

SCH 4UI **UNIT 3 Energy Changes and Rates of Reaction**

Section 5.1 con't and Section 5.2 Thermochemical Equations

Temperature is defined as the average kinetic energy of all the particles of a sample of matter

Heat is defined as the transfer of energy from a hot to cool

Watch Video Eureka – Episode 21 Temperature vs Heat

Remember enthalpy ΔH is defined as the total energy of the system

$$\Delta H = \Delta E + \Delta PV \dots \text{for a solids and liquids } \Delta PV = 0$$

Therefore; $\Delta H = \Delta E = Q \dots$ We can use these equations to calculate the amount of heat that is released or absorbed by a substance

$$Q = m c \Delta T$$

Specific heat capacity, c – is the amount of energy required to raise the temperature of 1 gram of a substance 1 °C

Units J/g°C ... this is unique for each substance, refer to chart in text

Example the specific heat capacity for water is 4.2 J/g°C

Heat capacity, C – is the amount of energy that is required to raise the temperature of an object 1°C or 1 K

Practice:

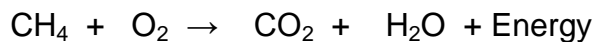
How much energy is required to heat 50g of water 10 °C? **See pages 280-281, PP 1-10**

Thermochemical Equations: See pages 292-299, PP11-20

Remember:

Endothermic Rxtns mean energy is absorbed and **Exothermic Rxtns** mean energy is released

Example



*If 890.8kJ of energy is produced during the combustion of methane, write the thermochemical equation.

Draw the enthalpy diagram for the combustion of methane.

The synthesis reaction of nitrogen dioxide requires energy, 66.4 kJ of energy per mole of nitrogen gas, write the thermochemical equation and draw an enthalpy diagram.

The ΔH_{comb} for butane is -2877 kJ/mol. Write the thermochemical equation and determine the amount of heat produced if 50g of butane burns.

A **calorimeter** is a device that is used to measure the heat released or absorbed by a physical or chemical process taking place within it.

Calorimetry involves the use of a calorimeter to study the changes associated with physical and chemical reactions.

The basis of calorimeters lies with the **second law of thermodynamics**, which states ...

Thermal energy is spontaneously transferred from an object at a higher temperature to an object at a lower temperature until the two objects reach the same temperature.

“This law ensures that the temperature that you measure after a process has taken place is the equilibrium temperature of all systems that are in thermal contact.”

The energy that is lost or gained can be determined by measuring the thermal energy transfer within the calorimeter.

$$Q_{rxn} = - Q_{soln}$$

Sample Question:

Using a simple calorimeter (2 nested Styrofoam cups and a lid) determine the enthalpy of neutralization when 50.0 ml of 0.5 M of HCl is added to 65 ml of NaOH. The initial temperature of the solutions is 17°C and the final temperature of 25°C. Calculate the enthalpy in units of kJ/mol of HCl. Assume the specific heat capacity for the solutions to be that of water.

What assumptions must be made when using a simple calorimeter?

Other calorimeters include Bomb Calorimeter (constant volume), Flame calorimeter and Constant Pressure calorimeter.

-Hess' Law is a method used to determine the enthalpy change for simple reactions to very complex and sometimes very dangerous reactions

Hess' Law States:

The enthalpy change of a physical or chemical process depends only on the initial and final conditions of the process. The enthalpy change of a multistep process is the sum of the enthalpy changes of its individual steps.

Illustration:

Complete the following questions to understand how Hess' law is used and learn how reactions can be manipulated to obtain desired results. le What can you do and what can't you do?

1. For the reaction below, which statement is true?

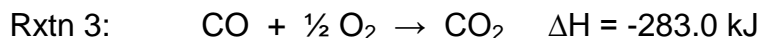
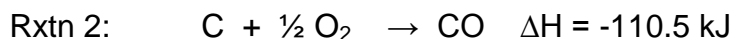
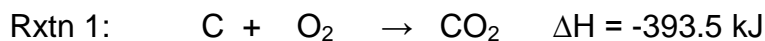
- a) Rxtn 1 + Rxtn 2 = Rxtn 3
- b) Rxtn 2 + Rxtn 3 = Rxtn 1
- c) Rxtn 1 + Rxtn 3 = Rxtn 2

Rxtn 1 : 1 bike \rightarrow 2 bicycle tires + 1 frame

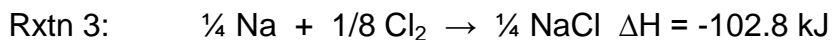
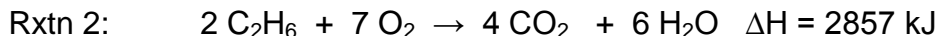
Rxtn 2 : Rubber + water + 1 frame \rightarrow 1 bike

Rxtn 3 : Rubber + water \rightarrow 2 bicycle tires

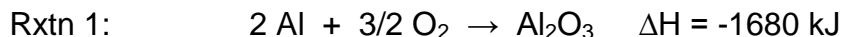
Apply the same concept to 3 chemical reactions. Which 2 reactions add up to the overall reaction? Show how the reactions add up to the overall reaction, and indicate what happens to the change in enthalpy values.



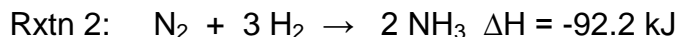
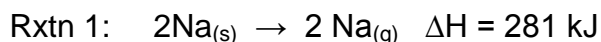
2. For the following equations write the equations so that the substance underlined only forms one mole of that substance. Don't forget to change the change in enthalpy value as well.



3. Rewrite the equations below to remove any fractions, again remember any changes you make to the equations you must apply to the change in enthalpy.



4. Rewrite the equations so that the products become the reactants and the reactants become the products. I.e. "flip" the equation. In so doing you must flip the sign. If the reaction initially had $\Delta H = +$, when the equation is flipped $\Delta H = -$ and vice versa.



Random Question... things that make you go hmmmmmm, good question:

5. When adding multiple equations together, substances on either side of the arrow can cancel one another out. Do these substances have to...

a) Be in the same state? I.e. liquid, solid or gas... Yes / No, explain

b) What happens if the substances do not have equal number of moles?

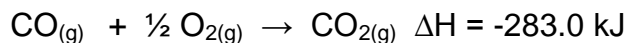
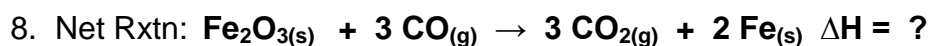
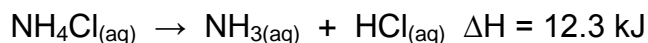
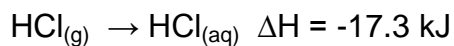
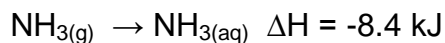
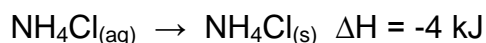
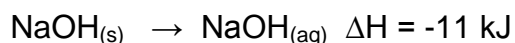
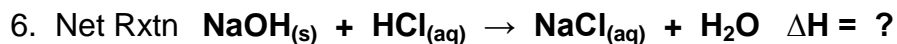
Summarize all the tricks you can use when manipulating equations and apply the tricks to the remaining questions. As always you must indicate what you have done to the reaction and show the new reaction as well as the new enthalpy change.

General Guidelines to aid in communicating your answers:

1. Assign reaction numbers to the reactions by writing numbers beside the initial reactions given
2. Indicate what you are going to do to the reaction ie, X4, flip, /2
3. the write the equation with the changes applied
4. include the new ΔH value

----- sorry guys/gals there are no short cuts here-----

TIP: Keep the arrows in the question lined up when adding, much easier to see which is a reactant and which is a product



***Formation Reactions:** substances formed from elements in their standard states

*Standard states are states at 25°C and 100 kPa

ΔH_f = standard molar enthalpy of formation

-is the amount of energy released or absorbed when one mole of a compound is formed directly from its elements in standard states

-this is the only time you can use fractions in balancing equations

***Calculating Enthalpy Changes**

- ΔH_f can be used to calculate ΔH of a reaction at standard temp and Pressure... using the following formula

*Calculate ΔH using ΔH_f for the combustion of ethane...

- 1) **MUST BALANCE EQUATION FIRST!**
- 2) Find ΔH_f from tables in back of textbook, watch for the subscripts!

*The rate of a reaction is measured by the change in concentration of the reactants with respect to the rate of the formation of the products.

Given the equation: $aA + bB \rightarrow \text{Products}$

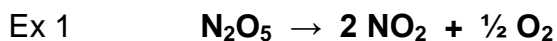
$$\text{Rate} = k[A]^m[B]^n$$

*exponents, indicated the "order" of the reaction

*k, the rate constant, indicates the speed of a reaction

Determining the rate law of a reaction using experimental data

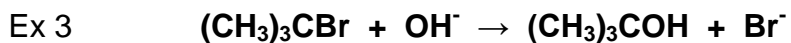
*Initial rates method, enables you to determine the rate of a reaction without having to wait for the entire reaction to be completed



Trial	$[\text{N}_2\text{O}_5]$	Rate of formation of O_2 (mol/L s^{-1})
1	0.45 M	2.7×10^{-4}
2	0.90 M	5.4×10^{-4}
3	1.35 M	8.2×10^{-4}



Trial	$[\text{CO}]$	$[\text{NO}_2]$	Rate of formation of CO_2 (mol/L s^{-1})
1	0.10 M	0.10 M	5.0×10^{-3}
2	0.10 M	0.20 M	20.0×10^{-3}
3	0.20 M	0.10 M	10.0×10^{-3}



Trial	$[(\text{CH}_3)_3\text{CBr}]$	$[\text{OH}^-]$	Rate (mol/L s^{-1})
1	0.10 M	0.10 M	4.0×10^{-3}
2	0.20 M	0.10 M	8.0×10^{-3}
3	0.10 M	0.20 M	4.0×10^{-3}

Collision Theory: in order for a chemical reaction to take place the reacting molecules must collide with each other

*The rate of a reaction depends on the number of collisions between reacting molecules

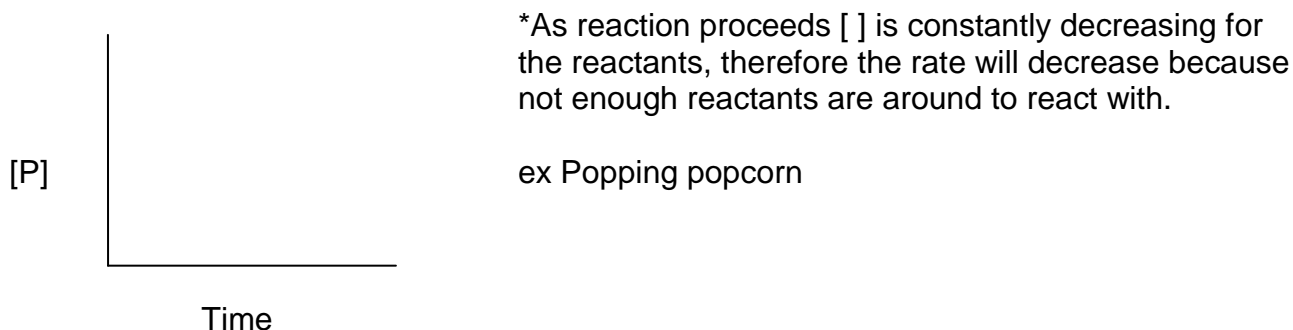
Apply Collision Theory (CT) to Factors that Affect Rate of Reaction:

***Temperature:** increase in T, increase in Kinetic Energy and therefore increase in movement and the number of collisions

***Increase in Surface Area:** more surface area to collide with will also increase the number of desired collision, ie leading to a reaction

***Concentration:** increase in concentration, rate tends to increase due to more collisions with the desired reactant. In dilute solutions there are lots of collisions but less of a chance of colliding with the correct reactant

*Why does the rate of a reaction decrease with respect to time?



-One problem with collision theory is that it makes the assumption that every collision will cause a reaction.... **NOT true**

PROOF: 1 L volume of gas at 25°C and atmospheric pressure has 1×10^{30} collisions per second. If all the collisions caused a reaction then the reactions in gas phase would be instantaneous... this is definitely not true!

-2 Factors must be considered... a) **orientation** and b) the **amount of energy** the reactants have or possess

-If the molecules do not have both the correct alignment and the minimum amount of energy, no reaction will take place and the reactants will bounce off one another still a reactant.

-If both factors are present then the bonds within the reactant will break and the bonds for the product will form

This can be compared to playing a game of billiards, aka pool

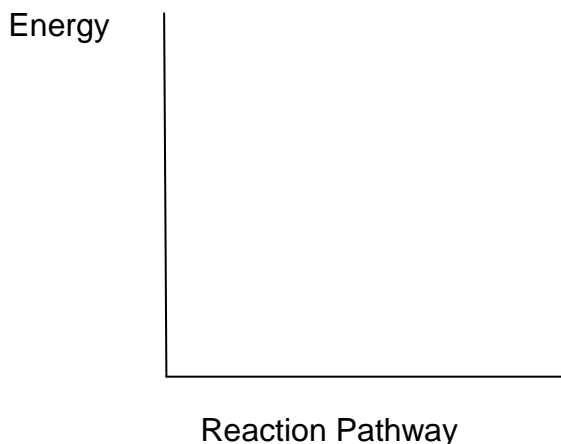
-If not enough energy is put into striking the cue ball or the angle is wrong when striking the cue ball the ball will not go into the pocket. The same can be said about a reactant molecule colliding with another reactant molecule, the wrong angle or not enough energy will not result in a reaction.

*If a reaction occurs a transition state will occur

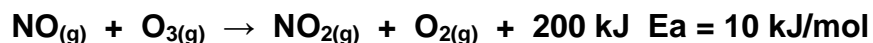
-**Transition state** is...the point in which the reactants are forming the products

-**Activated Complex** ...the unstable complex of reactants breaking bonds and forming new ones, this is rarely seen because the complex is too unstable. See page 293 for a visual example

Energy Diagrams are used to show the change in energy for the reaction

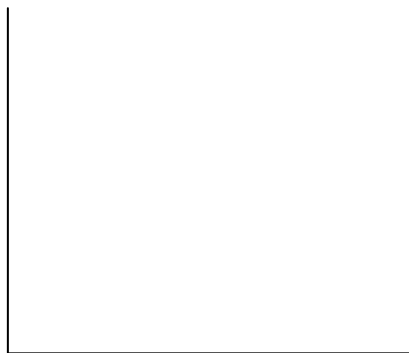


Practice: Draw an energy diagram for the forward and reverse direction for the following reaction, include all labels



Forward Reaction

Reverse Reaction



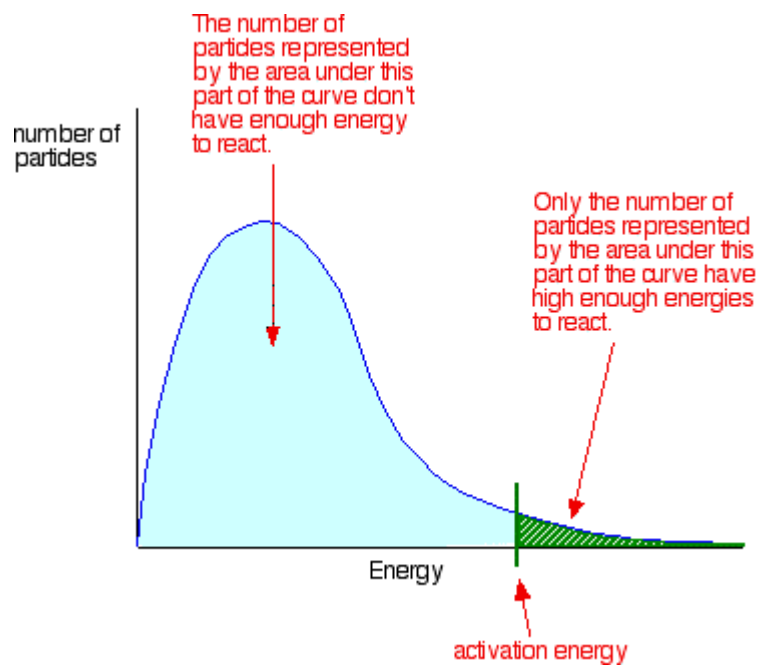
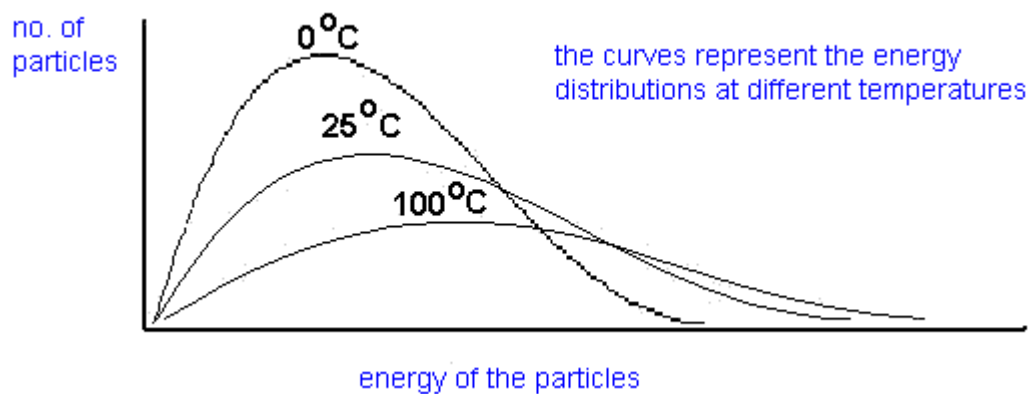
Draw the activated complex that forms for the above reaction... Hint, which bonds are breaking and which ones are forming?

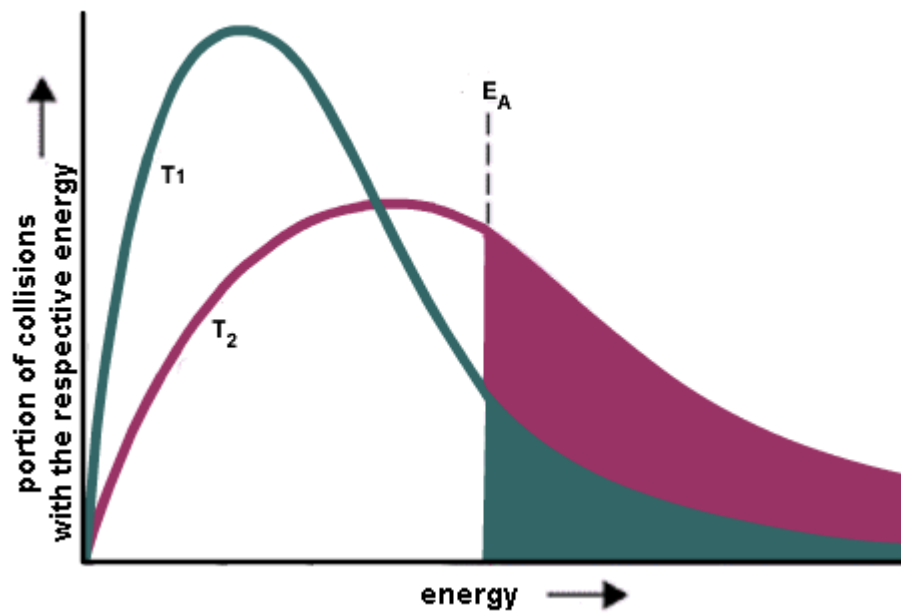
How does Temperature Affect Activation Energy?

*Increase in temperature causes 1) molecules to move faster and therefore increases the number of collisions and 2) the average molecular kinetic energy increases, therefore during the collisions more molecules will possess enough energy for the reaction to occur.

-Illustration – overlap Maxwell Distribution Curve with Energy diagrams ...

Maxwell Boltzmann Curves...

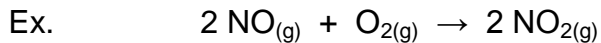




*Reactions are classified into 2 categories

- 1) Simple – involve one elementary step
- 2) Complex – involve a series of steps

Mechanism – is/are the steps or series of steps that make up a reaction



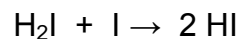
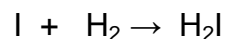
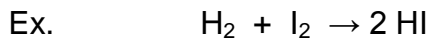
Mechanism:

Net Rxtn:

* N_2O_2 is considered a reaction intermediate...

Note: Must use experimental evidence to determine if a reaction is simple or complex, based on mechanism

Molecularity – indicates the number of reactant molecules used in each elementary step



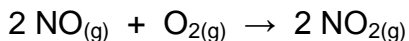
*Step 1 of mechanism is ...

*Step 2 and 3 are ...

-Termolecular – 3 molecules are rare, because it is very difficult for 3 molecules to collide with the right amount of energy and the correct orientation... low success rate

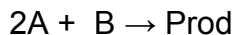
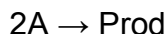
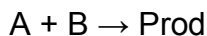
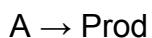
Rate Determining Step:

-this is the step that takes the longest to be completed, ie the slowest step



Mechanism:

***For an **elementary reaction or step** (within the mechanism), the exponents in the rate law equation are the same as the stoichiometric coefficients for each reactant in the elementary reaction...

Elementary Step**Rate Law****-Evaluating Mechanisms:**

In evaluating mechanisms they must satisfy the following criteria;

- 1) Equations of the elementary steps must combine to give the overall reaction
- 2) Proposed elementary steps must be reasonable
- 3) Mechanism must support the experimentally determined rate law

Practice by applying 1,2 and 3 to the above reaction

Info to determine the experimentally determined rate law for Eval Mech step 3

Trial #	[NO]	[O ₂]	Rate
1	0.2	0.2	3
2	0.2	0.4	6
3	0.4	0.2	12

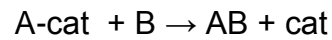
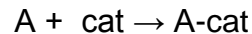
Catalysts:

-the role of catalysts is to increase the rate of a reaction without being consumed itself

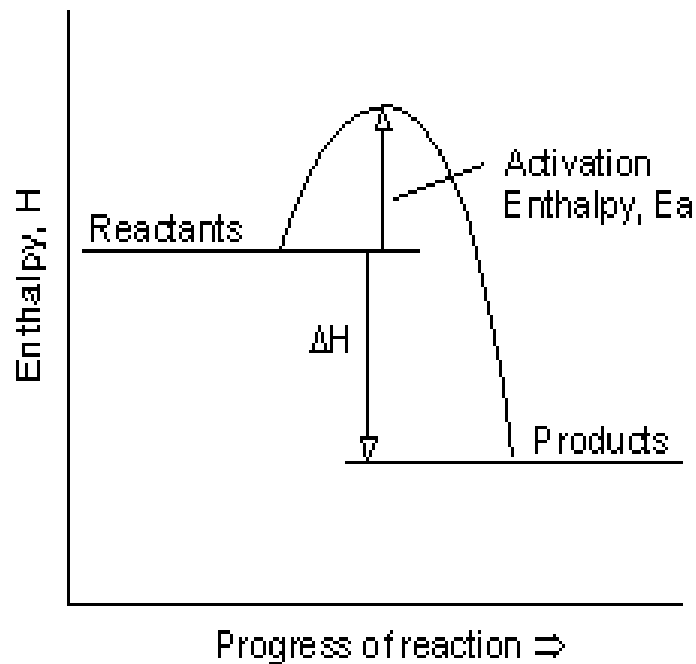
*This is not always true...



Mechanism:



*Catalysts work by reducing the activation energy by providing an alternative pathway...



Homogeneous Catalysts

-One phase, same as reactants

-Heterogeneous Catalysts

-catalyst is in a different state than the reactants
For example the addition reaction of hydrogen
Gas and ethene uses platinum as a catalyst.

Half Lives... Read pages 285-287, pp 9-12

*Half life refers to the time it takes for reactant mass or concentration to decrease by one half's of it's initial value.

*SI Unit is Seconds

*Other units used are hours or days if the reaction is slow or seconds or milliseconds, if the reaction is quick

*For first order reactions...

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

example: $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$

rate = $k [\text{SO}_2\text{Cl}_2]$ at 320°C , $k = 2.2 \times 10^{-5} \text{ s}^{-1}$

- Calculate the half life
- Time for $[\text{SO}_2\text{Cl}_2]$ to decrease by $\frac{1}{4}$