

Unit 2: Thermodynamics & Kinetics

Change in Matter and Energy (pg 298)

Thermochemistry: study of the energy changes that accompany physical or chemical changes in matter

When you are studying transfers of energy, it is important to distinguish between the substances undergoing a change (**chemical system**) and the system's environment (**surroundings**).

Thermal energy: energy available from a substance as a result of the motion of its molecules. So a bucket of cold water will have more thermal energy than a glass of hot water because the bucket simply has more molecules to move around. The amount of energy transferred between substances is referred to as **heat**.

Transfer of Heat between system & surroundings

Exothermic: heat flows into surroundings

Endothermic: absorption of heat from surroundings

Classifying Chemical Systems

Open system: matter & energy can move in or out

Eg. Boiling water in a beaker

Closed system: only energy can move in or out

Eg. Boiling water in a covered container

Isolated system: matter & energy cannot move in or out

Eg. Bomb calorimeter (see Fig 4 pg 299)

Practice pg 300 # 3-5

Measuring Energy Changes: Calorimetry (pg 300)

Calorimetry: technological process of measuring energy changes in a chemical system

When measuring heat, three factors have to be considered – mass, temperature change, and substance type. This yields the following formula:

$$q = mc\Delta T$$

q = heat (J)

m = mass (g)

c = specific heat capacity – J/(g·°C)

ΔT = change in temperature (°C)

Specific heat capacity: quantity of heat required to raise the temperature of a unit mass of a substance 1°C or 1K

Specific Heat Capacities of Substances (Table 1 pg 301)

Substance	Specific Heat Capacity J/(g·°C)
Ice	2.01
Water	4.18
Steam	2.0.1
Aluminum	0.900
Iron	0.444
Methanol	2.918

The study of chemical reactions that involve HEAT is called **thermodynamics!**

Example 1 (pg 301)

When 600 mL of water in an electric kettle is heated from 20°C to 85°C to make a cup of tea, how much heat flows into the water?

Example 2 (pg 301)

What would the final temperature be if 250.0 J of heat were transferred into 10.0 g of methanol at 20.0°C?

Practice pg302 # 9-13

Heat Transfer and Enthalpy Change (pg 302)

A chemical system contains both **kinetic** (movements/vibrations) & **potential** (bonds) energies.

The total energy of a chemical system is the sum of all the KE and PE of the particles in the system and is called its **internal energy** or $E_{(\text{system})}$

$$E_{(\text{system})} = \mathbf{KE}_{(\text{system})} + \mathbf{PE}_{(\text{system})}$$

** it's very difficult to measure $E_{(\text{system})}$ but you can measure ΔE when the chemical system undergoes a change

$$\Delta E = \mathbf{q \text{ (heat involved)}} + \mathbf{w \text{ (work done)}}$$

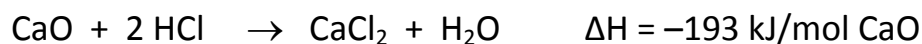
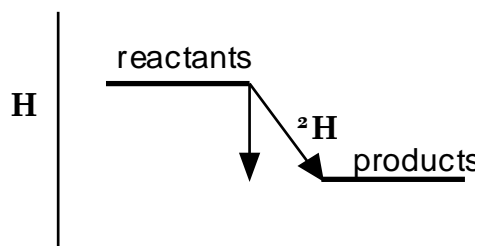
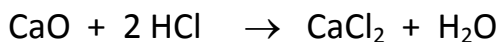
When little to no work is done (i.e. the reaction takes place in an open container) then chemists use another quantity to indicate the amount of heat involved in a chemical change – **enthalpy – H**.

Enthalpy change (ΔH): energy absorbed from or released to the surroundings during a chemical reaction

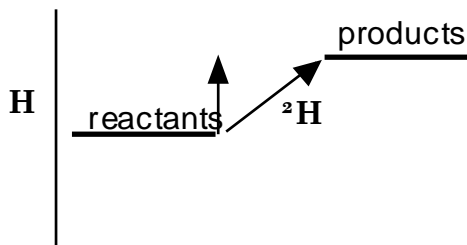
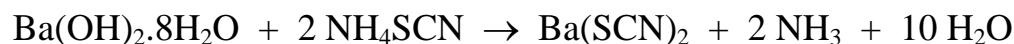
$$\Delta H_{\text{system}} = \pm |q_{\text{surroundings}}|$$

Enthalpy values can tell you important information about the reaction occurring:

1) ΔH is negative = exothermic reaction



2) ΔH is positive = endothermic reaction



Molar Enthalpies (pg 306)

Molar enthalpy (ΔH_x): enthalpy change involving one mole of a substance

** x represents the type of change occurring (eg. Solution, combustion, vaporization, freezing, neutralization, formation, etc.)

See Table 1 pg 306

To calculate ΔH for a substance other than one mole, use:

$$\Delta H = n \Delta H_x$$

ΔH = enthalpy change (kJ)

n = moles (mol)

ΔH_x = molar enthalpy value kJ (from a source) – see table 2 pg 307

Example 1. (pg 307)

A common refrigerant (Freon-12, molar mass 120.91 g/mol) is alternately vaporized in tubes inside a refrigerator, absorbing heat, and condensed in tubes outside the refrigerator, releasing heat. This results in energy being transferred from the inside to the outside of the refrigerator. The molar enthalpy of vaporization for the refrigerant is 34.99 kJ/mol. If 500.0 g of the refrigerant is vaporized, what is the expected enthalpy change ΔH ?

Example 2. (pg 308)

What amount of ethylene glycol would vaporize while absorbing 200.0 kJ of heat?

Practice 308 # 1-3

Calorimetry of Physical Changes (pg 308)

When we investigate energy changes we base our analysis on the **law of conservation of energy**: the total energy change of the chemical system is equal to the total energy change of the surroundings

$$\Delta H_{\text{system}} = \pm |q_{\text{surroundings}}|$$

From this and combining our other two formulae, we can come up with the following equation:

$$n\Delta H_x = mc\Delta T$$

n = moles (mol)

ΔH_x = molar enthalpy (J) – probably need to convert this 1st!

m = mass (g)

c = specific heat capacity in J/(g·°C)

ΔT = temperature change (°C)

Example 1. (pg 309)

In a calorimetry experiment, 7.46 g of potassium chloride is dissolved in 100.0 mL (100.0g) of water at an initial temperature of 24.1°C. The final temperature of the solution is 20.0°C. What is the molar enthalpy of solution of potassium chloride?

Example 2 (pg 310)

What mass of lithium chloride must have dissolved if the temperature of 200.0 g of water increased by 6.0°C? The molar enthalpy of solution of lithium chloride is -37 kJ/mol.

Practice pg 310 # 4,5

Pg 312 # 1-3 (note #1: ethane = C₂H₆)

Representing Enthalpy Changes (pg 313)

Enthalpy changes are represented in one of 4 ways:

1) *Thermochemical Equation with Energy Terms*



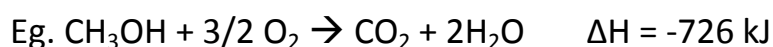
Example 1. (pg 314)

Write a thermochemical equation to represent the exothermic reaction that occurs when 2 moles of butane (C₄H₁₀) burn in excess oxygen gas. The molar enthalpy of combustion of butane is -2871 kJ/mol.

Example 2 (pg 315)

Write a thermochemical equation to represent dissolving one mole of silver nitrate in water. The molar enthalpy of solution is +22.6 kJ/mol.

2) *Thermochemical Equations with ΔH values*



Example 1. (pg 315)

Sulfur dioxide and oxygen react to form sulfur trioxide. The molar enthalpy for the combustion of sulphur dioxide, ΔH_{comb} , in this reaction is -98.9 kJ/mol SO_2 . What is the enthalpy change for this reaction?

Example 2 (pg 315)

Write a thermochemical equation, including a ΔH value to represent the exothermic reaction between xenon gas and fluorine gas to produce solid xenon tetrafluoride, given that the reaction produces 251 kJ per mol of Xe reacted.

3) Molar Enthalpies of Reaction

$$\Delta H_{\text{comb}} = -726 \text{ kJ/mol CH}_3\text{OH}$$

4) Potential Energy Diagrams

See Fig 2 pg 313

Practice pg 319 # 1-3

Hess's Law of Additivity of Reaction Enthalpies (pg 322)

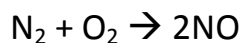
Hess's Law: the value ΔH for any reaction that can be written in steps equals the sum of the values of ΔH for each of the individual steps

Rules for Hess's Law

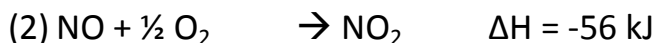
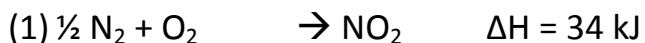
- 1) if a chemical equation is reversed, then the sign of ΔH changes
- 2) if the coefficients of a chemical equation are altered by multiplying or dividing by a constant factor, then the ΔH is altered in the same way

Example1. (pg 324)

What is the enthalpy change for the formation of 2 moles of nitrogen monoxide from its elements?

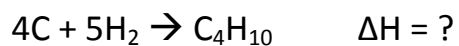


The following equations are known:

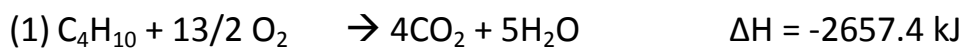


Example 2. (pg 325)

What is the enthalpy change for the formation of one mole of butane (C₄H₁₀) gas from its elements? The reaction is:



The following known equations are provided:



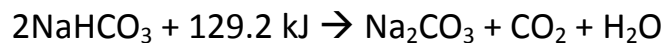
Practice pg 326 #1-3

Multistep Energy Calculations (pg 327)

Using all the formulae so far and Hess's Law, you can now do multi-step calculations.

Example 1. (pg 327)

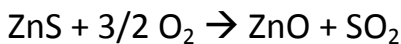
In the Solvay process for the production of sodium carbonate (or washing soda), one step is the endothermic decomposition of sodium hydrogen carbonate:



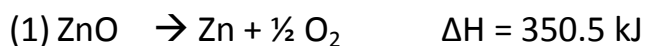
What quantity of chemical energy, ΔH , is required to decompose 100.0 kg of sodium hydrogen carbonate?

Example 2. (pg 328)

How much energy can be obtained from the roasting of 50.0 kg of zinc sulphide ore?



You are given the following thermochemical equations:



Practice pg 329 # 4, 5 (note: #4 ethyne = C₂H₂)

Pg 330 # 2

Standard Enthalpies of Formation (pg 331)

Standard enthalpy of formation: the quantity of energy associate with the formation of one mole of a substance from its elements in their standard states

Standard state refers to the most stable state of the element or compound at SATP.

Example 1. (pg 331)

Write the formation equation for liquid ethanol, C₂H₅OH.

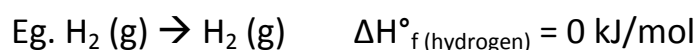
Example 2. (pg 332)

Write the formation equation for liquid carbonic acid.

Practice pg 332 #1

Using Standard Enthalpies of Formation (pg 332)

ΔH°_f for elements: The standard enthalpy of formation of an element already in standard state is zero



Graphite is the more stable form of carbon at SATP, so $\Delta H^\circ_{f(\text{graphite})} = 0$

However diamond is slightly less stable so:



You can use standard enthalpies to calculate ΔH using the following equation:

$$\Delta H = \sum(n\Delta H^\circ_{f(\text{products})}) - \sum(n\Delta H^\circ_{f(\text{reactants})})$$

ΔH = enthalpy change (kJ)

Σ = represents sum

n = moles (mol)

ΔH°_f = standard enthalpy of formation (kJ/mol)

See table on reverse of senior (orange) periodic table **or** C6 pg 799

**note values in text and on table are slightly different. It doesn't matter which ones you use. The answers to text questions correspond to the ones in the book, but I will post answers that correspond to the periodic table on the website.

Example 1(pg 334)

The main component in natural gas used in home heating or laboratory burners is methane (CH_4). What is the molar enthalpy of combustion of methane fuel?

Example 2. (pg 334)

The standard enthalpy of combustion of benzene (C_6H_6) to carbon dioxide and liquid water is -3273 kJ/mol . What is the standard of formation of benzene, given the tabulated values for carbon dioxide and liquid water?

Practice pg 335 # 5

Spontaneity (pg 494)

Spontaneous reactions: reactions that proceed without continuous outside assistance.

Studying energy flow in chemical changes allows us to predict what is possible and what is not.

1st Law of Thermodynamics: P.E. tends only to decrease spontaneously.

Since ΔH is primarily ΔPE then any chemical system that is exothermic ($\Delta H = -ve$) should be spontaneous.

BUT some endothermic reactions are also spontaneous. There must be another driving force pushing these reactions into products.

Enthalpy and Entropy Changes Together Determine Spontaneity (pg 495)

Entropy (S): measure of disorder or randomness

An increase in entropy means an increase in disorder. A change in entropy is calculated by:

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

When $\Delta S > 0$, then $S_{\text{products}} > S_{\text{reactants}}$

When $\Delta S < 0$, then $S_{\text{products}} < S_{\text{reactants}}$

It seems to be a universal phenomenon that a change resulting in an increase in entropy is more likely to occur than a decrease in entropy. The tendency for systems to achieve greater disorder is simply a result of the laws of probability.

Predicting the Sign of ΔS (pg497)

A system will experience an increase in entropy ($\Delta S > 0$) if,

- The volume of the gaseous system increases
- The temperature of a system increases
- The physical state of a system changes from solid to liquid or gas, or liquid to gas ($S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$)

In chemical reactions, entropy increases ($\Delta S > 0$) when

- Fewer moles of reactant molecules form a greater number of moles or product molecules
- Complex molecules are broken down into simpler units
- Solid reactants become liquid or gaseous products (or liquids become gases)

Practice pg 498 #1

ΔH and ΔS

To predict spontaneity, there are 4 possibilities

$\Delta H = +ve / \Delta S +ve$ (reaction is spontaneous at all temperatures)

$\Delta H = +ve / \Delta S -ve$ (rx cannot be spontaneous at any temp)

$\Delta H = -ve / \Delta S -ve$ (rxn tends to be spontaneous at low temp)

$\Delta H = +ve / \Delta S +ve$ (rx tends to be spontaneous at high temp)

Rate of Reaction (pg 360)

Chemical kinetics: study of ways to make a chemical reaction speed up or slow down

Rate of reaction: the speed at which a chemical change occurs

$$r = \Delta c / \Delta t$$

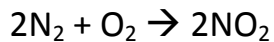
r = rate in mol/(L·min)

Δc = change in concentration (mol/L)

Δt = change in time (min)

Example 1. Pg 360

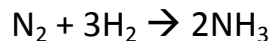
What is the overall rate of production of nitrogen dioxide in the system



If the concentration of nitrogen dioxide changes from 0.32 mol/L to 0.80 mol/L in 3 min?

Example 2. (pg 361)

What is the average rate of production of ammonia for the system, between 1.0 and 4.0 min,



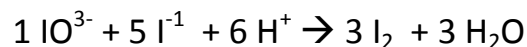
If the concentration of ammonia is 3.5 mol/L after 1.0 min and 6.2 mol/L after 4.0 min?

Practice pg 361 # 1, 2

Reaction rates can also be determined for various substances if the rate of one substance is known in a chemical reaction.

Example 1 (pg 363)

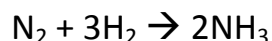
Consider the reaction of iodate, iodide, and hydrogen ions to yield iodine and water.



What are the rates of reaction with respect to the various reactants and products? The rate of reaction with respect to iodate ions (rate of consumption of IO_3^-) is determined experimentally to be $3.0 \times 10^{-5} \text{ mol}/(\text{L}\cdot\text{s})$

Example 2. (pg 364)

When nitrogen and hydrogen gases react to produce ammonia gas, the reaction is



What is the rate of consumption of each of the reactants when the rate of production of ammonia is $4.0 \times 10^{-3} \text{ mol}/(\text{L}\cdot\text{s})$?

Practice 364 # 3, 4

Factors Affecting Reaction Rate (pg 367)

There are 5 factors that affect the rate of reaction:

1) Chemical Nature of Reactants

- Some materials are prone to react faster than others based on their chemical make-up
- There is no specific rule but generally
 - Monatomic ions (eg. Ag^+ , Cl^-) react extremely fast
 - Molecular substances react slower

Eg. $\text{C}_6\text{H}_{12}\text{O}_6$ reacts slower with MnO_4^- than Fe^{2+} reacts with MnO_4^-

2) Concentration

- Increasing the concentration of a substance increases the reaction rate

Eg. Concentrated sulphuric acid burns more quickly than diluted sulphuric acid

3) Temperature

- Increasing the temperature of a substance increases the reaction rate

Eg. Dissolving sugar in hot water is faster than in cold water

4) Presence of a Catalyst

- **Catalyst:** substance that alters the rate of a chemical reaction without itself being permanently changed
- Using a catalyst will speed up a reaction

Eg. Enzymes in the body assist other molecules in basic function so processes can be carried out faster

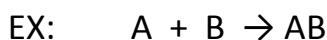
5) Surface Area

- Increasing the surface area of a substance increases the rate
Eg. Chopped food will cook faster than food left whole

Practice pg 371 # 1

Collision Theory and Rate of Reaction (pg 383)

For a reaction to occur a collision must occur between the reactants. The rate of a reaction reflects the probability of this collision.



If you have only 1A & 1B - there is only 1 chance of collision

If you have only 2A & 1B - there are 2 chances of collision

If you have only 3A & 1B - there are 3 chances of collision

If you have only 3A & 2B - there are 6 chances of collision

If you have only 3A & 4B - there are 12 chances of collision

So increasing the # of collisions, causes an increase in reaction rate.

Evidence:

1) Concentration: an increase in concentration means more particles are present so the chance of collision is higher. This will result in more collisions = \uparrow reaction rate!

2) Temperature: increasing temperature increases the speed at which particles move. The faster speed increases change of collision = \uparrow reaction rate!

3) Catalyst: assist molecules to react with each other and increase probability of collision. This means \uparrow reaction rate!

4) Surface Area: a higher surface area means there are more spaces for the particles to collide with each other. Again, \uparrow reaction rate!

Activation Energy (pg 384)

Activation energy: the minimum increase in potential energy of a system required for molecules to react

So a lower activation energy will increase rate of reaction. Adding a catalyst or changing the nature of the reactants will lower the activation energy, making it easier for the reaction to occur.

Rate Laws and Order of Reaction (pg 372)

The rate of a reaction is exponentially proportional to the product of the initial concentrations of the reactants. So if you know the rate of reaction and starting concentrations of the reactants, you can determine the effects of changing the concentration of the various reactants on the reaction rate.

Rate Law Equation

$$r = k [X]^m [Y]^n$$

r = rate of reaction in mol/L's

k = rate constant

$[X]$ = concentration of reactant X (mol/L)

$[Y]$ = concentration of reactant Y (mol/L)

m & n = **order of reaction** (exponent value that describes the initial concentration dependence of a particular reactant)

Example

For the reaction $2X + 2Y + 3Z \rightarrow$ products

you are told the rate law equation is:

$$r = k[X]^1[Y]^2[Z]^0$$

So this means:

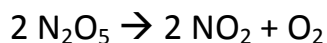
X: increases equally with rate, so doubling X, doubles rate **or** tripling X, triples rate

Y: increases rate by a power of 2; so doubling Y, quadruples rate ($2^2=4$) **or** tripling Y will multiply rate by 9 (3^2)

Z: since the power is zero, no matter what you do to the concentration of Z, you will not affect the reaction rate

Example 1 (pg 374)

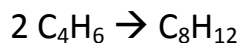
The decomposition of dinitrogen pentoxide,



Is first order with respect to N_2O_5 . If the initial rate of consumption is 2.1×10^{-4} mol/ (L·s) when the initial concentration of N_2O_5 is 0.40 mol/L, predict what the rate would be if another experiment were performed in which the initial concentration of N_2O_5 were 0.80 mol/L.

Example 2 (pg 374)

The dimerization reaction 1,3-butadiene (C_4H_6)



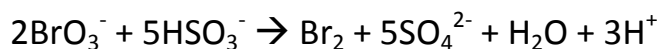
Is second order with respect to C_4H_6 . If the initial rate of reaction were 32 mmol $C_4H_6/(L \cdot min)$ at a given initial concentration of C_4H_6 , what would be the initial rate of reaction if the initial concentration of C_4H_6 were doubled?

Practice pg 377 # 2

Determining Rate Law Equations (pg 375)

Example 1 (pg 375)

When aqueous bromate and bisulfite ions react to produce bromine, the overall equation is

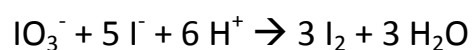


Consider the series of experiments recorded below, in which initial reactant concentrations are varied and rates are compared. From the evidence provided, determine a rate equation.

Trial	Initial $[BrO_3^-]$ (mmol/L)	Initial $[HSO_3^-]$ (mmol/L)	Initial rate of Br_2 production (mmol/L·s)
1	4.0	6.0	1.60
2	2.0	6.0	0.80
3	2.0	3.0	0.20

Example 2 (pg 376)

Mixing an acidic solution containing iodate, IO_3^- , ions with another solution containing I^- ions begins a reaction that proceeds, in several reaction steps to finally produce molecular iodine as one of the products.



The data below is obtained for rate of production of iodine.

Trial	Initial $[\text{IO}_3^-]$ (mmol/L)	Initial $[\text{I}^-]$ (mmol/L)	Initial $[\text{H}^+]$ (mmol/L)	Rate of production of iodine (mmol/L's)
1	0.10	0.10	0.10	5.0×10^{-4}
2	0.20	0.10	0.10	1.0×10^{-3}
3	0.10	0.30	0.10	1.5×10^{-3}
4	0.10	0.30	0.20	6.0×10^{-3}

- a) What is the rate equation for this reaction?
- b) What will the rate of reaction be when $[\text{IO}_3^-] = 0.200 \text{ mmol/L}$, $[\text{I}^-] = 0.40 \text{ mmol/L}$, and $[\text{H}^+] = 0.10 \text{ mmol/L}$?

Practice pg 377 #3, 4, 6

Chemical Kinetics & Half-Life (pg 379)

Half-life: time for half of the nuclei in a radioactive sample to decay, or half the amount of a reactant to be used up

Formulae for half-life:

$$\frac{\ln [A]_0}{[A]_t} = kt \quad \text{and} \quad [A]_t = [A]_0 e^{-kt}$$

ln & e (see calculator)

$[A]_0$ = initial concentration (mol/L)

$[A]_t$ = concentration at designated time

k = rate constant

t = time

Half-life & first order reactions

The following equation applies **only** to reactions that are **1st order**:

$$kt_{1/2} = 0.693$$

k = rate constant

$t_{1/2}$ = half-life

Example 1 (pg 380)

The radioisotope lead-212 has a half-life of 10.6 h. What is the rate constant for this isotope?

Example 2 (pg 380)

If the mass of an antibiotic in a patient is 2.464 g, what mass of antibiotic will remain after 6.0 h, if the half-life is 2.0 h, and no further drug is taken?

Practice pg 381 # 7, 8

Pg 381 #4

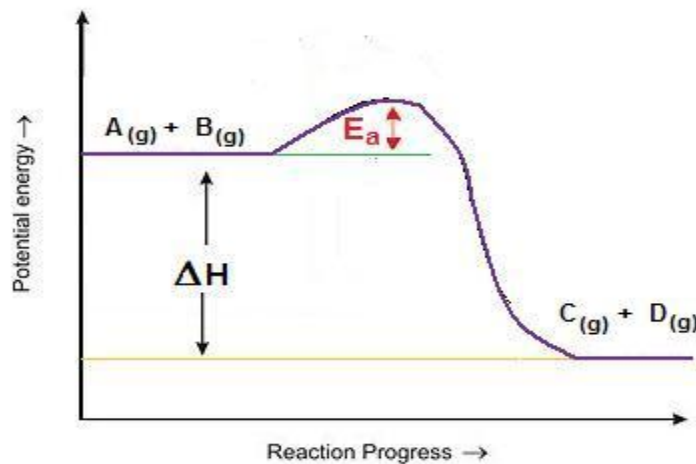
Reaction Mechanisms (pg 387)

Reaction mechanism: series of elementary steps that make up an overall reaction

Elementary step: step in a reaction mechanism that only involves one-, two-, or three-particle collisions

Essentially in a chemical reaction there are a series of “mini-steps” that occur before the overall reaction is completed.

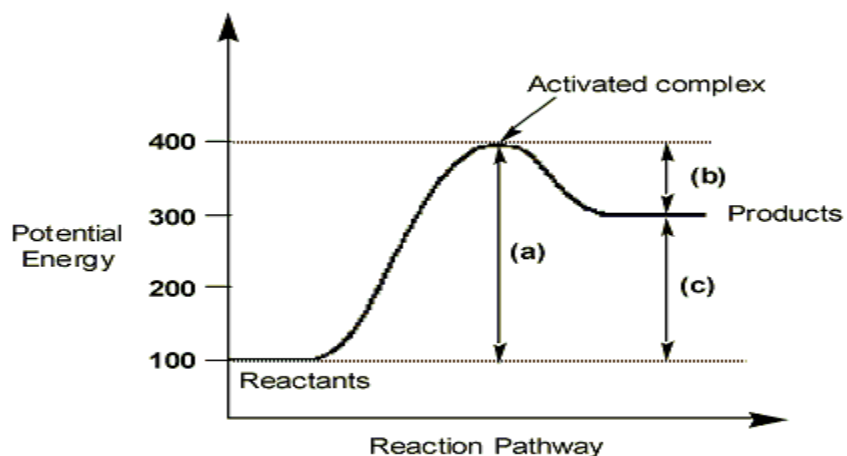
Potential Energy Changes During an Exothermic Reaction



E_a : activation energy

So in an exothermic reaction, there is a decrease in the initial energy of the reaction meaning that the energy is being transferred to the surroundings.

Potential Energy Changes During an Endothermic Reaction



(b) = activation energy

(c) = ΔH

So in an endothermic reaction, there is an increase in the initial energy of the reaction meaning that the energy is being absorbed from the surroundings.

Activated complex: unstable chemical species containing partially broken and partially formed bonds

Rate-determining step: slowest step in a reaction mechanism

Reactions rates are determined by the rate-determining step. Regardless of how fast any of the other steps of a reaction are, the slowest step decides rate.

Furthermore, if a reaction requires a lower activation energy to occur, then the rate-determining step will be sped up when compared to a reaction with a higher activation energy.

Practice pg 387 #1

Pg 391 #3