

# Ancillary Chemistry-II

## Thermodynamics



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BSC-04A

**Ancillary Chemistry-II (BASIC ASPECTS OF CHEMISTRY)**

Credits: 2

- SK ← ① Union of elements and its electronic basis. Ionic, covalent and hydrogen bonds. Energetics of chemical bond formation. Bond energy, average bond energy, bond lengths and bond angles.
- JS ← ② Conventional and non-conventional energy sources;  
a. Petroleum products: their origin and separation into different fractions. Octane and Cetane number.  
b. Brief discussion of hydrogen-hydride and lead storage battery.
- SK ← ③ Brief discussion of basic concept of electrode potential and its applications in the metallurgical operations with special reference to iron. The phenomenon of rusting of iron and its prevention through anodic protection.
- SK ← ④ The chemical basis of photosynthesis and respiration (only elementary treatments).
- I. Natural:
- SK → a) Photosynthesis: light reaction, Dark reaction, Factors affecting photosynthesis, Photorespiration.
- JS → b) Respiration: Discussion of the role of Hemoglobin and Myoglobin in carrying  $O_2$ , Aerobic and Anaerobic respiration, different steps in aerobic respiration (in brief), respiratory quotient (RQ).
- JS → II Polymers: Natural and synthetic polymers:  
a) Polysaccharides: carbohydrates  
b) Polypeptides: protein and enzymes, primary, secondary, tertiary and quaternary structures. Molecular disease and primary structure of protein.  
c) Enzymes: types of enzymes, co-factor and prosthetic group, denaturation of enzyme.  
d) Rubber and vulcanization of rubber.
- III Synthetic: Polyneoprene and Bu-na-S rubber, Nylon, Polyesters, Bakelite and Teflon. Health hazards and environmental problems created by polymers.

Chemical Thermodynamics:

Systems and surroundings.

Extensive and intensive thermodynamic properties,

Open, closed and adiabatic systems.

Spontaneous and Non-spontaneous processes.

Thermodynamic basis for the spontaneity of a process.





# Systems and surroundings

## System, Surroundings, Types of Systems, Intensive and Extensive Properties

### System

A thermodynamic system is defined as a definite quantity of matter or a region in space upon which attention is focussed in the analysis of a problem. We may want to study a quantity of matter contained within a closed rigid walled chamber, or we may want to consider something such as gas pipeline through which the matter flows. The composition of the matter inside the system may be fixed or may change through chemical and nuclear reactions. A system may be arbitrarily defined. It becomes important when exchange of energy between the system and the everything else outside the system is considered. The judgement on the energetics of this exchange is very important.

## **Surroundings**

Everything external to the system is surroundings. The system is distinguished from its surroundings by a specified boundary which may be at rest or in motion. The interactions between a system and its surroundings, which take place across the boundary, play an important role in thermodynamics. A system and its surroundings together comprise a universe.

## Energy States

- **Unstable:**  
falling or rolling
- **Stable:**  
at rest in lowest energy state
- **Metastable:**  
in low-energy perch

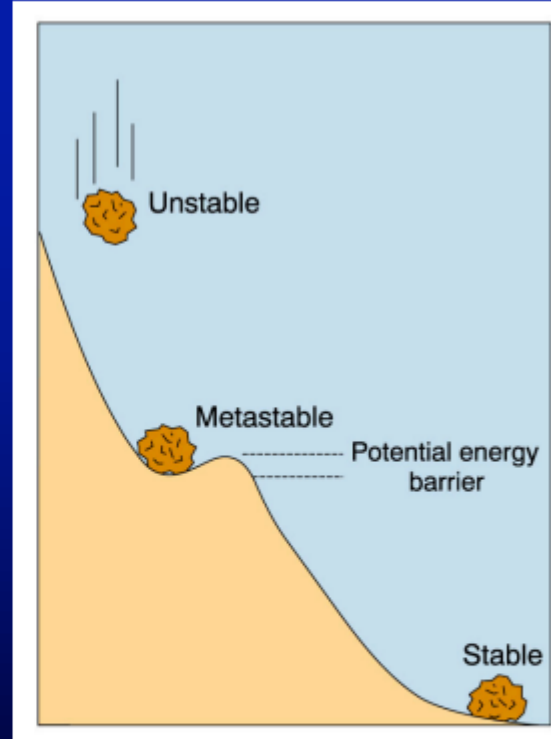


Figure 5-1. Stability states. Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.



The word THERMODYNAMICS means “Heat in Motion”.

“THERMODYNAMICS is basically a branch of science which focuses on the study of energy transfer and its effect on various physical properties of the system.”

“THERMODYNAMICS is the study of three E’s i.e. Energy, Entropy and Equilibrium.”

“THERMODYNAMICS is a science that governs following:

- ☐ Energy and its transformation.
- ☐ Feasibility of a process involving transformation of energy.
- ☐ Feasibility of a process involving transfer of energy.
- ☐ Equilibrium process.

Thus, we can say that THERMODYNAMICS deals with energy conversion, energy exchange and the direction of exchange.

## **THERMODYNAMIC SYSTEM**

- System is that part of universe which is under investigation or under the study of observer.
- Properties of the system are observed when the exchange of energy i.e. work or heat, takes place.
- There is no arbitrary rule for selection of system but proper selection makes the calculations easy.

## **SURROUNDINGS**

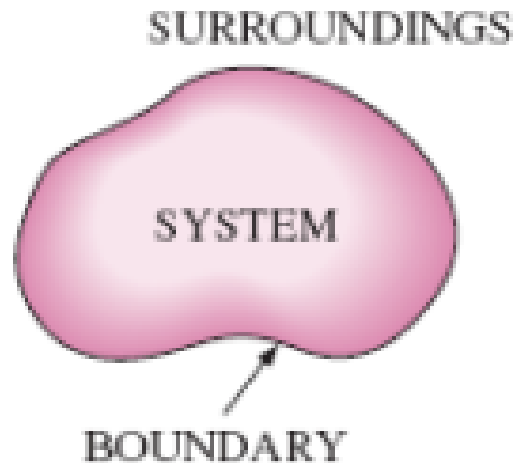
- The remaining portion of universe which is external to the system is called as surrounding.
- The exchange of energy takes place between system and surroundings; hence surroundings may be influenced by the changes taking place in system.

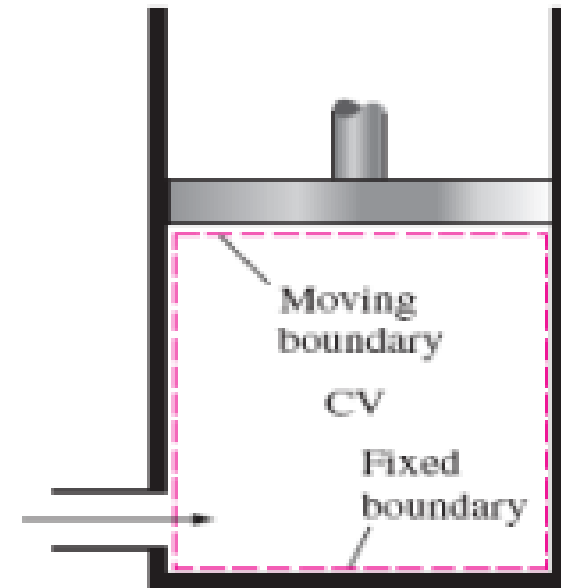
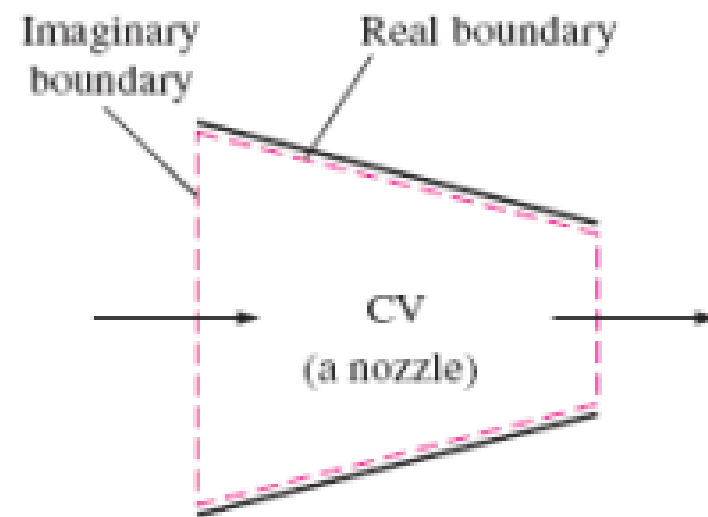
## **UNIVERSE**

- System and surroundings together constitutes Universe i.e.  $\text{System} + \text{Surroundings} = \text{Universe}$ .

## SYSTEM BOUNDARY

- System and surroundings in the universe are separated by System boundary.
- A system boundary has zero thickness.
- Boundary may be Real or Hypothetical and Fixed or Moving.
- It is a surface, and since a surface is a two-dimensional object, it has zero volume. Thus, it attains neither mass nor volume





## **DIFFERENCE BETWEEN SURROUNDINGS, IMMEDIATE SURROUNDINGS AND ENVIRONMENT**

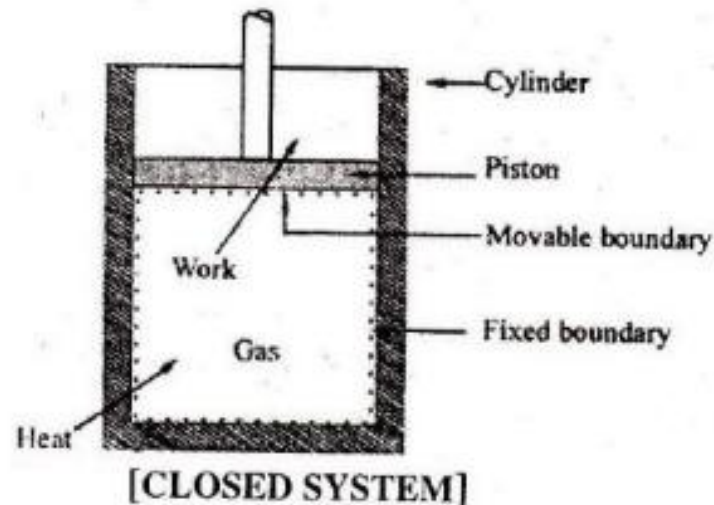
- ☐ Surroundings are everything outside the system boundaries.
- ☐ The immediate surroundings refer to the portion of the surroundings that is affected by the process, and
- ☐ Environment refers to the region beyond the immediate surroundings whose properties are not affected by the process at any point.

## CLASSIFICATION OF THERMODYNAMIC SYSTEM

On the basis of mass and energy transfer across / through the system boundaries, a thermodynamic system can be classified as follows:

### **CLOSED SYSTEM (OR NON FLOW SYSTEM)**

The system which can exchange energy with surroundings but which cannot transfer matter across the boundaries are known as closed system.



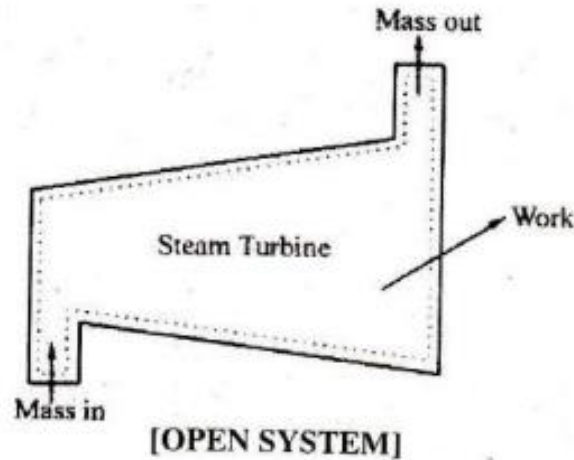
# Closed System

- ☐ Heat and work (energy) crosses the boundary.
- ☐ No mass transfer takes place i.e. mass of system is fixed, hence it is also called as NON FLOW SYSTEM.
- ☐ Due to fixed mass, we also define closed system as CONTROL MASS.
- ☐ Boundary of the system is not fixed but arbitrarily selected.
- ☐ Since boundary may change, volume of the system is not necessarily fixed.
- ☐ Energy transfer can be experienced only at boundaries.
- ☐ e.g. Piston cylinder arrangement, gas being compressed by a piston in a closed cylinder.

The fluid contained in the cylinder can receive or reject heat, can expand or contract, hence changing the volume, but no matter (fluid) can flow out or into the cylinder, i.e. mass remains fixed.

## OPEN SYSTEM (OR FLOW SYSTEM)

The system that can exchange both energy and matter with their environment.





## **OPEN SYSTEM (OR FLOW SYSTEM)**

Heat and work crosses the boundary.

- ☐ Mass transfer also takes place i.e. mass of system is not fixed; hence it is also called as FLOW SYSTEM.
- ☐ System boundary is known as CONTROL SURFACE which always remains fixed.
- ☐ Volume of the system does not change; hence open system is also defined as CONTROL VOLUME.
- ☐ e.g. Steam generator or boiler

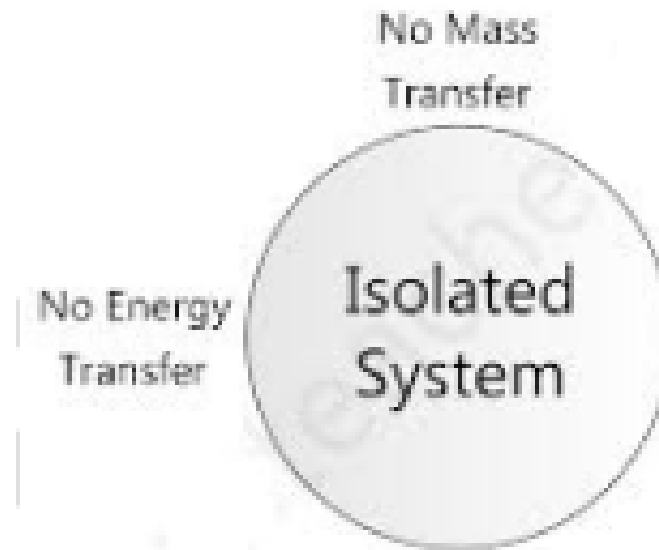
A steam generator converts water into steam by gaining heat from furnace. Hence water flows into the system and steam flows out of the system; hence matter is crossing the boundary of system.

## ISOLATED SYSTEM

An isolated system exchanges neither matter nor energy with its surroundings.

Isolated System

- ☐ Heat and work does NOT cross the boundary.
- ☐ Mass of the system remains fixed i.e. No mass transfer takes place.
- ☐ e.g. Thermos flask.
- ☐ Neither heat flows into/out of the system nor the matter flows.



Thus, a special type of closed system that does not interact with its surroundings is called an Isolated System.



## Open system

- ⊙ Heat and work crosses the boundary. Mass transfer also takes place *i.e.* mass of system is not fixed
- ⊙ Known as FLOW SYSTEM.
- ⊙ Volume of the system does not change.

## Closed System

- ⊙ Heat and work (energy) crosses the boundary. No mass transfer takes place.
- ⊙ Known as NON FLOW SYSTEM.
- ⊙ Volume of the system change.

## Isolated System

- ⊙ Heat and work does not cross the boundary. No mass transfer takes place.

## BASIC TERMINOLOGIES

There are some basic terms one should know for the good study of thermodynamics:

### HOMOGENEOUS AND HETEROGENEOUS SYSTEM

A phase is defined as the quantity of matter which is homogeneous throughout in chemical composition i.e. chemical composition does not vary within system; and physical structure i.e. solid, liquid or gas.

© The system consisting of single phase is called a homogeneous system.  
e.g. air, mixture of water and sugar etc.

© The system which consists of more than one phase is called heterogeneous system. e.g. mixture of water and oil etc

## THERMODYNAMIC EQUILIBRIUM

When a system is in equilibrium with regard to all possible changes in state, the system is in thermodynamic equilibrium. For example, if the gas that comprises a system is in thermal equilibrium, the temperature will be the same throughout the entire system.

## CONTROL VOLUME

A control volume is a fixed region in space chosen for the thermodynamic study of mass and energy balances for flowing systems. The boundary of the control volume may be a real or imaginary envelope. The control surface is the boundary of the control volume.

# **STEADY STATE**

Steady state is that circumstance in which there is no accumulation of mass or energy within the control volume, and the properties at any point within the system are independent of time.



## **THERMODYNAMIC PROCESS**

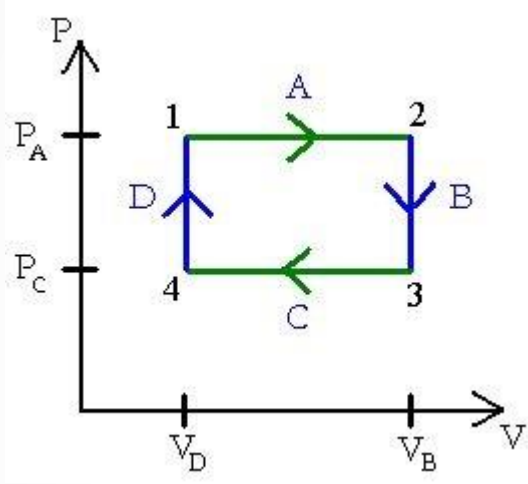
Whenever one or more of the properties of a system change, a change in the state of the system occurs. The path of the succession of states through which the system passes is called the thermodynamic process. One example of a thermodynamic process is increasing the temperature of a fluid while maintaining a constant pressure. Another example is increasing the pressure of a confined gas while maintaining a constant temperature.

## **CYCLIC PROCESS**

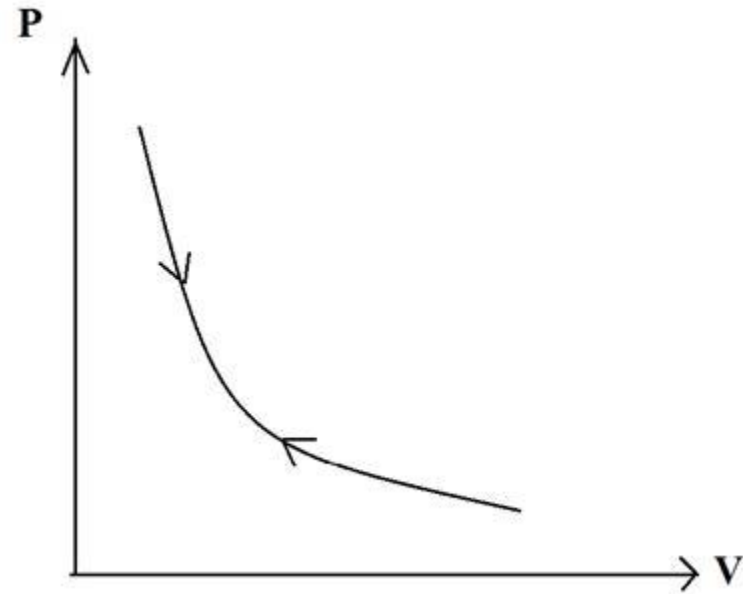
When a system in a given initial state goes through a number of different changes in state (going through various processes) and finally returns to its initial values, the system has undergone a cyclic process or cycle. Therefore, at the conclusion of a cycle, all the properties have the same value they had at the beginning. Steam (water) that circulates through a closed cooling loop undergoes a cycle.

## **REVERSIBLE PROCESS**

A reversible process for a system is defined as a process that, once having taken place, can be reversed, and in so doing leaves no change in either the system or surroundings. In other words the system and surroundings are returned to their original condition before the process took place. In reality, there are no truly reversible processes; however, for analysis purposes, one



*PV Curve for a Cyclic Process*



*PV Curve for a Reversible Process*

# CYCLIC PROCESS VERSUS REVERSIBLE PROCESS

A cyclic process is a chemical process that comes back to the initial state after progression

Can be reversible or irreversible

Have an enclosed PV curve

A reversible process is a process that can be reversed in order to obtain the initial state of a system

Essentially reversible

Not an enclosed PV curve

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uses reversible to make the analysis simpler, and to determine maximum theoretical efficiencies. Therefore, the reversible process is an appropriate starting point on which to base engineering study and calculation. Although the reversible process can be approximated, it can never be matched by real processes. One way to make real processes approximate reversible process is to carry out the process in a series of small or infinitesimal steps. For example, heat transfer may be considered reversible if it occurs due to a small temperature difference between the system and its surroundings. For example, transferring heat across a temperature difference of  $0.00001\text{ }^{\circ}\text{F}$  "appears" to be more reversible than for transferring heat across a temperature difference of  $100\text{ }^{\circ}\text{F}$ . Therefore, by cooling or heating the system in a number of infinitesimally small steps, we can approximate a reversible process.

## IRREVERSIBLE PROCESS

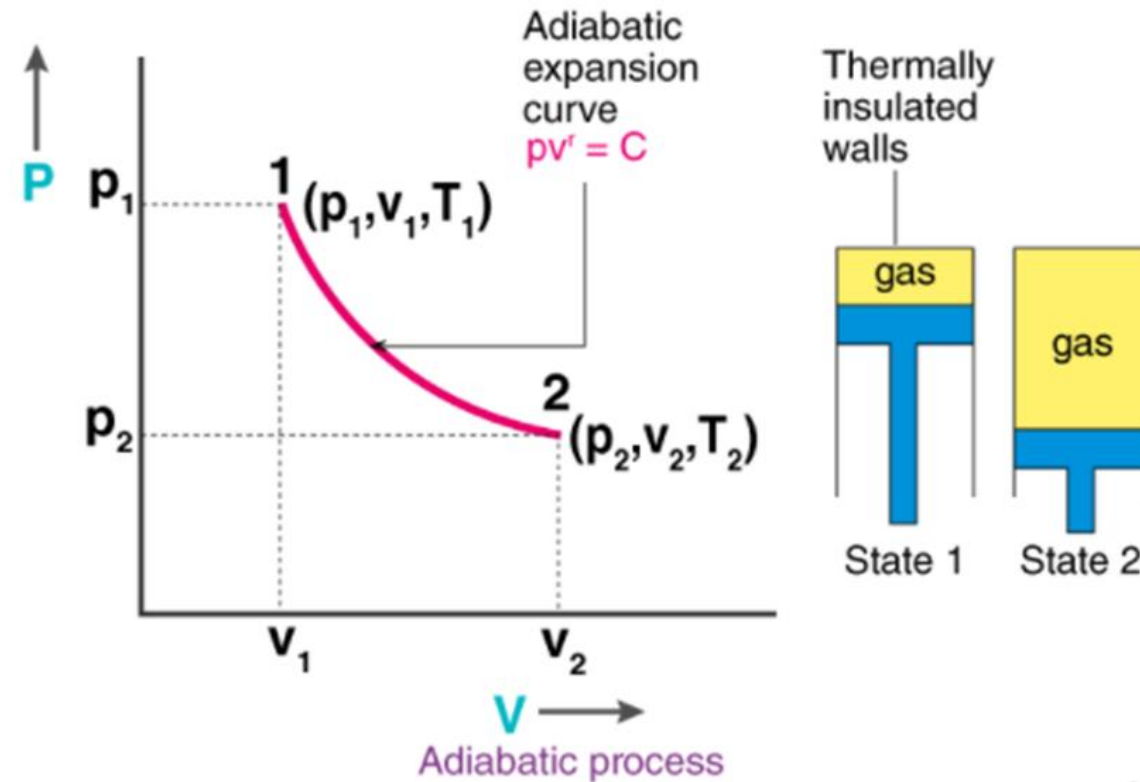
An irreversible process is a process that cannot return both the system and the surroundings to their original conditions. That is, the system and the surroundings would not return to their original conditions if the process was reversed. For example, an automobile engine does not give back the fuel it took to drive up a hill as it coasts back down the hill. There are many factors that make a process irreversible. Four of the most common causes of irreversibility are friction, unrestrained expansion of a fluid, heat transfer through a finite temperature difference, and mixing of two different substances. These factors are present in real, irreversible processes and prevent these processes from being reversible.

## **ADIABATIC PROCESS**

An adiabatic process is one in which there is no heat transfer into or out of the system. The system can be considered to be perfectly insulated.

The adiabatic process can be either **reversible** or **irreversible**. Following are the essential conditions for the adiabatic process to take place:

- The system must be perfectly insulated from the surrounding.
- The process must be carried out quickly so that there is a sufficient amount of time for heat transfer to take place.





For instance, the [gas compression](#) within an engine cylinder is expected to happen so fast that on the compression process timescale, a minimum amount of the energy of the system could be produced and sent out in the form of heat.

Despite the cylinders being not insulated and having a conductive nature, the process is deemed to be adiabatic. The same could be considered to be true for the enlargement process of such a system.

Following is the adiabatic process equation:

$$PV^\gamma = \text{constant}$$

Where,

- $P$  is the pressure of the system
- $V$  is the volume of the system
- $\gamma$  is the adiabatic index and is defined as the ratio of heat capacity at constant pressure  $C_p$  to heat capacity at constant volume  $C_v$

## Reversible Adiabatic Process

Reversible adiabatic process is also called an Isentropic Process. It is an idealized thermodynamic process that is adiabatic and in which the work transfers of the system are frictionless; there is no transfer of heat or of matter and the process is reversible. Such an idealized process is useful in engineering as a model of and basis of comparison for real processes.

## What is Adiabatic Expansion?

Adiabatic expansion is defined as an ideal behaviour for a closed system, in which the pressure is constant and the temperature is decreasing.

## What is Adiabatic Compression?

Adiabatic compression of the air is defined as the compression in which no heat is added or subtracted from the air and the internal energy of the air is increased which is equal to the external work done on the air. The pressure of the air is more than the volume as the temperature increases during compression.

***Interested to learn more about other concepts related to the adiabatic process, below are the links:***

- [Adiabatic Process Derivation](#)
- [Difference Between Isothermal and Adiabatic process](#)

## Adiabatic Process Example

There are several instances, some are stated below:

- It is a process where there is a gas compression and heat is generated. One of the simplest examples would be the release of air from a pneumatic tire.
- Adiabatic Efficiency is applied to devices such as nozzles, compressors, and turbines. One of the good applications of the adiabatic process.
- The pendulum oscillating in a vertical plane is an example of it.
- A quantum harmonic oscillator is also an example of an adiabatic system.
- When we put the ice into the icebox, no heat goes out and no heat comes in.

<b>Isothermal process</b>	<b>Adiabatic process</b>
An isothermal process is defined as one of the thermodynamic processes which occur at a constant temperature	An adiabatic process is defined as one of the thermodynamic processes which occur without any heat transfer between the system and the surrounding
Work done is due to the change in the net heat content in the system	Work done is due to the change in its internal energy
The temperature cannot be varied	The temperature can be varied
There is a transfer of heat	There is no transfer of heat

## ISENTROPIC PROCESS

An isentropic process is one in which the entropy of the fluid remains constant. This will be true if the process the system goes through is reversible and adiabatic. An isentropic process can also be called a constant entropy process.

## POLYTROPIC PROCESS

When a gas undergoes a reversible process in which there is heat transfer, the process frequently takes place in such a manner that a plot of the Log P (pressure) vs. Log V (volume) is a straight line. Or stated in equation form  $PV^n = \text{constant}$ . This type of process is called a polytropic process. An example of a polytropic process is the expansion of the combustion gases in the cylinder of a water-cooled reciprocating engine.

## THROTTLING PROCESS

A throttling process is defined as a process in which there is no change in enthalpy from state one to state two,  $h_1 = h_2$  ; no work is done,  $W = 0$ ; and the process is adiabatic,  $Q = 0$ . To better understand the theory of the ideal throttling process let's compare what we can observe with the above theoretical assumptions.

## PROPERTIES OF A SYSTEM

- Properties are the descriptive and measurable characteristics of the system.
- Properties describe the state of a system i.e. has a definite value when system is in a particular state.
- These are macroscopic in nature and hence, can be measured very easily.
- Their differential is exact i.e. value can be determined by simply integrating from one state to another.
- They depend only upon the state of system but not on the path followed by the process, hence are Point function or State function.

# INTENSIVE AND EXTENSIVE PROPERTIES

Properties of system may be classified as Intensive or Extensive properties.

- INTENSIVE PROPERTIES are those which are independent of mass of system.

- Property of small portion of the system defines the property of whole of the system.

- Intensive properties are expressed in lower case letters except Pressure (P), temperature (T).

- All the specific properties are intensive properties. □ e.g. Pressure (P), temperature (T), density( $\rho$ ) etc.

- EXTENSIVE PROPERTIES are mass dependent. Hence their value depends upon the size of the system.

An extensive property when expressed as per unit mass becomes an intensive property (Specific property).

- ☐ Extensive properties are expressed in upper case letter except mass.
- ☐ e.g. mass (m), energy (E), enthalpy (H), entropy (S) etc.



$$\frac{\text{Extensive}}{\text{Extensive}} = \text{intensive}$$

$m$	$\frac{1}{2} m$	$\frac{1}{2} m$	} Extensive properties
$V$	$\frac{1}{2} V$	$\frac{1}{2} V$	
$T$	$T$	$T$	} Intensive properties
$P$	$P$	$P$	
$\rho$	$\rho$	$\rho$	

Intensive properties are those which will be unchanged by any process, whereas those properties whose values are increased or decreased in proportion to the enlargement or reduction of the system are called extensive properties.

If the system consists of mixture of different phases, the phases are separated from each other by phase boundary. The thermodynamic properties change abruptly at the phase boundary, even though the intensive properties like temperature and pressure are identical.

## Spontaneous Processes

### Comparing and Contrasting the Three Laws of Thermodynamics

The three laws of thermodynamics are given in the table from a chemist's point of view. • The sign conventions for heat,  $q$ , and work,  $w$ , are given below: •  $q$  is positive for an endothermic process (absorbs heat). •  $q$  is negative for an exothermic process (releases heat). •  $w$  is positive when work is done on the system by the surroundings. •  $w$  is negative when work is done by the system on the surroundings.

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  - $w$  is negative when work is done by the system on the surroundings.

<b>Laws of Thermodynamics</b>		
<b><i>Law</i></b>	<b><i>Statement</i></b>	<b><i>Equation</i></b>
1 <sup>st</sup> Law	Energy can be converted from one form to another, but cannot be created or destroyed.	$\Delta E = q + w$ Remember the sign conventions for heat and work.
2 <sup>nd</sup> Law	The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.	For a spontaneous process, $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$ For an equilibrium process, $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$
3 <sup>rd</sup> Law	The entropy of a perfect crystalline substance is zero at the absolute zero of temperature.	

### Spontaneous Processes

- Water runs downhill but never uphill.
- A lump of sugar dissolves in coffee but never reverses the process.
- Heat flows from a hotter object to a colder one but never reverses the process.
- Iron exposed to water and oxygen forms rust, but rust never spontaneously reverts to iron.
- A large number of exothermic reactions are spontaneous.
  - Ex.  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = -890.4 \text{ kJ/mole}$
  - Ex.  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = -56.2 \text{ kJ/mole}$
- However, sometimes the assumption that spontaneous processes always decrease a system's energy (i.e. exothermic reactions are always spontaneous) fails:
  - $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = +6.01 \text{ kJ/mole}$
  - $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \quad \Delta H^\circ = +25 \text{ kJ/mole}$
- Exothermicity favors the spontaneity of a reaction 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. To make this kind of prediction, we need another thermodynamic quantity called entropy.

## Entropy

- Entropy,  $\Delta S$ , is a measure of disorder or randomness for a system.
- When entropy increases,  $\Delta S > 0$ , and when entropy decreases,  $\Delta S < 0$ .
  - Processes (or comparisons) that increase in entropy:
    - Solid  $\rightarrow$  Liquid  $\rightarrow$  Gas
    - Solute  $\rightarrow$  Solution
    - Lower temperature  $\rightarrow$  Higher temperature
    - Fewer particles  $\rightarrow$  More particles
    - Fewer atoms in a molecule  $\rightarrow$  More atoms in a molecule
- Standard entropy is the absolute entropy of a substance at 1 atm and 25°C. (Recall that the standard state refers only to 1 atm. The reason for specifying 25°C is that many processes are carried out at room temperature.)
- Ex. Predict whether the entropy change is greater or less than zero for each of the following processes: (a) freezing ethanol (b) evaporating a beaker of liquid bromine at room temperature (c) dissolving glucose in water (d) cooling nitrogen gas from 80°C to 20°C.

## Second Law of Thermodynamics

- The connection between entropy and the spontaneity of a reaction is expressed by the second law of thermodynamics: The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.
- Mathematically, the second law of thermodynamics states that:
  - for a spontaneous process,  $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$ ,
  - and for an equilibrium process,  $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$ .
- Entropy changes in the surroundings are represented by  $\Delta S_{surroundings} = \frac{-\Delta H_{system}}{T}$  where  $T$  is the Kelvin temperature.



## Absolute Entropy and the Third Law of Thermodynamics

### Third Law of Thermodynamics

- According to the third law of thermodynamics, the entropy of a perfect crystalline substance is zero at the absolute zero of temperature.
- The important point about the third law of thermodynamics is that it enables us to determine the absolute entropies of substances.

### Calculating Entropy Changes

- Suppose that a system is represented by  $a A + b B \rightarrow c C + d D$ , then  
$$\Delta S_{rxn}^{\circ} = \sum n S^{\circ}(\text{products}) - \sum m S^{\circ}(\text{reactants})$$
. Also see the related equations in the table of Similar Thermodynamic Calculations for a System.
- The standard entropy,  $S^{\circ}$ , values for a large number of compounds appear in Appendix 3.
- Ex. From the standard entropy values in Appendix 3, calculate the standard entropy changes for the following reactions at 25°C:  
(a)  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$   
(b)  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$                       (c)  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g})$

Similar Thermodynamic Calculations for a System		
Quantity	Calculation	Comments

Standard enthalpy of reaction, $\Delta H_{rxn}^o$	$\Delta H_{rxn}^o = \sum nH_f^o(\text{products}) - \sum mH_f^o(\text{reactants})$	The standard enthalpy of formation of any element in its most stable form is zero.
Standard entropy of reaction, $\Delta S_{rxn}^o$	$\Delta S_{rxn}^o = \sum nS^o(\text{products}) - \sum mS^o(\text{reactants})$	
Standard free-energy of reaction, $\Delta G_{rxn}^o$	$\Delta G_{rxn}^o = \sum nG_f^o(\text{products}) - \sum mG_f^o(\text{reactants})$	The standard free-energy of formation of any element in its most stable form is zero.

- General rules for quickly evaluating  $\Delta S_{rxn}^o$  :
  - $\Delta S_{rxn}^o$  is positive if a reaction produces more gas molecules than it consumes.
  - $\Delta S_{rxn}^o$  is negative if the total number of gas molecules decreases.
  - $\Delta S_{rxn}^o$  can be either a small positive or a small negative number if there is no net change in the total number of gas molecules.
- Ex. Predict whether the entropy change of the system in each of the following reactions is positive or negative.
 

(a)  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$

(b)  $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$

(c)  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{HBr}(\text{g})$
- Entropy changes in the surroundings are represented by  $\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$  where  $T$  is the Kelvin temperature.



### Gibbs Free Energy

- Substituting  $\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$  into  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$  and multiplying both sides by -1 gives  $-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} < 0$ . Replacing  $-T\Delta S_{\text{universe}}$  with  $\Delta G$  gives  $\Delta G = \Delta H_{\text{system}} - T\Delta S_{\text{system}} < 0$  for a spontaneous reaction.
- Thus, the change in free energy,  $\Delta G$ , for a constant-temperature process is represented by  $\Delta G = \Delta H - T\Delta S$  in which  $\Delta H$  is the enthalpy of the system,  $\Delta S$  is the entropy of the system, and  $T$  is the Kelvin temperature.
  - If  $\Delta G$  is negative, the reaction is spontaneous (it proceeds in the forward direction).
  - If  $\Delta G$  is positive, the reaction is nonspontaneous (it proceeds in the reverse direction).
  - If  $\Delta G = 0$ , the system is at equilibrium. There is no net change.
- The standard free-energy of reaction,  $\Delta G_f^\circ$ , is the free-energy change for a reaction when it occurs under standard-state conditions, when reactants in their standard states are converted to products in their standard states.
- Suppose that a system is represented by  $a A + b B \rightarrow c C + d D$ , then  $\Delta G_{\text{rxn}}^\circ = \sum n G_f^\circ(\text{products}) - \sum m G_f^\circ(\text{reactants})$ . Also see the related equations in the table of Similar Thermodynamic Calculations for a System.
- The standard free-energy of formation,  $\Delta G_f^\circ$ , of any element in its most stable form is zero.

- Ex. Calculate the standard free-energy changes for the following reactions at 25°C.  
 (a)  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$       (b)  $2 \text{MgO}(\text{s}) \rightarrow 2 \text{Mg}(\text{s}) + \text{O}_2(\text{g})$   
 Use Appendix 3 to find the  $\Delta G_f^\circ$  values.

### Temperature and Spontaneity

- At the temperature at which a phase transition occurs, the system is at equilibrium ( $\Delta G = 0$ ) and  $\Delta G = \Delta H - T\Delta S = 0$ . From this, we can write  $\Delta S = \frac{\Delta H}{T}$ .
- For example, for the ice  $\rightarrow$  water transition,  $\Delta H$  is the molar heat of fusion and  $T$  is the melting point. The entropy change is  $\Delta S_{\text{ice} \rightarrow \text{water}} = \frac{6010 \text{ J/mole}}{273 \text{ K}} = 22.0 \text{ J/K-mole}$ . Similarly, for the water  $\rightarrow$  ice transition, the change is  $\Delta S_{\text{water} \rightarrow \text{ice}} = \frac{-6010 \text{ J/mole}}{273 \text{ K}} = -22.0 \text{ J/K-mole}$ .
- Ex. The molar heats of fusion and vaporization of benzene are 10.9 kJ/mole and 31.0 kJ/mole, respectively. Calculate the entropy changes for the solid  $\rightarrow$  liquid and liquid  $\rightarrow$  vapor transitions for benzene. At 1 atm pressure, benzene melts at 5.5°C and boils at 80.1°C.
- Under what conditions will we have a spontaneous reaction (negative  $\Delta G$ )? See the Factors Affecting the Sign of  $\Delta G$  table to see how the signs of  $\Delta H$  and  $\Delta S$  affect  $\Delta G$ . Note that the thinking process to produce the conclusions of the table is as important as the conclusions themselves.

<b>Factors Affecting the Sign of <math>\Delta G</math> in the Relationship <math>\Delta G = \Delta H - T\Delta S</math></b>			
<i>Sign of <math>\Delta H</math></i>	<i>Sign of <math>\Delta S</math></i>	<i>Sign of <math>\Delta G</math></i>	<i>Is Reaction Spontaneous?</i>
Negative	Positive	Always negative	Yes, always
Positive	Negative	Always positive	No, always
Positive	Positive	Negative at high temperature	Yes, at high temperature
Negative	Negative	Negative at low temperature	Yes, at low temperature

### **Free Energy and Chemical Equilibrium**

#### **Free Energy and Chemical Equilibrium**

- During the course of a chemical reaction, not all the reactants and products will be in their standard states. Under this condition, the relationship between  $\Delta G$  and  $\Delta G^\circ$ , which can be derived from thermodynamics, is  $\Delta G = \Delta G^\circ + RT \ln Q$  where  $R$  is the gas constant (8.314 J/mole-K,  $T$  is the absolute temperature of the reaction, and  $Q$  is the reaction quotient.
- At equilibrium, by definition,  $\Delta G = 0$  and  $Q = K$  where  $K$  is the equilibrium constant. Thus,  $\Delta G = \Delta G^\circ + RT \ln Q = 0$  and  $\Delta G^\circ = -RT \ln K$ .
- In the equation  $\Delta G^\circ = -RT \ln K$ ,  $K_p$  is used for gases and  $K_c$  is used for reactions in solution. Note that the larger the  $K$  is, the more negative  $\Delta G^\circ$  is.



- $\Delta G^\circ = -RT \ln K$  allows chemists to calculate equilibrium constants from thermodynamic data.
- **Note that it is the sign of  $\Delta G$  and not that of  $\Delta G^\circ$  that determines the direction of reaction spontaneity.** The sign of  $\Delta G^\circ$  only tells us the relative amounts of products and reactants when equilibrium is reached, not the direction of the net reaction. See the table for additional information.

Relation Between $\Delta G^\circ$ and $K$ as Predicted by the Equation $\Delta G^\circ = -RT \ln K$			
$K$	$\ln K$	$\Delta G^\circ$	Comments
$>1$	Positive	Negative	Products are favored over reactants at equilibrium.
$=1$	0	0	Products and reactants are equally favored at equilibrium.
$<1$	Negative	Positive	Reactants are favored over products at equilibrium.

- Ex. Using the data listed in Appendix 3, calculate the equilibrium constant ( $K_p$ ) for the following reaction at 25°C:  $2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$
- Ex. In Chapter 16, we discussed the solubility product of slightly soluble substances. Using the solubility product of silver chloride at 25°C ( $1.6 \times 10^{-10}$ ), calculate  $\Delta G^\circ$  for the following process:  $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- Ex. The equilibrium constant ( $K_p$ ) for the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$  is 0.113 at 298 K, which corresponds to a standard free-energy change of 5.40 kJ/mole. In a certain experiment, the initial pressures are  $P_{\text{NO}_2} = 0.122 \text{ atm}$  and  $P_{\text{N}_2\text{O}_4} = 0.453 \text{ atm}$ . Calculate  $\Delta G$  for the reaction at these pressures and predict the direction of the net reaction toward equilibrium.

### **Influence of Temperature on Equilibrium Constants**

Higher reaction temperatures increase the equilibrium constant of an endothermic reaction but decrease the equilibrium constant of an exothermic reaction.

The slope of a plot of  $\ln K$  (y-axis) versus  $1/T$  (x-axis) for an equilibrium system is used to determine the standard enthalpy for the equilibrium,  $\Delta H_{rxn}^{\circ}$ , and the y-intercept of the plot is used to determine the standard entropy change,  $\Delta S_{rxn}^{\circ}$ . The corresponding equation of the line for this plot is  $\ln K = -\frac{\Delta H_{rxn}^{\circ}}{R} \left( \frac{1}{T} \right) + \frac{\Delta S_{rxn}^{\circ}}{R}$ .

### **Driving the Human Engine: Coupled Reactions**

Many important biochemical processes, including glycolysis and phosphorylation, are made possible by coupled spontaneous and nonspontaneous reactions. The free energy released in the spontaneous processes going on in the body is used to drive nonspontaneous processes.

### **: Microstates: A Quantized View of Entropy**

In 1868, Boltzmann showed that the entropy of a system is given by  $S = k \ln W$  in which  $k$  is the Boltzmann constant  $1.38 \times 10^{-23}$  J/K and  $W$  is the number of microstates for the system. A system with fewer microstates (smaller  $W$ ) among which to spread its energy has a lower entropy.