

Outline		
	Thermodynamics & Equilibrium	Dates
01	To rationalize bulk properties and processes using thermodynamics and also apply the knowledge to decide the feasibility of a given process	Introduction, Concept of internal energy, enthalpy and entropy 03.07.19, 05.07.19
02		Entropy calculations involving ideal gases (expansion, mixing etc.) 05.07.19
03		Concept of free energy (A and G), Gibb's-Helmholtz equation, conditions of spontaneity and equilibrium, thermodynamic parameters accompanying cell operation 10.07.19, 11.07.19
04		Derivation and applications of van't Hoff isotherm and isochore 12.07.19
05		Derivation and applications of Clapeyron-Clausius equation 17.07.19, 18.07.19
06		Partial molar properties, concept of chemical potential, Gibb's-Duhem equation & application 19.07.19, 24.07.19

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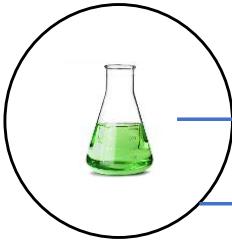
## Introduction Thermodynamics

The branch of science which deals with the quantitative relationships between heat and other forms of energy" because other forms of energy can be converted into heat.

### Terms in Thermodynamics

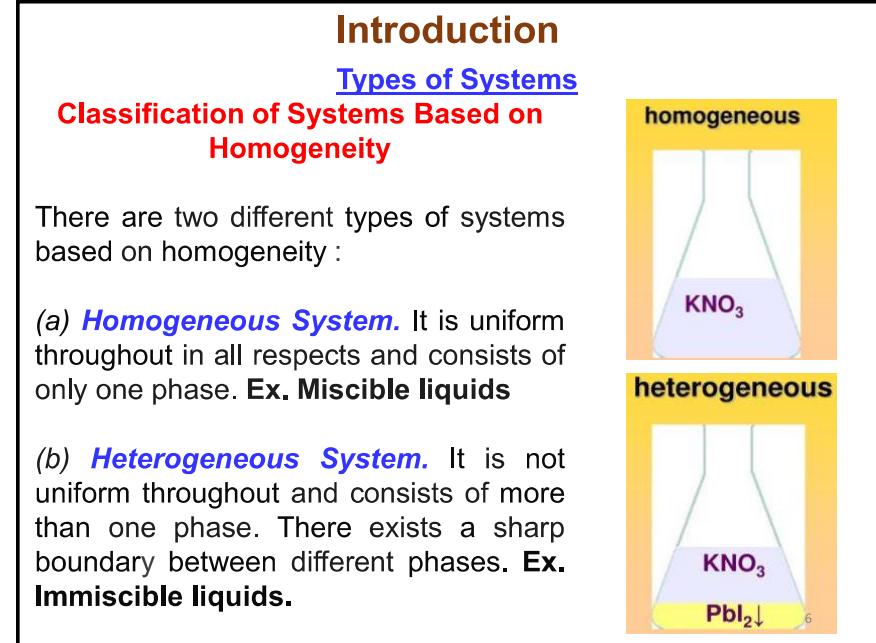
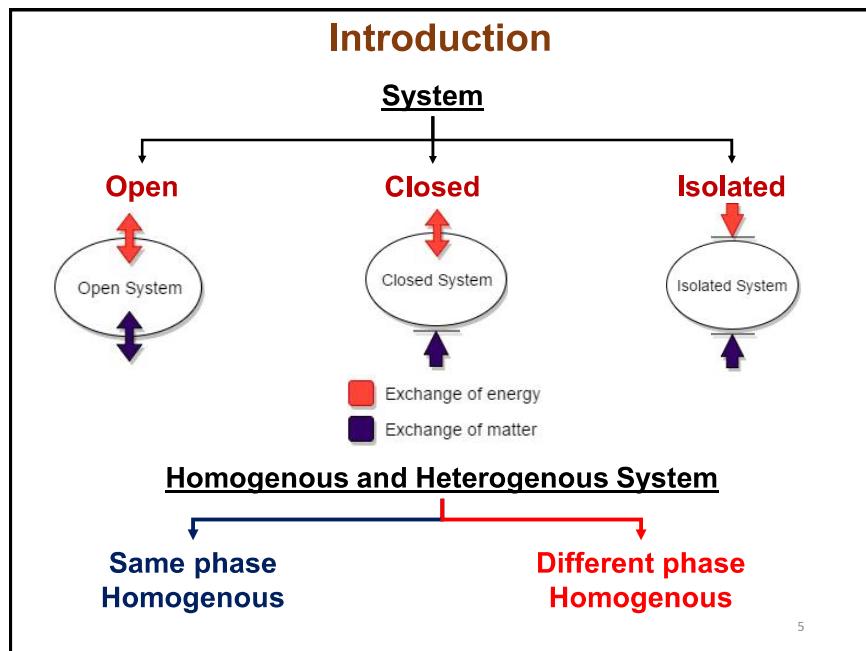
"**System** can be defined as the part of the universe which is selected for study and is separated from the rest of the universe by definite boundary."

Rest of the universe, other than system is known as surroundings. System and surroundings may or may not be in a position to exchange energy and matter.



System + Surrounding = Universe

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## Introduction

### Types of Systems

#### Classification of Systems Based on Interaction between System and Surroundings

(a) **Open systems.** Exchange of both matter and energy is possible. Due to these exchanges, **matter and energy do not remain constant** in open system. Hot liquid taken in a beaker is an example of open system.

(b) **Closed system.** A system which can exchange energy but not matter with the surrounding. In closed system, **matter remains constant and only the energy changes**. Hot liquid taken in a closed lid is an example of closed system.

(c) **Isolated system.** In an isolated system, there is no interaction between system and surroundings. **Both matter and energy of such systems remain constant**. Hot liquid taken in a thermally insulated closed flask is an example of isolated system.

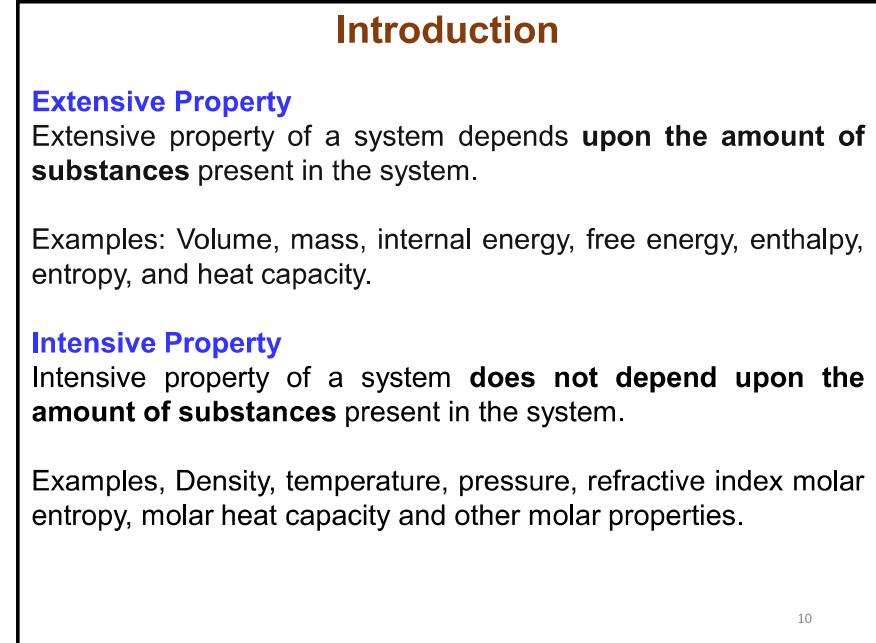
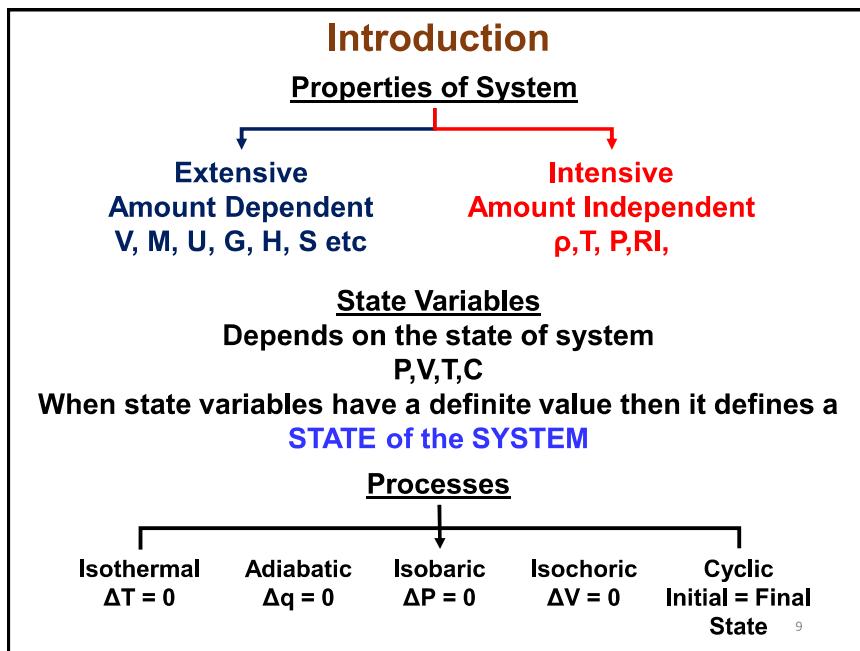
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## Introduction

### Types of Systems



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## Introduction

### State Variables

The **measurable properties of a system** which completely define the state of a system are called state variables or thermodynamic variables.

Examples: Pressure, volume, temperature and concentration.

State variables are directly measurable from experiments and are inter-related by an equation of state.

Example, The equation of state for an ideal gas is

$$pV = nRT$$

### State of a System

A thermodynamic system is said to be in a **definite state when the state variables have definite values**. Any change in the value of these variables will change the state of the system.

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## Introduction

### Process

A thermodynamic process is defined as the method of operation with the help of which a system **changes from one state to another**.

### Isothermal Process

This type of process is carried out at constant temperature. For such a process, change in temperature ( $\Delta T = 0$ ).

### Adiabatic Process

This type of process is carried out in a system which is enclosed by adiabatic walls and hence there is no heat exchange between system and surroundings. ( $\Delta q = 0$ )

### Isochoric Process

System's volume remains constant in isochoric process. For isochoric process  $\Delta V = 0$

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## Introduction

### Isobaric Process

This type of process is carried out under conditions of constant pressure. ( $\Delta P = 0$ ).

### Cyclic Process.

When the system follows a cyclic path for undergoing a series of changes in its state and finally the system comes back to its initial state. (**Initial State = Final State**)

### Reversible Process

If the driving force is only infinitesimally greater than the opposing force at any instant, then the **system does not deviate from equilibrium by more than an infinitesimal amount**.

### Irreversible Process

This type of process takes finite time for completion and it occurs spontaneously. **Natural or laboratory reactions are irreversible**

## Concept of Equilibrium

### Thermodynamic Equilibrium

A system in which the observable properties of the system do not undergo any change with time is said to be in thermodynamic equilibrium

### Thermal Equilibrium

When the **temperature remains same** in all parts of the system and there is no flow of heat from one part of the system to another

### Chemical Equilibrium

When the **composition of the system**, remains constant and uniform throughout

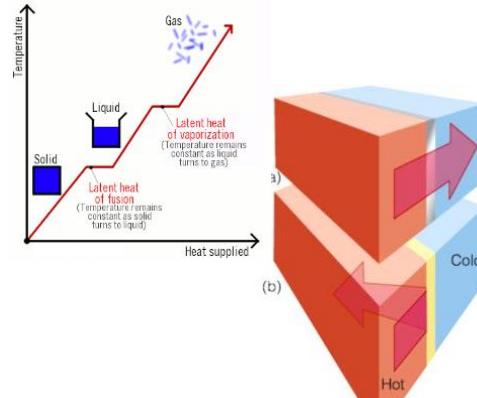
### Mechanical Equilibrium

When the **pressure remains same** in all parts of the system and there is no mechanical work done by one part of the system to another

## Concept of Heat

### Heat

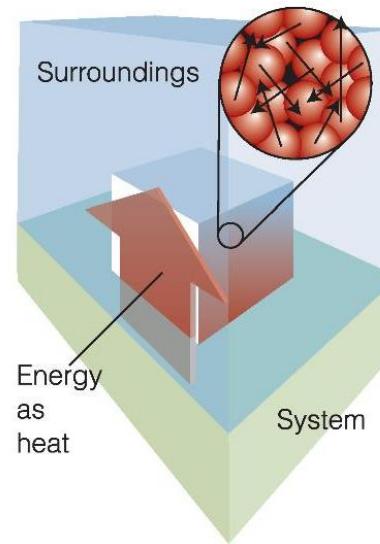
When a system and its surroundings are at different temperatures, the form of the energy exchanged between them is commonly known as heat. Heat **always flow from higher temperature to lower temperature spontaneously.**



**Fig. 1.3** (a) A diathermic wall permits the passage of energy as heat; (b) an adiabatic wall does not, even if there is a temperature difference across the wall.

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## Molecular Concept of Heat



Heat is the mode of transfer of energy that achieves or utilizes random motion in the surroundings.

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## Concept of Work

**Work**

**Mechanical work (w) = Applied force (F) x Displacement of the object (dl).**

**Pressure Volume work done =  $P_{\text{ext}} \times \Delta V$**

$$(N\text{H}_2)_2\text{CO}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g})$$

**Fig. 1.4** When urea reacts with oxygen, the gases produced (carbon dioxide and nitrogen) must push back the surrounding atmosphere (represented by the weight resting on the piston) and hence must do work on its surroundings. This is an example of energy leaving a system as work. 17

## Molecular Concept of Work

Work is the transfer of energy that achieves or utilizes uniform motion in the surroundings.

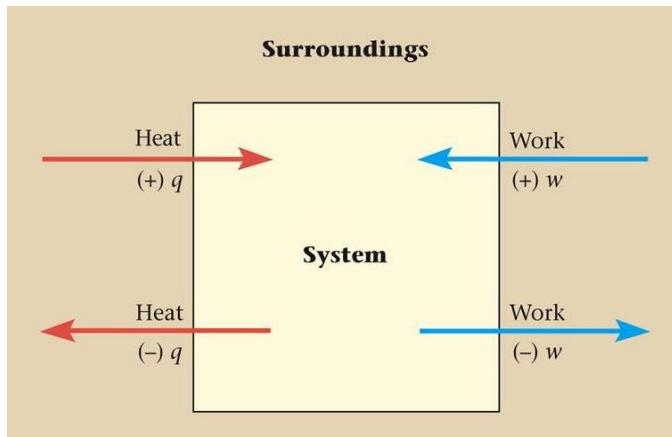
Electrical work, corresponds to electrons being pushed in the same direction through a circuit.

Mechanical work corresponds to atoms being pushed in the same direction against an opposing force.

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## Sign Convention for Heat and Work

### The Happiness Rule



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## Science on Move

### Neural nets to simulate molecular motion cast

Machine learning allows quantum mechanics to be efficiently applied to molecular simulations

Date: July 2, 2019

Source: DOE/Los Alamos National Laboratory

Summary: New work is showing that artificial neural nets can be trained to encode quantum mechanical laws to describe the motions of molecules, supercharging simulations potentially across a broad range of fields.



1.Justin S. Smith, Benjamin T. Nebgen, Roman Zubatyuk, Nicholas Lubbers, Christian Devereux, Kipton Barros, Sergei Tretiak, Olexandr Isayev, Adrian E. Roitberg. **Approaching coupled cluster accuracy with a general-purpose neural network potential through transfer learning.** *Nature Communications*, 2019; 10 (1) DOI: [10.1038/s41467-019-10827-4](https://doi.org/10.1038/s41467-019-10827-4)

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## Internal Energy

To understand how **chemical or physical or biological processes can store and release energy**, we need to be familiar with a very important law that relates work and heat to changes in the energy of all the constituents of a system.

**Internal energy**,  $U$ , of the system, the sum of all the kinetic and potential contributions to the energy of all the atoms, ions, and molecules in the system.

It is an **extensive property** because 2 kg of iron at a given temperature and pressure, for instance, has twice the internal energy of 1 kg of iron under the same conditions. It's a **state function**.

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## Internal Energy

In practice, we do not know and **cannot measure the absolute value of the total energy of a sample** because it includes the kinetic and potential energies of all the electrons and all the components of the atomic nuclei.

All practical applications of thermodynamics deal with  $\Delta U$ , not with  $U$  itself. A change in internal energy is written

$$\Delta U = q + w$$

where :  $w$  is the energy transferred to the system by doing work and  $q$  is the energy transferred to it by heating

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## Enthalpy

### Enthalpy or Heat Content (H)

The energy stored within the substance or the system that is available for conversion into heat is called enthalpy or heat content of the substance or the system.

It is denoted by H and is given by:

$$H = E + PV \text{ ----- Eqn.1}$$

When a system moves from an initial state to final state we have

$$\Delta H = \Delta E + P \Delta V \text{ ----- Eqn.2}$$

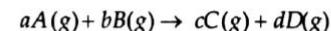
When no additional work is done than heat supplied to the system at constant P is same as enthalpy

$$\Delta H = q_p \text{----- Eqn.3}$$

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## Enthalpy for Chemical Reaction

Consider a reaction in gaseous phase at constant temperature (T) and pressure (P)



Let  $n_R$  = Number of moles of gaseous reactants ( $= a + b$ ),

$n_P$  = Number of moles of gaseous products ( $= c + d$ ),

$V_R$  and  $V_P$  = Total volume of gaseous reactants and products,

From ideal gas equation :  $PV = nRT$

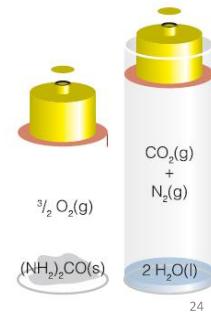
$$PV_R = n_R RT \text{ and } PV_P = n_P RT$$

$$\therefore P(V_P - V_R) = (n_P - n_R) RT$$

$$\Rightarrow P\Delta V = \Delta n_g \cdot RT$$

$$\text{But } \Delta H = \Delta E + P\Delta V$$

$$\therefore \Delta H = \Delta E + \Delta n_g RT$$



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## Internal Energy and Enthalpy-Numericals

1. The heat of formation of methane at constant pressure at 25 °C is -74.85 kJ/mol. What will be the heat of formation at constant volume?

**Solution.** Given :  $C(s) + 2 H_2(g) \longrightarrow CH_4(g)$  :  $\Delta H = -74.85 \text{ kJ/mol}$

$$T = 25^\circ C = 25 + 273 = 298 \text{ K}$$

Now  $\Delta n_g = 1 - 2 = -1$

Moreover  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

As  $\Delta H = \Delta E + \Delta n_g RT$

$$\begin{aligned}\Delta E &= \Delta H - \Delta n_g RT \\ &= (-74850) - \{(-1) \times 8.314 \times 298\} \\ &= -72,372 \text{ J/mol} = -72.37 \text{ kJ/mol.}\end{aligned}$$

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## Internal Energy and Enthalpy

2. The combustion of heptane  $C_7H_{16}$  in a constant volume calorimeter gave the value of  $q_v = -4793 \text{ kJ}$  at 25° C. What will be the enthalpy change of the process at 25° C?

**Solution.**  $C_7H_{16}(l) + 11 O_2(g) \longrightarrow 7 CO_2(g) + 8 H_2O(l)$

$$\therefore \Delta n_g = 7 - 11 = -4 \text{ moles}$$

Given  $T = 25^\circ C = 25 + 273 = 298^\circ K$ ;

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

$$q_v = -4793 \times 10^3 \text{ J}$$

Hence,  $\Delta H = \Delta E + \Delta n_g RT$

$$= q_v + \Delta n_g RT$$

$$= (-4793 \times 10^3) + \{(-4) \times 8.314 \times 298\}$$

$$= -4802910.3 \text{ J} = -4802.9 \text{ kJ}$$

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## Heat Capacity

### Heat Capacity of a System (C)

It is defined as the amount of heat (q) required to increase the temperature of the system from the lower temperature ( $T_1$ ) to the higher temperature ( $T_2$ ) divided by the temperature difference ( $T_2 - T_1$ )

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$$

$$C_p - C_V = n R$$

$$C_{p,m} - C_{V,m} = R$$



**The climate of islands and towns situated near river banks and sea-shore is much more equable due to large heat capacity of water.**

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## State and Path Functions

### State Functions

Properties like internal energy and enthalpy that are independent of how a sample is prepared are called state functions.

**The Greek letter  $\Delta$ (delta) is used to indicate changes in state functions in a thermodynamic process.**

$$\Delta V = V_{\text{final}} - V_{\text{initial}}$$

### Path Functions

Properties like heat and work that are dependent on how a sample is prepared are called path functions.

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## Exact and Inexact Differential

An **exact differential** is an **infinitesimal\*** quantity which, when integrated, gives a result that is independent of the path between the initial and final states.

For example, if we heat a system, its internal energy changes from the initial to the final state which is sum (integral) of all the infinitesimal changes along the path.

$$\Delta E = \int_i^f dE$$

However, when a system is heated, the total energy transferred as heat is the sum of all individual contributions at each point of the path :

$$q = \int_{i, \text{path}}^f dq$$

In the above equation, we do not write  $\Delta q$  since  $q$  is not a state function and energy supplied as heat cannot be expressed as  $q_f - q_i$ . Hence it is an inexact differential.

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## First Law of Thermodynamics

### Statements of First Law of Thermodynamics

It is basically law of conservation of Energy which states that Energy can neither be created nor destroyed although it can be converted from one form into another.

### Mathematical Expression of First law of Thermodynamics In Terms of $\Delta E$

Let us consider a system whose internal energy is  $E_1$ .

Now, if the system absorbs  $q$  amount of heat, and if work ( $w$ ) is done on the system, then the

Internal energy of the system increases and becomes  $E_1 + q + w$ ,  
Thus,

$$\begin{aligned} E_2 &= E_1 + q + w \\ \Rightarrow E_2 - E_1 &= q + w \\ \Rightarrow \Delta E &= q + w \end{aligned}$$

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### First Law of Thermodynamics

1. Estimate the change in the internal energies : (a) When an electric motor produced 15 kJ of energy each second and lost 2 kJ as heat to the surroundings. (b) When a spring was wound, 100 J of work was done on it but 15 J escaped to the surroundings as heat.

**Solution.** (a)  $\Delta E = (-q) + (-w) = -2 - 15 = -17 \text{ kJ}$   
 (b)  $\Delta E = (-q) + (w) = -15 + 100 = +85 \text{ J}$

2. Calculate the work done when 63 gm of iron reacts with hydrochloric acid in (i) a closed vessel of fixed volume, (ii) an open beaker at 25 °C.

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### First Law of Thermodynamics

3. The latent heat of vaporisation of Bromine at 59 °C and 1 atm is 29.2 kJ/mol. What are  $\Delta H$  and  $\Delta E$  of this process ?

**Solution.** Latent heat is equal to  $\Delta H$ ,

$$\text{hence } \Delta H = q_p = 29.2 \text{ kJ/mol.}$$

The work in the process of vaporisation

$$\begin{aligned} w &= P\Delta V \\ \Rightarrow w &= P(V_g - V_l) = PV_g = RT = 8.314 (\text{JK}^{-1} \text{mol}^{-1}) \times 332 \text{ K} \\ \Rightarrow w &= 2760.25 \text{ J mol}^{-1} = 2.76 \text{ kJ/mol.} \\ \therefore \Delta E &= \Delta H - w = 29.2 - 2.76 = 26.44 \text{ kJ/mol.} \end{aligned}$$

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## First Law of Thermodynamics

4. In a constant volume calorimeter, at 298 °K, 0.01 mole of TNT was detonated when 8180 calories of heat was released. Each mole of TNT gives six moles of gaseous products on detonation. Calculate  $\Delta E$  and  $\Delta H$  per mole of TNT exploded.

$$\text{Solution. (i)} \quad \Delta E = q_v = \frac{-8180}{0.01} = -818,000 \text{ cal / mol.}$$

$$\begin{aligned} \text{(ii)} \quad \Delta H &= \Delta E + \Delta n_g RT \\ &= -818,000 + 6 \times 2 \times 298 = -814,424 \text{ cal / mol.} \end{aligned}$$

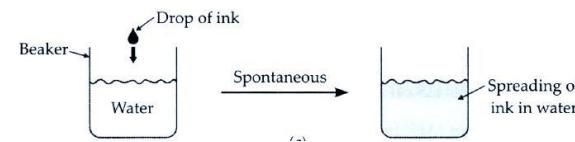
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## Spontaneous Process

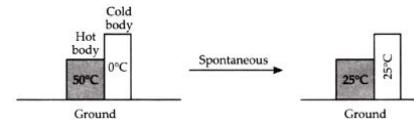
A process which proceeds by its own without any outside assistance is called as spontaneous process.

Driving forces for a spontaneous reaction are :

(i) **Tendency of a system to attain maximum randomness (or maximum entropy).**  
For example, when a drop of ink is put in a beaker full of water, it spreads uniformly quickly (Fig. II(a)) and thereby the randomness (and hence entropy) increases.



(ii) **Tendency of a system to acquire maximum stability or minimum energy (or minimum enthalpy) :** For example, heat flows from hot body to cold body



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## Spontaneous Process

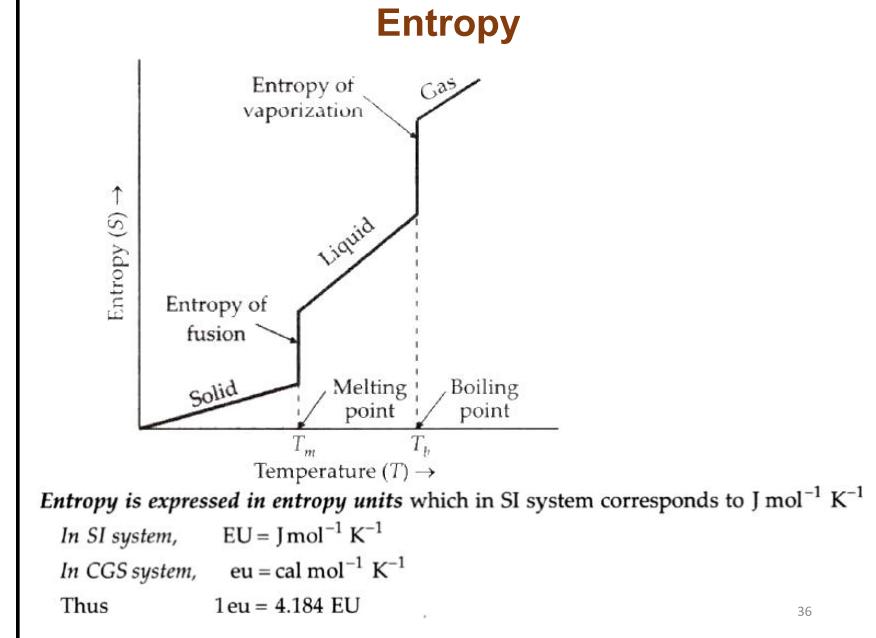
### Criteria of Spontaneity

1. A spontaneous change is **unidirectional**.
2. For unstable system (when the system is not in equilibrium), a **spontaneous process is inevitable**. And this process will continue till equilibrium state is reached.
3. **Increase in randomness** favours a spontaneous process. For example, melting of ice.

### Statement of Second Law of Thermodynamics

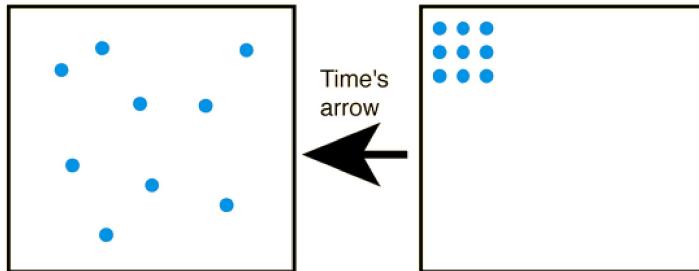
- (a) Heat cannot pass from a colder body to a warmer body.
- (b) Entropy increases in irreversible processes.

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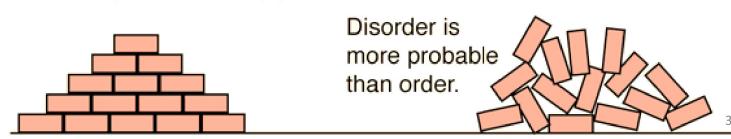


## Imagining Entropy

If the particles represent gas molecules at normal temperatures inside a closed container, which of the illustrated configurations came first?



If you tossed bricks off a truck, which kind of pile of bricks would you more likely produce?



## Entropy

- Entropy is the measure of the randomness or disorder of the system. It is denoted by S.
- Entropy helps us in judging if a thermodynamic process is spontaneous or non spontaneous.
- If  $S_{\text{final}} > S_{\text{initial}}$  then the process is regarded as spontaneous.**

$$\Delta S = S_f - S_i$$

- In terms of entropy the second law of thermodynamics is stated as:

The entropy of an isolated system increases in the course of spontaneous change.

For a reversible change taking place at a fixed temperature (T), the change in entropy (dS) is equal to heat energy absorbed or evolved divided by the temperature (T)

$$ds = \frac{dq_{\text{rev}}}{T} \quad (\text{For infinitesimally slow change}) \quad \text{Eq.1}$$

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## Entropy

For a reversible change taking place at a fixed temperature (T), the change in entropy (dS) is equal to heat energy absorbed or evolved divided by the temperature (T)

$$\int dS = \frac{dq_{rev}}{T} \quad (\text{For infinitesimally slow change}) \quad \text{Eq.1}$$

**The change in entropy is inversely proportional to the temperature at which the transfer takes place.**

### Molecular Concept:

At low T, the molecules in a system are less disorganized. A small additional transfer of energy (or heat) will **have a pronounced effect on the degree of disorder.**

BUT

At high T, the molecules in a system are highly disorganized. A small additional transfer of heat will result in a **relatively small additional disorder.**

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## Entropy

*Rank the following in order of increasing entropy :*

- (i) 1 mol of  $H_2O_{(l)}$  at 25°C and 1 atm. pressure.
- (ii) 2 mol of  $H_2O_{(s)}$  at 0°C and 1 atm. pressure.
- (iii) 1 mol of  $H_2O_{(v)}$  at 100°C and 1 atm. pressure.
- (iv) 1 mol of  $H_2O_{(l)}$  at 0°C and 1 atm. pressure.

**Solution.** (ii) < (iv) < (i) < (iii)

*Predict in which of the following, entropy decreases/increases :*

- (i)  $H_2(g) \longrightarrow 2 H(g)$
- (ii)  $2 NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$
- (iii) Temperature of a crystalline solid is raised from 0 K to 115 K.
- (iv) A liquid crystallizes into a solid.

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## Entropy

Predict whether the conversion of oxygen into oxide via.



will be spontaneous or not at 25 °C.

*Given :  $\Delta S_r^\circ = -217 \text{ JK}^{-1}\text{mol}^{-1}$  and  $\Delta H_r^\circ = -1202 \text{ kJ/mol}$ .*

**Solution.**  $\Delta S_{\text{system}}^\circ = \Delta S_r^\circ = -217 \text{ JK}^{-1}\text{mol}^{-1}$

$$\begin{aligned}\Delta S_{\text{surroundings}}^\circ &= -\frac{\Delta H_r^\circ}{T} = \frac{-(-1202 \times 10^3 \text{ J mol}^{-1})}{298 \text{ K}} \\ &= 4033.5 \text{ JK}^{-1}\text{mol}^{-1}\end{aligned}$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{system}}^\circ + \Delta S_{\text{surroundings}}^\circ$$

$$= -217 + 4033.5 = +3816.5 \text{ JK}^{-1}\text{mol}^{-1}_{41}$$

## Entropy

### Entropy Change for a Reaction

Standard entropy change for a reaction or the standard reaction entropy ( $\Delta S_r^\circ$ ) is defined as the difference in molar entropy between the products and the reactants in their standard states

$$\sum y S_m^\circ \text{ (Products)} - \sum z S_m^\circ \text{ (Reactants)}$$

For a general chemical reaction



$$\Rightarrow \Delta S_r^\circ = \{cS_m^\circ \text{ (C)} + dS_m^\circ \text{ (D)}\} - \{aS_m^\circ \text{ (A)} + bS_m^\circ \text{ (B)}\}$$

where  $S_m^\circ$  stands for standard molar entropy at a given temperature.

## Entropy

*Is oxidation of iron*



*spontaneous at 298 K ?*

$$\text{Given : } S_m^\circ [Fe_2O_3(s)] = 87.4 \text{ JK}^{-1} \text{ mol}^{-1},$$

$$S_m^\circ [O_2(g)] = 205.1 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$S_m^\circ [Fe(s)] = 27.3 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\text{and } \Delta H_r^\circ = -1648 \text{ kJ/mol.}$$

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## Entropy

$$\begin{aligned}\text{Solution. } \Delta S_{\text{system}}^\circ &= \Delta S_r^\circ = [2S_m^\circ [Fe_2O_3(s)] - 4S_m^\circ [Fe(s)] + 3S_m^\circ [O_2(g)]] \\ &= [2 \times 87.4] - [4 \times 27.3 + 3 \times 205.1] = -549.7 \text{ JK}^{-1} \text{ mol}^{-1}.\end{aligned}$$

$$\text{Now } \Delta S_{\text{surroundings}}^\circ = \frac{-\Delta H_r^\circ}{T} = \frac{-(-1648 \times 10^3 \text{ J mol}^{-1})}{298 \text{ K}} = 5530 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\therefore \Delta S_{\text{total}}^\circ = \Delta S_{\text{system}}^\circ + \Delta S_{\text{surroundings}}^\circ = -549.7 + 5530 = +4980.6 \text{ JK}^{-1} \text{ mol}^{-1}.$$

This overall increase in the entropy makes the oxidation of iron spontaneous.

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## Entropy

### Entropy Change for an Ideal Gas

Consider one mole of an ideal gas enclosed in a cylinder fitted with a frictionless, weightless and movable piston at constant pressure. Suppose the gas is undergoing reversible expansion from volume  $V_1$  to  $V_2$ .

As the process is reversible, the pressure of the gas is approximately equal to the external pressure against which the gas is expanding at all stages. Hence, under these conditions, maximum work done by the gas is equal to  $P \cdot dV$

From first law of thermodynamics we have

$$dq = dE + dW$$

$$dq = dE + P dV$$

As  $C_V = \frac{dE}{dT}$  and  $PV = RT \quad \therefore \quad P = \frac{RT}{V}$

Thus,  $dq = C_V dT + RT \frac{dV}{V}$

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## Entropy

Dividing by  $T$ , we get

$$\frac{dq}{T} = C_V \frac{dT}{T} + R \frac{dV}{V}$$

From the definition of entropy,

$$\frac{dq}{T} = dS$$

$$\therefore dS = C_V \frac{dT}{T} + R \frac{dV}{V}$$

For a definite change from initial state to final state, the total change in entropy is given by  $\Delta S$

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### Entropy

$$\Delta S = \int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow \Delta S = C_V \ln(T_2/T_1) + R \ln(V_2/V_1) \quad \dots(i)$$

#### Notes

- $\int \frac{dx}{x} = \ln x + \text{constants}$

- $\int_1^2 \frac{dx}{x} = \ln x_2 - \ln x_1 = \ln\left(\frac{x_2}{x_1}\right)$

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### Entropy

For an ideal gas,  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\Rightarrow V_2/V_1 = (P_1/P_2) \times (T_2/T_1)$$

$$\therefore \Delta S = C_V \ln(T_2/T_1) + R \ln(P_1/P_2) + R \ln(T_2/T_1)$$

$$\Rightarrow \Delta S = (C_V + R) \ln(T_2/T_1) + R \ln(P_1/P_2) \quad \dots(ii)$$

We know :  $C_p - C_V = R \quad \therefore C_p = (C_V + R)$

Thus,  $\Delta S = C_p \ln(T_2/T_1) + R \ln(P_1/P_2)$

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## Entropy

**Case I.** When  $T_1 = T_2$  i.e., at constant temperature, for isothermal expansion of ideal gas

$$(\Delta S)_T = n R \ln(V_2/V_1) = n R \ln(P_1/P_2)$$

$$\Rightarrow (\Delta S)_T = 2.303 n R \log(P_1/P_2)$$

**Case II.** When  $P_1 = P_2$  i.e., at constant pressure, for isobaric process

$$(\Delta S)_P = n C_P \ln(T_2/T_1)$$

$$\Rightarrow (\Delta S)_P = 2.303 n C_P \log(T_2/T_1)$$

$$\text{As } (\Delta S)_P = S_2 - S_1 \quad \therefore \quad S_2 = S_1 + n C_P \ln(T_2/T_1)$$

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## Entropy

**Case III.** When  $V_1 = V_2$  i.e., at constant volume, for isochoric process

$$(\Delta S)_V = n C_V \ln(T_2/T_1)$$

$$\Rightarrow (\Delta S)_V = 2.303 n C_V \log(T_2/T_1)$$

Ten moles of an ideal gas expands reversibly from a volume of 1 dm<sup>3</sup> and temperature 25 °C to a volume of 2 dm<sup>3</sup> and temperature 50 °C. Assume  $C_V = 3/2 R$ , calculate the entropy change for the process.

**Solution.**  $\Delta S = n[C_V \ln(T_2/T_1) + R \ln(V_2/V_1)]$

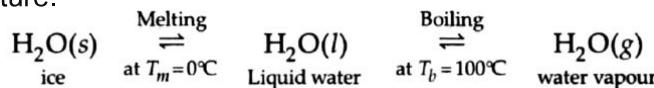
$$\therefore \Delta S = 10 \left[ \frac{3}{2} (8.314) \ln\left(\frac{323}{298}\right) + (8.314) \ln\left(\frac{2}{1}\right) \right] = 67.68 \text{ JK}^{-1}$$

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## Entropy

### The Entropy of Phase Transition at the Transition Temperature

Consider a system and its surroundings are at a temperature (at 1 atm) when its two phase are in equilibrium. This temperature is known as transition temperature, like melting or boiling temperature.



Because at the transition temperature, the two phases in the system are in equilibrium so any transfer of heat between the system and surroundings is reversible.

Because at constant pressure,

$$q = \Delta H_{\text{trans}}$$

$$\therefore \Delta S_{\text{trans}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{trans}}}{T}$$

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## Entropy

But since melting and vaporizing are endothermic processes so both will be accompanied by an increase in the system's entropy.

$$\therefore \Delta S_{\text{fusion}}^{\circ} = \frac{\Delta H_{\text{fusion}}^{\circ}}{T} ; \quad \Delta S_{\text{vap}}^{\circ} = \frac{\Delta H_{\text{vap}}^{\circ}}{T}$$

$$\Delta S_{\text{vap}} > \Delta S_{\text{fusion}}$$

**This is because vaporization creates more disorder than the melting process.**

When any liquid evaporates and becomes a gas, then a comparable amount of disorder is generated. Hence, all liquids can be expected to have similar standard entropies of vaporization (about  $85 \text{ JK}^{-1}\text{mol}^{-1}$ ). **This empirical observation is called Trouton's rule.**

Liquid	Cyclohexane	$\text{CCl}_4$	Benzene	$\text{H}_2\text{S}$	Methane	$\text{H}_2\text{O}$
$\Delta S_{\text{vap}}^{\circ} (\text{JK}^{-1}\text{mol}^{-1})$	+ 85.1	+ 85.8	+ 87.2	+ 87.9	+ 73.2	+ 109.1

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## Entropy

Predict the enthalpy of vaporization of ethane from its boiling point- 88.6°C.

**Solution.** Assuming, ethane will obey Trouton's rule, so its

$$\Delta S_{\text{vap}} = 85 \text{ JK}^{-1} \text{ mol}^{-1}$$

Since  $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$       ∴       $\Delta H_{\text{vap}} = T_b (\Delta S_{\text{vap}})$

Given  $T_b = -88.6^\circ\text{C} = -88.6 + 273 = 184.4 \text{ K}$   
 Thus,  $\Delta H_{\text{vap}} = (184.4) (85) = 15674 \text{ J mol}^{-1} = +15.7 \text{ kJ/mol.}$

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## Work Function

*Work function is defined as*

$$A = E - TS \quad \text{-----Eqn-1}$$

where  $A$  is work function,  
 $E$  is internal energy,  
 $T$  is temperature,  
 and  $S$  is entropy.

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## Work Function

Suppose a system goes from state 1 to state 2 at a constant temperature,  $T$ . As Helmholtz energy or work function is a state function

$$\begin{aligned}\therefore \Delta A &= A_2 - A_1 \\ &= (E_2 - TS_2) - (E_1 - TS_1) \\ &= (E_2 - E_1) - T(S_2 - S_1)\end{aligned}$$

$$\Rightarrow \Delta A = \Delta E - T\Delta S$$

For a cyclic process,  $\Delta A = 0$   
Work function is an extensive property of the system.

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## Work Function

### Significance of Work Function

$$A = E - TS$$

$$dA = dE - TdS - SdT \quad \text{-----Eqn-2}$$

From first law of thermodynamics,

$$dq = dE + W_{rev}$$

From the definition of entropy,

$$dS = \frac{dq}{T} \quad \Rightarrow \quad dq = TdS$$

$$TdS = dE + W_{rev} \quad \Rightarrow \quad dE = TdS - W_{rev}$$

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## Work Function

From the definition of entropy,

$$dS = \frac{dq}{T} \Rightarrow dq = TdS$$

$$TdS = dE + W_{rev} \Rightarrow dE = TdS - W_{rev} \text{-----Eqn-3}$$

Substituting this value of  $dE$  from equation (3) in equation (2), we get

$$dA = TdS - W_{rev} - TdS - SdT = -[W_{rev} + SdT]$$

A decrease in work function at constant temperature gives the maximum reversible work done by the system, which includes both mechanical and non-mechanical work

**Variation of Work Function with Temperature and Volume (Assignment)**

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## Work Function

### Gibbs Helmholtz Equation in terms of work function

For initial and final states, can be written as :

$$\text{Initial State} \quad \left( \frac{\partial A_1}{\partial T} \right)_V = -S_1 \text{-----Eqn-1}$$

$$\text{Final State} \quad \left( \frac{\partial A_2}{\partial T} \right)_V = -S_2 \text{-----Eqn-2}$$

Subtracting Eqn-1 from Eqn-2

$$\begin{aligned} \left( \frac{\partial A_2}{\partial T} \right) - \left( \frac{\partial A_1}{\partial T} \right) &= -S_2 - (-S_1) \\ \Rightarrow \left[ \frac{\partial(A_2 - A_1)}{\partial T} \right] &= -(S - S_1) \end{aligned}$$

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### Work Function

$$\begin{aligned} \left( \frac{\partial A_2}{\partial T} \right) - \left( \frac{\partial A_1}{\partial T} \right) &= -S_2 - (-S_1) \\ \Rightarrow \left[ \frac{\partial(A_2 - A_1)}{\partial T} \right] &= -(S - S_1) \\ \Rightarrow \left[ \frac{\partial(\Delta A)}{\partial T} \right]_V &= -\Delta S \quad \text{Eqn.3} \end{aligned}$$

Substituting this value of  $\Delta S$  in the following equation, we get

$$\begin{aligned} \Delta A &= \Delta E - T\Delta S \\ \Rightarrow \Delta A &= \Delta E + T \left[ \frac{\partial(\Delta A)}{\partial T} \right]_V \quad \text{Eqn.4} \end{aligned}$$

**Equation (4), is Gibbs Helmholtz equation in terms of work function change and internal energy change.**

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### Work Function

When 1 mol glucose is oxidised to carbon dioxide and water at 298 K, calorimetric measurements give  $\Delta E^\circ_r = -2808 \text{ kJ/mol}$  and  $\Delta S_r = +182.4 \text{ J K}^{-1} \text{ mol}^{-1}$ . How much of this energy change can be extracted as (a) heat at constant pressure (b) work.

**Solution.** (a) The combustion reaction of glucose is :



$$\therefore \Delta n_g = 6 - 6 = 0$$

$$\begin{aligned} \text{Since } \Delta H_r &= \Delta E_r + \Delta n_g RT \\ &= \Delta E_r + 0 \times RT = \Delta E_0 = -2808 \text{ kJ/mol.} \end{aligned}$$

(b) As  $A = E - TS$

At const. Temp. ( $T = 298 \text{ K}$ ),

$$\Delta A_r = \Delta E_r - T\Delta S_r$$

$$\begin{aligned} \therefore \Delta A_r &= (-2808 \times 10^3) - (298)(+182.4) \\ &= -2862355.2 \text{ J mol}^{-1} = -2862.3 \text{ kJ mol}^{-1}. \end{aligned}$$

## Gibbs Free Energy

Gibbs free energy can be defined as "the maximum amount of energy available to a system during a process for doing useful work under constant temperature and pressure conditions". where

Mathematically,

$$G = H - TS \text{ -----Eqn-1}$$

G is Gibbs' free energy, H is enthalpy, T is temperature and S is entropy.

Gibbs' free energy is a state function

$$\Delta G = G_2 - G_1$$

$$\Rightarrow \Delta G = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\Rightarrow \Delta G = (H_2 - H_1) - T(S_2 - S_1)$$

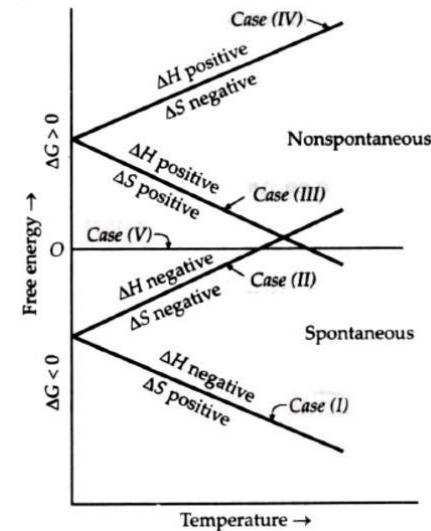
$$\Rightarrow \Delta G = \Delta H - T\Delta S$$

For a cyclic process  $\Delta G = 0$  and It is extensive property of the system

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## Gibbs Free Energy

### Significance of Gibbs' Free Energy



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## Gibbs Free Energy

### Significance of Gibbs' Free Energy

#### **Case I. When $\Delta H$ is negative and $\Delta S$ is positive**

$$\Delta G = \text{Energy factor} - \text{Entropy factor}$$

In this case, both energy factor and entropy factor are favourable and make the value of  $\Delta G$  negative.

#### **Case II. When $\Delta H$ is negative and $\Delta S$ is negative**

The reaction will only occur when enthalpy factor is greater than the entropy factor.

#### **Case III. When $\Delta H$ is positive and $\Delta S$ is positive**

The reaction will only occur when entropy factor is greater than the enthalpy factor.

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## Gibbs Free Energy

### Significance of Gibbs' Free Energy

#### **Case IV. When $\Delta H$ is positive and $\Delta S$ is negative**

The reaction will not occur.

#### **Case IV. When $\Delta H = T\Delta S$ is**

The reaction has achieved a state of equilibrium

Discuss the feasibility of the reaction:



at 100° C and 1000° C. Given  $\Delta H = + 31400$  cal and  $\Delta S = + 32$  eu

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## Gibbs Free Energy

**Example 40** Discuss the feasibility of the reaction :  $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$   
at 100°C and 1000°C. Given  $\Delta H = +31400\text{ cal}$  and  $\Delta S = +32\text{ eu}$

**Solution.** As  $\Delta G = \Delta H - T\Delta S$

$$\therefore \Delta G_{373} = (31400) - 373(32) = +19464\text{ cal}$$

$$\Delta G_{1273} = (31400) - 1273(32) = -9336\text{ cal}$$

Since  $\Delta G_{1273}$  is negative so reaction will be spontaneous at 1000°C. However positive value of  $\Delta G_{373}$  indicates that reaction will not occur at 100°C.

**Example 42** For a reaction at 298 K,  $2A + B \rightarrow C$ .

$\Delta H = 100\text{ k Cal}$  and  $\Delta S = 0.50\text{ k Cal K}^{-1}$ . Assuming  $\Delta H$  and  $\Delta S$  to be constant over the temperature change, at what temperature the reaction will become spontaneous.

**Solution.** Given :  $\Delta H = 100\text{ k Cal}$

$$\Delta S = 0.50\text{ k Cal K}^{-1}$$

$$\text{As } \Delta G = \Delta H - T\Delta S \Rightarrow T = \left( \frac{\Delta H - \Delta G}{\Delta S} \right)$$

Substituting the values of  $\Delta H$  and  $\Delta S$  in the above equation, when  $\Delta G = 0$ , we have

$$T = \left( \frac{100 - 0}{0.50} \right) = 200\text{ K}$$

So, if  $T = 200\text{ K}$ ,  $\Delta G = 0$

Thus, if  $T > 200\text{ K}$ ,  $\Delta G = \text{negative}$ .

Hence, the given reaction will be spontaneous above 200 K.

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## Gibbs Free Energy

### Relationship between $\Delta G$ and $\Delta A$

$$\Delta G = \Delta H - T\Delta S \quad \text{Eqn-1}$$

$$\Delta H = \Delta E + P\Delta V \quad \text{Eqn-2}$$

Substituting the value of  $\Delta H$  from Eqn-2 in Eqn-1 we have

$$\Delta G = (\Delta E + P\Delta V) - T\Delta S$$

$$\Delta G = (\Delta E - T\Delta S) + P\Delta V \quad \text{Eqn-3}$$

We know that

$$\Delta A = \Delta E - T\Delta S \quad \text{Eqn-4}$$

Using equation (4), equation (3) becomes

$$\Delta G = \Delta A + P\Delta V \quad \text{Eqn-5}$$

Equation 5 represents a relationship between  $\Delta G$  and  $\Delta A$

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## Gibbs Free Energy

Standard Gibbs Energy of Reaction ( $\Delta G_f^\circ$ )

The standard free energy change is defined as:-

The free energy change for a process at a specified temperature in which the reactants are in their standard states are converted to products in their standard states

For a general chemical reaction



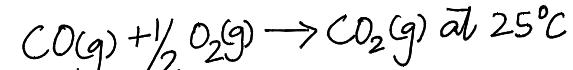
$$\Delta G_f^\circ = \{c\Delta G_{f,C}^\circ + d\Delta G_{f,D}^\circ\} - \{a\Delta G_{f,A}^\circ + b\Delta G_{f,B}^\circ\}$$

where  $\Delta G_f^\circ$  = Standard Gibbs Energy of Formation

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## Gibbs Free Energy

Calculate the standard Gibbs Energy of the reaction



$$\text{Given:- } \Delta G_f^\circ(CO_2(g)) = -394.4 \text{ kJ/mole}$$

$$\Delta G_f^\circ(CO(g)) = -137.2 \text{ kJ/mole}$$

$$\text{Solution. } \Delta G_f^\circ = \{\Delta G_f^\circ(CO_2, g)\} - \{\Delta G_f^\circ(CO, g) + \frac{1}{2} \Delta G^\circ(O_2, g)\}$$

$$= \{-394.4\} - \{(-137.2) + \frac{1}{2}(0)\} \text{ kJ/mol} = -257.2 \text{ kJ/mol}$$

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### Vant Hoff Isotherm

*Relationship Between  $\Delta G^\circ$  and Equilibrium Constant*

From thermodynamics we have:-

$$(dG)_T = VdP$$

For one mole of ideal gas,

$$PV = RT$$

$$\Rightarrow V = \frac{RT}{P}$$

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### Vant Hoff Isotherm

Hence at constant temperature free energy change is given by

$$dG = RT \frac{dP}{P}$$

On integration we get,

$$\int dG = RT \int \frac{dP}{P}$$

$$\Rightarrow G = G^\circ + RT \ln P \quad \text{----- Eqn.1}$$

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### Vant Hoff Isotherm

Now consider a general reaction:-



Let  $G_A$ ,  $G_B$ ,  $G_C$  and  $G_D$  are free energy/mole of the reactants and products at their respective pressure  $P_A$ ,  $P_B$ ,  $P_C$  and  $P_D$ .

So the free energy change for the chemical reaction is given by

$$\Delta G = (cG_C + dG_D) - (aG_A + bG_B) \quad \text{--- Eqn.2}$$

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### Vant Hoff Isotherm

Expressing Eqn-2 in form of Eqn-1 we have

$$\Delta G = [(cG_C^0 + cRT \ln P_C) + (dG_D^0 + dRT \ln P_D)] - [(aG_A^0 + aRT \ln P_A) + (bG_B^0 + bRT \ln P_B)]$$

Regrouping and Rearranging we have

$$\Delta G = \Delta G^0 + RT \ln \left[ \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b} \right] \quad \text{--- Eqn.3}$$

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### Vant Hoff Isotherm

At Equilibrium

$$\Delta G = 0$$

$$\Rightarrow \Delta G^{\circ} + RT \ln \left[ \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b} \right] = 0$$

$$\Rightarrow \Delta G^{\circ} + RT \ln K_{eq} = 0$$

$$\Rightarrow \Delta G^{\circ} = -RT \ln K_{eq} \quad \text{--- Eqn-4}$$

Putting the value of  $\Delta G^{\circ}$  from Eqn-4 in Eqn-3 we have

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### Vant Hoff Isotherm

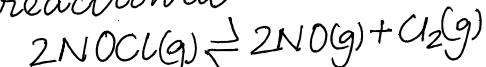
$$\Delta G^{\circ} = -RT \ln K_{eq} + RT \ln \left[ \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b} \right]$$

--- Eqn-5

The above equation-5 is known as

VANT HOFF ISOTHERM

Calculate the equilibrium constant of the reaction at 400K



Given  $\Delta H^{\circ} = 80 \text{ kJ/mol}$ ,  $\Delta S^{\circ} = 120 \text{ J/K.mol}$

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### Vant Hoff Isochore

This is mainly used for calculating equilibrium constants ( $K_2$ ) at temperature ( $T_2$ ) of its value ( $K_1$ ) at temperature ( $T_1$ ) is known

So we have

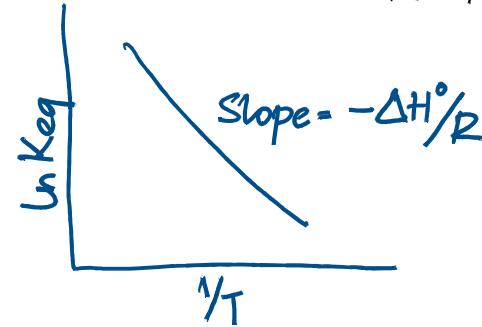
$$\begin{aligned}\Delta G^\circ &= -RT \ln K_{\text{eq}} \\ \Rightarrow \ln K_{\text{eq}} &= \frac{-\Delta G^\circ}{RT} \\ &= \frac{-(\Delta H^\circ - T\Delta S^\circ)}{RT}\end{aligned}$$

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### Vant Hoff Isochore

$$\Rightarrow \ln K_{\text{eq}} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\Rightarrow \ln K_{\text{eq}} = \text{constant} - \frac{\Delta H^\circ}{R} \times \frac{1}{T}$$



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### Vant Hoff Isochore

Hence we have

$$\ln K_1 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT_1}$$

$$\ln K_2 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT_2}$$

$$\ln K_2 - \ln K_1 = \frac{\Delta H^\circ}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\Rightarrow \log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \quad \text{Eqn-6}$$

Eqn(6) is known as VANT HOFF ISOCHORE

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### Gibbs Helmholtz Equation

The equation gives temperature dependence of free energy

We have:-

$$dG = VdP - SdT$$

For a isobaric change  $dP=0$

$$(dG)_P = -SdT \quad \text{--- Eqn-1}$$

$$\Rightarrow (\partial G / \partial T)_P = -S \quad \text{--- Eqn-2}$$

But as  $G = H - TS$

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### Gibbs Helmholtz Equation

$$\Rightarrow \Delta G = H + T \left( \frac{\partial G}{\partial T} \right)_P$$

For a finite change

$$\Delta G = \Delta H + T \left( \frac{\partial \Delta G}{\partial T} \right)_P \quad \text{--- Eqn-3}$$

Eqn 3 is known as Gibbs Helmholtz equation

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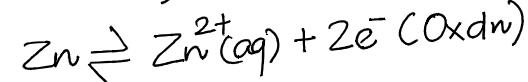
### Applications Gibbs Helmholtz Equation

► To electrolytic cell

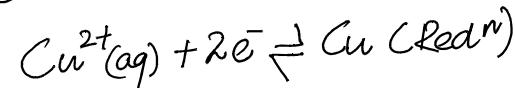
Consider a Daniel cell



Anode (Zn electrode) :-



Cathode (Cu electrode) :-



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### Applications Gibbs Helmholtz Equation

Let e.m.f of the reversible cell =  $E$  volts

Quantity of electricity passing =  $n$  Faradays  
 $= nF$  coulombs

Therefore the electrical work done  
 $= nFE$  joules

Hence  $-\Delta G_f = W_{net} = nFE$   
 $\Rightarrow \Delta G_f = -nFE$  ----- (1)

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### Applications Gibbs Helmholtz Equation

The relationship on substituting in  
 Gibbs Helmholtz equation we have

$$-nFE = \Delta H - nFT \left( \frac{\partial E}{\partial T} \right)_P$$

$$\Rightarrow \Delta H = -nF \left[ E - T \left( \frac{\partial E}{\partial T} \right)_P \right] \text{ --- Eqn-2}$$

Comparing Gibbs Helmholtz equation with  
 $\Delta G_f = \Delta H - T\Delta S$  we have

$$\Delta S = - \left[ \frac{\partial (\Delta G_f)}{\partial T} \right]_P$$

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### Applications Gibbs Helmholtz Equation

$$\text{As } \Delta G = -nFE$$

$$\Rightarrow \Delta S = -\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = nF\left(\frac{\partial E}{\partial T}\right)_P \quad \dots(2)$$

The free energy change ( $\Delta G$ ) accompanying a given process is - 86 kJ at 298 K and - 84 kJ at 308 K. Calculate the change in enthalpy ( $\Delta H$ ) for the process at 303 K.

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### Partial Molar Quantities

The term  $\left(\frac{\partial Z}{\partial n_i}\right)_{T, P, n_1, n_2, \dots}$  is called the partial molar quantity of any component  $i$

It is mainly defined as :-

The rate of change of property with the change in amount of  $i$ th component when temperature, pressure and amounts of other components remains constant

Ex :-  $(\partial V/\partial n_i)_{T, P, n_j}$  - Partial Molar volume

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## Partial Molar Gibbs Free Energy

### Chemical Potential

The partial molar Gibbs free energy has been given a specific symbol ( $\mu$ ) and name *chemical potential* because of its universality in dealing with various aspects of thermodynamic studies.

Chemical potential of  $i$ th component is defined as

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j}$$

Chemical potential is the increase in Gibbs free energy per mole that results when a small amount ( $dn_i$  moles) are added to the system keeping temperature, pressure and all other compositions constant. It is an intensive property of the system.

### Physical significance:

The reactions with low chemical potential has a lower ability to drive a reaction forward.

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## Gibbs-Duhem Equation

Let  $n_A$  and  $n_B$  are the number of moles of component A and & and  $\mu_A$  and  $\mu_B$  are their partial molar Gibbs energies, then total Gibbs energy of the mixture ( $G$ ) can be calculated by using the following equation :

$$G = n_A \mu_A + n_B \mu_B \quad \dots \dots (1)$$

Equation 1 gives the total Gibbs energy of a binary mixture

When the compositions are changed infinitesimally,

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B \quad \dots \dots (2)$$

In an open system

$$dG = VdP - SdT + \mu_A dn_A + \mu_B dn_B \quad \dots \dots (3)$$

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### Gibbs-Duhem Equation

At constant T and P

$$dG = \mu_A dn_A + \mu_B dn_B \quad \dots \dots (4)$$

Comparing eqn (2) and eqn (4) we have

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \dots \dots (5)$$

The equation (5) is the Gibbs Duhem equation. Its significance is that the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components. If  $\mu_A$  increases, then  $\mu_B$  must decrease,

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A \quad \dots \dots (6)$$

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### Clapeyron Clausius Equation

Let us consider the change of a pure substance from phase I to another phase II in equilibrium with it at a given temperature and pressure.

Let  $G_I$  = free energy per mole of the substance in the initial phase I, and

$G_{II}$  = free energy per mole of the substance in the final phase II.

At equilibrium, there will be no change in free energy,

$$\begin{aligned} \Delta G &= G_{II} - G_I = 0 \\ \Rightarrow G_I &= G_{II} \end{aligned}$$

If the temperature of such a system is raised, say, from  $T$  to  $(T + dT)$ , in order to maintain the equilibrium. The pressure will also have to change, say from  $P$  to  $(P + dP)$ .

The relationship between  $dT$  and  $dP$  can be derived from thermodynamics.

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### Clapeyron Clausius Equation

Let  $G_I + dG_I$  = free energy per mole of the substance in phase I at the new temperature and pressure.

and  $G_{II} + dG_{II}$  = free energy per mole of the substance in phase II at the new temperature and pressure.

As the two phases are still in equilibrium, hence,

$$G_I + dG_I = G_{II} + dG_{II} \quad \dots \dots \dots (1)$$

But when a system undergoes reversibly a change of temperature ( $dT$ ) and a change of pressure ( $dP$ ), the change of free energy is given by the expression

$$dG = VdP - SdT$$

For the two phases, this equation can be written as

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### Clapeyron Clausius Equation

$$\text{For phase I } dG_I = V_I dP - S_I dT \quad \dots \dots \dots 2$$

$$\text{For phase II } dG_{II} = V_{II} dP - S_{II} dT \quad \dots \dots \dots 3$$

$$\text{As } G_I = G_{II}$$

$$\therefore dG_I = dG_{II} \quad \dots \dots \dots (4)$$

$$\Rightarrow V_I dP - S_I dT = V_{II} dP - S_{II} dT$$

$$\Rightarrow (V_{II} - V_I) dP = (S_{II} - S_I) dT$$

$$\Rightarrow \frac{dP}{dT} = \frac{S_{II} - S_I}{V_{II} - V_I} = \frac{\Delta S}{\Delta V} \quad \dots \dots \dots 5$$

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### Clapeyron Clausius Equation

Let the heat exchanged reversibly per mole of the substance during phase transformation at constant temperature 'T' be  $q$ , then the change in entropy is given by :-

$$\Delta S = q/T$$

Putting the value of  $\Delta S$  we have

$$\frac{dP}{dT} = \frac{q}{T\Delta V} \quad \text{--- (6)}$$

The above equation (6) is known as CLAPEYRON - CLAUSIUS EQUATION

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### Clapeyron Clausius Equation

Derive the Clapeyron Clausius equation for Liquid Vapour equilibria.

(ASSIGNMENT)

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