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Unit I
Thermodynamics

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Introduction

• The branch of science which deals with the quantitative relationship between heat and other forms of energies is called thermodynamics

• For example,

• Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air.

• The chemical energy used to do mechanical work when a fuel burns in an engine

• The chemical energy used to provide electrical energy through a galvanic cell like dry cell.

• The study of these energy transformations forms the subject matter of thermodynamics

The System And The Surrounding

- The part of universe in which observations are made or which is under investigation is called system.

- Surroundings is the part of universe other than system .

- The surroundings include everything other than the system.

- System and the surroundings together constitute the universe .

- The universe = The system + The surroundings

Types of the System

Open System

• There is exchange of energy and matter between system and surroundings.

• For example. the presence of reactants in an open beaker.

• Here the boundary is an imaginary

Closed System

• There is no exchange of matter, but exchange of energy is possible between system and the surroundings.

• For example, the presence of reactants in a closed vessel made of conducting material.

Isolated System

• There is no exchange of energy and matter between the system and the surroundings

• For example, the presence of reactants in a thermos flask or any other closed insulated vessel

Reversible Processes
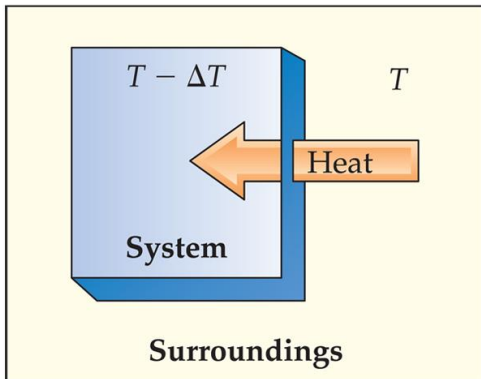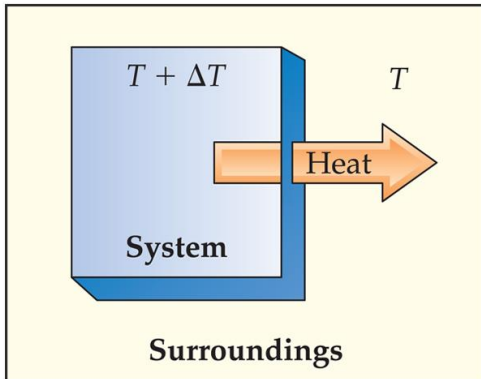
- In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

- Changes are infinitesimally **small** in a reversible process.

Irreversible Processes
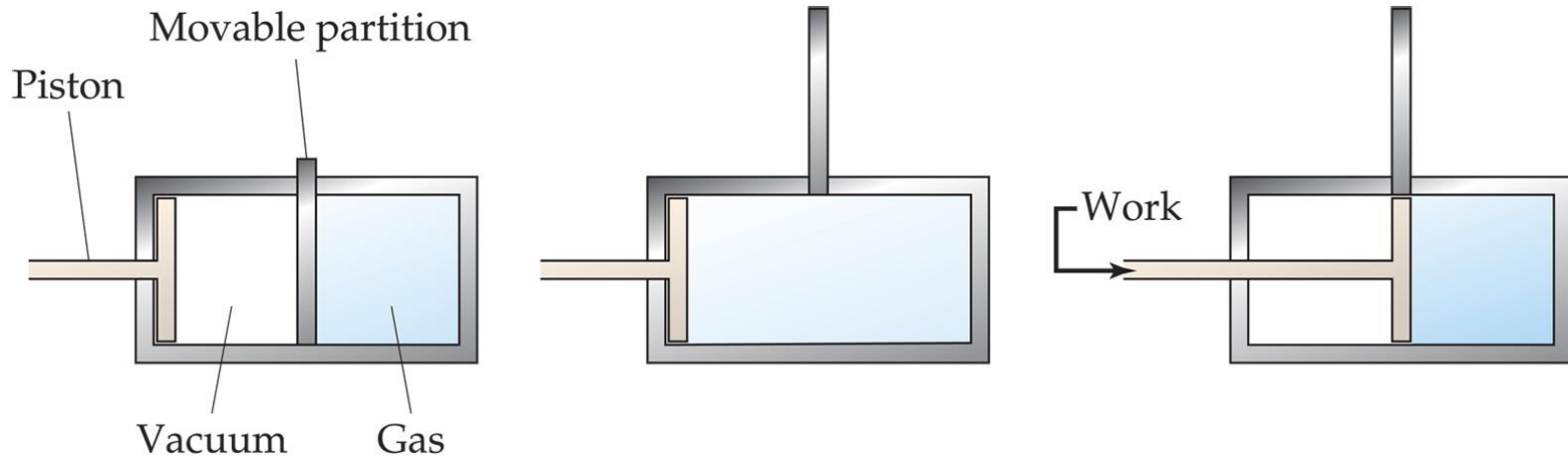
- Irreversible processes cannot be undone by exactly reversing the change to the system.

- All Spontaneous processes are irreversible.

- All Real processes are irreversible.

Spontaneous Processes

- Spontaneous processes are those that can proceed without any outside intervention.
- The gas in vessel *B* will spontaneously effuse into vessel *A*, but once the gas is in both vessels, it will *not* spontaneously
- Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.
- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above 0°C it is spontaneous for ice to melt.
- Below 0°C the reverse process is spontaneous.

A   B

Evacuated   1 atm

Spontaneous   Not spontaneous

A   B

0.5 atm   0.5 atm
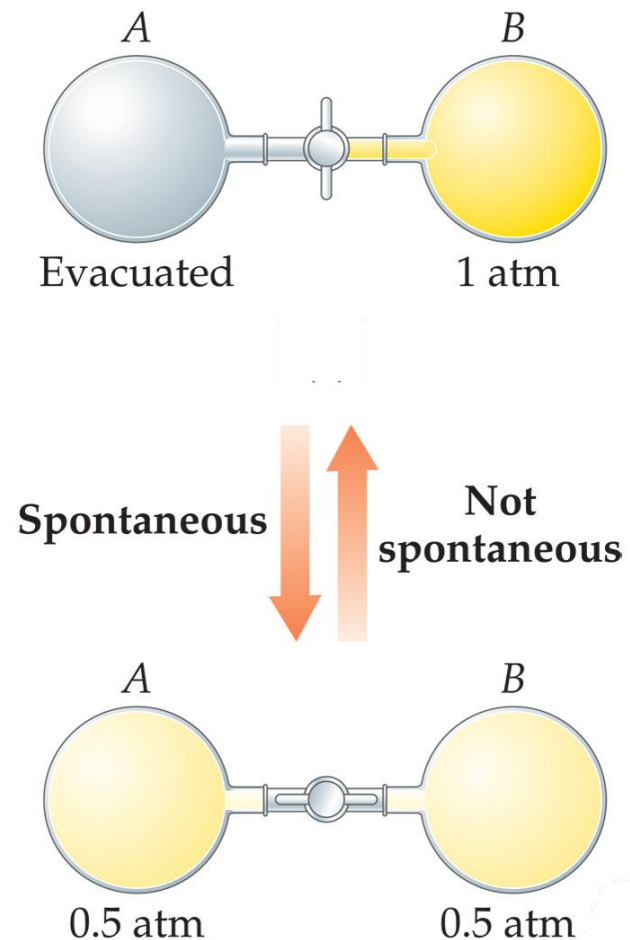
ENTROPY

Entropy is a measure of the degree of randomness or disorder in the system.
• The greater the disorder in an isolated system, the higher is the entropy.
• Qualitatively, Order of entropy :
Solid(lowest entropy) < Liquid < gas (highest entropy)
• Entropy is a state function and ΔS is independent of path.
• Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system.
• A system at higher temperature has greater randomness in it than one at lower temperature.
• Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature.
• This suggests that the entropy change is inversely proportional to the temperature.

ΔS is related with q and T for a reversible reaction as $\Delta S = \frac{q_{rev}}{T}$

• When a system is in equilibrium, the entropy is maximum, and the change in entropy, ΔS = 0.
• Entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero.
• Since entropy is a state property, we can calculate the change in entropy of a reversible process by Both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, ΔU = 0, but ΔStotal i.e., ΔSsys + ΔSsurr is not zero for irreversible process.
• Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.
• ΔStotal > 0 Process is spontaneous
• ΔStotal < 0 Process is Non-spontaneous
• ΔStotal = 0 System is in equilibrium
• ΔSsys alone can not decide the spontaneity of the process for closed and open system

Entropy and Second Law of Thermodynamics

- Entropy is the loss of energy available to do work.

- Another form of the second law of thermodynamics states that the total entropy of a system either increases or remains constant; it never decreases.

- Entropy is zero in a reversible process; it increases in an irreversible process.

- Entropy of any isolated system always increases.

- In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

Absolute Entropy and Third Law of Thermodynamics

- The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics.

- The importance of the third law is that absolute values of entropy of pure substance can be determined.

Standard Entropies

- These are molar entropy values of substances in their standard states.
- Standard entropies tend to increase with increasing molar mass.
- Larger and more complex molecules have greater entropies.

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	$S°$, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Ideal and Non-Ideal Solutions

Ideal solution	Non-ideal solution
(i) Obey's Raoult's law over the entire range of concentration.	Does not obey Raoult's law over the entire range of concentration.
(ii) There is no change in enthalpy when the solution is formed from their components. $$\Delta H_{mix} = 0$$	There is change in enthalpy when the solution is formed from their components. $$\Delta H_{mix} \neq 0$$
(iii) There is no change in volume when the solution is formed from their components. $$\Delta V_{mix} = 0$$	There is change in volume when the solution is formed from their components. $$\Delta V_{mix} \neq 0$$
(iv) The interactions between the components in solution are similar to those in the pure components.	The interaction between the components in solution are different from those of the pure components.