**Unit 1- Thermochemistry, Energy and Rates of Reaction (Chap.5-6)**

**Review of Grade 11 Material**

From here on, in this course you will be working with moles, molarity, volumes, mass and other measuring concepts. YOU NEED TO REVIEW GRADE 11 MATERIALS! If you cannot do these review question talk to your teacher.

The three equations you need to know are the three different expressions for the mole in a pure sample, a solution and a gas. The terms and equations are given below.

n= moles (units mol) [ X ], C or M (molarity) are all used for molar concentration units = moles/L

m= mass (units g) V = Volume (units L) Mm = molar mass (units g/mol)

Equations for Moles ****

****

****

When a system is expressed as a substance dissolved in solution the first two equations can be combined, giving:



For diluting solutions: moles concentrated = moles diluted



**REVIEW CHALLENGE**

4.2 g of Mg(s) reacts with 15.0 mL of 3.00 M HCl(aq). What volume of H2(g) is produced at 18°C and 101.2 kPa?

Always show full solutions for your work. For stoichiometry problems, after a balanced equation has been written, write a mole ratio based on the balanced equation.

1. What mass of NaOH is required to make 250. mL of a 0.150M solution? *(ans. 1.50g)*

2. What volume of 17.5M acetic acid is required to make 2.00L of 0.500M acetic acid? *(ans. 57.1 mL)*

3. a) How many moles of CaCl2 are found in 75.0 mL of 1.50M solution of CaCl2? *(ans. 0.112 mol)*

b) How many moles of Cl-  ions are found in the solution? *(ans. 0.224 mol)*

4. A 100. mL solution contains 5.35g of NH4Cl. Calculate the molar concentration of the solution. *(ans. 1.00M)*

5. It is determined that 75.0 mL of 0.100M solution contain 0.439g of a substance. Calculate the molar mass of the substance. *(ans.58.5 g/mol)*

6.a) Calculate the number of moles of CuSO4.5H2O contained in 25.0mL of 0.200M solution. *(ans. 5.0 x 10-3 mol)*

b) What mass of CuSO4.5H2O is contained in this solution? *(ans. 1.25g)*

7. NH4Cl has a ΔHºsolution = 14.78 kJ/mol. If you dissolved 2.68g of NH4Cl in water, calculate the ΔHº for this amount of NH4Cl. Enthalpy or ΔHºsolution tells us the energy change (in kJ) that occurs when a salt is dissolved in water to make a solution. *(ans. 0.74 kJ)*

8. When sodium hydroxide dissolves in water, the temperature of the solution increases. Calculate the ΔH solution in kJ/mol NaOH if the enthalpy change is 11.1 kJ when 10.0g of NaOH is dissolved. *(ans. 44.4 kJ/mol)*

**Energy Definitions (**Text page 286)

**Energy** is the capacity of a system to do work (i.e. make an object move).

**Thermochemistry** is the study of energy changes during physical and chemical changes.

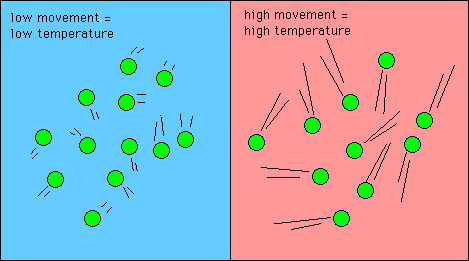
**Potential energy** is energy due to position or composition. The energy associated with chemical bonds is an example of potential energy. If during a chemical reaction the bond energy changes from reactants to products releasing energy, the temperature increases (for example when gasoline is burned) indicating an energy change.

**Kinetic energy** is the energy of motion. When the temperature of a substance increases, the particles of that substance move faster with more kinetic energy.

**Internal energy** is the total potential and kinetic energy of a substance.

**Heat** is a verb for the thermal energy transferred from a hot object to a cooler object. When two object of differing temperature interact they will transfer heat until they reach the same temperature. Energy must be conserved during these heat transfers, so the energy lost by one substance must be equivalent to the energy gained by the other substance.

**Temperature** is a measurement of the average kinetic energy of a substance. All matter has a temperature associated with it that is a direct measure of the motion of the molecules:



The more kinetic energy matter has the higher temperature it will also have. If heat is loss or gain by matter kinetic energy is loss or gain with a corresponding decrease or increase in temperature.

**Specific Heat:** Specific heat is a physical property of matter. It is defined as the energy needed to raise the temperature of one gram of a substance by one degree Celsius. Units: J/g⋅°C

Specific Heat = energy absorbed or c = **q** mass of sample × temperature change in °C m × ΔT

Rearranging the equation **q = m** × **c** × **ΔT** givesus an equation for energy

**Molar heat capacity:** is the energy required to raise the temperature of one mole of a substance by 1 °C (J/mol⋅°C)

Consider the specific heat of copper, 0.385 J/g ºC.

What does this mean?

|  |  |
| --- | --- |
| **Some common specific heats capacities:** | |
| Substance | *c*  (J/g 0C) |
| Air | 1.01 |
| Aluminum | 0.900 |
| Copper | 0.385 |
| Carbon (graphite) | 0.710 |
| Gold | 0.129 |
| Iron | 0.444 |
| Mercury | 0.140 |
| Methanol(l) | 2.92 |
| NaCl | 0.864 |
| Ice | 2.03 |
| Water | 4.179 |

**Example 1**: How much energy does it take to raise the temperature of 50. g of copper by 10. ºC? *(Ans. 190 J)*

**Example 2**: If we add 30. J of heat to 10. g of aluminum, by how much will its temperature increase? *(Ans. 3.3ºC)*

**Example 3:** Find the molar specific heat capacity for Copper.

**Calorimetry and Hess’s Law (Chapters 5.1 and 5.2)**

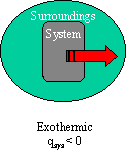
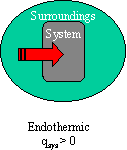
**Calorimetry**

Energy changes occur when 1) two materials at different temperature exchange energy

2) energy is lost or gained during a chemical reaction when reactants are converted to products. (Text page 288)

**Type 1 Problems: Heat exchange**

*Endothermic* q > 0 *Exothermic* q < 0



**Type 2 Problems: Chemical to Thermal Energy Exchange**

Reactants

Products

Δ*EP*

Products

Δ*EP*

*Released to Surroundings*

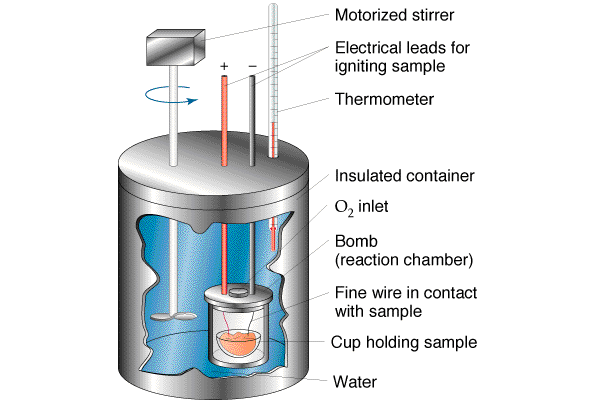
*Absorbed from Surroundings*

Reactants

**Demo**: Endothermic and Exothermic reactions.

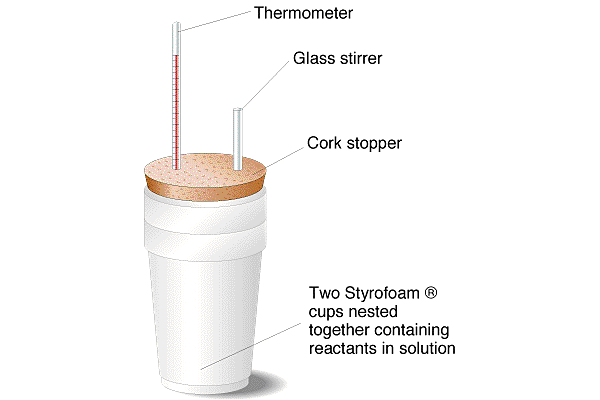
The measurement of the **amount** of energy lost or gained by the system to the surroundings is called calorimetry. A Calorimeter is the instrument used to measure temperature changes that are then related to energy changes. There are two types of calorimeters, constant volume and constant pressure calorimeters.

**Calorimeters:**



The following diagram depicts a **constant volume** or 'bomb' calorimeter used for reactions that involve gases. The container is sealed so the gases cannot escape.

**qsurr = C × T**



For reactions that do not involve gases a constant pressure calorimeter is used. A much simpler, but less accurate calorimeter of this type is a coffee cup calorimeter.

**qsurr = m× c × T**

* The calorimeter either has a heat capacity (c with units J/°C) associated with it where **qsurr = CT,** or the mass of water in the calorimeter is known (the remainder of the calorimeter is considered to have negligible heat capacity) and the equation **qsurr = m c T** is used with the mass and specific heat capacity of the water as the surroundings.

**Enthalpy Changes (Chap 5.2)**

The thermal energy of a substance is called its enthalpy (*H*). The specific enthalpy of one substance cannot be determined by measurement. However, changes in enthalpy can be measured if it is assumed that the quantity of energy lost or gained by the system is equal in quantity to the energy transferred to or from the surroundings respectively.

**Type 1 Problems: Heat exchange (refer to CP pg. 5 for diagram):**

When two substance of different temperature are combined (but do not react or physically change in any way) and are allowed to equilibrate to a new common temperature. The calorimeter is always considered the surroundings.

* **q for the system is positive** if energy goes into the system and the temperature of the surroundings decreases.
* **q for the system is negative** if the system loses heat to the surroundings and the temperature of the surroundings increases
* The overall energy must be conserved **qsystem = -qsurroundings**

*Example:*

*In a coffee cup calorimeter, an unknown mass of iron heated to 75oC is added to 50. mL of water. The temperature of the solution rises from 20.oC to 27oC. Calculate the mass of iron.*

**Type 2 Problems: Chemical to Thermal Energy Exchange (refer to CP pg. 5 for diagram):**

When a physical or chemical change occurs that releases or absorbs energy.

* thermal (kinetic) energy from the surroundings is converted to bond energy for the system in endothermic reactions
* bond energy from the system is converted to thermal energy in the surroundings in an exothermic reactions
* The overall energy must be conserved **∆Hsystem = -qsurroundings**

The units of enthalpy are kilojoules (**kJ**)

* If the amount of substance that reacted is given, the enthalpy can be expressed as a molar quantity or molar enthalpy (**∆Hrxn)**. The question will usually indicate which reactant or product it requires a molar enthalpy calculation for. **n × ∆Hrxn = -qsurroundings**

The units of molar enthalpy are kilojoules per mol (**kJ/mol**).

*Example*

*0.500 gram of H2CO, is combusted in a bomb calorimeter, and the temperature of the bath in the calorimeter (150 g H2O) changes from 24.0 to 39.2oC.*

*a) What amount of thermal energy was released to the surroundings? (Answer in kJ)*

*b) What is the molar enthalpy of combustion* ***∆Hcomb*** *for H2CO? (Answer in kJ/mol)*

More Examples of Calorimeter Calculations in Text p. 294- 297

***Note:*** *∆Hx, the molar enthalpy, can refer to any physical or chemical change that involves a temperature change. For example ∆H****neut*** *is the energy change when a mole of acid or base is* ***neutralized*** *and ∆H****sol*** *is the energy change when a mole of a solid is dissolved to make a* ***solution****. The quantity of energy is specific to the equation and will change if reactant or products have different phases or coefficients. For example H2O(s) → H2O****(l)*** *will not have the same enthalpy change as H2O(s) → H2O****(g)*** *and 2 H2(g) + O2(g) → 2H2O****(l)*** *will not have the same enthalpy as H2(g) + ½ O2(g) → H2O****(l)****.*

**Specific Heat and Heat Capacity Worksheet**

1. The temperature of 335 g of water changed from 24.5oC to 26.4oC. How much energy did this sample absorb? c for water = 4.18 J/goC *(ans. 2.66 kJ)*

2. How much energy in kilojoules has to be removed from 225g of water to lower its temperature from 25.0oC to 10.0oC? *(ans. –14.1 kJ)*

3. To bring 1.0 kg of water from 25oC to 99oC takes how much energy input is required? *(ans. 3.1 x 102 kJ)*

4. An insulated cup contains 75.0g of water at 24.00oC. A 26.00g sample of metal at 82.25oC is added. The final temperature of the water and metal is 28.34oC. What is the specific heat of the metal? *(ans. 0.971 J/goC )*

5. A calorimeter has a heat capacity of 1265 J/oC. A reaction causes the temperature of the calorimeter to change from 22.34oC to 25.12oC. How many joules of energy were released in this process?

*(ans. 3.517 kJ released)*

6. What is the specific heat of silicon if it takes 192J to raise the temperature of 45.0g of Si by 6.0oC? *(ans. 0.71 J/goC)*

7. Aqueous silver ion reacts with aqueous chloride ion to yield a white precipitate of solid silver chloride. When 10.0 mL of 1.00M AgNO3 solution is added to 10.0mL of 1.00 M NaCl solution at 25oC in a calorimeter a white precipitate of AgCl forms and the temperature of the aqueous mixture increases to 32.6oC. Assuming that the specific heat of the aqueous mixture is 4.18 J/goC, that the density of the mixture is 1.00 g/mL, and that the calorimeter itself absorbs a negligible amount of energy, calculate the amount of energy absorbed by water in kJ/mol of Ag+. *(ans. -64 kJ/mol)*

8. When 25 mL of 1.0M H2SO4 is added to 50 mL of 1.0 M NaOH at 25oC in a calorimeter, the temperature of the aqueous solution increases to 33.9 oC. Assuming that the specific heat of the solution is 4.18 J/g°C, that its density is 1.00 /mL, and that the calorimeter itself absorbs a negligible amount of energy, calculate the amount of energy absorbed by the surroundings for the reaction. *(ans. 2.8 kJ heat absorbed)*

9. Titanium metal is used as a structural material in many high-tech applications such as jet engines. What is the specific heat of titanium in J/g°C if it takes 89.7 J to raise the temperature of a 33.0g block by 5.20°C? What is the molar heat capacity of titanium in J/mol °C? *(ans. 25.0 J/molºC)*

10. Sodium metal is sometimes used as a cooling agent in heat exchange units because of its relatively high molar heat capacity of 28.2 J/mol°C. What is the specific heat of sodium in J/g°C? *(ans. 1.23 J/gºC)*

**Homework:**

* **Text p.301 Practice questions # 1- 4,**
* **Print Hess’s Law Lab**

**Writing Thermochemical Equations** (p.301)

* Thermochemical equations include the ΔH values
* The equations are always interpreted in terms of moles
* These equations are the only ones that allow fractional coefficients

*Ex.*

*CH4(g) + 2 O2(g) → CO2(g) + 2H2O(l) + 890.32 kJ*

*CH4(g) + 2 O2(g) → CO2(g) + 2H2O(l) ΔHcomb =* ***–*** *890.32 kJ*

1. *Is this reaction endothermic or exothermic? \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_*
2. *What is the enthalpy change for each mole of oxygen reacted?*
3. *If 20.0 g of methane are burned, what will the enthalpy change be?*

***n× ∆Hcomb = ∆H***

**Textbook Questions: p. 306 # 2- 4, 6, 7**

##### Enthalpy Practice Problems

1. For the reaction

S(s) + O2 (g) → SO2 (g) ΔHrxn=-296 kJ

1. How much heat is evolved when 275g sulfur is burned in excess O2? *(ans: -2.54×103 kJ)*
2. How much heat is evolved when 25mol sulfur is burned in excess O2? *(ans: -7.4×103 kJ)*
3. How much heat is evolved when 150g sulfur dioxide is produced? *(ans: -693kJ)*

2. In a coffee-cup calorimeter, 50.0mL of 0.100M AgNO3 and 50.0mL of 0.100HCl are mixed to yield the following reaction:

Ag+ (aq) + Cl- (aq) → AgCl (s)

The two solutions were initially at 22.60ºC, and the final temperature is 23.40ºC. Calculate the molar enthalpy change for this reaction in kJ/mol of AgCl formed. Assume that the combined solution has a mass of 100.0g and has a specific heat capacity of 4.18 J/ºC ·g. *(ans: -66 kJ/mol)*

3. Consider the dissolution of CaCl2: CaCl2(s) → Ca2+ (aq) + 2Cl- (aq) ΔHsol= -81.5kJ

An 11.0 g sample of CaCl2 is dissolved in 125 g of water, with both substances at 25.0 ºC. Calculate the final temperature of the solution assuming no heat loss to the container and assuming the density of the solution is 1.00 g/mL with a specific heat capacity of 4.18 J/ºC·g. *(ans 40.4ºC)*

\*\*Note: In the Nelson Text, the mass of the surroundings is assumed to be the mass of water only, not the mass of the CaCl2 solution, 125 g vs 136 g. This is an assumption error just like assuming the container has a negligible heat capacity and the density and heat capacity of the solution is the same as that of pure water. The answer is based on a 136 g mass.

4. Camphor (C10H16O) has an enthalpy of combustion of -5903.6 kJ/mol. The temperature of the calorimeter increases by 2.28ºC when a 0.1204 g sample of camphor is burned in a bomb calorimeter. Calculate the **heat capacity (C)** of the calorimeter. *(ans 2.05 kJ/ºC)*

**Hess’s Law** (p.314- 317)

Enthalpy is a state function; the change in enthalpy in going from some initial state to some final state is independent of the pathway. This means that in going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. This principle is known as Hess’s Law after the Swiss-born chemist Germain Henri Hess.

For example, the addition of hydrogen to acetylene to form ethane can be carried out

in one step:

HC≡CH(g) + 2H2(g)  H3C-CH3(g) ΔH = -311.42 kJ

or in two steps:

HC≡CH(g) + 1H2(g) H2C=CH2(g) ΔH = -174.47 kJ

H2C=CH2(g) + 1H2(g) H3C-CH3(g) ΔH = – 136.95 kJ

Sum of the reactions:

In order to use Hess’s Law to calculate changes in enthalpy for reactions, it is important to understand two characteristics of ΔH for a reaction:

1. If a reaction is reversed, the sign of ΔH is also reversed.

2. The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced equation are multiplied by an integer, the value of ΔH is multiplied by the same integer.

For example: Use the following equations to calculate ΔH in kJ for the combustion of methane.

We want to find ΔH for: CH4(g) + 2O2(g) → CO2(g) + 2 H2O(l)

We are given: #1 CH4(g) + O2(g) → CH2O(g ) + H2O(g) ΔH = -284 kJ ×1

#2 CH2O(g) + O2(g) → CO2(g) + H2O(g) ΔH = - 518 kJ ×1

#3 H2O(l) → H2O(g) ΔH = 44.0 kJ × ̵ 2

Given Overall: CH4 + 2O2 → CO2 + 2 H2O ΔH =?

*thought process: want CH4 as a reactant, so keep #1 as is… want CO2 as product and CH2O to disappear altogether so keep #2 as is and we want 2 waters in liquid state so reverse #3 and ×2.*

(ans: ΔH = - 890 kJ)

See more sample problems on page 316 and 317

**Textbook Questions: p. 317 #1- 3; p. 318 # 1, 4- 8**

**Hess’ Law Practice Problems**

1. Calculate the ΔHrxn for the following reaction: **Ca(s) + 2C(s)  + 3 O2(g)  → 2 CaCO3(s)**

Given:*(Ans: -2413.8 kJ)*

2 Ca(s) + O2(g) → 2 CaO(s) Δ H2 = -1270.18 kJ

C(graphite) + O2(g) → CO2(g) Δ H3 = - 393.51 kJ

CaO(s) + CO2(g) → CaCO3(s) Δ H 4 = -178.32 kJ

1. Calculate ΔHrxn for **Sn(s) + Cl2(g) → SnCl2(s)** *(Ans: -349.8 kJ)*

Given:

Sn(s) + 2 Cl2(g) → SnCl4(l) Δ Hr = -545.2 kJ

SnCl2(s) + Cl2(g) ) → SnCl4(l)  Δ Hr = -195.4 kJ

1. For the reaction **2 KClO3(s) → 2 KCl(s) + 3O2(g)** Δ Ho = -91.0 kJ

a) What is the Δ Ho for the reaction 2 KCl(s) + 3O2(g) ) → 2 KClO3(s)

b) What is ΔHo for the reaction KClO3(s) ) → KCl(s) + 3/2 O2(g)

*(Ans: a) 91.0 kJ, b) –45.5 kJ)*

1. Calculate ΔHr for the reaction **MnO2(s) + 2C(graphite) ) → Mn(s) + 2CO(g)** from the following information : *(Ans: 298.99 kJ)*

Mn(s) + O2(g) ) → MnO2(S) ΔH = -520.03 kJ

2C (graphite) + O2(g) ) → 2 CO(g) ΔH = -221.04 kJ

1. Given: S(s) + O2(g) ) → SO2(g) ΔH = -296.83 kJ

2S(s) + 3O2(g) ) -→ 2 SO3(g) ΔH = - 791.44 kJ

Use Hess’s Law to calculate the ΔH for the reaction

**2SO2(g) + O2(g) → 2SO3(g)**

*(Ans: -197.78 kJ)*

1. Calculate the enthalpy change for the reaction: **WO3(s) + 3H2(g) ) → W(s) + 3H2O(g)**

from the following information : *(Ans: 125.94 kJ)*

2W(s) + 3O2(g) ) → 2WO3(s) ΔH = -1685.4 kJ

2H2(g) + O2(g) ) → 2H2O(g) ΔH = -477.84 kJ

1. Given: **2H2(g) + O 2(g) ) → 2H2O(l)** ΔH = -571.66 kJ

N2O5(g) + H2O(l) ) → 2HNO3(l) ΔH = -92.0 kJ

N2(g) + 3O2(g) + H2(g) ) → 2 HNO3(l) ΔH = -348.2 kJ

Calculate the heat of reaction for: 2N2(g) + 5O2(g) ) → 2 N2O5(g) *(Ans: 59.26kJ)*

##### Text

**Standard Enthalpies of Formation/ Standard Heats of Formation**  (p. 319-324)

**Formation** **reactions**are *reactions in which a compound is formed from its element.*

For example: methane, CH4 is formed from the elements solid carbon (graphite) and hydrogen gas.

C(s) + 2H2(g) → CH4(g)

The formation equation for calcium hydroxide is:

Ca(s) + O2(g) + H2(g) → Ca(OH)2(s)

Calcium hydroxide can also be formed by synthesis reaction

CaO(s) + H2O(l) → Ca(OH)2(s)

but this is **not** a formation reaction because CaO and H2O are **compounds**, not elements.

A set of **standard conditions** has been defined so that results can be compared between laboratories easily. Both the reactants and products in the formation equation must be under standard conditions.

**Conventional Definitions of Standard State (\_\_**°**)**

From this point onwards, the superscript “**°**”, e.g. ΔHf**°**, refers to a specific set of conditions, outlined as follows. Standard ambient temperature (in SATP) is 25oC = 298 K.

**For a compound:**

* for a gaseous substance is at a pressure of 1 atm or 101.3 kPa.
* for non-gaseous pure substances, the standard state is pure liquid or solid
* for a dissolved substance in solution, the standard state is at a concentration of exactly 1.0 M.

**For an element:**

* the standard state of an element is the form in which the element exists under STAP conditions of 1 atm (101.3 kPa) and 25°C = 298K.

**Standard Enthalpy Change**, Δ**H°** , is the enthalpy change that accompanies a reaction when the reactants and products are in their standard states.

**Standard Enthalpy of Formation**, **ΔH°f**, is the enthalpy change that results when **one mole** of the substance is formed from its elements with all substances in their standard states.

The standard enthalpies of formation of for any element already in its standard states is zero.

A table of **ΔH°f**values is given in your text book on page 320. Note the units for standard heat of formation ΔH°f are kJ/mol. The list in your text is very limited so a second table from a University textbook has also been provided.

X2  in element form:H O F Br I N Cl

**Remember: Elements → 1 Compound**

Practice:

1. Write the formation equation for each of the following:
2. Mg(OH)2(s) b) C3H8 (g)
3. Write heat of formation equations for the following:

a) CH3OH (l) b) H2O(g) c) CaSO4(s)  d) NH4ClO4(s) e) SiCl4(l) f) CO (g) g) O(g) h) H2O(l)

\*Note: Many useful values can be calculated from this data. For example

i) if you double equation g) it gives the energy to break a O=O bond under standard conditions.

ii) the difference between the standard heats of formation of b) and h) is the energy released when water is condensed under standard conditions.

*Answers for first two problems:*

# *a) C(s) + 2 H2(g) + ½ O2(g)→ CH3OH (l) ΔH°f = -239.1 kJ/mol (value from text page 320)*

*b) H2(g) + ½ O2 (g)* ***→***  *H2O(g) ΔH°f* *= -241.8 kJ/mol*

**Using Standard Heats of Formation in Hess’s Law** (p.320-323)

The standard heats of formation can be used to calculate the heat of reaction for any chemical reactions. The concept is that in order to form the products there is a two-step process :

Step 1) **reactants** broken down → into their **elements** in standard state

Step 2) **elements** in standard state assembled→ into the new **products** in their standard states

(Page 321 text- atomic diagram)

CH4(g) + 2O2(g) → C(s) + 2H2(g) + 2 O2(g) → CO2(g) + 2 H2O(l)

**ΔHr° = sum of (moles × standard enthalpies - sum of (moles × standard enthalpies**

**of formation of products) of formation of reactants)**

**ΔHr° = nΔH°f products - nΔH°f reactants**

Because ΔH°f values are given on a per-mole basis, we must multiply the ΔH°f value for each substance by the stoichiometic coefficient of that substance in the balanced chemical equation.

*Example: CH4(g) + 2O2(g) → CO2(g) + 2 H2O(l) ΔH = ??*

See examples in text page 322 to 323

**Textbook Questions: p. 324 # 1- 10**

**Calculating ΔH using Bond Energies (**p. 307-312)

## This is a less accurate method than calorimetry.

Bond energy is the **average** energy needed to break a given type of bond. From the table below, you can see that a double bond is not only shorter than a single bond but also stronger.

# Bond Lengths and Strengths:

**Bond Length (in pm) Bond energy (in kJ/mol) Example**

C—C 154 347 H3C – CH3

C=C 134 614 H2C=CH2

C≡C 120 839 HC≡CH

# Bond Energy and Enthalpy (ΔH)

Bond energy values can be used to calculate **approximate** energies for reactions.

ΔH = sum of the energies required to break old bonds (positive signs) plus the sum of the energies released in the formation of new bonds (negative signs).

**ΔH = Σ n×D (bonds broken) - Σ n×D (bonds formed)**

D = bond energy per mole of bonds

n = moles (based on equation coefficients)

Σ = sum of terms

A chart of bond energies is given in your textbook on page 307.

*Example 1) Determine the enthalpy change for the reaction: H2(g) + F2(g) → 2 HF(g) given the bond energies*

*DH-H = 432 kJ/mol DF-F = 154 kJ/mol DH-F = 565 kJ/mol*

ΔH = 1molH-H × DH-H + 1 molF-F × DF-F – 2 molH-F × DH-F

= 1~~mol~~H-H (432 kJ/~~mol~~) + 1 ~~mol~~F-F (154 kJ/~~mol~~) - 2~~mol~~H-F (565 kJ/~~mol~~)

= - 544 kJ or ΔHsyn = -544 kJ/molrxn

1. Calculate the energy change for the combustion of ethanol (CH3CH2OH) using bond energies.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Bond | C-C | C-H | C-O | C=O\* | O-H | O=O |
| Energy (kJ/mol) | 347 | 413 | 358 | 799 | 467 | 495 |

\*CO2

1. ***Write a balanced chemical equation for the combustion reaction***
2. ***Draw structural diagrams of the molecules to determine the type and number of bonds that will be broken and made.***
3. ***Write the enthalpy equation, look up the bond energies and plug them into the equation***
4. ***Solve***

2) Calculate the enthalpy change for the reaction in which methane gas, CH4(g), is combined with chlorine gas and fluorine gas to produce Freon-12 gas, CF2Cl2(g).

CH4(g) + 2Cl2(g) +2F2(g) 🡪 CF2Cl2(g) + 2HF(g) + 2HCl(g)

**Textbook Questions: page 313 # 1-6, 9, 12, 13**

**Thermodynamics, Entropy and Gibb’s Free Energy** (Not in textbook)

Some reactions, such as the combustion of hydrocarbon fuels, are very fast and react almost to completion. Other reactions, such as the combination of gold and oxygen, hardly occur at all. Still other reactions like the industrial synthesis of ammonia from nitrogen and hydrogen gases are very slow without a catalyst and with a catalyst the final mixture contains appreciable amounts of both reactants and products. What fundamental properties of nature determine the speed and extent of a particular chemical reaction? The study of reaction rates is called kinetics and will be covered in university since it requires knowledge of calculus. Whether a reaction will or will not occur is determined by examining the enthalpy, entropy and Gibb’s Free Energy for a reaction.

# Spontaneous Processes

A spontaneous process is defined as one that proceeds on its own without any external influence. The reverse of a spontaneous process is always nonspontaneous and takes place only in the presence of some continuous external influence. Consider the combination of hydrogen and oxygen in the presence of a platinum catalyst:

2H2(g) + O2(g)  2H2O(g)

The reaction occurs spontaneously, but the reverse reaction, decomposition of water into its elements, does not occur on its own. Water can only be broken down into its elements by electrolysis, where electrical energy is the external influence.

Spontaneous does not mean “fast”. A spontaneous reaction can be slow --- the decaying process, the gradual rusting of iron. Thermodynamics tells us if the reaction occurs spontaneously, but will not indicate how slow or fast the reaction will be.

**Enthalpy, Entropy and Spontaneous Reactions**

Based on enthalpy, reactions that lower the energy of the system (potential energy is converted to thermal energy in an exothermic reaction) are energetically preferred. But not all exothermic reactions are spontaneous and conversely not all endothermic reactions are nonspontaneous. So enthalpy alone cannot determine the spontaneity of a reaction. There is a second driving force involved.

The second driving force is nature’s tendency to move to a preferred condition of maximum randomness or disorder. Leaves blow randomly, never into an organized pile. Your locker never organizes itself. Molecular systems behave in the same manner. **Molecular systems tend to move spontaneously to a state of maximum randomness or disorder.**

Molecular randomness or disorder is called **entropy**. The symbol for entropy is S and the entropy change for a process is given the symbol **ΔS** where:

**ΔS = Sfinal — Sinitial**

Units of S: Joule/Kelvin × mole = **J/mol•K**

**ΔS is (+) when randomness or disorder of a system increases**

**ΔS is (–) when randomness or disorder of a system decreases**

Example:

HgCl2(s) → HgCl2(aq)  ΔS = 9 J/K mol

NaCl(s) → Na+(aq) + Cl-(aq) ΔS = 43 J/K mol

***Practice:***

*Predict the sign of ΔS in the system for each of the following processes:*

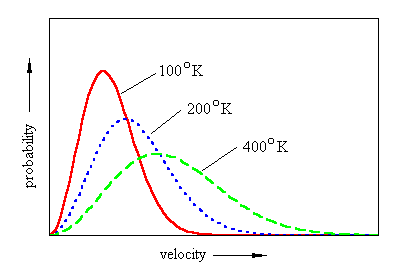
*a) CO2(s) → CO2(g) ( sublimation of dry ice ) c) N2(g) + 3 H2(g) → 2 NH3(g)*

*b) CaSO4(s) → CaO(s) + SO3(g) d) I2(s) → I2(aq)*

##### Entropy and Temperature

Entropy is associated with molecular motion. Disordered crystals have higher entropy than ordered crystals, and expanded gases have higher entropy than compressed gases.

As the temperature of a substance increases, random molecular motion increases, and there is a corresponding increase in the average kinetic energy of the molecules. But not all the molecules have the same kinetic energy. There is a distribution of molecular speeds in a gas, a distribution that broadens and shifts to higher speeds with increasing temperature. In solids, liquids and gases, the total energy of a substance can be distributed among the individual molecules in a number of ways, a number that increases as the total energy increases. Therefore the entropy of a substance increases with increasing temperature.



**The Third Law of Thermodynamics**:

The entropy of a perfectly ordered crystalline substance at 0 K is zero.

As a solid is heated, the entropy increases with a jump at the melting point because there are many more ways of arranging the molecules in the liquid than in the solid phase. When the liquid reaches its boiling point, there is an even greater jump in entropy because molecules in the gas are free to occupy a much larger volume.

Standard Molar Entropies and Standard Entropies of Reaction

The standard molar entropy of a substance, denoted by S°, is the entropy of 1 mol of the pure substance under standard conditions (1 atm pressure (101.3 kPa) and a specified temperature, usually 25°C). The units of S° are Joules per Kelvin•mole (J/K• mol) and the values are found in the handout.

Like enthalpies, standard molar entropy changes **ΔS°** can be calculated for a chemical reaction by subtracting the standard molar entropies of the reactants from the standard molar entropies of the products.

**ΔS° = Σ n × S° (products) – Σ n × S° (reactants)**

S° values are also given on a per-mole basis, so they are multiplied by the stoichiometic coefficient of that substance in the balanced chemical equation.

*Example: Calculate the ΔS° for the reaction N2O4(g) → 2 NO2(g) given S°NO2 = 240.5 J/K∙mol. and S°N2O4 = 304 J/K∙mol (ans. 177 J/K)*

\*\*Note: Unlike ΔH° values, for the elements in their standard state, ***S*° values ≠ 0. Only perfect crystals at absolute zero have zero entropy.**

**Entropy and Gibbs Free Energy**

The value ΔG is a measure of the maximum amount of work a system can do as it approaches the end of the reaction, hence the name “free energy”….or free work. Free energy is a state function like enthalpy and entropy. There are two ways to calculate the standard free-energy change for a reaction.

# Applications of Enthalpy, Entropy and Gibbs

The free energy of a substance, like enthalpy and entropy, depends on temperature, pressure, the physical state of the substance (solid, liquid or gas) and its concentration, in the case of solutions. As a result, free energy changes for chemical reactions must be compared under standard-state conditions, solids, liquids and gases in pure form at 1 atm pressure, solutes at 1M concentration and a specified temperature, usually 25°C. The symbol ΔG°, is used for the standard free energy change.

The equation which relates free energy to enthalpy and entropy changes is: **ΔG° = ΔH° – TΔS°**

**ΔG° is negative (**–) f**or a \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ reaction** (if there is a lowering of Gibbs Free Energy)

**ΔG° is positive (+) for a \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ reaction.**

**ΔG° = 0 for a system that has both the forward and reverse reaction occurring at the same rate so the amount of products and reactants do not change.**

Rate ( Reactants → products) = Rate (Products → reactants)

**Spontaneity of a reaction is temperature-dependent**:

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | ∆H | |
|  |  | + | - |
| ∆S | + | Spontaneous  only at high T | Spontaneous  at all T |
| ̶ | Non-spontaneous  at all T | Spontaneous  only at low T |

**Calculating ΔG° values (under standard conditions):**

**Method 1:** Use the equation **ΔG° = ΔH°–TΔS°.** If the ΔH° and ΔS° values for the reaction are given, this is a very simple problem. If they are not, you must use the ΔH°f and ΔS° values for the reactants and products from the handout to calculate them (lots of work). Remember T must be the Kelvin temperature and the units of energy must match. ΔH°f values are in kJ/mol and ΔS°values are in J/mol•K. You must convert them to the same units, either J or kJ.

**Method 2:** Use the equation **ΔGrxn° = Σn ×ΔG°f(products) – Σn ×ΔG°f(reactants).** Similar to the standard enthalpy of formation **ΔH°f ,**  the standard free energy of formation, ΔG°f of a substance is the free energy change that results when one mole of the substance is formed from its elements with all substances in their standard states. These values are found in the handout. The **standard free energies of formation, ΔG°f, for elements in their most stable or most common form are zero**. Use ΔG°f values from the handout.

The method you use depends on the information you are given in the problem.

***Method 1*** *Example: Given the information below, determine if the following reaction is* ***spontaneous****.*

*N2(g) + 3H2(g) → 2NH3(g)*

*ΔH° = -92.2 kJ; ΔS° = –198.7 J/ K; T = 25°C+ = \_\_\_\_\_\_\_\_\_K*

*ΔG° = ΔH° – TΔS°*

*=*

***Method 2*** *Example: Calculate ΔG° in kJ for the following reaction: 2NO(g) + O2(g) → 2NO2(g)*

ΔGrxn° = Σn ×ΔG°f(products) – Σn ×ΔG°f(reactants)

*(ans: –70 kJ)*

**Estimation of Temperature at which Direction of Spontaneous Change Reverses**

If both ΔH and ΔS have the same sign (+ and + or – and – ), temperature determines if the reaction is spontaneous or not. **ΔG° = ΔH°– TΔS°** can be used to estimate the temperature at which the spontaneity of a reaction changes. For phase changes, these changes occur at the melting point and boiling point and can be used to estimate the temperature a liquid boils or freezes at. At the normal boiling point of a liquid, vapour is forming at the same rate as liquid is condensing so **ΔG = O**.

|  |  |  |
| --- | --- | --- |
|  | **ΔH°f** | **S°** |
| CH3OH(l) | -239 kJ/mol | 127 J/K∙mol |
| CH3OH(g) | -201 kJ/mol | 240 J/K∙mol |

Ex. 1) Estimate the boiling point temperature for methanol, CH3OH given the data:

CH3OH(l) 👎 CH3OH(g)

Step 1: Calculate the values of ΔH° and ΔS°

Step 2: Substitute into the equation ΔG° = ΔH° – TΔS°, noting **ΔG = O** at the boiling point. Rearrange the equation and solve for T.

***ΔH°*=**

***ΔS°*=**

T = ΔH°

ΔS°

**ΔG = O** also equals zero at thetemperature where the spontaneity of a reaction changes.

Ex.2)Methanol (CH3OH), an alcohol used in the manufacture of adhesives, fibers and plastics, is synthesized industrially by the reaction:

CO(g) + 2H2(g) → CH3OH(l)

a) Calculate the standard enthalpy, entropy and free energy change for this reaction at 25°C.

b) Is the reaction spontaneous at 25°C? Explain.

HH

c) If it is spontaneous at 25°C, estimate the temperature at which the reverse reaction becomes spontaneous.

*Ans: a) ΔH° = –128.5 kJ, ΔS° = –333 J/K, ΔG° = –29.3 kJ b) yes, ΔG° is negative c) 386 K*

**Entropy Practice Problems**

1. Using the entropy values from the chart, calculate the standard entropy for the following reactions:
2. C2H4(g) + H2(g) → C2H6(g)
3. N2(g) + 3H2(g) → 2NH3(g)
4. CO(g) + 2H2(g) → CH3OH(l)
5. 2C2H6(g) + 7O2(g) → 4CO2(g) + 6H2O(l)
6. Ca(OH)2 + H2SO4(l) → CaSO4(s) + 2H2O(l)

*Ans: a) –120.9 J/K b) –198.3 J/K c) –332.1 J/K d) –619.8 J/K e) 7 J/K*

2. Predict the sign of ΔS° and then calculate ΔS° for each of the following reactions:

1. 2H2S(g)+ SO2(g) → 3S(s) + 2H2O(g)
2. 2SO3(g) → 2SO2(g) + O2(g)
3. Fe2O3(s) + 3H2(g) → 2Fe(s) + 3H2O(g)

*Ans: a) -186 J/K b) + 187 J/K c) +138 J/K*

3. Predict the sign of ΔS° and then calculate ΔS° for each of the following reactions:

* 1. H2(g) + ½ O2(g) → H2O(l)
  2. N2(g) + 3H2(g) → 2NH3(g)
  3. HCl(g) → H+(aq) + Cl- (aq)

*Ans: a) -164 J/K b) -199 J/K c) -130 J/K*

**Thermodynamics Practice Questions**

1. Use the standard molar entropies in the handout to calculate ΔS° at 25°C for each of the following:
   1. 2 S(s) + 3O2(g) → 2 SO3(g) *(ans: -165 J/K)*
   2. SO3(g) + H2O(l) → H2SO4(aq) *(ans: -307 J/K)*
   3. AgCl(s) → Ag+ (aq) + Cl-(aq) *(ans: 34 J/K)*
2. Use the data in the handout to calculate ΔH° and ΔS° of the following reactions. From the values of ΔH° and ΔS°, calculate ΔG° at 25° C and predict whether each reaction is spontaneous under standard state conditions.
   1. N2(g) + 2 O2(g) → 2 NO2(g)
   2. 2 KClO3(s) → 2 KCl(s) + 3 O2(g)
3. Use the ΔG°f values in the handout to calculate ΔG° at 25°C for each reaction.
   1. 2 SO2(g) + O2(g) → 2 SO3(g)
   2. N2(g) + 2 H2(g) → N2H4(l)
4. Which of the following reactions (unbalanced) would be expected to be spontaneous at 25°C and 1 atm? You must balance the reactions first.
5. PbO(s) + NH3(g) → Pb(s) + N2(g) + H2O(g) *(note: ΔG°f PbO = –187.9 kJ/mol)*
6. NaOH(s) + HCl(g) → NaCl(s) + H2O(l)
7. Al2O3(s) + Fe(s) → Fe2O3(s) + Al(s) *(note: ΔG°f Al2O3 = –1576.4 kJ/mol)*
8. 2CH4(g) → C2H6(g) + H2(g)

*Ans: i) –89 kJ, spont. ii) –145 kJ, spont. iii) 836 kJ not spont. iv) 69 kJ not spont.*

1. Calculate ΔG° in kJ for the following reactions, using the data in the handout:
2. Ca(OH)2 (s) + 2HCl(g) → CaCl2(s) + 2H2O(g) *(note: ΔG°f CaCl2 = –750.2 kJ/mol)*
3. 2HCl(g) + CaO(s) → CaCl2(s) + H2O(g)
4. H2SO4(l) + 2NaCl(s) → 2HCl(g) + Na2SO4(s)  *(note: ΔG°f Na2SO4 = –1266.8 kJ/mol)*
5. 3NO2(g) + H2O(l) → 2HNO3(l) + NO(g)

*Ans: a) –119.2 kJ b) –185 kJ c) 1.2 kJ d) 6 kJ*

**REACTION KINETICS – Factors Affecting Rates (pages 362-371)**

\*DEMO: Santa Can

**Rates of Reactions**

Chemical kinetics is the study of how fast chemical reactions take place. Studies of reaction rates are an important source of information about reaction mechanisms. A reaction mechanism is a detailed molecular level picture of how a reaction takes place. Reaction mechanisms are theories that explain experimental observations.

**Factors Affecting Chemical Reactions:** (Read p. 362- 364 and p.369-371)

1. **Nature of the reactant**

Some substances are more reactive than others. We discovered this experimentally when we did the activity series lab. Some metals like Magnesium are much more reactive in acid than other metals like copper. Some acids like hydrochloric acid are much more corrosive than others like acetic acid. Bond type, strength and number are all important in determining reaction rates as well as collision geometry.

1. **Concentration**

From experience we know that the greater the concentration of an acid or base the more corrosive or reactive it is. The greater the concentration the more collisions there are between reactants.

1. **Surface area**

Powdered forms of substances react much faster than clumps of solids (**Santa Can demo**). This is the reason why most reactants are grounded into a powder or dissolved into solutions. The greater the reactant’s surface area, the more possible collisions can occur between reactants.

1. **Temperature**

Usually as you heat a sample it will react faster. We refrigerate our foods to slow down the decomposition process.

1. **Catalysts**

A catalyst is a substance that speeds up a reaction without being consumed. Catalysts may be homogeneous (same phase as the reactants) or heterogeneous (a different phase from the reactants). Biological catalysts are called enzymes. They are very specific to the reactants they will bind with and the reactions they catalyze, so the body can be full of different substances but the catalyst will only interact with one of these substances. Industrial catalysts are not as specific so care is taken to use only the reactants required for the reaction during industrial processes.

**Textbook Questions: p.365 #1**

**Theories of Reaction Rates**  (page 366)

<http://www.chemguide.co.uk/physical/basicratesmenu.html#top>

**Collision Theory:**

Based on the kinetic molecular theory of gases, this theory holds that for a chemical reaction to occur the reacting molecules must collide with each other with enough force to overcome the electrostatic repulsions experienced by the reactants. If the molecules do not collide, there will be no reaction. The theory also states that the rate of the reaction depends on the number of reactant collisions in a period of time. This explains the dependence of reaction rates on the concentration of the reactants. As a reaction proceeds the reactants are consumed, their concentration decreases, the number of collisions decreases and the reaction slows down over time.

## Factors Influencing Collisions

Not every collision leads to a reaction. This conclusion is based on the fact that many gaseous reactions can have up to 1 x 1030 collisions every second but never react at the speed expected by this number of collisions. Not all collisions are “successful”.

Two factors influence whether a collision will or will not be successful:

* + 1. **Orientation** (also called collision geometry)

For **NO + O3 → NO2 + O2**

The way the molecules are facing each other (their orientation to each other) can be very important.

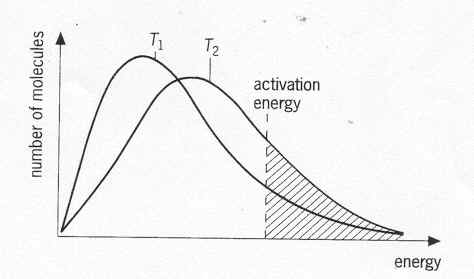
**N**

Reaction

##### No reaction

For Nitrogen monoxide to react with ozone (O3) the nitrogen atom of the NO molecule must collide with one of the oxygen atoms of the ozone molecule. The NO molecule must be in the correct orientation when it collides with the ozone molecule for a reaction to occur which yields an NO2 molecules + and O2 molecule. The more selective the geometry, the slower the reaction.

* + 1. **Energy of colliding molecules**

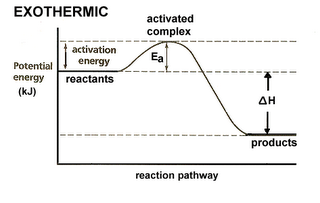


Even if the molecules collide with the correct orientation, a reaction will only occur if the molecules involved have sufficient kinetic energy to overcome electrostatic repulsion between reacting molecules and break the reactant bonds to form products. This energy requirement is called the activation energy, Ea. In a large sample of reactant molecules there is usually only a fraction of molecules with the correct energy. At higher temperatures, a greater number of the reactants will have the required activation energy giving a faster reaction. Higher temperatures also cause the reactants to more faster, increasing the frequency of collisions.

**Activation Energies and Transition States** (p.367-368)

An energy diagram shows how the energy of the reacting system changes as the reaction proceeds. The energy of both reactants and products is indicated along the vertical axis. The progress of the reaction is plotted along the horizontal axis or reaction pathway. The transition state is the highest energy point of the graph where the activated complex is formed. An **effective collision** is one in which the reactants collide with the correct orientation and energy to form an activated complex that leads to the formation of products.

# Energy Diagram for an Exothermic Reaction



In this case, the product has (more or less) energy than the reactant,

∴ ΔH is (positive or negative) and the reaction is exothermic.

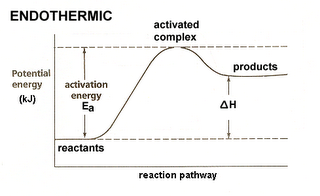
On the energy diagram, **activation energy** is the amount of energy required to reach the activated complex. It can be more or less than the enthalpy change. Reactions with high Ea tend to be slower reactions. Even if there is the same number of collisions, there will be less **effective** collisions.

Exothermic:

* E products is less than E reactants
* ΔH is negative or Energy is released

1. **Energy Diagram for an Endothermic Reaction**

The enthalpy of the **products is higher** than that of the **reactants**, so energy has been taken in by the system. As a result the ΔH of the reaction is positive and the activation energy is greater than the enthalpy change.

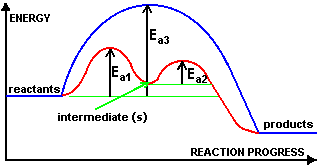
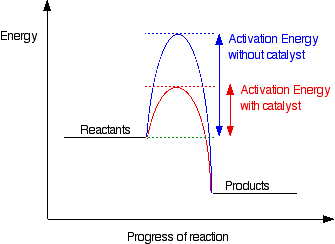


**Catalysts** (p.371)

A catalyst is a substance that increases the reaction rate without increasing the number of collisions and without being consumed itself. A catalyst provides an alternate pathway with lower activation energy. Thus at the same temperature, more molecules will have sufficient energy to overcome the new, smaller activation energy barrier, and the reaction will be faster. It is believed that catalysts alter the pathway or steps in a reaction but still give the same product and overall enthalpy change.

**A + y → Ay** (**Ay** is an intermediate)

**A + B  C + D Ay + B → C + D + y y** is a catalyst (usually heterogeneous) **y** is a catalyst (usually homogeneous)



OR

**Textbook Questions: p.372** #**1, 2, 4- 6**

**Reaction Mechanisms** (p. 383-384)

**Reaction Mechanisms**: Reactions can be classified as being either simple or complex. A complex reaction consists of a number of steps. Each of these steps involves one collision and is known as an **elementary step**. A simple reaction consists of one elementary step. The step or **series of steps** that make up a reaction is known as the **mechanism of that reaction**. From a reaction equation it is not possible to determine if it is simple or complex.

Nitrogen monoxide is a pollutant in automobile exhaust. The mechanism, whereby nitrogen monoxide reacts with oxygen to form nitrogen dioxide (another pollutant), is believed to consist of the following elementary steps.

Step (1) 2 NO → N2O2

Step (2) N2O2 + O2 → 2 NO2

If the two steps are added together: 2 NO + N2O2 + O2 → N2O2 + 2 NO2

They give the overall reaction equation: 2 NO(g) + O2(g) → 2 NO2(g)

The dinitrogen dioxide cancels out and does not appear as part of the overall equation. It is produced in the first elementary step and used up in the second. Species such as dinitrogen dioxide are known as reaction **intermediates**. Intermediates can be atoms, molecules or ions that are produced as a product in an early step then used up as a reactant in a subsequent step. They are not found in the overall reaction equation and are usually very short lived and difficult to isolate.

## Rate Determining Step

Every mechanism has a rate-determining step. This is the **slowest step** in the reaction. If the first elementary step of the mechanism is the rate-determining step, then we can say that the overall reaction rate depends on this initial step **and** on the concentrations of the species involved in this step.

Any subsequent step is faster and does not affect the overall rate.

For the nitrogen monoxide equation, if the first step is the slow step, then the rate of the reaction would be dependent on the concentration of NO. It would not change with different concentration of O2 since oxygen is not in the rate determining step.

An analogy of washing dishes can be used:

Step 1 (washing) dirty dishes → clean wet dishes

Step 2 (drying) clean wet dishes → clean dry dishes

The dirty dishes represent the reactants and the clean dry dishes are the products. If the person washing the dishes is very slow, then the drier will have no trouble keeping up and in fact will probably be waiting for clean wet dishes. In this case the reaction intermediate (clean wet dishes) will be short lived and the overall speed of doing dishes will depend on just how slowly the washer performs the first task.

But if the person washing the dishes is speedy and the drier is slow, the clean wet dishes accumulate (lots of intermediate present) and the drying step is the rate determining step. If the second step is the rate determining step it is possible to observe intermediates in the mechanism.

A proposed mechanism is only valid if the following occur:

* 1. The sum of the elementary steps must give the overall balanced equation for the reaction (intermediates and catalysts must cancel out)

1. Each elementary step involves no more than three reactants because the probability of a collision involving 4 or more reactants is too unlikely.
2. The slowest step in a reaction mechanism is the rate determining step and must coincide with the experimentally determined rate law equation.

Examples of slow elementary steps and their corresponding rate law equation are given in the table below.

|  |  |
| --- | --- |
| **Elementary step** | **Rate Law Equation** |
| A → products | Rate = k[A] |
| A + A → products | Rate = k[A]2 |
| A + B → products | Rate = k[A][B] |

Kinetic experiments on the reaction of nitrogen dioxide with carbon monoxide giving the products nitrogen monoxide and carbon dioxide, show that the rate of this reaction depends on the concentration of the nitrogen dioxide according to the rate equation r = k **[NO2]**2. Further experimental evidence indicates the existence of nitrogen trioxide as a reaction intermediate. A proposed mechanism for this reaction would then be the following:

**step 1 NO2 + NO2 → NO3 + NO slow step**

step 2 NO3 + CO → NO2 + CO2 fast step

Addition of the two steps gives the correct overall equation:

NO2(g) + CO(g) → NO(g) + CO2(g)

What happens if it was proposed that the second step is slow?

step 1 NO2 + NO2 → NO3 + NO fast step

**step 2 NO3 + CO → NO2 + CO2 slow step**

The overall equation is the same but the rate law would be dependent on [CO] and [NO3],

r = k[CO] [NO3]. You cannot have an intermediate in a rate law equation so the concentration of the intermediate must be dependent on the concentration of the reactants that led to its formation and will lead to a much more complex rate law equation. However, CO is not in the experimental rate law equation so this is not a possible equation.

Video:

<https://www.youtube.com/watch?v=ShzW1LoQgoc>

*Sample Problem 1:*

The rate law of a chemical reaction was found to be : rate = k[NO(g)][Cl2(g)]

The following elementary steps have been proposed:

NO(g) + Cl2(g) → NOCl2(g)

NOCl2(g) + NO(g) → 2NOCl(g)

1. Determine the overall reaction.
2. Identify any reaction intermediates.
3. Determine the slowest step in the mechanism. Explain your choice.
4. Determine the rate law equation for the fast step.

*Solution:*

**Homework: 1) Text Questions: p. 386 practice #2, 3**

**p. 387 # 3, 5, 8, 9**

**2) Print `Factors Affecting Rates` Lab**

**SUMMARY**

* The rate of a chemical reaction can be followed by measuring changes in the physical properties of the species involved.
* Reaction rate depends on a number of factors including concentration and form of the reactants, phase and temperature of the reaction, agitation of the reaction solution, and presence of visible or UV light.
* Collision theory explains reaction rates in terms of molecular collisions.
* Transition state theory explains a reaction in terms of an intermediate product called the activated complex.
* Increased temperature increases the reaction rate. At higher temperatures more molecules are involved in collisions which have enough energy to overcome the activation energy barrier.
* Although the reaction rate is normally dependent in some way on the concentration of the reactants, the actual relationship must be determined by experiment; it cannot be deduced from the balanced reaction equation.
* A reaction mechanism is the series of elementary steps making up the reaction, with the slowest step being the rate-determining step.
* An intermediate is produced as a product in an early step then used up as a reactant in a subsequent step, so it is not found in the overall reaction equation.
* A catalyst speeds up the reaction by providing an alternate pathway having lower activation energy.
* A catalyst starts as a reactant so it is consumed in an early step of the mechanism, but is produced again as a product in a subsequent step, so it is not found in the overall equation.

**PRACTICE QUESTIONS:**

1. A student is asked to determine the molar enthalpy of neutralization, ΔHneut, for the reaction represented below. The student combines equal volumes of 1.0M HCl and 1.0M NaOH in an open polystyrene cup calorimeter. The heat released by the reaction is determined using the equation

q = mcΔT. HCl (aq) + NaOH (aq) → H2O(l) + NaCl (aq)

 + OH → H2O(l)

Assume the following:

* Both solutions are at the same temperature before they are combined
* The densities of all the solutions are the same as that of water. (1g/mL)
* Any heat lost to the calorimeter or to the air is negligible.
* The specific heat capacity of the combined solutions is the same as that of water.

1. Give appropriate units for each of the terms in the equation q = mcΔT
2. List the measurements that must be made in order to obtain the value of q.
3. Explain how to calculate each of the following.

i) The number of moles of water formed during the experiment

ii) The value of the molar enthalpy of neutralization, for the reaction between HCl(aq) and NaOH (aq).

1. The student repeats the experiment with the same equal volumes, but this time uses 2.0M HCl and 2.0M NaOH.

i) Indicate whether the value of q increases, decreases or stays the same when compared to the first experiment. Justify your prediction.

ii) Indicate whether the value of the molar enthalpy of neutralization increases, decreases or stays the same when compared to the first experiment. Justify your prediction.

1. Suppose that a significant amount of water were lost to the air during the experiment. What effect would this have on the calculated value of the molar enthalpy of neutralization? Justify your answer.
2. For the reaction,

**2 NO (g) + Br2 (g) → 2 NOBr (g)** , the rate law equation is r = k[NO][Br2]

The following is a proposed mechanism for the above reaction:

Br2 (g) + NO (g) → NOBr2 (g) slow

NOBr2 (g) + NO (g) → 2NOBr (g) fast

Is this a possible mechanism for this reaction? Explain your answer.

1. Given the following data, calculate ΔH for the reaction: **S(s)+O2 → SO2 (g)**

S(s) + 3/2 O2 (g) → SO3(g)  ΔH=-395.2 kJ

2SO2(g) + O2(g) → 2SO3 (g)  ΔH=-198.2kJ

*(ans. -296.1kJ)*

1. Given the following data, calculate the ΔH for the reaction: **2C(s) + H2(g) → C2H2 (g)** C2H2(g) + 5/2O2(g) → 2CO2 (g) +H2O (l) ΔH=-1300. kJ

C(s) + O2 (g) → CO2 (g) ΔH=-394 kJ

H2(g) + ½ O2(g) → H2O (l) ΔH=-286kJ

*(ans. 226 kJ)*

1. The bombardier beetle uses an explosive discharge as a defensive measure. The chemical reaction involved is the oxidation of hydroquinone by hydrogen peroxide to produce quinone and water:

**C6H4(OH)2 (aq) +H2O2(aq) → C6H4O2(aq) + 2H2O (l)**

Calculate ΔH for this reaction from the following data:

C6H4(OH)2(aq) → C6H4O2 (aq) + H2 (g) ΔH=+177.4 kJ

H2(g) + O2(g) → H2O2 (aq) ΔH= -191.2kJ

H2(g) + ½ O2(g) → H2O (g) ΔH=-241.8kJ

H2O(g) → H2O (l) ΔH=-43.8 kJ

*(ans. -202.6 kJ)*

1. Given the following data, Calculate ΔH for the reaction **2N2(g) +5O2(g) → 2N2O5 (g)**:

H2 (g) + ½ O2 (g) → H2O(l) ΔH=-285.8kJ

N2O5 (g) +H2O(l) → 2HNO3 (l) ΔH=-76.6 kJ

½ N2(g) + 3/2 O2 (g) +1/2 H2 (g) → HNO3 (l) ΔH=-174.1 kJ

*(ans. 28.4kJ)*

1. Use ΔH°f  from the handout chart to calculate the enthalpy of reaction for the following:

a) 2KClO3(s) → 2 KCl(s) + 3O2 (g) *(ans.-90 kJ)*

b) 3NO2(g) + H2O(l) → 2 HNO3(l) + NO(g) *(ans.-74kJ)*

c) CH3CH2OH(l) + 3O2(g) → 2CO2(g) + 3H2O(l) *(ans.-1367kJ)*

d) 2CH4(g) + 3O2(g) → 2CO(g) + 4 H2O(l) *(ans.-1215kJ)*

e) 4NH3(g) + 5O2(g) → 4NO(g) + 6H2O(l) *(ans.-1172kJ)*

f) HCl(g) + NaOH(s) → NaCl(s) + H2O(l) *(ans.-178kJ)*

g) NaHCO3(s) → CO2(g) + NaOH(s) *(ans.127.5kJ)*

**Enthalpy Review**

1. A pot containing 1.00 L of water at 23°C is warmed to 68°C when 5.00 g of butter is burned (source of energy). Calculate the heat absorbed by the water.

(specific heat of: water 4.1796 J/g°C, Butter 1.90 J/g°C)

1. 3.0x104 J of heat energy is transferred to a 1.0 kg block of aluminum initially at 10.0°C. What will be the final temperature?
2. When 100. g of metal at 94°C is placed in 100. g of water at 10°C, the final temperature of the water is 17°C. Calculate the specific heat capacity of the metal.
3. Aluminum metal and iron (III) oxide react and form aluminum oxide and iron. For each mole of aluminum used, 429.6 kJ of energy is released under standard conditions. Write the thermochemical equation that shows the consumption of 4 moles of aluminum.
4. The absolute value of ΔHº for the combustion reaction of benzene C6H6

2C6H6 (l) + 15 O2 (g) → 12CO2 (g) + 6H2O(l)

is 6542 kJ. What is the ΔHº for the combustion of 1.500 mol of benzene?

1. Hydrogen chloride gas can be generated by heating a mixture of sulphuric acid and potassium chloride according to the reaction

KCl (s) + H2SO4 (l) → HCl (g) + K2SO4 (s)

Calculate the ΔHº for this reaction from the following thermochemical equations.

KOH (s) + HCl (g) → KCl (s) + H2O(l) ΔHº= -203.6 kJ

2 KOH (s) + H2SO4 (l) → 2 H2O(l) + K2SO4 (s) ΔHº= -342.4 kJ

1. Using the following equations, find the ΔHº for this reaction: 3 C2H2 → C6H6

C2H2 + 5/2 O2 (g) → 2CO2 (g) + H2O(l) ΔHº= -1299 kJ

C6H6 + 15/2 O2 (g) → 6CO2 (g) + 3 H2O(l) ΔHº= -3267 kJ

1. Calculate the ΔHº for the combustion of acetylene C2H2(g) using the heats of formation.

* 1. Calculate the ΔH for the following reaction using heats of formation
  2. NH3(g) + HCl (g) → NH4Cl(s)
  3. Is the reaction exothermic or endothermic?
  4. Do the products have a greater or smaller enthalpy than the reactants?

1. Why is the rate of a reaction affected by each of the following?

a) frequency of collisions

b) kinetic energy of the collisions

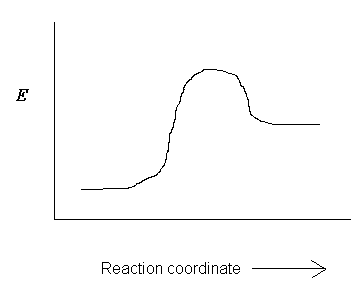
c) orientation of the collisions

1. For the following reaction profile, indicate:

a) the positions of the reactants and products

b) the activation energy

c) ΔH for the reaction



1. The activation energy for the reaction H2 (g) + I2 (g) → 2 HI (g) is 167 kJ/mol and ΔH for the reaction is +28 kJ/mol. What is the activation energy for the decomposition of HI?
2. How does a catalyst increase the rate of a chemical reaction?

**Textbook Review Questions:**

**page 395 #1-5; page 396 # 1 – 4, 7, 8, 25 – 35, 54 -57, 60 – 62, 74, 75**