

CHAPTER THREE

Introduction to Chemical

Thermodynamics

Part one

Thermodynamics

- **Thermodynamics** is the study of energy and its transformation.
- In a chemical reaction, thermodynamics determines whether a reaction is possible and how much product can be formed.
- Thermodynamics deals with energy changes and applies to physical as well as chemical changes.
- However, it does not give any information about the duration of time required for the related processes.

Common Thermodynamic Terms

There are three types of thermodynamic systems based on the boundary between the system and its surroundings.

- An **open system**— is a system that can exchange mass and energy, usually in the form of heat, with its surroundings.
- For example, an open system may consist of a quantity of water in an open container,

Thermodynamics

- A **closed system** – is a system which transfers energy, but not mass across its boundary with its surroundings.
- If you close the flask,, so that no water vapor can escape from or condense into the container, you create a closed system.
- An **isolated system** – is a system in which neither the transfer of mass nor that of energy takes place across its boundary with the surroundings. By placing the water in a totally insulated container,

Thermodynamics

The properties of a system can be intensive or extensive based on its dependence on amount of a substance.

Intensive properties are those that do not depend on the amount of matter present.

Some examples include colour, temperature and density.

Extensive properties are those properties, that depend on the amount of matter, for

example, mass, internal energy, volume, and pressure.

Thermodynamics

- ✓ A **spontaneous process** is a process that occurs without external influence. Once started, requires no action from outside in order to continue
- ✓ Example -A rock that is rolling down from the top of a hill continues to roll down.
 - Heat flows from an object of high temperature to an object of low temperature
 - Iron rusts in moist air.
- ✓ **non-spontaneous process** will not occur unless some external action is continuously applied. example freezing of water in to ice

Thermodynamics

- ✓ **isothermal process** is a process in which temperature remains constant, $\Delta T = 0$
- ✓ This typically occurs when a system is in contact with an outside thermal reservoir (heat bath)
- ✓ An alternative special case in which a system exchanges no heat with the surroundings ($\Delta q = 0$) is called an **adiabatic process**.
- ✓ In an isothermal process, the value of $\Delta T = 0$ but $\Delta q \neq 0$, while in an adiabatic process, $\Delta T \neq 0$ but $\Delta q = 0$.
- ✓ **Path function**-it depends on the path how to prepare the state of a system
- ✓ example work, heat
- ✓ **State function**-depends on the initial and final state of system example energy, volume, pressure

THE FIRST LAW OF THERMODYNAMICS AND SOME THERMODYNAMIC QUANTITIES

Internal Energy (E)

- ✓ The **internal energy** (E) of a system is the total energy contained within a system, partly as kinetic energy and partly as potential energy
- ✓ When a chemical system changes from reactants to products and the product return to the starting reactant, the internal energy has changed
- ✓ To determine this change, ΔE , we measure the difference between the systems internal energy after the change (E_{final}) and before the change (E_{initia}).

$$\Delta E = E_{\text{final}} - (E_{\text{initia}})$$

Thermodynamics

The kinetic energy component of internal energy consists of various types of molecular motion and the movement of electrons within molecules.

Potential energy is a factor of:

- * attractive and repulsive interaction between molecules;
- * attractive interactions between electrons and nuclei within molecules;
- * repulsive interactions between electrons within molecules; and
- * repulsive interactions between nuclei within molecule.

Heat

- Heat (thermal energy) is the energy transferred between a system and its surroundings as a result of a difference in their temperatures.
- Heat passes spontaneously from the region of higher temperature to the region of lower temperature.
- Heat transfer stops when the system and surroundings reach the same temperature and therefore the system and surroundings are at **thermal equilibrium**.

Heat and Calorimetry

- chemical reaction or a physical change that releases heat is said to be an **exothermic** process.

Example -The burning of charcoal, freezing process

- A reaction or a physical change that absorbs heat is an **endothermic** process.
- The melting of ice is an endothermic process, because heat is absorbed when ice melts
- The SI unit of heat is joule(J). Another unit of heat is calorie.
- A **calorie (Cal)** is the amount of heat, or other energy, necessary to raise the temperature of 1 g of water by 1 degree Celsius
- The measurement of heat flow is called **calorimetry**.
- An apparatus that measures heat is called a **calorimeter**

Heat

- Heat capacity is defined as the amount of heat energy required to raise its temperature by 1° (or 1 K)
- The heat capacity of 1 mol of a substance is called its **molar heat capacity**
- The heat capacity of 1g of a substance is called its **specific heat**.
- Specific heat of a substance can be determined experimentally by measuring the temperature change (ΔT) for a known mass (m) of a substance that gains or loses a specific quantity of heat, q .
- Specific heat(C)= $\frac{q}{m \times \Delta T}$, $q = mc\Delta T$

Heat

- Heat capacity = $\frac{\text{quantity of heat trasfered}}{\text{temperature change}}$
- $q = mC\Delta T$ where $\Delta T = T_{\text{final}} - T_{\text{initial}}$
- q -amount of heat transferred
- C -specific heat capacity
- ΔT -change in temperature, the same in degree Celsius and kalvin scale

A 466 g sample of water is heated from 8.5°C to 74.6°C. Calculate the amount of heat absorbed by the water in kilojoules

How much heat is required to raise the temperature of 250 g of water from 22°C to near its boiling point, 98°C?

Work (W)

- Work, like heat, is an energy transferred between a system and its surroundings
- Work is defined as a force applied over a given distance
- Work is defined as a force applied over a given distance, so if the piston moves a distance Δh , then the magnitude of the work is

$$\text{work} = \text{force} * \text{distance} = F * \Delta h$$

$$\text{since } P = \frac{F}{A}, F = P * A, \quad W = P * A * \Delta h$$

The product of the cross-sectional area of the cylinder, A , and the height, Δh , represents the change in volume of the gas, which is designated by the symbol ΔV , hence $W = P * \Delta V$

Heat

- The product of pressure and a change in volume is usually called “pressure-volume” work.
- When a gas expands, ΔV is positive, and the work is negative. Such type of work is called work done by the system or work done on the surrounding
- $W = -P * \Delta V$
- A negative quantity of work signifies that the system loses energy, and that this, energy is transferred from the system to the surroundings.
- When a gas is compressed by its surroundings, ΔV is negative, the quantity of work is positive and energy is gained by the system. Such type of work is called work done on the system or work done by the surrounding

The First Law of Thermodynamics

- The first law of thermodynamics, which is a restatement of the law of conservation of energy, states that the total amount of energy in the universe is constant.

$$\Delta E = q + \Delta W$$

- Thermodynamic quantities always consist of two parts:
 - a number plus units, which gives the magnitude of the change; and
 - a sign that indicates the direction of the flow.

If q is positive-heat is absorbed by the system

- heat flows in to the surrounding
- the system energy is increasing

If q is negative-heat is released by the system

- heat flows out of the system
- the system energy is decreasing

Heat

- The sign reflects the system's point of view.
- For example, if a quantity of energy flows into the system as heat, q is equal to $+q$, where the positive sign indicates that the system's energy is increasing.
- On the other hand, when energy flows out of the system as heat, q equal to $-q$, where the negative sign indicates that the system's energy is decreasing.
- This suggests that we need sign conventions to be used with the first law of thermodynamics.
- The conventions are as follows:
 - * If heat is absorbed by the system, $q > 0$. If work is done on a system, $W > 0$.
 - * If heat is given off by a system, $q < 0$. If work is done by a system, $W < 0$.

A gas does 135 J of work while expanding and at the same time, it absorbs 156 J of heat. What is the change in internal energy?

Calculate ΔE for a process in which the system absorbs 65 J of heat and 12 J of work is done on it by the surroundings

THERMOCHEMISTRY

- Thermochemistry is the study of energy changes that occur during chemical reactions

Heats of Reactions

- In the first law of thermodynamics, you have learned that

$$E = q + p\Delta V$$

- If a reaction occurs at constant volume, then $\Delta V = 0$ and no pressure-volume work is done. Thus, $\Delta E = (q)_V$. Where the subscript V indicates a constant-volume process.

Enthalpy

- What is enthalpy? The heat absorbed or released by a system at constant pressure is called enthalpy (H).
- Enthalpy is defined as the sum of the internal energy and the pressure-volume product of a system.
- $H = E + pV$
- or $\Delta H = \Delta E + P \Delta V$ (at constant pressure)
- $\Delta E = q - P \Delta V$
- then $\Delta H = q - P \Delta V + P \Delta V$
- $\Delta H = (q)_p$
- Thus, the change in enthalpy equals the heat gained or lost at constant pressure.

Enthalpy

- What is the relationship between ΔH and ΔE ?
- In case of an ideal gas, we can express change in enthalpy, using the ideal-gas law:
- $PV = nRT$
- $\Delta H = \Delta E + \Delta(PV)$
- $\Delta H = \Delta E + \Delta(nRT)$
- If the temperature is constant

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta H = \Delta H - \Delta(nRT)$$

where $\Delta n = \sum n_P - \sum n_R$ of the gaseous substances.

Calculate the change in enthalpy when 2 moles of CO is converted to 2 moles of CO₂ at 1 atm and 25°C.



Some Properties of Enthalpy

- Enthalpy is an extensive property. The enthalpy of a system depends on the quantities of substances present. Consider the formation of ammonia from nitrogen and hydrogen;



- The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction
- The enthalpy change for a reaction depends on the state of the reactants and the products



Thank you
End of part one

CHAPTER THREE
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Thermodynamics
Part Two

Standard States

- The standard state for a substance is the most stable form at temperature of 25°C and at atmospheric pressure of 1 atm.
- We can define the standard enthalpy of combustion, ΔH°_c , as the change in enthalpy that accompanies the combustion of 1 mole of a substance in oxygen at standard conditions.
- Most chemical reactions that produce heat are combustion reactions.

Standard Enthalpies of Formation

- The standard enthalpy of formation, ΔH_f° , is the change in enthalpy in the reaction when one mole of a substance is formed from the elements in their standard states.
- By definition, the standard enthalpy of formation of the most stable form of any element is **zero**

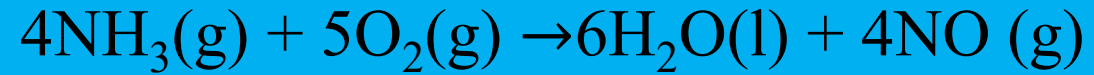
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- Now let us explore how we can use standard enthalpies of formation to determine standard enthalpy changes of chemical reactions.
- We sum the enthalpies of formation of all reaction products, taking care to multiply each molar enthalpy of formation by the coefficient of that substance in a balanced equation.
- From this, we subtract a similar sum of the enthalpies of formation for the reactants:

$$\sum n\Delta H^\circ_{f(\text{product})} - \sum m\Delta H^\circ_{f(\text{reactant})}$$

- where, n and m are the stoichiometric coefficients of the chemical reaction.

The standard enthalpies of formation of NH_3 , H_2O and NO are -46.2 , -241.8 and 90.3 kJ/mol, respectively. Calculate the enthalpy of the reaction:



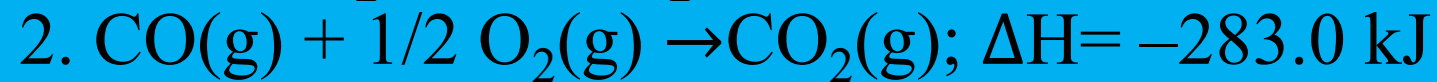
Calculate ΔH° for combustion of propane, C_3H_8 , from the ΔH_f° values of the products and reactants. $\text{C}_3\text{H}_8 (\text{g}) + 5\text{O}_2 (\text{g}) \rightarrow 3\text{CO}_2 (\text{g}) + 4\text{H}_2\text{O} (\text{l})$

Hess's Law

Hess's law states that if different processes are used to bring about the same change the enthalpy changes during these processes are the same.

- It states that if the reaction is the sum of two or more other reactions then the enthalpy change for the overall process must be the sum of ΔH of the constituent reactions
- $\Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$

The enthalpies of combustions, of C to CO₂ and CO to CO₂ are −393.5 kJ/mol and −283.0 kJ/mol, respectively.



Using these data, calculate the enthalpy of combustion of C to CO.



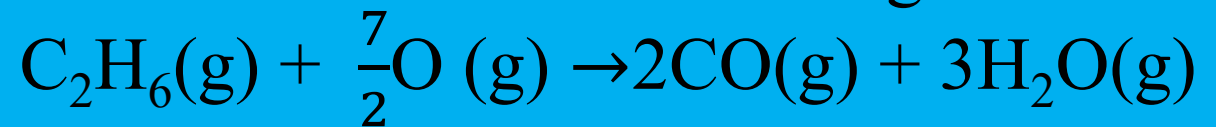
Calculate the enthalpy for the following reaction: $\text{C (graphite)} \rightarrow \text{C (diamond)}$
Given the data:

1. $\text{C (graphite)} + \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}); \Delta H = -393.5 \text{ kJ}$
2. $\text{C (diamond)} + \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}); \Delta H = -395.4 \text{ kJ}$

Bond Energies

- ✓ Bond energy is the enthalpy required to break a particular bond in 1 mole of gaseous molecules.
- ✓ Bond breaking is endothermic process while bond forming is exothermic process
- ✓ The greater Bond energy is the stronger bond
- ✓ This energy is generally expressed in kilojoules per mole of bonds (kJ/mol).
- ✓ $\text{bond energies} = \sum \text{energy of bonds broken} - \sum \text{energies of bonds formed}$

Estimate ΔH for the following reaction:



Estimate the enthalpy of the formation of gaseous hydrazine, $\text{N}_2\text{H}_4(\text{g})$

$$\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2\text{H}_4(\text{g})$$

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

Entropy and Spontaneous Process

- ✓ A spontaneous process(change) is a change in a system that proceeds without any outside influence on the system.
- ✓ For example, when we add solid salt to water, the solid dissolves without any outside influence. The dissolution is spontaneous.
- ✓ We know well that certain other processes don't occur by themselves. They are said to be non-spontaneous. For example, water does not freeze to form ice at room temperature.
- ✓ A non-spontaneous process is one that cannot take place without outside influence on the
- ✓ system

Entropy and Entropy Change

Entropy (S) is the thermodynamic property of a system that is related to its degree of randomness, or disorder.

The greater the randomness, or disorder, in a system, the higher is its entropy.

Every substance has entropy and entropy is state function

The SI unit of entropy is JK^{-1} (Joule per Kelvin), which is the same unit as that of heat capacity

The entropy change, ΔS , for a chemical change is equal to the sum of the entropies of the products minus the sum of the entropies of the reactants.

- $$\Delta S_{\text{rxn}} = \sum m S_{(\text{product})} - \sum n S_{(\text{reactant})}$$

Entropy and Entropy Change

where m and n are the amounts of the individual species represented by their coefficients in the balanced equation. For a reaction,

$aA + bB \rightarrow cC + dD$, the entropy change is

$$\Delta S = (c \times S_c + d \times S_d) - (a \times S_a + b \times S_b)$$

where S_a is the entropy of A, S_b is the entropy of B, and so on.

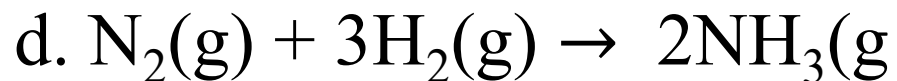
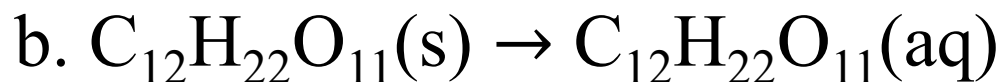
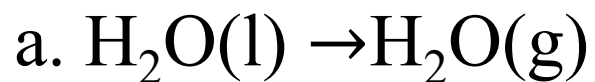
* $\Delta S > 0$ indicates an increase in randomness, or disorder, during the change.

• $\Delta S < 0$ indicates a decrease in randomness, or an increase in order

$$S_{\text{gas}} \gg S_{\text{liquid}} \gg S_{\text{solid}}$$

Entropy and Entropy Change

- Predict whether each of the following leads to an increase or decrease in the entropy.



The Second Law of Thermodynamics

- The connection between entropy and the spontaneity of a reaction is expressed by the second law of thermodynamics, which states that “*The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.*”
- Because the universe is made up of the system and its surroundings, the entropy change in the universe (ΔS_{univ}) for any process is the sum of the entropy changes in the system (ΔS_{sys}) and the surroundings (ΔS_{sur}).
- Mathematically, we can express the second law of thermodynamics as follows:
- For a spontaneous process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$
- For a non spontaneous process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} < 0$
- For an equilibrium process: $\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$

The Second Law of Thermodynamics

- For a spontaneous process, the second law says that ΔS_{univ} must be greater than zero, but it does not place a restriction on either ΔS_{sys} or ΔS_{sur} .
- Thus it is possible for either ΔS_{sys} or ΔS_{sur} to be negative, as long as the sum of these two quantities is greater than zero.
- For an equilibrium process, ΔS_{univ} is zero. In this case ΔS_{sys} and ΔS_{sur} must be equal in magnitude but opposite in sign.

The Second Law of Thermodynamics

free energy and free energy change

free energy it also called gibbs free energy because it was developed by the American mathematician J. Willard Gibbs

✓ It is state function

$G = H - TS$ where T is the absolute temperature,

S is an entropy and

H is an enthalpy

For a process occurring at constant temperature, the change in free energy is given by the expression $\Delta G = \Delta H - T\Delta S$

The Second Law of Thermodynamics

For a change in which $\Delta H < 0$ and $\Delta S > 0$, the change in Gibbs free energy becomes less than zero ($\Delta G < 0$), and the process is spontaneous.

- * If $\Delta H > 0$ and $\Delta S < 0$, the change in Gibbs free energy becomes positive ($\Delta G > 0$), and the process is non-spontaneous.
- * If $\Delta H > 0$ and $\Delta S > 0$, ΔG may or may not be negative, but only if $\Delta H < T\Delta S$, $\Delta G < 0$.
- * If $\Delta H < 0$ and $\Delta S < 0$, $\Delta G < 0$ if $T\Delta S$ is small. This occurs at small value of temperature.
- * If ΔG is zero, the process is at equilibrium and there is no driving force tending to make the reaction go in either direction.

The Second Law of Thermodynamics

Case	ΔH	ΔS	ΔG	Result	Example
1.	-	+	-	Spontaneous at all T	$2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$
2.	-	-	-	Spontaneous toward low T	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
	-	-	+	Non-spontaneous toward high T	
3.	+	+	+	Non-spontaneous toward low T	$2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
	+	+	-	Spontaneous toward high T	
4.	+	-	+	Non-spontaneous at all T	$2\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g})$

The reaction of calcium oxide with the pollutant sulfur trioxide has been proposed as one way of removing SO_3 from burning high sulfur coal.

$\text{CaO(s)} + \text{SO}_3\text{(g)} \rightarrow \text{CaSO}_4\text{(s)}$ Using the following ΔH°_f and S°_{298} values, calculate the standard free-energy change for the reaction under standard state conditions and predict whether the reaction is spontaneous or non spontaneous.

CaO(s) : $\Delta H^\circ_f = -635.5 \text{ kJ/mol}$; $S^\circ_{298} = 40 \text{ J/mol K}$

$\text{SO}_3\text{(g)}$: $\Delta H^\circ_f = -395.7 \text{ kJ/mol}$; $S^\circ_{298} = 256.6 \text{ J/mol K}$

$\text{CaSO}_4\text{(s)}$; $\Delta H^\circ_f = -1432.7 \text{ kJ/mol}$; $S^\circ_{298} = 107 \text{ J/mol K}$

Thank you
End of part two

