overall reaction equation?

Created then used!

c) Draw a potential energy curve for the three-step mechanism.



Reaction Intermediate: Species that are produced in one step of a reaction, then used in a later step.

HOBr and HBr are reaction intermediates from the last example. Reaction intermediates may not be part of the overall reaction if they happen to "cancel out" when determining the overall reaction.

Exception: eg. $A + F \longrightarrow B + 2C$



Overall: $A + F \longrightarrow 2B + D + C$ (BUT, C is still a rxn intermediate)

The first place you see a reaction intermediate is on the PRODUCTS' side and then it is used as a REACTANT.

Example:

Step 1: $O_3 + NO + \text{energy} \Rightarrow NO_2 + O_2$ rate: fast

Step 2: $NO_2 + O \Rightarrow NO + O_2 + \text{energy}$ rate: slow

a) What is the overall reaction?



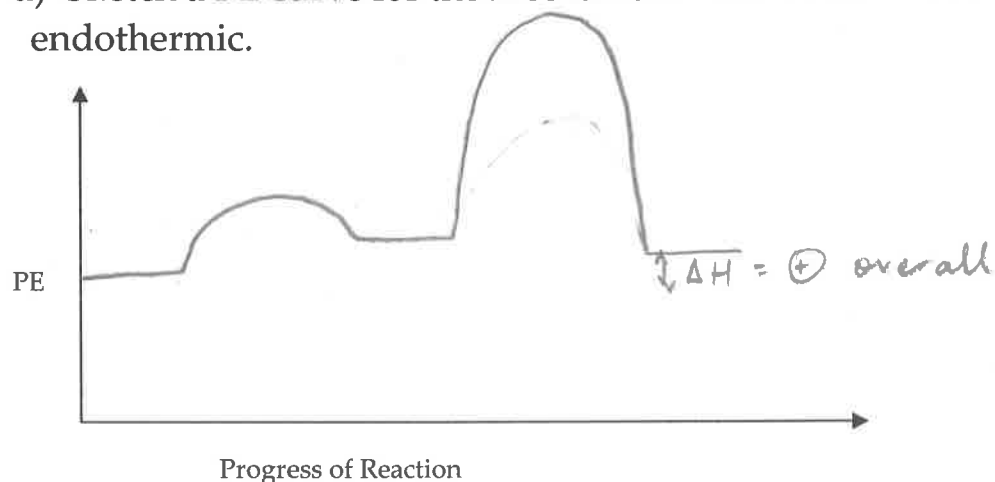
b) Find all reaction intermediates.



c) Which is the rate-determining step?

Step 2

d) Sketch a PE curve for the mechanism. The overall reaction is endothermic.



Catalyst: a substance that increases reaction rate without being consumed in a reaction.

Which substance acted as a catalyst in the last example?

NO

A catalyst is not part of the overall reaction as it always "cancels out".

A catalyst is a REACTANT first, and then a PRODUCT.

Why do all catalyzed reactions have at least 2-step mechanisms (this refers more generally to homogeneous catalysts, but can also include heterogeneous)?

Catalyst used in one step then reproduced in a later step.

Assignment 12: Reaction Mechanism Exercises

1) Step 1: $2\text{NO} + \text{H}_2 \Rightarrow \text{N}_2 + \text{H}_2\text{O}_2$ rate: slow

Step 2: $\text{H}_2\text{O}_2 + \text{H}_2 \Rightarrow 2\text{H}_2\text{O}$ rate: fast

a) What is the overall reaction?



b) Which is the rate-determining step?

Step 1

c) Identify any reaction intermediates.

H_2O_2

2) Step 1: rate: fast

Step 2: $\text{N}_2\text{O}_2 + \text{Br}_2 \Rightarrow 2\text{NOBr}$ rate: slow

Overall: $2\text{NO} + \text{Br}_2 \Rightarrow 2\text{NOBr}$

a) Find Step 1. $2\text{NO} \longrightarrow \text{N}_2\text{O}_2$

b) If it was possible to increase the rate of step 1, how would this affect the overall reaction rate? *Not very profoundly at all.*

c) Identify any reaction intermediates.

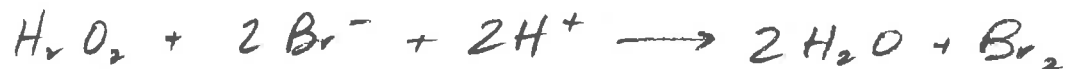
N_2O_2

3) Overall: $2\text{H}_2\text{O}_2 \Rightarrow 2\text{H}_2\text{O} + \text{O}_2$

Step 1: $\text{Br}_2 + \text{H}_2\text{O}_2 \Rightarrow 2\text{Br}^- + 2\text{H}^+ + \text{O}_2$

Step 2:

a) Find step 2.



b) Identify any reaction intermediates.

Br^- and H^+

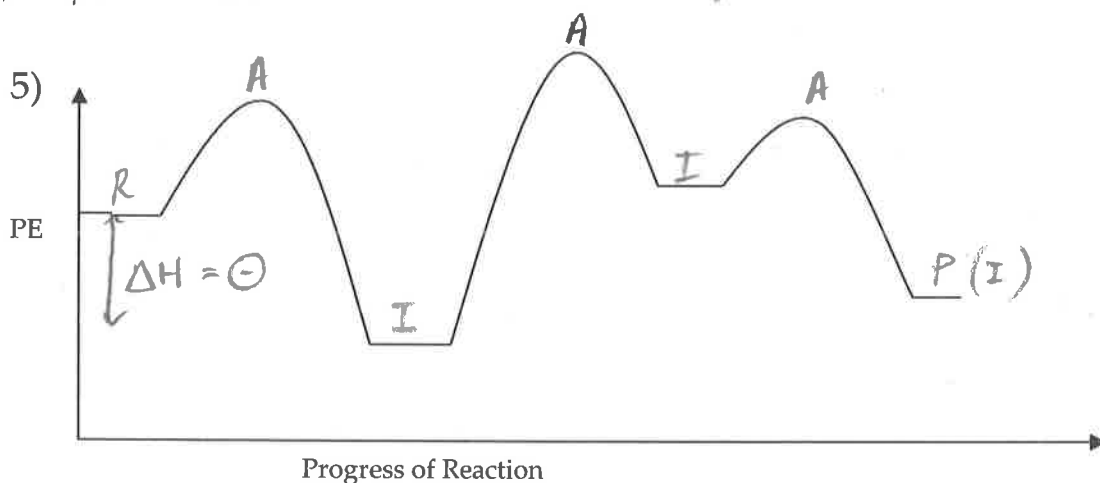
c) Identify any catalysts.

Br_2

4) Why does the following reaction have a multi-step mechanism?



Low probability that 8 molecules would collide at the same time with sufficient KE/PE and proper orientation to form an activated complex.



a) How many steps are in the reaction mechanism?

3

b) State whether each step is endothermic or exothermic.

1 - exo

3 - exo

2 - endo

c) Is the overall reaction endothermic or exothermic?

exo

d) Which is the rate-determining step? How can you tell? Step 2 - largest E_a

e) Label ΔH for the overall reaction on the curve.

f) On the curve, label an A wherever you would find an activated complex and an I wherever you would find a reaction intermediate. How do the two differ?
A.C. → high PE; unstable; short-lived
R.I. → lower PE; more stable; longer-lived.

6) Consider the following mechanism:



Step 2:



a) Find Step 2.



b) Identify a catalyst.

c) Identify any reaction intermediates.



d) What would be the chemical formula of the activated complex in Step 3? *Too complicated to DRAW in Chem. 12!!!



7) Step 1: $\text{H}^+ + \text{H}_2\text{O}_2 \Rightarrow \text{H}_3\text{O}_2^+$ rate: fast

Step 2: rate: slow



a) Find Step 2.



b) Identify any reaction intermediates.



c) Which is the rate-determining step?

Step 2

d) What is the formula for the activated complex in Step 2?

(don't forget to sum charges!)





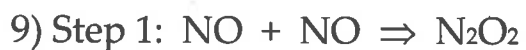
a) What is the overall reaction?



b) What would the chemical formula be for the activated complex in Step 1? (don't forget to sum charges!)



c) Identify any reaction intermediates.



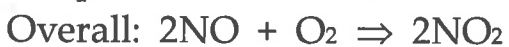
exothermic / rate: fast

Step 2:

endothermic / rate: slow



exothermic / rate: fast

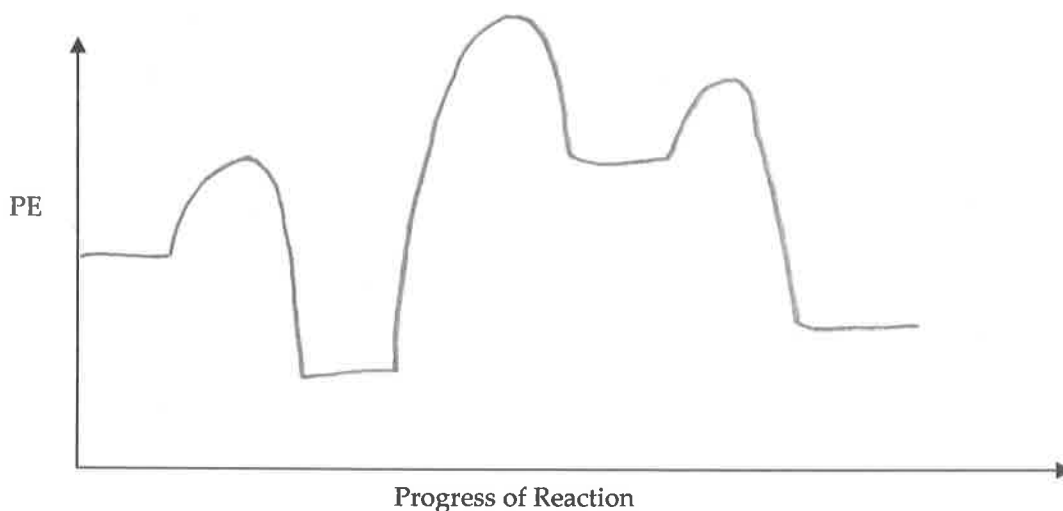


exothermic

a) Find Step 2.



b) Sketch a PE diagram for the reaction mechanism.



QUIZ 3

Specific Uses of Catalysts

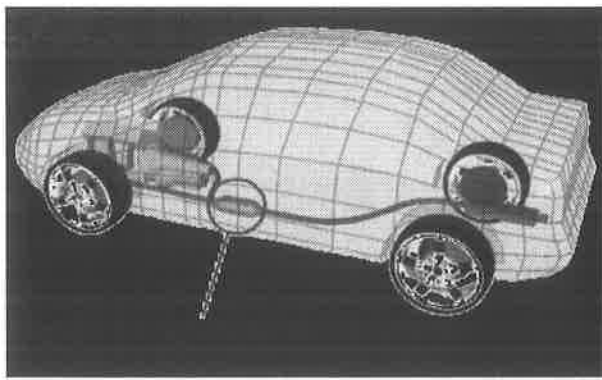
i. Automobile Catalytic Converters

- Vehicle engines produce NO (nitric oxide) as a result of the synthesis of N_2 and O_2 from the air and the high temperature of the combustion within engines.
- NO can then oxidize to produce NO_2 which can form ACID RAIN when released into the atmosphere.
- Furthermore, CO (carbon monoxide) and other harmful un-oxidized hydrocarbons are also released in exhaust.

SOLUTION?? Catalytic Converter (since 1981) – consists of two chambers that lessen the amount of pollutants released in exhaust fumes – the converter itself is part of the exhaust system.

Chamber 1: contains a transition metal or a transition metal oxide which converts NO back into N_2 and O_2 .

Chamber 2: contains a PLATINUM catalyst that serves to help convert CO and un-oxidized hydrocarbons to CO_2 and H_2O .



ii. Hydrogen Peroxide Decomposition: $2 \text{H}_2\text{O}_2 \longrightarrow 2 \text{H}_2\text{O} + \text{O}_2$

Background:

- H_2O_2 is a harmful metabolic by-product formed mainly via the oxidation of fatty acids in animals (predominantly occurs in the liver), and via photorespiration of glucose in plants (one of the many respiration pathways in plants).
- H_2O_2 kills cells non-specifically by disrupting cell membranes; sometimes used as a wound cleaner to kill bacteria -- but within organisms, excess H_2O_2 can be harmful.

Three Catalysts Utilized to Decompose H_2O_2 :

1. Manganese (IV) oxide (MnO_2) – used in the lab (the “burning splint” reaction).
2. Raw liver (animals) – liver tissue contains many peroxisomes (organelle) that possess the enzyme *catalase* which decomposes H_2O_2 so as to protect animal cell membranes from disruption.
3. Raw potato (plants) – Catalase evident in potato cell peroxisomes.

iii. Autocatalysis

- *Autocatalysis* occurs when the product of a reaction serves as a catalyst for the same reaction.
- the reaction starts slowly but picks up speed once the catalyst begins to form.

eg. Reduction of acidified permanganate ion by the oxalate ion with Mn^{2+} catalyst:



*products form faster if Mn^{2+} is provided at the beginning of the rxn.

Assignment 13: Catalyst Exercises

1. READ pp. 34 – 36 before attempting questions.
2. In the upper atmosphere, chlorofluorocarbons (from many aerosol products and volcano emissions) absorb sunlight and subsequent fragmentation produces radical Cl atoms. **Now**, do question 62 on page 36 in Hebden.
3. Do question 63 on p. 36 in Hebden.

