

THERMODYNAMICS



Classical thermodynamics... is the only physical theory of universal physical theory of universal content which I am convinced... will never be overthrown.

Albert Einstein



Rudolf Clausius
(1822-1888)

Learning Objectives:

After studying this unit, students will be able to

- distinguish between the system and surroundings
- define closed, open and isolated systems
- distinguish between state and path functions
- describe the relation between internal energy, work and heat
- state four laws of thermodynamics
- correlate internal energy change (ΔU) and enthalpy change (ΔH) and their measurement.
- calculate enthalpy changes for various types of reactions
- apply Hess's law to calculate lattice energy of crystals
- define spontaneous and non spontaneous processes
- establish the relationship between thermodynamic state functions enthalpy (H), entropy (S) and Gibbs free energy (G)
- list the factors that determines spontaneity of the process
- establish the link between ΔG and spontaneity, and the relationship between ΔG^0 and equilibrium constant

7.1 Introduction

The term 'Thermodynamics' means flow of heat and is derived from the Greek 'Thermos' (heat) and 'dynamics' (flow). In our daily life, we come across many useful reactions such as burning of fuel to produce heat energy, flow of electrons through circuit to produce electrical energy, metabolic reactions to produce the necessary energy for biological functions and so on. Thermodynamics, the study of the transformation of energy, explains all such processes quantitatively and allows us to make useful predictions.

In the 19th century, scientists tried to understand the underlying principles of steam engine which were already in operation, in order to improve their efficiency. The basic problem of the investigation was the transformation of heat into mechanical work. However, over time, the laws of thermodynamics were developed and helped to understand the process of steam engine. These laws have been used to deduce powerful mathematical relationships applicable to a broad range of processes.

Thermodynamics evaluates the macroscopic properties (heat, work) and their inter relationships. It deals with properties of systems in equilibrium and is independent of any theories or properties of the individual molecules which constitute the system.

The principles of thermodynamics are based on three laws of thermodynamics. The first two laws (First and second law) summarise the actual experience of inter

conversion of different forms of energy. The third law deals with the calculation of entropy and the unattainability of absolute zero Kelvin. Thermodynamics carries high practical values but bears certain limitations. It is independent of atomic and molecular structure and reaction mechanism. The laws can be used to predict whether a particular reaction is feasible or not under a given set of conditions, but they cannot give the rate at which the reaction takes place. In other words, thermodynamics deals with equilibrium conditions quantitatively, but does not take into account the kinetic approach to the equilibrium state.

7.2 System and Surrounding

Before studying the laws of thermodynamics and their applications, it is important to understand the meaning of a few terms used frequently in thermodynamics.

System:

The universe is divided into two parts, the system and its surroundings. The system is the part of universe which is under thermodynamic consideration. It is separated from the rest of the universe by real or imaginary boundaries.

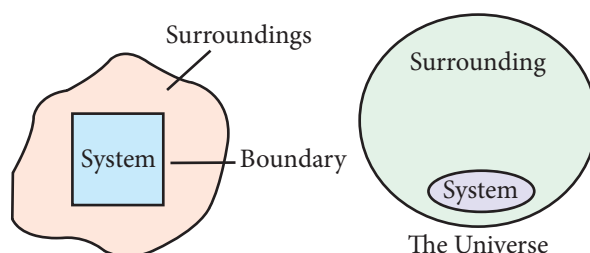


Figure 7.1 System, surrounding & boundary Homogeneous and heterogeneous systems

Example:

The system may be water in a beaker, a balloon filled with air, an aqueous solution of glucose etc.

On the basis of physical and chemical properties, systems can be divided into two types.

A system is called homogeneous if the physical state of all its constituents are the same. Example: a mixture of gases, completely miscible mixture of liquids etc.

A system is called heterogeneous, if physical state of all its constituents is not the same.

Example: mixture of oil and water

Surrounding:

Everything in the universe that is not the part of the system is called surroundings.

Boundary:

Anything which separates the system from its surrounding is called boundary.

7.2.1 Types of systems:

There are three types of thermodynamic systems depending on the nature of the boundary.

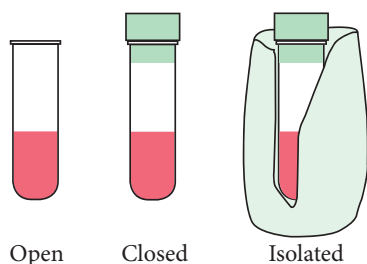


Figure 7.2 Types of Systems

Isolated system:

A system which can exchange neither matter nor energy with its surroundings is called an isolated system. Here boundary is sealed and insulated. Hot water contained in a thermos flask, is an example for an isolated system. In this isolated system both energy (heat) and matter (water vapour) neither enter nor leave the system.

Closed system:

A system which can exchange only energy but not matter with its surroundings is called a closed system. Here the boundary is sealed but not insulated. Hot water contained in a closed beaker is an example for a closed system. In this system energy (heat) is transferred to the surroundings but no matter (water vapour) can escape from this system. A gas contained in a cylinder fitted with a piston constitutes a closed system.

Open system:

A System which can exchange both matter and energy with its surrounding is called an open system. Hot water contained in an open beaker is an example for open system. In this system both matter (water vapour) and energy (heat) is transferred to the surrounding.

All living things and chemical reactions are open systems because they exchange matter and energy with the surroundings.

7.2.2 Properties of the system:

Intensive and extensive properties

Some of the properties of a system depend on its mass or size whereas other properties do not depend on its mass or size. Based on this, the properties of a system are grouped as **extensive** property and **intensive** property.

Extensive properties:

The property that depends on the mass or the size of the system is called an extensive property.

Examples: Volume, Number of moles, Mass, Internal energy, etc.,

Intensive properties:

The property that is independent of the mass or the size of the system is called an intensive property.

Examples : Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume, etc.,

Table: 7.1 Typical List of Extensive and Intensive properties

Extensive properties	Intensive properties
volume, mass, amount of substance (mole), energy, enthalpy, entropy, free energy, heat capacity	molar volume, density, molar mass, molarity, mole fraction, molality, specific heat capacity

7.2.3 Thermodynamic processes

The method of operation which can bring about a change in the system is called thermodynamic process. Heating, cooling, expansion, compression, fusion, vaporization etc., are some examples of a thermodynamic process.

Types of processes:

A thermodynamic process can be carried out in different ways and under different conditions. The processes can be classified as follows:

Reversible process:

The process in which the system and surrounding can be restored to the initial state from the final state without producing any changes in the thermodynamic properties of the universe is called a reversible process. There are two important conditions for the reversible process to occur. Firstly, the process should occur infinitesimally slowly and secondly throughout the process, the system and surroundings must be in equilibrium with each other.

Irreversible Process:

The process in which the system and surrounding cannot be restored to the initial state from the final state is called an irreversible process. All the processes occurring in nature are irreversible processes. During the irreversible process the system and surroundings are not in equilibrium with each other.

Adiabatic process:

An adiabatic process is defined as one in which there is no exchange of heat (q) between the system and surrounding during the process. Those processes in which no heat can flow into or out of the system are called **adiabatic processes**. This condition is attained by thermally insulating the system. In an adiabatic process if work is done by the system its temperature decreases, if work is done on the system its temperature increases, because, the system cannot exchange heat with its surroundings.

For an adiabatic process $q = 0$

Isothermal process :

An isothermal process is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. The system exchanges heat with its surrounding and the temperature of the system remains constant. For this purpose the experiment is often performed in a thermostat.

For an isothermal process $dT = 0$

Isobaric process

An isobaric process is defined as one in which the pressure of the system remains constant during its change from the initial to final state.

For an isobaric process $dP = 0$.

Isochoric process

An isochoric process is defined as

the one in which the volume of system remains constant during its change from initial to final state. Combustion of a fuel in a bomb calorimeter is an example of an isochoric process.

For an isochoric process, $dV = 0$.

Cyclic process:

When a system returns to its original state after completing a series of changes, then it is said that a cycle is completed. This process is known as a cyclic process.

For a cyclic process $dU = 0$, $dH = 0$, $dP = 0$, $dV = 0$, $dT = 0$

Table: 7.2 Overview of the process and its condition

Process	Condition
Adiabatic	$q = 0$
Isothermal	$dT = 0$
Isobaric	$dP = 0$
Isochoric	$dV = 0$
Cyclic	$dE = 0$, $dH = 0$, $dP = 0$, $dV = 0$, $dT = 0$

State functions, path functions:

State function

A thermodynamic system can be defined by using the variables P , V , T and n . A state function is a thermodynamic property of a system, which has a specific value for a given state and does not depend on the path (or manner) by which the particular state is reached.

Example : Pressure (P), Volume (V), Temperature(T), Internal energy (U), Enthalpy (H), free energy (G) etc.

Path functions:

A path function is a thermodynamic property of the system whose value depends on the path by which the system changes from its initial to final states.

Example: Work (w), Heat (q).

Work (w) will have different values if the process is carried out reversibly or irreversibly.

Internal Energy (U)

The internal energy is a characteristic property of a system which is denoted by the symbol U. The internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules. The total energy of all molecules in a system is equal to the sum of their translational energy (U_t), vibrational energy (U_v), rotational energy (U_r), bond energy (U_b), electronic energy (U_e) and energy due to molecular interactions (U_i).

Thus:

$$U = U_t + U_v + U_r + U_b + U_e + U_i$$

The total energy of all the molecules of the system is called internal energy. In thermodynamics one is concerned only with the change in internal energy (ΔU) rather than the absolute value of energy.

Importance of Internal energy

The internal energy possessed by a substance differentiates its physical structure. For example, the allotropes of carbon, namely, graphite C(graphite) and diamond C(diamond), differ from each other because they possess different internal energies and have different structures.

Characteristics of internal energy (U):

- The internal energy of a system is an extensive property. It depends on the amount of the substances present in the system. If the amount is doubled, the internal energy is also doubled.
- The internal energy of a system is a state function. It depends only upon the state variables (T, P, V, n) of the system. The change in internal energy does not depend on the path by which the final state is reached.
- The change in internal energy of a system is expressed as $\Delta U = U_f - U_i$
- In a cyclic process, there is no internal energy change. $\Delta U_{(cyclic)} = 0$
- If the internal energy of the system in the final state (U_f) is less than the internal energy of the system in its initial state (U_i), then ΔU would be negative.

$$\Delta U = U_f - U_i = -ve \quad (U_f < U_i)$$

- If the internal energy of the system in the final state (U_f) is greater than the internal energy of the system in its initial state (U_i), then ΔU would be positive.

$$\Delta U = U_f - U_i = +ve \quad (U_f > U_i)$$

HEAT(q)

The heat (q) is regarded as an energy in transit across the boundary separating a system from its surrounding. Heat changes lead to temperature differences between system and surrounding. Heat is a path function.

Units of heat:

The SI unit of heat is joule (J). Heat quantities are generally measured in calories (cal). A calorie is defined as the quantity of heat required to raise the temperature of 1 gram of water by 1°C in the vicinity of 15°C .

Sign convention of heat:

The symbol of heat is q .

If heat flows into the system from the surrounding, energy of a system increases. Hence it is taken to be positive (+ q).

If heat flows out of the system into the surrounding, energy of the system decreases. Hence, it is taken to be negative (– q).

Work(w)

Work is defined as the force (F) multiplied by the displacement(x).

$$-w = F \cdot x \quad \text{-----}(7.1)$$

The negative sign (–) is introduced to indicate that the work has been done by the system by spending a part of its internal energy.

The work,

- (i) is a path function.
- (ii) appears only at the boundary of the system.
- (iii) appears during the change in the state of the system.
- (iv) In thermodynamics, surroundings is so large that macroscopic changes to surroundings do not happen.

Units of work:

The SI unit of work is joule (J), which is defined as the work done by a force of one Newton through a displacement of one meter ($J = \text{Nm}$). We often use kilojoule (kJ) for large quantities of work. $1 \text{ kJ} = 1000 \text{ J}$.

Sign convention of work:

The symbol of work is ' w '.

If work is done by the system, the energy of the system decreases, hence by convention, work is taken to be negative (– w).

If work is done on the system, the energy of the system increases, hence by convention, the work is taken to be positive (+ w).

Pressure - volume work

In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as pressure-volume work, PV work or expansion work.

Work involved in expansion and compression processes:

In most thermodynamic calculations we are dealing with the evaluation of work involved in the expansion or compression of gases. The essential condition for expansion or compression of a system is that there should be difference between external pressure (P_{ext}) and internal pressure (P_{int}).

For understanding pressure-volume work, let us consider a cylinder which contains 'n' moles of an ideal gas fitted with a frictionless piston of cross sectional area A . The total volume of the gas inside is V_i and pressure of the gas inside is P_{int} .

If the external pressure P_{ext} is greater than P_{int} , the piston moves inward till the pressure inside becomes equal to P_{ext} . Let this change be achieved in a single step and the final volume be V_f .

In this case, the work is done on the system (+w). It can be calculated as follows

$$w = -F \cdot \Delta x \quad \text{----- (7.2)}$$

where dx is the distance moved by the piston during the compression and F is the force acting on the gas.

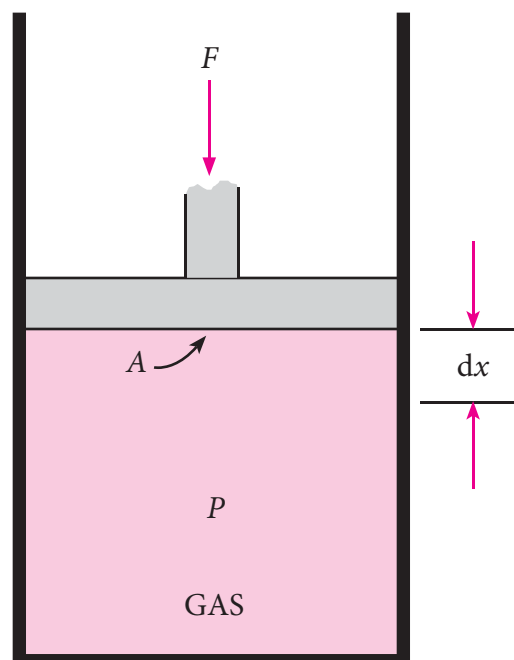


Figure 7.3 showing work involved in compression processes

$$F = P_{\text{ext}} A \quad \text{---- (7.3)}$$

Substituting 7.3 in 7.2

$$w = - P_{\text{ext}} \cdot A \cdot \Delta x$$

$$A \cdot \Delta x = \text{change in volume} = V_f - V_i$$

$$w = - P_{\text{ext}} \cdot (V_f - V_i) \quad \text{----- (7.4)}$$

$$w = - P_{\text{ext}} \cdot (-\Delta V) \quad \text{----- (7.5)}$$

$$= P_{\text{ext}} \cdot \Delta V$$

Since work is done on the system, it is a positive quantity.

If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV . In such a case we can calculate the work done on the gas by the relation

$$w_{rev} = - \int_{V_i}^{V_f} P_{ext} dV$$

In a compression process, P_{ext} the external pressure is always greater than the pressure of the system.

$$\text{i.e. } P_{ext} = (P_{int} + dP).$$

In an expansion process, the external pressure is always less than the pressure of the system

$$\text{i.e. } P_{ext} = (P_{int} - dP).$$

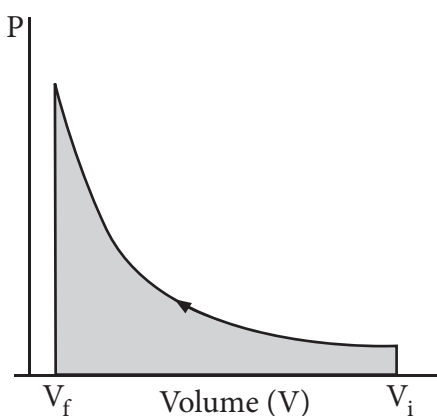


Figure 7.4

When pressure is not constant and changes in infinitesimally small steps (reversible conditions) during compression from V_i to V_f , the P-V plot looks like in fig 7.4. Work done on the gas is represented by the shaded area.

In general case we can write,

$P_{ext} = (P_{int} \pm dP)$. Such processes are called reversible processes. For a compression process work can be related to internal pressure of the system under reversible conditions by writing equation

$$w_{rev} = - \int_{V_i}^{V_f} P_{int} dV$$

For a given system with an ideal gas

$$P_{int} V = nRT$$

$$P_{int} = \frac{nRT}{V}$$

$$w_{rev} = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$w_{rev} = - nRT \int_{V_i}^{V_f} \left(\frac{dV}{V} \right)$$

$$w_{rev} = - nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$w_{rev} = - 2.303 nRT \log \left(\frac{V_f}{V_i} \right) \text{ ----- 7.6}$$

If $V_f > V_i$ (expansion), the sign of work done by the process is negative.

If $V_f < V_i$ (compression) the sign of work done on the process is positive.

Table: 7.3 Summary of sign conventions

1.	If heat is absorbed by the system	:	$+q$
2.	If heat is evolved by the system	:	$-q$
3.	work is done by the system	:	$-w$
4.	work is done on the system	:	$+w$

7.3 Zeroth law of thermodynamics:

The zeroth law of thermodynamics, also known as the law of thermal equilibrium, was put forward much after the establishment of the first and second laws of thermodynamics. It is placed

before the first and second laws as it provides a logical basis for the concept of temperature of the system.

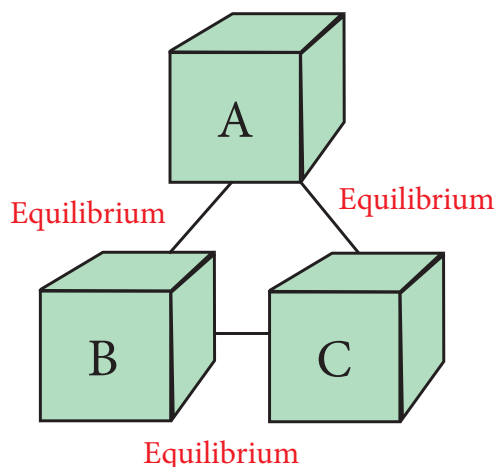


Figure : 7.5 Zeroth law of thermodynamics:

The law states that 'If two systems are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves'.

According to this law, if systems B and C separately are in thermal equilibrium with another system A, then systems B and C will also be in thermal equilibrium with each other. This is also the principle by which thermometers are used.

7.4 First Law of Thermodynamics:

The first law of thermodynamics, known as the law of conservation of energy, states that the total energy of an isolated system remains constant though it may change from one form to another.

When a system moves from state 1 to state 2, its internal energy changes from U_1 to U_2 . Then change in internal energy

$$\Delta U = U_2 - U_1.$$

This internal energy change is brought about by the either absorption or evolution of heat and/or by work being done by/on the system.

Because the total energy of the system must remain constant, we can write the mathematical statement of the First Law as:

$$\Delta U = q + w \text{ -----(7.7)}$$

Where q - the amount of heat supplied to the system; w - work done on the system

Other statements of first law of thermodynamics

- (1) Whenever an energy of a particular type disappears, an equivalent amount of another type must be produced.
- (2) The total energy of a system and surrounding remains constant (or conserved)
- (3) "Energy can neither be created nor destroyed, but may be converted from one form to another".
- (4) "The change in the internal energy of a closed system is equal to the energy that passes through its boundary as heat or work".
- (5) "Heat and work are two ways of changing a system's internal energy".

7.4.1 Mathematical statement of the first law

The mathematical statement of the first law of thermodynamics is

$$\Delta U = q + w \text{ ----- 7.7}$$

Case 1 : For a cyclic process involving isothermal expansion of an ideal gas,

$$\Delta U = 0.$$

$$\text{eqn (7.7)} \Rightarrow \therefore q = -w$$

In other words, during a cyclic process, the amount of heat absorbed by the system is equal to work done by the system.

Case 2 : For an isochoric process (no change in volume) there is no work of expansion. i.e. $\Delta V = 0$

$$\begin{aligned} \Delta U &= q + w \\ &= q - P\Delta V \\ \Delta V &= 0 \\ \Delta U &= q_v \end{aligned}$$

In other words, during an isochoric process, the amount of heat supplied to the system is converted to its internal energy.

Case 3 : For an adiabatic process there is no change in heat. i.e. $q = 0$. Hence

$$q = 0$$

$$\text{eqn (7.7)} \Rightarrow \Delta U = w$$

In other words, in an adiabatic process, the decrease in internal energy

is exactly equal to the work done by the system on its surroundings.

Case 4 : For an isobaric process. There is no change in the pressure. P remains constant. Hence

$$\begin{aligned} \Delta U &= q + w \\ \Delta U &= q - P\Delta V \end{aligned}$$

In other words, in an isobaric process a part of heat absorbed by the system is used for PV expansion work and the remaining is added to the internal energy of the system.

Problem: 7.1

A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J of thermal energy from its surroundings. Determine the change in internal energy of system.

Solution:

Given data $q = 400 \text{ J}$ $V_1 = 5 \text{ L}$ $V_2 = 10 \text{ L}$

$\Delta u = q - w$ (heat is given to the system (+q); work is done by the system (-w))

$$\begin{aligned} \Delta u &= q - PdV \\ &= 400 \text{ J} - 1 \text{ atm} (10 - 5) \text{ L} \\ &= 400 \text{ J} - 5 \text{ atm L} \\ &[\therefore 1 \text{ L atm} = 101.33 \text{ J}] \\ &= 400 \text{ J} - 5 \times 101.33 \text{ J} \\ &= 400 \text{ J} - 506.65 \text{ J} \\ &= -106.65 \text{ J} \end{aligned}$$

7.5 Enthalpy (H)

The enthalpy (H), is a thermodynamic property of a system, is defined as the sum of the internal energy (U) of a system and the product of pressure and volume of the system. That is,

$$H = U + PV \text{ -----(7.8)}$$

It reflects the capacity to do mechanical work and the capacity to release heat by the system. When a process occurs at constant pressure, the heat involved (either released or absorbed) is equal to the change in enthalpy.

Enthalpy is a state function which depends entirely on the state functions T, P and U. Enthalpy is usually expressed as the change in enthalpy (ΔH) for a process between initial and final states at constant pressure.

$$\Delta H = \Delta U + P\Delta V \text{ -----(7.9)}$$

The change in enthalpy (ΔH) is equal to the heat supplied at the constant pressure to a system (as long as the system does no additional work).

$$\Delta H = q_p$$

In an endothermic reaction heat is absorbed by the system from the surroundings that is $q > 0$ (positive). Therefore, ΔH is also positive. In an exothermic reaction heat is evolved by the system to the surroundings that is, $q < 0$ (negative). If q is negative, then ΔH will also be negative.

7.5.1 Relation between enthalpy 'H' and internal energy 'U'

When the system at constant pressure undergoes changes from an initial state with H_1 , U_1 and V_1 to a final state with H_2 , U_2 and V_2 the change in enthalpy ΔH , can be calculated as follows:

$$H = U + PV$$

In the initial state

$$H_1 = U_1 + PV_1 \text{ -----(7.10)}$$

In the final state

$$H_2 = U_2 + PV_2 \text{ -----(7.11)}$$

change in enthalpy is (7.11) - (7.10)

$$(H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$$

$$\Delta H = \Delta U + P\Delta V \text{ ----- (7.12)}$$

As per first law of thermodynamics,

$$\Delta U = q + w$$

Equation 7.12 becomes

$$\Delta H = q + w + P\Delta V$$

$$w = -P\Delta V$$

$$\Delta H = q_p - P\Delta V + P\Delta V$$

$$\Delta H = q_p \text{ ----- (7.13)}$$

q_p – is the heat absorbed at constant pressure and is considered as heat content.

Consider a closed system of gases which are chemically reacting to form gaseous products at constant temperature

and pressure with V_i and V_f as the total volumes of the reactant and product gases respectively, and n_i and n_f as the number of moles of gaseous reactants and products, then,

For reactants (initial state) :

$$PV_i = n_i RT \text{ ----- (7.14)}$$

For products (final state) :

$$PV_f = n_f RT \text{ ----- (7.15)}$$

$$(7.15) - (7.14)$$

$$P (V_f - V_i) = (n_f - n_i) RT$$

$$P \Delta V = \Delta n_{(g)} RT \text{ ----- (7.16)}$$

Substituting in 7.16 in 7.12

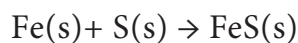
$$\Delta H = \Delta U + \Delta n_{(g)} RT \text{ ----- (7.17)}$$

7.5.2 Enthalpy Changes for Different Types of Reactions and Phase Transitions:

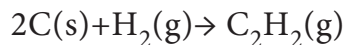
The heat or enthalpy changes accompanying chemical reactions is expressed in different ways depending on the nature of the reaction. These are discussed below.

Standard heat of formation

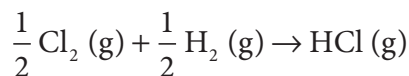
The standard heat of formation of a compound is defined as "the change in enthalpy that takes place when one mole of a compound is formed from its elements, present in their standard states (298 K and 1 bar pressure)". By convention the standard heat of formation of all elements is assigned a value of zero.



$$\Delta H_f^0 = -100.42 \text{ kJ mol}^{-1}$$



$$\Delta H_f^0 = +222.33 \text{ kJ mol}^{-1}$$



$$\Delta H_f^0 = -92.4 \text{ kJ mol}^{-1}$$

The standard heats of formation of some compounds are given in Table 7.4.

Table: 7.4 standard heat of formation of some compounds

Substance	ΔH_f^0 (kJ mol ⁻¹)	Substance	ΔH_f^0 (kJ mol ⁻¹)
H ₂ O(l)	-242	CH ₄ (g)	-74.85
HCl(g)	-92.4	C ₂ H ₆ (g)	-84.6
HBr(g)	-36.4	C ₆ H ₆ (g)	+49.6
NH ₃ (g)	-46.1	C ₂ H ₂ (g)	+222.33
CO ₂ (g)	-393.5	CH ₃ OH(l)	-239.2

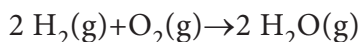
7.6 Thermochemical Equations:

A thermochemical equation is a balanced stoichiometric chemical equation that includes the enthalpy change (ΔH). The following conventions are adopted in thermochemical equations:

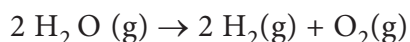
- The coefficients in a balanced thermochemical equation refer to number of moles of reactants and products involved in the reaction.

- (ii) The enthalpy change of the reaction ΔH_r has to be specified with appropriate sign and unit.
- (iii) When the chemical reaction is reversed, the value of ΔH is reversed in sign with the same magnitude.
- (iv) The physical states (gas, liquid, aqueous, solid in brackets) of all species are important and must be specified in a thermochemical reaction, since ΔH depends on the physical state of reactants and products.
- (v) If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also multiplied by the same number.
- (vi) The negative sign of ΔH_r indicates that the reaction is exothermic and the positive sign of ΔH_r indicates an endothermic reaction.

For example, consider the following reaction,



$$\Delta H_r^0 = -967.4 \text{ kJ}$$



$$\Delta H_r^0 = +967.4 \text{ kJ}$$

Standard enthalpy of reaction (ΔH_r^0) from standard enthalpy of formation (ΔH_f^0)

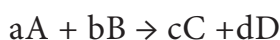
The standard enthalpy of a reaction is the enthalpy change for a reaction

when all the reactants and products are present in their standard states. Standard conditions are denoted by adding the superscript 0 to the symbol (ΔH^0)

We can calculate the enthalpy of a reaction under standard conditions from the values of standard enthalpies of formation of various reactants and products. The standard enthalpy of reaction is equal to the difference between standard enthalpy of formation of products and the standard enthalpies of formation of reactants.

$$\Delta H_r^0 = \sum \Delta H_f^0 (\text{products}) - \sum \Delta H_f^0 (\text{reactants})$$

For a general reaction

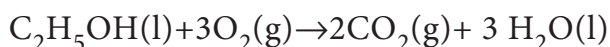


$$\Delta H_r^0 = \sum \Delta H_f^0 (\text{products}) - \sum \Delta H_f^0 (\text{reactants})$$

$$\Delta H_r^0 = \{c \Delta H_f^0 (\text{C}) + d \Delta H_f^0 (\text{D})\} - \{a \Delta H_f^0 (\text{A}) + b \Delta H_f^0 (\text{B})\}$$

Problem : 7.2

The standard enthalpies of formation of $\text{C}_2\text{H}_5\text{OH}(\text{l})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are - 277, -393.5 and -285.5 kJ mol^{-1} respectively. Calculate the standard enthalpy change for the reaction

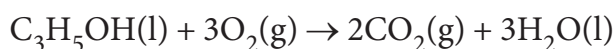


The enthalpy of formation of $\text{O}_2(\text{g})$ in the standard state is Zero, by definition

Solution:

For example, the standard enthalpy change for the combustion of ethanol can be calculated from the standard enthalpies of formation of $\text{C}_2\text{H}_5\text{OH}(\text{l})$, $\text{CO}_2(\text{g})$

and $\text{H}_2\text{O}(\text{l})$. The enthalpies of formation are -277 , -393.5 and $-285.5 \text{ kJ mol}^{-1}$ respectively.



$$\Delta H_r^0 = \left\{ (\Delta H_f^0)_{\text{products}} - (\Delta H_f^0)_{\text{reactants}} \right\}$$

$$\Delta H_r^0 = \left[2(\Delta H_f^0)_{\text{CO}_2} + 3(\Delta H_f^0)_{\text{H}_2\text{O}} \right] - \left[1(\Delta H_f^0)_{\text{C}_2\text{H}_5\text{OH}} + 3(\Delta H_f^0)_{\text{O}_2} \right]$$

$$\Delta H_r^0 = \left[\begin{array}{l} 2\text{mol}(-393.5)\text{kJ mol}^{-1} \\ + 3\text{mol}(-285.5)\text{kJ mol}^{-1} \end{array} \right] - \left[\begin{array}{l} 1\text{mol}(-277)\text{kJ mol}^{-1} \\ + 3\text{mol}(0)\text{kJ mol}^{-1} \end{array} \right]$$

$$= [-787 - 856.5] - [-277]$$

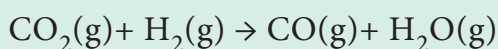
$$= -1643.5 + 277$$

$$\Delta H_r^0 = -1366.5 \text{ KJ}$$

Evaluate Yourself - 1



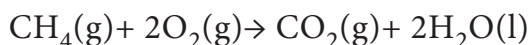
Calculate ΔH_f^0 for the reaction



given that ΔH_f^0 for $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -393.5 , -111.31 and -242 kJ mol^{-1} respectively.

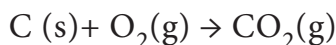
Heat of combustion

The heat of combustion of a substance is defined as “The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen”. It is denoted by ΔH_C . For example, the heat of combustion of methane is $-87.78 \text{ kJ mol}^{-1}$



$$\Delta H_C = -87.78 \text{ kJ mol}^{-1}$$

For the combustion of carbon,



$$\Delta H_C = -394.55 \text{ kJ mol}^{-1}$$

Combustion reactions are always exothermic. Hence the enthalpy change is always negative.

Molar heat capacities

When heat (q) is supplied to a system, the molecules in the system absorb the heat and hence their kinetic energy increases, which in turn raises the temperature of the system from T_1 to T_2 . This increase ($T_2 - T_1$) in temperature is directly proportional to the amount of heat absorbed and the mass of the substance. In other words,

$$q \propto m\Delta T$$

$$q = c m \Delta T$$

$$c = q/m \Delta T$$

The constant c is called heat capacity.

$$c = \left(\frac{q}{m(T_2 - T_1)} \right) \text{ ----- (7.18)}$$

when $m=1 \text{ kg}$ and $(T_2 - T_1) = 1 \text{ K}$ then the heat capacity is referred as specific heat capacity. The equation 7.18 becomes

$$c = q$$

Thus specific heat capacity of a

system is defined as “The heat absorbed by one kilogram of a substance to raise its temperature by one Kelvin at a specified temperature”.

The heat capacity for 1 mole of substance, is called molar heat capacity (c_m). It is defined as “The amount of heat absorbed by one mole of the substance to raise its temperature by 1 kelvin”.

Units of Heat Capacity:

The SI unit of molar heat capacity is $\text{JK}^{-1}\text{mol}^{-1}$

The molar heat capacities can be expressed either at constant volume (C_v) or at constant pressure (C_p).

According to the first law of thermodynamics

$$U = q + w \quad \text{or} \quad U = q - PdV$$

$$q = U + PdV \text{ -----(7.19)}$$

Differentiate (7.19) with respect to temperature at constant volume i.e $dV=0$,

$$\left(\frac{\partial q}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \text{ -----7.20}$$

Thus the heat capacity at constant volume (C_v) is defined as the rate of change of internal energy with respect to temperature at constant volume.

Similarly the molar heat capacity at constant pressure (C_p) can be defined as

the rate of change of enthalpy with respect to temperature at constant pressure.

$$c_p = \left(\frac{\partial H}{\partial T}\right)_p \text{ ----- (7.21)}$$

Relation between C_p and C_v for an ideal gas.

From the definition of enthalpy

$$H = U + PV \text{ -----(7.8)}$$

for 1 mole of an ideal gas

$$PV = nRT \text{ -----(7.22)}$$

By substituting (7.22) in (7.8)

$$H = U + nRT \text{ ---- (7.23)}$$

Differentiating the above equation with respect to T,

$$\frac{\partial H}{\partial T} = \frac{\partial U}{\partial T} + nR \frac{\partial T}{\partial T}$$

$$\begin{aligned} C_p &= C_v + nR \quad (1) \\ C_p - C_v &= nR \text{(7.24)} \end{aligned} \left[\begin{array}{l} \because \left(\frac{\partial H}{\partial T}\right)_P = C_P \\ \text{and } \left(\frac{\partial U}{\partial T}\right)_V = C_V \end{array} \right]$$

At constant pressure processes, a system has to do work against the surroundings. Hence, the system would require more heat to effect a given temperature rise than at constant volume, so C_p is always greater than C_v

Calculation of ΔU and ΔH

For one mole of an ideal gas, we have

$$c_v = \frac{dU}{dT}$$

$$dU = C_V dT$$

For a finite change, we have

$$\Delta U = C_V \Delta T$$

$$\Delta U = C_V (T_2 - T_1)$$

and for n moles of an ideal gas we get

$$\Delta U = n C_V (T_2 - T_1) \text{ ----- (7.25)}$$

Similarly for n moles of an ideal gas we get

$$\Delta H = n C_P (T_2 - T_1) \text{ ----- (7.26)}$$

Problem 7.3

Calculate the value of ΔU and ΔH on heating 128.0 g of oxygen from 0°C to 100°C . C_V and C_P on an average are 21 and 29 J mol⁻¹ K⁻¹. (The difference is 8 J mol⁻¹ K⁻¹ which is approximately equal to R)

Solution.

We know

$$\Delta U = n C_V (T_2 - T_1)$$

$$\Delta H = n C_P (T_2 - T_1)$$

$$\text{Here } n = \frac{128}{32} \text{ 4 moles ;}$$

$$T_2 = 100^\circ \text{C} = 373\text{K}; T_1 = 0^\circ \text{C} = 273\text{K}$$

$$\Delta U = n C_V (T_2 - T_1)$$

$$\Delta U = 4 \times 21 \times (373 - 273)$$

$$\Delta U = 8400 \text{ J}$$

$$\Delta U = 8.4 \text{ kJ}$$

$$\Delta H = n C_P (T_2 - T_1)$$

$$\Delta H = 4 \times 29 \times (373 - 273)$$

$$\Delta H = 11600 \text{ J}$$

$$\Delta H = 11.6 \text{ kJ}$$



Evaluate Yourself -2

Calculate the amount of heat necessary to raise 180 g of water from 25°C to 100°C . Molar heat capacity of water is 75.3 J mol⁻¹ K⁻¹

7.7 Measurement of ΔU and ΔH using Calorimetry.

Calorimeter is used for measuring the amount of heat change in a chemical or physical change. In calorimetry, the temperature change in the process is measured which is directly proportional to the heat capacity. By using the expression $C = q/m\Delta T$, we can calculate the amount of heat change in the process. Calorimetric measurements are made under two different conditions

i) At constant volume (q_V)

ii) At constant pressure (q_P)

(A) ΔU Measurements

For chemical reactions, heat evolved at constant volume, is measured

in a *bomb calorimeter*.

The inner vessel (the bomb) and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws.

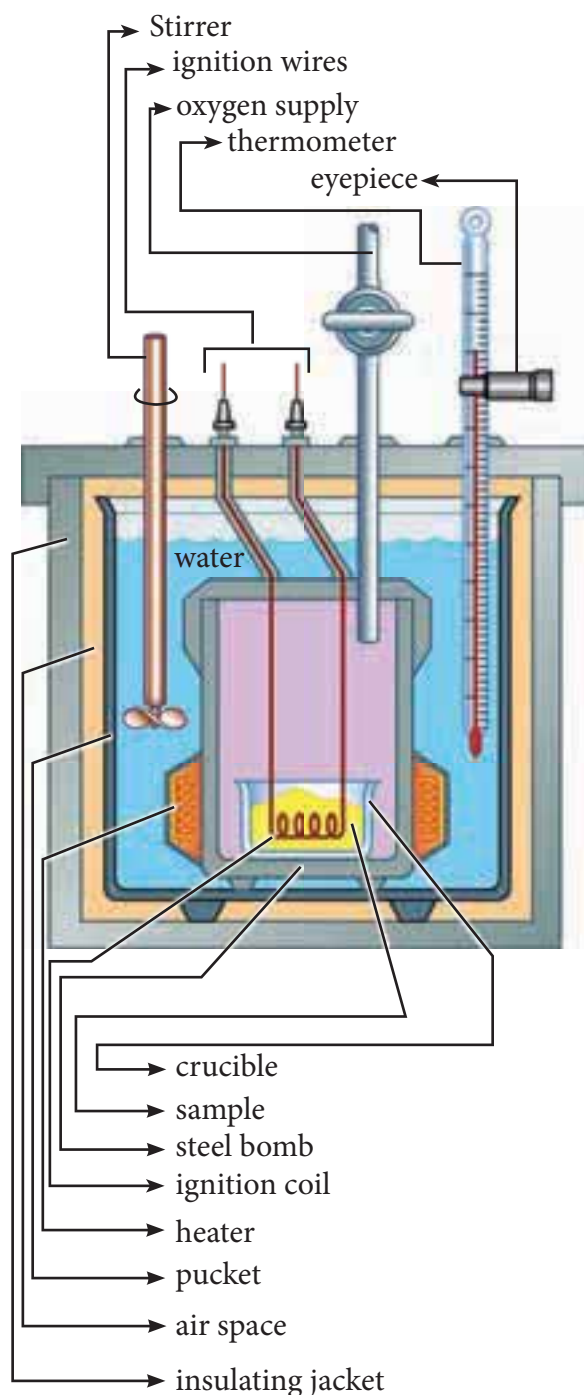


Figure 7.6 Bomb calorimeter

A weighed amount of the substance is taken in a platinum cup connected with

electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurized with excess oxygen. The bomb is immersed in water, in the inner volume of the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred, uniformly. The reaction is started by striking the substance through electrical heating.

A known amount of combustible substance is burnt in oxygen in the bomb. Heat evolved during the reaction is absorbed by the calorimeter as well as the water in which the bomb is immersed. The change in temperature is measured using a Beckman thermometer. Since the bomb is sealed its volume does not change and hence the heat measurements is equal to the heat of combustion at a constant volume (ΔU)_c.

The amount of heat produced in the reaction (ΔU)_c is equal to the sum of the heat absorbed by the calorimeter and water.

Heat absorbed by the calorimeter

$$q_1 = k \cdot \Delta T$$

where k is a calorimeter constant equal to $m_c C_c$ (m_c is mass of the calorimeter and C_c is heat capacity of calorimeter)

Heat absorbed by the water

$$q_2 = m_w C_w \Delta T$$

where m_w is molar mass of water

C_w is molar heat capacity of water (4,184 kJ K⁻¹ mol⁻¹)

$$\begin{aligned}\text{Therefore } \Delta U_c &= q_1 + q_2 \\ &= k \cdot \Delta T + m_w C_w \Delta T \\ &= (k + m_w C_w) \Delta T\end{aligned}$$

Calorimeter constant can be determined by burning a known mass of standard sample (benzoic acid) for which the heat of combustion is known ($-3227 \text{ kJ mol}^{-1}$)

The enthalpy of combustion at constant pressure of the substance is calculated from the equation (7.17)

$$\Delta H_C^0 (\text{pressure}) = \Delta U_C^0 (\text{Vol}) + \Delta n_g RT$$

Applications of bomb calorimeter:

1. Bomb calorimeter is used to determine the amount of heat released in combustion reaction.
2. It is used to determine the calorific value of food.
3. Bomb calorimeter is used in many industries such as metabolic study, food processing, explosive testing etc.

(b) ΔH Measurements

Heat change at constant pressure (at atmospheric pressure) can be measured using a coffee cup calorimeter. A schematic representation of a coffee cup calorimeter is given in Figure 7.7. Instead of bomb, a styrofoam cup is used in this calorimeter. It acts as good adiabatic wall and doesn't allow transfer of heat produced during the reaction to its surrounding. This entire heat energy is absorbed by the water inside the cup. This method can be used for the reactions where there is no

appreciable change in volume. The change in the temperature of water is measured and used to calculate the amount of heat that has been absorbed or evolved in the reaction using the following expression.

$$q = m_w C_w \Delta T$$

where m_w is the molar mass of water and C_w is the molar heat capacity of water ($4184 \text{ kJ K}^{-1} \text{ mol}^{-1}$)

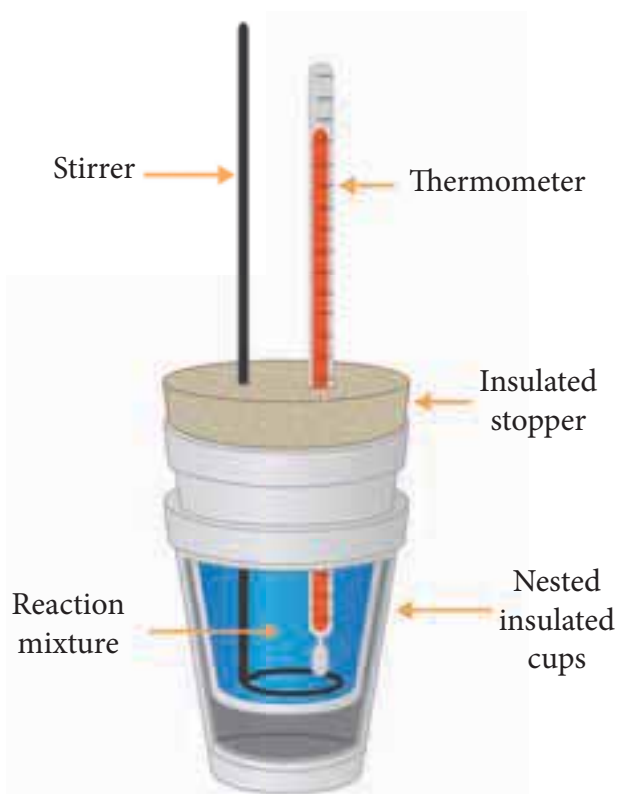
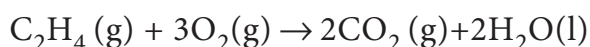


Figure 7.7 Coffee cup Calorimeter

Problem 7. 4

Calculate the enthalpy of combustion of ethylene at 300 K at constant pressure, if its heat of combustion at constant volume (ΔU) is -1406 kJ .

The complete ethylene combustion reaction can be written as,



$$\Delta U = -1406 \text{ kJ}$$

$$\Delta n = n_{\text{p}(\text{g})} - n_{\text{r}(\text{g})}$$

$$\Delta n = 2 - 4 = -2$$

$$\Delta H = \Delta U + RT\Delta n_{\text{g}}$$

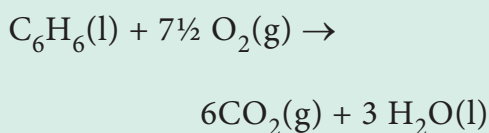
$$\Delta H = -1406 + (8.314 \times 10^{-3} \times 300 \times (-2))$$

$$\Delta H = -1410.9 \text{ kJ}$$

Evaluate Yourself - 3



From the following data at constant volume for combustion of benzene, calculate the heat of this reaction at constant pressure condition.



$$\Delta U \text{ at } 25^\circ \text{C} = -3268.12 \text{ kJ}$$

Applications of the heat of combustion:

(1) Calculation of heat of formation: Since the heat of combustion of organic compounds can be determined with considerable ease, they are employed to calculate the heat of formation of other compounds.

For example let us calculate the standard enthalpy of formation ΔH_f^0 of CH_4 from the values of enthalpy of combustion for H_2 , $\text{C}(\text{graphite})$ and CH_4 which are -285.8, -393.5, and -890.4 kJ mol^{-1} respectively.

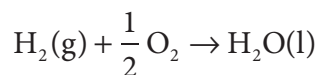
Let us interpret the information

about enthalpy of formation by writing out the equations. It is important to note that the standard enthalpy of formation of pure elemental gases and elements is assumed to be zero under standard conditions. Thermochemical equation for the formation of methane from its constituent elements is,

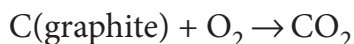


$$\Delta H_f^0 = X \text{ kJ mol}^{-1} \text{--- (i)}$$

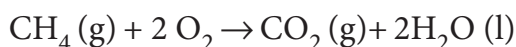
Thermo chemical equations for the combustion of given substances are,



$$\Delta H^0 = -285.8 \text{ kJ mol}^{-1} \text{---(ii)}$$

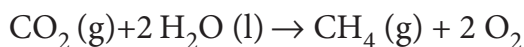


$$\Delta H^0 = -393.5 \text{ kJ mol}^{-1} \text{--- (iii)}$$



$$\Delta H^0 = -890.4 \text{ kJ mol}^{-1} \text{--- (iv)}$$

Since methane is in the product side of the required equation (i), we have to reverse the equation (iv)



$$\Delta H^0 = +890.4 \text{ kJ mol}^{-1} \text{--- (v)}$$

In order to get equation (i) from the remaining,

$$(i) = [(ii) \times 2] + (iii) + (v)$$

$$X = [(-285.8) \times 2] + [-393.5] + [+890.4]$$

$$= -74.7 \text{ kJ}$$

Hence, the amount of energy required for the formation of 1 mole of methane is -74.7 kJ

The heat of formation methane = $-74.7 \text{ kJ mol}^{-1}$

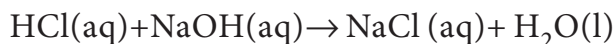
(2) Calculation of calorific value of food and fuels: The calorific value is defined as the amount of heat produced in calories (or joules) when one gram of the substance is completely burnt. The SI unit of calorific value is J kg^{-1} . However, it is usually expressed in cal g^{-1} .

Heat of solution:

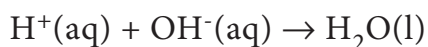
Heat changes are usually observed when a substance is dissolved in a solvent. The heat of solution is defined as the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.

Heat of neutralisation:

The heat of neutralisation is defined as “The change in enthalpy when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base or vice versa in dilute solution”.



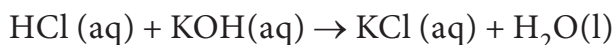
$$\Delta H = - 57.32 \text{ kJ}$$



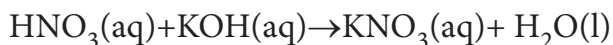
$$\Delta H = - 57.32 \text{ kJ}$$

The heat of neutralisation of a strong acid and strong base is around $- 57.32 \text{ kJ}$, irrespective of nature of acid or base used which is evident from the below

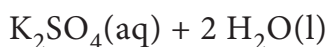
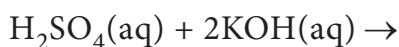
mentioned examples.



$$\Delta H = - 57.32 \text{ kJ}$$

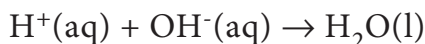


$$\Delta H = - 57.32 \text{ kJ}$$



$$\Delta H = - 57.32 \text{ kJ}$$

The reason for this can be explained on the basis of Arrhenius theory of acids and bases which states that strong acids and strong bases completely ionise in aqueous solution to produce H^+ and OH^- ions respectively. Therefore in all the above mentioned reactions the neutralisation can be expressed as follows.

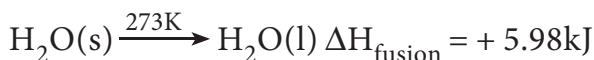


$$\Delta H = - 57.32 \text{ kJ}$$

Molar heat of fusion

The molar heat of fusion is defined as “the change in enthalpy when one mole of a solid substance is converted into the liquid state at its melting point”.

For example, the heat of fusion of ice can be represented as

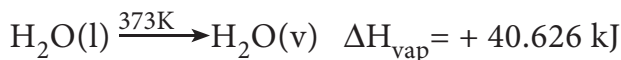


Molar heat of vapourisation

The molar heat of vaporisation is defined as “the change in enthalpy when

one mole of liquid is converted into vapour state at its boiling point”.

For example, heat of vaporisation of water can be represented as



Molar heat of sublimation

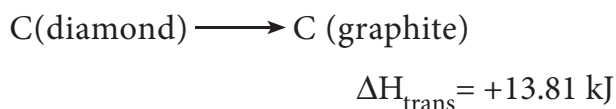
Sublimation is a process when a solid changes directly into its vapour state without changing into liquid state. Molar heat of sublimation is defined as “the change in enthalpy when one mole of a solid is directly converted into the vapour state at its sublimation temperature”. For example, the heat of sublimation of iodine is represented as



Another example of sublimation process is solid CO_2 to gas at atmospheric pressure at very low temperatures.

Heat of transition

The heat of transition is defined as “The change in enthalpy when one mole of an element changes from one of its allotropic form to another. For example, the transition of diamond into graphite may be represented as



Similarly the allotropic transitions in sulphur and phosphorous can be represented as follows,



$$\Delta H_{\text{trans}} = - 0.067 \text{ kJ}$$



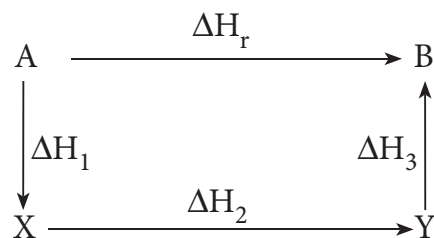
$$\Delta H_{\text{trans}} = - 4.301 \text{ kJ}$$

7.8 Hess's law of constant heat summation

We have already seen that the heat changes in chemical reactions are equal to the difference in internal energy (ΔU) or heat content (ΔH) of the products and reactants, depending upon whether the reaction is studied at constant volume or constant pressure. Since ΔU and ΔH are functions of the state of the system, the heat evolved or absorbed in a given reaction depends only on the initial state and final state of the system and not on the path or the steps by which the change takes place.

This generalisation is known as **Hess's law** and stated as:

The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps provided the initial and final states are same.



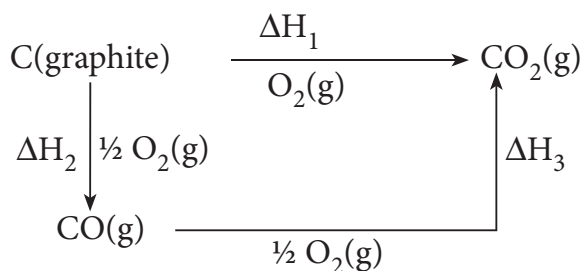
$$\Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Application of Hess's Law: Hess's law can be applied to calculate enthalpies of reactions that are difficult to measure. For example, it is very difficult to measure the heat of combustion of graphite to give pure CO .

However, enthalpy for the oxidation of graphite to CO_2 and CO to CO_2 can easily be measured. For these conversions, the heat of combustion values are -393.5 kJ and -283.5 kJ respectively.

From these data the enthalpy of combustion of graphite to CO can be calculated by applying Hess's law.

The reactions involved in this process can be expressed as follows



According to Hess law,

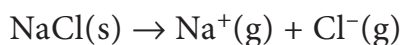
$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

$$-393.5 \text{ kJ} = X - 283.5 \text{ kJ}$$

$$X = -110.5 \text{ kJ}$$

7.9 Lattice energy ($\Delta H_{\text{lattice}}$)

Lattice energy is defined as the amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance. It is also referred as lattice enthalpy.



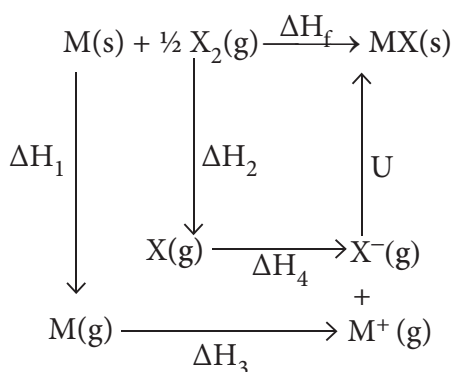
$$\Delta H_{\text{lattice}} = +788 \text{ kJ mol}^{-1}$$

From the above equation it is clear that 788 kJ of energy is required to separate Na^+ and Cl^- ions from 1 mole of NaCl .

Born - Haber cycle

The Born-Haber cycle is an approach to analyse reaction energies. It was named after two German scientists Max Born and Fritz Haber who developed this cycle. The cycle is concerned with the formation of an ionic compound from the reaction of a metal with a halogen or other non-metallic element such as oxygen.

Born-Haber cycle is primarily used in calculating lattice energy, which cannot be measured directly. The Born-Haber cycle applies Hess's law to calculate the lattice enthalpy. For example consider the formation of a simple ionic solid such as an alkali metal halide MX , the following steps are considered.



ΔH_1 - enthalpy change for the sublimation M(s) to M(g)

ΔH_2 - enthalpy change for the dissociation of $\frac{1}{2} \text{X}_2(\text{g})$ to X(g)

ΔH_3 - Ionisation energy for M(g) to $\text{M}^+(\text{g})$

ΔH_4 - electron affinity for the conversion of X(g) to $\text{X}^-(\text{g})$

U - the lattice enthalpy for the formation of solid MX

ΔH_f - enthalpy change for the formation of solid MX directly from elements

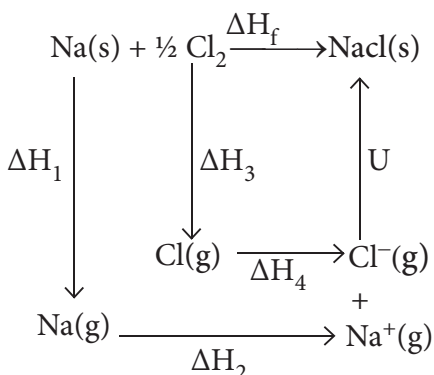
According to Hess's law of heat summation

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + U$$

Let us use the Born - Haber cycle for determining the lattice enthalpy of NaCl as follows:

Since the reaction is carried out with reactants in elemental forms and products in their standard states, at 1 bar, the overall enthalpy change of the reaction is also the enthalpy of formation for NaCl. Also, the formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

Let us calculate the lattice energy of sodium chloride using Born-Haber cycle



ΔH_f = heat of formation of sodium chloride = $-411.3 \text{ kJ mol}^{-1}$

ΔH_1 = heat of sublimation of Na(S) = $108.7 \text{ kJ mol}^{-1}$

ΔH_2 = ionisation energy of Na(S) = $495.0 \text{ kJ mol}^{-1}$

ΔH_3 = dissociation energy of $\text{Cl}_2(\text{S})$ = 244 kJ mol^{-1}

ΔH_4 = Electron affinity of Cl(S) = $-349.0 \text{ kJ mol}^{-1}$

U = lattice energy of NaCl

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \frac{1}{2} \Delta H_3 + \Delta H_4 + U$$

$$\therefore U = (\Delta H_f) - (\Delta H_1 + \Delta H_2 + \frac{1}{2} \Delta H_3 + \Delta H_4)$$

$$\Rightarrow U = (-411.3) - (108.7 + 495.0 + 122 - 349)$$

$$U = (-411.3) - (376.7)$$

$$\therefore U = -788 \text{ kJ mol}^{-1}$$

This negative sign in lattice energy indicates that the energy is released when sodium is formed from its constituent gaseous ions Na^+ and Cl^-

Evaluate Yourself - 4



When a mole of magnesium bromide is prepared from 1 mole of magnesium and 1 mole of liquid bromine, 524 kJ of energy is released.

The heat of sublimation of Mg metal is 148 kJ mol^{-1} . The heat of dissociation of bromine gas into atoms is 193 kJ mol^{-1} . The heat of vapourisation of liquid bromine is 31 kJ mol^{-1} . The ionisation energy of magnesium is 2187 kJ mol^{-1} and the electron affinity of bromine is -662 kJ mol^{-1} . Calculate the lattice energy of magnesium bromide.

7.10. Second Law of thermodynamics:

Need for the second law of thermodynamics:

We know from the first law of thermodynamics, the energy of the universe is conserved. Let us consider the following processes:

1. A glass of hot water over time loses heat energy to the surrounding and becomes cold.
2. When you mix hydrochloric acid with sodium hydroxide, it forms sodium chloride and water with evolution of heat.

In both these processes, the total energy is conserved and are consistent with the first law of thermodynamics. However, the reverse process i.e. cold water becoming hot water by absorbing heat from surrounding on its own does not occur spontaneously even though the energy change involved in this process is also consistent with the first law. However, if the heat energy is supplied to cold water, then it will become hot. i.e. the change that does not occur spontaneously and can be driven by supplying energy.

Similarly, a solution of sodium chloride does not absorb heat energy on its own, to form hydrochloric acid and sodium hydroxide. But, this process can not be driven even by supplying energy. From these kinds of our natural experiences, we have come to know that certain processes are spontaneous while the others are not, and some processes have a preferred direction. In order to explain the feasibility of a process, we need the second law of thermodynamics.

7.10.1 Various statements of the second law of thermodynamics

Entropy

The second law of thermodynamics introduces another state function called entropy. Entropy is a measure of the

molecular disorder (randomness) of a system. But thermodynamic definition of entropy is concerned with the change in entropy that occurs as a result of a process.

It is defined as, $dS = dq_{\text{rev}} / T$

Entropy statement:

The second law of thermodynamics can be expressed in terms of entropy. i.e. “the entropy of an isolated system increases during a spontaneous process”.

For an irreversible process such as spontaneous expansion of a gas,

$$\Delta S_{\text{total}} > 0$$

$$\Delta S_{\text{total}} > \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\text{i.e. } \Delta S_{\text{universe}} > \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

For a reversible process such as melting of ice,

$$\Delta S_{\text{system}} = - \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{universe}} = 0$$

Kelvin-Planck statement:

It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink. The second law of thermodynamics explains why even an ideal, frictionless engine cannot convert 100% of its input heat into work. Carnot on his analysis of heat engines, found that the maximum efficiency of a heat engine which operates reversibly, depends only on the two temperatures between which it is operated.

Efficiency = work performed / heat absorbed

$$\eta = \frac{|q_h| - |q_c|}{|q_h|}$$

q_h - heat absorbed from the hot reservoir

q_c - heat transferred to cold reservoir

$$\eta = 1 - \frac{|q_c|}{|q_h|} \quad \text{--- (7.27)}$$

For a reversible cyclic process

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

$$\frac{q_h}{T_h} = \frac{-q_c}{T_c}$$

$$\frac{-T_c}{T_h} = \frac{q_c}{q_h}$$

$$\frac{T_c}{T_h} = \frac{|q_c|}{|q_h|} \quad \text{--- 7.28}$$

Substituting 7.28 in 7.27

$$\Rightarrow \eta = 1 - \frac{T_c}{T_h} \quad \text{--- 7.29}$$

$$T_h \gg T_c$$

Hence, $\eta < 1$

efficiency in percentage can be expressed as

$$\text{Efficiency in percentage} = \left[1 - \frac{T_c}{T_h} \right] \times 100$$

Clausius statement:

It is impossible to transfer heat from a cold reservoir to a hot reservoir without doing some work.

Problem: 7.10

If an automobile engine burns petrol at a temperature of 816°C and if the surrounding temperature is 21°C , calculate its maximum possible efficiency.

Solution:

$$\% \text{ Efficiency} = \left[\frac{T_h - T_c}{T_h} \right] \times 100$$

Here

$$T_h = 816 + 273 = 1089 \text{ K};$$

$$T_c = 21 + 273 = 294 \text{ K}$$

$$\% \text{ Efficiency} = \left(\frac{1089 - 294}{1089} \right) \times 100$$

$$\% \text{ Efficiency} = 73\%$$

Evaluate Yourself - 5



An engine operating between 127°C and 47°C takes some specified amount of heat from a high temperature reservoir. Assuming that there are no frictional losses, calculate the percentage efficiency of an engine.

Unit of entropy:

The entropy (S) is equal to heat energy exchanged (q) divided by the temperature (T) at which the exchange takes place. Therefore, The SI unit of entropy is JK^{-1} .

Spontaneity and Randomness

Careful examination shows that in each of the processes viz., melting of ice and evaporation of water, there is an increase in randomness or disorder of the system. The water molecules in ice

are arranged in a highly organised crystal pattern which permits little movement. As the ice melts, the water molecules become disorganised and can move more freely. The movement of molecules becomes freer in the liquid phase and even more free in the vapour phase. In other words, we can say that the randomness of the water molecules increases, as ice melts into water or water evaporates. Both are spontaneous processes which result in an increase in randomness (entropy).

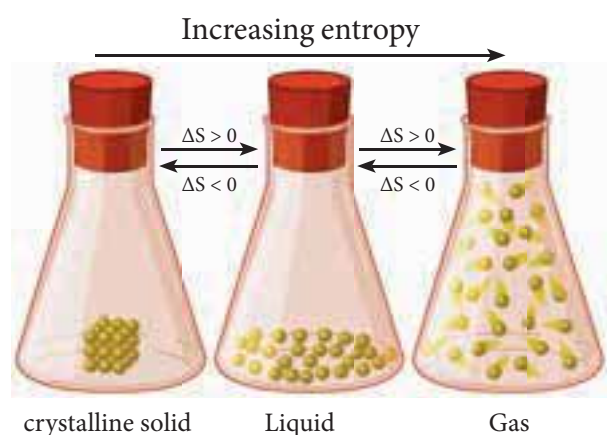


Figure 7.8 Illustration showing an increase in disorder.

Standard Entropy Change(ΔS°):

It is possible to calculate the actual entropy of a substance at any temperature above 0 K. The absolute entropy of a substance at 298 K and one bar pressure is called the standard entropy S° . The third law of thermodynamics states, according to Nernst, that the absolute entropy of elements is zero only at 0 K in a perfect crystal, and standard entropies of all substances at any temperature above 0 K always have positive values. Once we know the entropies of different substances, we

can calculate the standard entropy change (ΔS_r°) for chemical reactions.

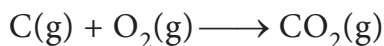
$$\Delta S_r^\circ = \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ \quad \text{----- (7.30)}$$

Standard Entropy of Formation:

Standard entropy of formation is defined as “the entropy of formation of 1 mole of a compound from the elements under standard conditions”. It is denoted as ΔS_f° . We can calculate the value of entropy of a given compound from the values of S° of elements.

Problem: 7.6

Calculate the standard entropy change for the following reaction(ΔS_f°), given the standard entropies of $\text{CO}_2(\text{g})$, $\text{C}(\text{s})$, $\text{O}_2(\text{g})$ as 213.6 , 5.740 and 205 JK^{-1} respectively.



$$\Delta S_r^\circ = \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ$$

$$\Delta S_r^\circ = \{S_{\text{CO}_2}^\circ\} - \{S_{\text{C}}^\circ + S_{\text{O}_2}^\circ\}$$

$$\Delta S_r^\circ = 213.6 - [5.74 + 205]$$

$$\Delta S_r^\circ = 213.6 - [210.74]$$

$$\Delta S_r^\circ = 2.86 \text{ JK}^{-1}$$

Evaluate Yourself- 6



Urea on hydrolysis produces ammonia and carbon dioxide. The standard entropies of urea, H_2O , CO_2 , NH_3 are 173.8, 70, 213.5 and 192.5 $\text{J mole}^{-1}\text{K}^{-1}$ respectively. Calculate the entropy change for this reaction.

Entropy change accompanying change of phase

When there is a change of state from solid to liquid (melting), liquid to vapour (evaporation) or solid to vapour (sublimation) there is a change in entropy. This change may be carried out at constant temperature reversibly as two phases are in equilibrium during the change.

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{rev}}}{T} \quad \text{----- (7.31)}$$

Entropy of fusion:

The heat absorbed, when one mole of a solid melts at its melting point reversibly, is called molar heat of fusion. The entropy change for this process is given by

$$\Delta S_{\text{rev}} = \frac{dq_{\text{rev}}}{T}$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f} \quad \text{----- (7.32)}$$

where ΔH_{fusion} is Molar heat of fusion. T_f is the melting point.

Entropy of vapourisation:

The heat absorbed, when one mole of liquid is boiled at its boiling point reversibly, is called molar heat of vapourisation. The entropy change is given by

$$\Delta S_v = \frac{\Delta H_v}{T_b} \quad \text{----- (7.33)}$$

where ΔH_v is Molar heat of vaporisation. T_b is the boiling point.

Entropy of transition:

The heat change, when one mole of a solid changes reversibly from one allotropic form to another at its transition temperature is called enthalpy of

transition. The entropy change is given

$$\Delta S_t = \frac{\Delta H_t}{T_t} \quad \text{----- (7.34)}$$

where ΔH_t is the molar heat of transition, T_t is the transition temperature.

Problem: 7.7

Calculate the entropy change during the melting of one mole of ice into water at 0°C and 1 atm pressure. Enthalpy of fusion of ice is 6008 J mol^{-1}

Given:

$$\Delta H_{\text{fusion}} = 6008\text{ J mol}^{-1}$$

$$T_f = 0^\circ\text{C} = 273\text{ K}$$



$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$\Delta S_{\text{fusion}} = \frac{6008}{273}$$

$$\Delta S_{\text{fusion}} = 22.007\text{ J K}^{-1}\text{ mole}^{-1}$$

Evaluate Yourself - 7



Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K . The molar heat of vaporisation of ethanol is 39.84 kJ mol^{-1}

7.11 Gibbs free energy (G)

One of the important applications of the second law of thermodynamics is to predict the spontaneity of a reaction under a specific set of conditions. A reaction that occurs under the given set of conditions without any external driving force is called a spontaneous reaction. Otherwise, it is said to be non-spontaneous. In our day today life, we observe many spontaneous physical and chemical

processes, which includes the following examples.

1. A waterfall runs downhill, but never uphill, spontaneously.
2. A lump of sugar dissolves spontaneously in a cup of coffee, but never reappears in its original form spontaneously.
3. Heat flows from hotter object to a colder one, but never flows from colder to hotter object spontaneously.
4. The expansion of a gas into an evacuated bulb is a spontaneous process, the reverse process that is gathering of all molecules into one bulb is not spontaneous.

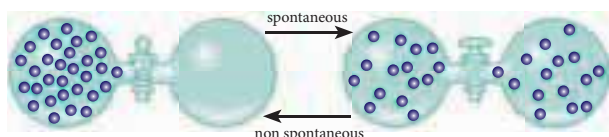
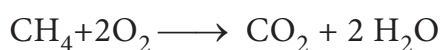


Figure 7.9 Spontaneous process illustration

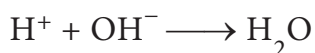
These examples show that the processes that occur spontaneously in one direction, cannot take place in opposite direction spontaneously.

Similarly a large number of exothermic reactions are spontaneous. An example is combustion of methane.



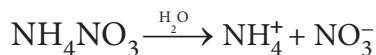
$$\Delta H^\circ = -890.4 \text{ kJ mol}^{-1}$$

Another example is acid-base neutralization reaction:



$$\Delta H^\circ = -57.32 \text{ kJ mol}^{-1}$$

However, some endothermic processes are also spontaneous. For example ammonium nitrate dissolves in water spontaneously though this dissolution is endothermic.



$$\Delta H^\circ = +25 \text{ kJ mol}^{-1}$$

From the above examples we can come to the conclusion that exothermicity favors the spontaneity but does not guarantee it. We cannot decide whether or not a chemical reaction will occur spontaneously solely on the basis of energy changes in the system. We know from second law of thermodynamics that in a spontaneous process, the entropy increases. But not all the processes which are accompanied by an increase in entropy are spontaneous. In order to predict the spontaneity of a reaction, we need some other thermodynamic function.

The second law of thermodynamics introduces another thermodynamic function called Gibbs free energy which finds useful in predicting the spontaneity of a reaction. The Gibbs free energy (G) was developed in the 1870's by Josiah Willard Gibbs. He originally termed this energy as the "available energy" to do work in a system. This quantity is the energy associated with a chemical reaction that can be used to do work.

Gibbs free energy is defined as below

$$G = H - TS \text{ ----- (7.35)}$$

Gibbs free energy (G) is an extensive property and it is a single valued

state function.

Let us consider a system which undergoes a change of state from state (1) to state (2) at constant temperature.

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T \Delta S \text{-----(7.36)}$$

Now let us consider how ΔG is related to reaction spontaneity.

We know that

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

For a reversible process (equilibrium), the change in entropy of universe is zero. $\Delta S_{\text{total}} = 0$ [$\because \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$]

Similarly, for an equilibrium process $\Delta G = 0$

For spontaneous process, $\Delta S_{\text{total}} > 0$, so

$$\Delta S_{\text{total}} > 0$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

$$\frac{\Delta H_{\text{sys}}}{T} - \Delta S_{\text{system}} > 0$$

$$\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} > 0$$

$$T \Delta S_{\text{sys}} - \Delta H_{\text{sys}} < 0$$

$$-(\Delta H_{\text{sys}} - T \Delta S_{\text{sys}}) > 0$$

$$-(\Delta G) > 0$$

hence for a spontaneous process,

$$\Delta G < 0$$

$$\text{i.e. } \Delta H - T \Delta S < 0 \text{-----(7.37)}$$

ΔH_{sys} is the enthalpy change of a reaction, $T \Delta S_{\text{sys}}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known

as the free energy of the reaction. For non spontaneous process, $\Delta G > 0$

Gibbs free energy and the net work done by the system:

For any system at constant pressure and temperature

$$\Delta G = \Delta H - T \Delta S \text{----- (7.36)}$$

We know that,

$$\Delta H = \Delta U + P \Delta V$$

$$\therefore \Delta G = \Delta U + P \Delta V - T \Delta S$$

from first law of thermodynamics

$$\Delta U = q + w$$

from second law of thermodynamics

$$\Delta S = \frac{q}{T} \quad \Delta G = q + w + P \Delta V - T \left(\frac{q}{T} \right)$$

$$\Delta G = w + P \Delta V$$

$$-\Delta G = -w - P \Delta V \text{.....(7.38)}$$

But $-P \Delta V$ represents the work done due to expansion against a constant external pressure. Therefore, it is clear that the decrease in free energy ($-\Delta G$) accompanying a process taking place at constant temperature and pressure is equal to the maximum work obtainable from the system other than the work of expansion.

7.11.1 Criteria for spontaneity of a process

The spontaneity of any process depends on three different factors.

- If the enthalpy change of a process is negative, then the process is exothermic and may be spontaneous. (ΔH is negative)
- If the entropy change of a process is positive, then the process may occur spontaneously. (ΔS is positive)
- The gibbs free energy which is the

combination of the above two ($\Delta H - T\Delta S$) should be negative for a reaction to occur spontaneously, i.e. the necessary condition for a reaction to be spontaneous is $\Delta H - T\Delta S < 0$

Table 7.5 Effect of Temperature on Spontaneity of Reactions:

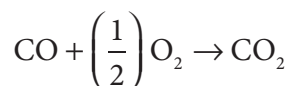
ΔH_r	ΔS_r	$\Delta G_r = \Delta H_r - T\Delta S_r$	Description	Example
–	+	– (at all T)	Spontaneous at all temperature	$2O_3(g) \rightarrow 3O_2(g)$
–	–	– (at low T)	spontaneous at low temperature	Adsorption of gases
		+ (at high T)	non-spontaneous at high temperature	
+	+	+ (at low T)	non-spontaneous at low temperature	Melting of a solid
		– (at high T)	spontaneous at high temperature	
+	–	+ (at all T)	non spontaneous at all temperatures	$2H_2O(g) + O_2(g) \rightarrow 2H_2O_2(l)$

The Table assumes ΔH and ΔS will remain the way indicated for all temperatures. It may not be necessary that way. The Spontaneity of a chemical reaction is only the potential for the reaction to proceed as written. The rate of such processes is determined by kinetic factors, outside of thermodynamical prediction.

Problem: 7. 8

Show that the reaction $CO + \left(\frac{1}{2}\right)O_2 \rightarrow CO_2$

at 300K is spontaneous. The standard Gibbs free energies of formation of CO_2 and CO are -394.4 and -137.2 kJ mole⁻¹ respectively.



$$\Delta G_{(reaction)}^0 = \sum G_{f(products)}^0 - \sum G_{f(reactants)}^0$$

$$\Delta G_{(reaction)}^0 = [G_{CO_2}^0] - \left[G_{CO}^0 + \frac{1}{2} G_{O_2}^0 \right]$$

$$\Delta G_{(reaction)}^0 = -394.4 + [137.2 + 0]$$

$$\Delta G_{(reaction)}^0 = -257.2 \text{ kJ mol}^{-1}$$

$\Delta G_{(reaction)}$ of a reaction at a given temperature is negative hence the reaction is spontaneous.

Evaluate Yourself - 8

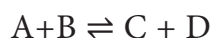


For a chemical reaction the values of ΔH and ΔS at 300K are -10 kJ mole⁻¹ and -20 J deg⁻¹ mole⁻¹ respectively. What is the value of ΔG of the reaction? Calculate the ΔG of a reaction at 600 K assuming ΔH and ΔS values are constant. Predict the nature of the reaction.

7.11.2 Relationship between standard free energy change (ΔG^0) and equilibrium constant (K_{eq}):

In a reversible process, the system is in perfect equilibrium with its surroundings at all times. A reversible chemical reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with decrease in free energy, which is impossible. It is possible only if at equilibrium, the free energy of a system is minimum. Lets consider a general

equilibrium reaction



The free energy change of the above reaction in any state (ΔG) is related to the standard free energy change of the reaction (ΔG^0) according to the following equation.

$$\Delta G = \Delta G^0 + RT \ln Q \text{ ----- (7.39)}$$

where Q is reaction quotient and is defined as the ratio of concentration of the products to the concentrations of the reactants under non equilibrium condition.

When equilibrium is attained, there is no further free energy change i.e. $\Delta G = 0$ and Q becomes equal to equilibrium constant. Hence the above equation becomes.

$$\Delta G^0 = -RT \ln K_{eq}$$

This equation is known as Van't Hoff equation.

$$\Delta G^0 = -2.303 RT \log K_{eq} \text{ ----- (7.40)}$$

We also know that

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 = -RT \ln K_{eq}$$

Problem: 7.9

Calculate ΔG^0 for conversion of oxygen to ozone $3/2 O_2 \rightleftharpoons O_{3(g)}$ at 298 K, if K_p for this conversion is 2.47×10^{-29} in standard pressure units.

Solution:

$$\Delta G^0 = -2.303 RT \log K_p$$

Where

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

$$K_p = 2.47 \times 10^{-29}$$

$$T = 298\text{K}$$

$$\Delta G^0 = -2.303(8.314)(298)\log(2.47 \times 10^{-29})$$

$$\Delta G^0 = 16300 \text{ Jmol}^{-1}$$

$$\Delta G^0 = 16.3 \text{ KJ mol}^{-1}$$

7.12 Third law of Thermodynamics

The entropy of a substance varies directly with temperature. Lower the temperature, lower is the entropy. For example, water above 100°C at one atmosphere exists as a gas and has higher entropy (higher disorder). The water molecules are free to roam about in the entire container. When the system is cooled, the water vapour condenses to form a liquid. The water molecules in liquid phase still can move about somewhat freely. Thus the entropy of the system has decreased. On further cooling, water freezes to form ice crystal. The water molecules in the ice crystal are highly ordered and entropy of the system is very low.

If we cool the solid crystal still further, the vibration of molecules held in the crystal lattice gets slower and they have very little freedom of movement (very little disorder) and hence very small entropy.

At absolute zero (0 K or -273K), theoretically all modes of motion stop.

Absolute zero is a temperature that an object can get arbitrarily close to but absolute zero will remain unattainable.

Thus the third law of thermodynamics states that the entropy of pure crystalline substance at absolute zero is zero. Otherwise it can be stated as it is impossible to lower the temperature of an object to absolute zero in a finite number of steps. Mathematically,

$$\lim_{T \rightarrow 0} S = 0 \text{ for a perfectly ordered crystalline state.}$$

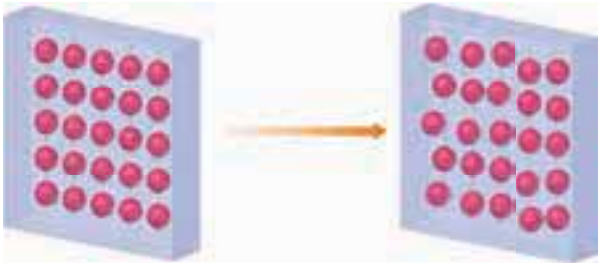


Figure 7.10 Third law of Thermodynamics

Crystals with defects (imperfection) at absolute zero, have entropy greater than zero. Absolute entropy of a substance can never be negative.

SUMMARY



The branch of science which deals the relation between energy, heat and work is called Thermodynamics. The main aim of the study of chemical thermodynamics is to learn (i) transformation of energy from one form into another form (ii) Utilization of various forms of energies.

System: A system is defined as any part of universe under consideration. There are three types of thermodynamic systems. They are (i) isolated system (ii) closed system and (iii) open system.

Surrounding: Everything in the universe that is not the part of the system is called surrounding.

Boundary: Anything which separates the system from its surrounding is called boundary.

Thermodynamic Properties: Any quantity that depends only on the state of system is called thermodynamic property of a system. There are two kinds of thermodynamic properties called (1) intensive - independent of the quantity of material and (2) extensive - directly proportional to the quantity of material. There are five basic thermodynamic properties. (U,H,S and G)

Thermodynamic Processes:

Adiabatic process in which no heat transfer takes place ($q = 0$)

Isothermal process in which

temperature remains constant ($dT = 0$).

Isobaric process in which pressure remains constant ($dP = 0$).

Isochoric process in which volume remains constant ($dV = 0$).

Cyclic process in which the system returns to its original state after completing a series of changes.

Internal energy (U): Internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules. The energy of a system of molecules is equal to the sum of its translational energy, vibrational energy, rotational energy, bond energy, electronic energy and energy due to molecular interactions.

Heat: Heat is regarded as the energy in transit across the boundary separating a system from its surrounding. Heat is a path function. The SI unit of heat is joule (J)

Work : Work is defined as the force (F) multiplied by the displacement - $w = F \cdot x$, work is measured in Joules, i.e the SI unit of work is Joule. During expansion or compression of a gas the work done is calculated by the relation $w = -P\Delta V$.

The sign conventions for heat and work are as follows:

If heat is absorbed by the system : $+q$

If heat is evolved by the system : $-q$

If work is done by the system : $-w$

If work is done on the system : $+w$

Laws of Thermodynamics:

Zeroth law : When two systems are separately in equilibrium with a third system, they are in equilibrium with each other.

First law: "Energy can neither be created nor destroyed, but may be converted from one form to another".

$$\Delta U = q + w.$$

Enthalpy is a thermodynamic property of a system. Enthalpy H is defined as the sum of the internal energy and pressure volume work.

$$H = U + PV. \text{ Enthalpy change, } \Delta H = \Delta U + \Delta n_g RT.$$

Hess's law: It states that "the enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps". Hess's law can be applied to calculate enthalpies of reactions that are difficult to measure.

Heat capacities: [C_p and C_v]

Heat capacity is defined as the amount of energy required to increase the temperature of one unit quantity of material by one degree, under specific conditions. It can be measured under two different conditions, namely,

(a) constant pressure $C_p = dH/dT$

(b) constant volume $C_v = dU/dT$

Second law of thermodynamics:

The second law of thermodynamics helps us to predict whether the reaction is feasible or not and also tells the direction of the flow of heat.

To predict spontaneity of a process, a new thermodynamic quantity namely entropy (S) was introduced. Entropy is a measure of the randomness or disorderliness of the system.

Entropy statement: "whenever a spontaneous process takes place, it is accompanied by an increase in the total entropy of the universe".

Kelvin-Planck statement: It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of that heat to a colder reservoir.

Clausius statement: This statement recognises that heat flows spontaneously from hot objects to cold objects and to get it flow in the opposite direction, we have to spend some work.

Gibbs Free Energy (G):

G is expressed as $G = H - TS$, free energy change of a process is given by the relation $\Delta G = \Delta H - T\Delta S$.

Standard free energy change and equilibrium constants are related by the equation $\Delta G^0 = -RT \ln K_{eq}$

Third law:

The entropy of a perfectly crystalline material at absolute zero is zero.

EVALUATION



I. Choose the best answer

- The amount of heat exchanged with the surrounding at constant temperature and pressure is given by the quantity
 a) ΔE b) ΔH c) ΔS d) ΔG
- All the naturally occurring processes proceed spontaneously in a direction which leads to
 a) decrease in entropy b) increase in enthalpy
 c) increase in free energy d) decrease in free energy
- In an adiabatic process, which of the following is true ?
 a) $q = w$ b) $q = 0$ c) $\Delta E = q$ d) $P \Delta V = 0$
- In a reversible process, the change in entropy of the universe is
 a) > 0 b) ≥ 0 c) < 0 d) $= 0$
- In an adiabatic expansion of an ideal gas
 a) $w = -\Delta u$ b) $w = \Delta u + \Delta H$ c) $\Delta u = 0$ d) $w = 0$
- The intensive property among the quantities below is
 a) mass b) volume c) enthalpy d) $\frac{\text{mass}}{\text{volume}}$
- An ideal gas expands from the volume of $1 \times 10^{-3} \text{ m}^3$ to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure at $1 \times 10^5 \text{ Nm}^{-2}$. The work done is
 a) -900 J b) 900 kJ c) 270 kJ d) -900 kJ
- Heat of combustion is always
 a) positive b) negative c) zero d) either positive or negative
- The heat of formation of CO and CO_2 are -26.4 kCal and -94 kCal , respectively. Heat of combustion of carbon monoxide will be
 a) $+26.4 \text{ kcal}$ b) -67.6 kcal c) -120.6 kcal d) $+52.8 \text{ kcal}$

10. $\text{C(diamond)} \rightarrow \text{C(graphite)}$, $\Delta H = -ve$, this indicates that
- graphite is more stable than diamond
 - graphite has more energy than diamond
 - both are equally stable
 - stability cannot be predicted
11. The enthalpies of formation of Al_2O_3 and Cr_2O_3 are -1596 kJ and -1134 kJ , respectively.
- ΔH for the reaction $2\text{Al} + \text{Cr}_2\text{O}_3 \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3$ is
- -1365 kJ
 - 2730 kJ
 - -2730 kJ
 - -462 kJ
12. Which of the following is not a thermodynamic function ?
- internal energy
 - enthalpy
 - entropy
 - frictional energy
13. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then
- $\Delta H > \Delta U$
 - $\Delta H - \Delta U = 0$
 - $\Delta H + \Delta U = 0$
 - $\Delta H < \Delta U$
14. Change in internal energy, when 4 kJ of work is done on the system and 1 kJ of heat is given out by the system is
- $+1 \text{ kJ}$
 - -5 kJ
 - $+3 \text{ kJ}$
 - -3 kJ
15. The work done by the liberated gas when 55.85 g of iron (molar mass 55.85 g mol^{-1}) reacts with hydrochloric acid in an open beaker at 25°C
- -2.48 kJ
 - -2.22 kJ
 - $+2.22 \text{ kJ}$
 - $+2.48 \text{ kJ}$
16. The value of ΔH for cooling 2 moles of an ideal monatomic gas from 125°C to 25°C at constant pressure will be $\left[\text{given } C_p = \frac{5}{2} R \right]$
- $-250 R$
 - $-500 R$
 - $500 R$
 - $+250 R$
17. Given that $\text{C(g)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ $\Delta H^0 = -a \text{ kJ}$; $2 \text{ CO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$ $\Delta H^0 = -b \text{ kJ}$; Calculate the ΔH^0 for the reaction $\text{C(g)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}$
- $\frac{b+2a}{2}$
 - $2a-b$
 - $\frac{2a-b}{2}$
 - $\frac{b-2a}{2}$

18. When 15.68 litres of a gas mixture of methane and propane are fully combusted at 0°C and 1 atmosphere, 32 litres of oxygen at the same temperature and pressure are consumed. The amount of heat released from this combustion in kJ is ($\Delta H_{\text{C}}(\text{CH}_4) = -890 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{C}}(\text{C}_3\text{H}_8) = -2220 \text{ kJ mol}^{-1}$)
- a) -889 kJ b) -1390 kJ c) -3180 kJ d) -653.66 kJ
19. The bond dissociation energy of methane and ethane are 360 kJ mol^{-1} and 620 kJ mol^{-1} respectively. Then, the bond dissociation energy of C-C bond is
- a) 170 kJ mol^{-1} b) 50 kJ mol^{-1} c) 80 kJ mol^{-1} d) 220 kJ mol^{-1}
20. The correct thermodynamic conditions for the spontaneous reaction at all temperature is (NEET Phase - I)
- a) $\Delta H < 0$ and $\Delta S > 0$
 b) $\Delta H < 0$ and $\Delta S < 0$
 c) $\Delta H > 0$ and $\Delta S = 0$
 d) $\Delta H > 0$ and $\Delta S > 0$
21. The temperature of the system, decreases in an _____
- a) Isothermal expansion b) Isothermal Compression c) adiabatic expansion
 d) adiabatic compression
22. In an isothermal reversible compression of an ideal gas the sign of q, ΔS and w are respectively
- a) +, -, - b) -, +, - c) +, -, + d) -, -, +
23. Molar heat of vapourisation of a liquid is 4.8 kJ mol^{-1} . If the entropy change is $16 \text{ J mol}^{-1} \text{ K}^{-1}$, the boiling point of the liquid is
- a) 323 K b) 27°C c) 164 K d) 0.3 K
24. ΔS is expected to be maximum for the reaction
- a) $\text{Ca(S)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaO(S)}$
 b) $\text{C(S)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
 c) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO(g)}$
 d) $\text{CaCO}_3(\text{S}) \rightarrow \text{CaO(S)} + \text{CO}_2(\text{g})$

25. The values of ΔH and ΔS for a reaction are respectively 30 kJ mol^{-1} and $100 \text{ JK}^{-1} \text{ mol}^{-1}$. Then the temperature above which the reaction will become spontaneous is
- a) 300 K b) 30 K c) 100 K d) 20°C
26. State the first law of thermodynamics.
27. Define Hess's law of constant heat summation.
28. Explain intensive properties with two examples
29. Define the following terms:
- a. isothermal process b. adiabatic process
- c. isobaric process d. isochoric process
30. What is the usual definition of entropy? What is the unit of entropy?
31. Predict the feasibility of a reaction when
- i) both ΔH and ΔS positive ii) both ΔH and ΔS negative
- iii) ΔH decreases but ΔS increases
32. Define is Gibbs's free energy.
33. Define enthalpy of combustion.
34. Define molar heat capacity. Give its unit.
35. Define the calorific value of food. What is the unit of calorific value?
36. Define enthalpy of neutralization.
37. What is lattice energy?
38. What are state and path functions? Give two examples.
39. Give Kelvin statement of second law of thermodynamics.
40. The equilibrium constant of a reaction is 10, what will be the sign of ΔG ? Will this reaction be spontaneous?
41. Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.

42. State the third law of thermodynamics.
43. Write down the Born-Haber cycle for the formation of CaCl_2
44. Identify the state and path functions out of the following: a) Enthalpy b) Entropy c) Heat d) Temperature e) Work f) Free energy.
45. State the various statements of second law of thermodynamics.
46. What are spontaneous reactions? What are the conditions for the spontaneity of a process?
47. List the characteristics of internal energy.
48. Explain how heat absorbed at constant volume is measured using bomb calorimeter with a neat diagram.
49. Calculate the work involved in expansion and compression process.
50. Derive the relation between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.
51. Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.
52. List the characteristics of Gibbs free energy.
53. Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.
54. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is 2.5 kJ K^{-1} . Calculate the enthalpy of combustion of the gas in kJ mol^{-1} .
55. Calculate the entropy change in the system, and surroundings, and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at 77°C to the surrounding at 33°C .
56. 1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710J and expands to 2 litres. Calculate the entropy change in expansion process.
57. 30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is $28.4 \text{ JK}^{-1} \text{ mol}^{-1}$. Calculate the melting point of sodium chloride.
58. Calculate the standard heat of formation of propane, if its heat of combustion is $-2220.2 \text{ kJ mol}^{-1}$. the heats of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -393.5 and $-285.8 \text{ kJ mol}^{-1}$ respectively.

59. You are given normal boiling points and standard enthalpies of vapourisation. Calculate the entropy of vapourisation of liquids listed below.

S. No	Liquid	Boiling points ($^{\circ}\text{C}$)	ΔH (kJ mol $^{-1}$)
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

60. For the reaction $\text{Ag}_2\text{O}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g})$: $\Delta H = 30.56 \text{ kJ mol}^{-1}$ and $\Delta S = 6.66 \text{ JK}^{-1} \text{ mol}^{-1}$ (at 1 atm). Calculate the temperature at which ΔG is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

61. What is the equilibrium constant K_{eq} for the following reaction at 400K.



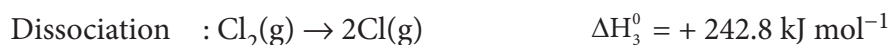
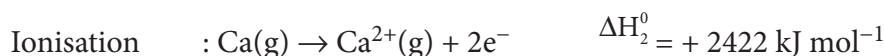
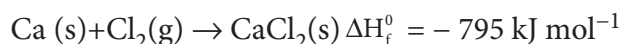
given that $\Delta H^{\circ} = 77.2 \text{ kJ mol}^{-1}$;

and $\Delta S^{\circ} = 122 \text{ JK}^{-1} \text{ mol}^{-1}$.

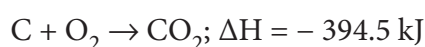
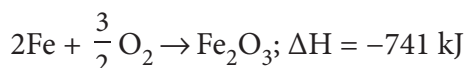
62. Cyanamide (NH_2CN) is completely burnt in excess oxygen in a bomb calorimeter, ΔU was found to be $-742.4 \text{ kJ mol}^{-1}$, calculate the enthalpy change of the reaction at 298K. $\text{NH}_2\text{CN}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ $\Delta H = ?$

63. Calculate the enthalpy of hydrogenation of ethylene from the following data. Bond energies of C – H, C – C, C = C and H – H are 414, 347, 618 and 435 kJ mol $^{-1}$.

64. Calculate the lattice energy of CaCl_2 from the given data



65. Calculate the enthalpy change for the reaction $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ from the following data.



66. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne(A) , 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C) the equilibrium was maintained at 175°C, calculate ΔG^0 for the following equilibria.



67. At 33K, N_2O_4 is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.
68. The standard enthalpies of formation of SO_2 and SO_3 are -297 kJ mol^{-1} and -396 kJ mol^{-1} respectively. Calculate the standard enthalpy of reaction for the reaction: $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$
69. For the reaction at 298 K : $2A + B \rightarrow C$
- $\Delta H = 400 \text{ J mol}^{-1}$; $\Delta S = 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$ Determine the temperature at which the reaction would be spontaneous.
70. Find out the value of equilibrium constant for the following reaction at 298K, $2 \text{ NH}_3(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{NH}_2\text{CONH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ Standard Gibbs energy change, ΔG_r^0 at the given temperature is $-13.6 \text{ kJ mol}^{-1}$.
71. A gas mixture of 3.67 lit of ethylene and methane on complete combustion at 25°C and at 1 atm pressure produce 6.11 lit of carbondioxide. Find out the amount of heat evolved in kJ, during this combustion. ($\Delta H_C(\text{CH}_4) = -890 \text{ kJ mol}^{-1}$ and ($\Delta H_C(\text{C}_2\text{H}_4) = -1423 \text{ kJ mol}^{-1}$

CONCEPT MAP

