## Module-1: Lecture-1: TeachUrSelf Metallurgical Thermodynamics

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## Some Important Terms of Thermodynamics

System:

- Substance or a group of substances in which we have special interest
- Part of universe set apart for our special consideration

Examples: Reaction vessel, distillation column, heat engine

## Process:

- Changes taking place in a system

Examples: Hydrocarbon and oxygen in a combustion chamber constitutes a system, combustion of fuel to form water and carbon dioxide constitutes a process

## Surroundings:

- Part of universe outside the system, separated from system by boundaries.
- Boundaries can be physical or imaginary, rigid or movable.
- Usually restricted to that portion of the universe which is in immediate vicinity of the system and are affected by changes occurring in the system.

Examples: when steam condensing in a shell and tube heat exchanger is treated as a system, the cooling water to which the latent heat of vaporization is transferred may be treated as the surroundings.

## Homogeneous system:

- Properties are same throughout or vary smoothly without showing any surface of discontinuity.

Examples: Liquid water in a beaker, a column of dust free air.

## Heterogeneous system:

- Consists of 2 or more distinct homogeneous phases separated by phase boundaries.
- Sudden change in properties occur at phase boundaries.

Examples: mixture of water and toluene, water and water vapor in a closed container

## Closed system:

- Can exchange energy with surroundings across boundaries, but not matter

Examples: Hot water filled in a closed steel container, batch reactor

## Open system:

- Can exchange both energy and matter with the surroundings

Examples: Tubular flow reactor, Cyclical processes like power and refrigeration cycles are closed when considered as a whole, whereas each component of the cycle such as compressor, pump, heat exchanger are open.

## Isolated system:

- Neither energy nor mass transfer across the boundaries.
- Totally unaffected by the changes in the surroundings.

Example: thermo-flask

State and Properties:

- Certain specifications such as pressure, volume, and temperature are necessary to define the conditions of a given system.
- Condition defined by such specifications - State of the system
- Variables used to define the state - State functions / properties of the system
- Minimum number of such variables required to represent the state - Degrees of freedom


## Intensive and Extensive Properties:

- Extensive properties depend on the quantity (or extend) of matter specified in the system.

Examples: Mass, Volume, Entropy, Enthalpy, Work, Heat.

- Total value of any extensive property is the sum of the values of the property of individual components into which the system can be subdivided.
- Intensive property is independent of the size of the system.

Examples: Pressure, Temperature, Specific volume, Density

- Some intensive properties are derived from the extensive properties by specifying the unit amount of substance concerned.

$$
\begin{gathered}
\text { density }=\frac{\text { mass }}{\text { volume }} \\
\text { Specific heat }=\frac{\text { heat capcity }}{\text { mass }}
\end{gathered}
$$

## State functions:

- Properties of a system describe its present state and do not give a record of its previous history.
- Fixed for a particular state of the system and do not depend on the path by which the state was arrived at.
- When a system is considered in two different states, the difference in property between two states depends solely upon these states themselves and not upon the manner in which the system changes from one state to the other.
- They are exact differentials.
- Change in state function / property is zero for a cyclic process.


## Path functions:

- Depends on the path from initial to final state.

Examples: Heat and Work

- Path - succession of equilibrium states passed through when system changes from one equilibrium state to another.
- They are inexact differentials


## First Law of Thermodynamics:

Heat, Work and Internal Energy:

The First Law of Thermodynamics is really a statement of the Principle of Conservation of Energy:

- Energy can neither be created, nor destroyed.
- Energy can be transported or converted from one form to another but cannot be either created or destroyed.
- Chemical and/or physical changes are accompanied by changes in energy.

The types of energy commonly encountered include:

- Heat energy
- Work or mechanical energy
- Electrical energy
- Chemical energy


## Heat (q):

Heat flows by virtue of a temperature difference. Heat will flow until temperature gradients disappear. When heat flows, energy is transferred. The sign convention is that heat is positive when it flows to the system from the surroundings and negative when it flows the system to the surroundings.


System is defined as a portion of the universe that is chosen for thermodynamics discussion and the surroundings is the remainder of the universe.

Work (w):

Work is the transfer of energy by interaction between the system and the surroundings.

There are many types of work:

- Mechanical work
- Electrical work
- Magnetic work
- Surface tension

For now, we will be dealing mainly with mechanical work.

The system can do work on the surroundings. The surroundings can also do work on the system. The sign convention employed in this text:

- If the system does work on the surroundings, then work (w) is positive.
- If the surroundings does work on the system, then work (w) is negative.


> System is defined as a portion of the universe that is chosen for thermodynamics discussion and the surroundings is the remainder of the universe.

## Internal Energy (U):

Energy contained in the system is called the internal energy.


- If heat $(q)$ is supplied to the system, the internal energy of the system (U) will increase.
- If the system does work (w) to the surroundings, energy will be expended and hence the internal energy ( U ) of the system will decrease.

Net change in the internal energy $(\Delta U)$ is then

$$
\Delta U=q-w
$$

This principle is referred to as the First Law of Thermodynamics: Energy may be converted from one form to another, but it cannot be created or destroyed.

As force $=$ area $\times$ pressure, the expression is correct. If the gas expands against the external pressure $P_{e x}$ from $L_{1}$ to $\boldsymbol{L}_{\mathbf{2}}$ in the figure, the work done by the system (i.e., the gas) is

$$
w=\int_{L_{1}}^{L_{2}} A P_{e x} d L=\int_{V_{1}}^{V_{2}} P_{e x} d V
$$



If the external pressure is continuously adjusted so that it is kept the same as the internal pressure P

$$
w=\int_{V_{1}}^{V_{2}} P d V
$$

Work under these conditions is called reversible work.

Work is a mode of energy transfer which occurs due to the existence of imbalance of forces between the system and the surroundings. When the forces are infinitesimally unbalanced throughout the process in which energy is transferred as work, then the process is said to be reversible.

- Thermodynamics is largely concerned with the relations between state functions which characterize systems.
- A state function can be integrated between the initial (A) and final (B) states, being independent of integration path.

$$
\Delta U=\int_{A}^{B} d U
$$

- An exact differential can be written in terms of partial derivatives. For instance, as

$$
\begin{gathered}
U=f(T, V) \\
d U=\left(\frac{\partial U}{\partial T}\right)_{V} d T+\left(\frac{\partial U}{\partial V}\right)_{T} d V
\end{gathered}
$$

- The order of differentiation of a state function is immaterial.

$$
\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_{V}\right]_{T}=\left[\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_{T}\right]_{V}
$$

- The First Law of Thermodynamics may be summarized by the following equation:



## More about $\boldsymbol{q}$ and $\boldsymbol{w}$

"Heat" and "work" are defined only for processes: heat and work are modes of energy transfer. A system cannot possess either heat or work. There is no function of state that can represent heat or work.

## Enthalpy (H):

If a process takes place at constant volume,

$$
w=P \Delta V=0
$$

From the first law of thermodynamics,

$$
\Delta U=q-w=q
$$

Therefore, the increase or decrease in internal energy of the system is equal to the heat absorbed or released, respectively, at constant volume. If a process is carried out at a constant pressure rather than at a constant volume, then the work done by the system as a result of the volume change is

$$
w=\int_{1}^{2} P d V=P \int_{1}^{2} d V=P\left(V_{2}-V_{1}\right)
$$

From the first law of thermodynamics:


## Rearrangement yields

$$
\left(U_{2}+P V_{2}\right)-\left(U_{1}+P V_{1}\right)=q
$$

The function $U+P V$ occurs frequently in chemical thermodynamics and hence it is given a special name, enthalpy and the symbol H .

$$
H=U+P V
$$

Then

$$
\Delta H=H_{2}-H_{1}=q
$$

For a system at constant pressure, therefore,


For changes at other than constant pressure, $\boldsymbol{\Delta H}$ still has a definite value, but $\boldsymbol{\Delta H} \neq \boldsymbol{q}$.

## Heat Capacity (C):

The heat capacity of a system is defined as the amount of heat, $q$, required to raise the temperature of the system by $\Delta T$. Thus,


$$
C=\frac{q}{\Delta T}
$$

where $C$ is the heat capacity.

For an infinitesimal change in T,

$$
C=\frac{d q}{d T}
$$

Heat capacity is the measure of the capacity of a system to take in energy as heat.

Recall that heat $q$ is not a state function, so that the change in $q$ depends on the other variable, for instance, $V$ or $P$, in addition to $T$. Therefore,

At constant volume:

$$
\delta q=d U \rightarrow C_{V}=\frac{d U}{d T}
$$

At constant pressure:

$$
\delta q=d H \rightarrow C_{P}=\frac{d H}{d T}
$$

Where, $C_{V}$ is the heat capacity at constant volume, and $C_{P}$ is the heat capacity at constant pressure. The variation with temperature of the heat capacity, $C_{P}$, for a substance is often given by an expression of the form:

$$
C_{P}=a+b T+c T^{-2}
$$

where $a, b$ and $c$ are constants to be determined empirically.


From the above diagram:

$$
T \rightarrow 0 \text { then } C_{V} \rightarrow 0
$$

## Thoughtful Examples:

Prove the following statements:

- For condensed phased, i.e., solids or liquids, $C_{V}$ and $C_{P}$ are quite similar in magnitude.
- $C_{V}$ and $C_{P}$ are significantly different for ideal gases.


## Solution:

For condensed phases:

$$
\begin{gathered}
\Delta H=\Delta U+\Delta(P V) \cong \Delta U \\
C_{V}=\left(\frac{\partial U}{\partial T}\right)_{V} \quad C_{P}=\left(\frac{\partial H}{\partial T}\right)_{P} \\
C_{P}=C_{V}
\end{gathered}
$$

For ideal gases:


## Thoughtful Example:

Substances usually expand with increase in temperature at constant pressure. Is $C_{P}$ usually larger than $C_{V}$

## Solution:

When heat is supplied to a substance:


Therefore, $C_{P}$ is larger than $C_{V}$.


The contribution to $C_{p}$ caused by change in the volume of the system against the constant external pressure

The contribution from the energy required for the change in volume against the internal cohesive forces acting between the constituent particles of a substance.
For liquids and solids, which have strong internal cohesive forces, the term $(\partial U / \partial T)$ is large.
For gases this term is usually small compared with $P$. An ideal gas is a gas consisting of non-interacting particles, and hence this term is zero.

$$
\begin{gathered}
C_{P}-C_{V}=P\left(\frac{\partial V}{\partial T}\right)_{P} \\
P V=R T \\
C_{P}-C_{V}=R \\
\hline
\end{gathered}
$$

## Thoughtful Examples:

In a reversible, adiabatic process of a system comprising of 1 mole of an ideal gas, prove that the following relationships:

- $d U=-\delta w$
- $C_{V} d T=-P d V$


## Solutions:

- $d U=\delta q-\delta w$, but $\delta q=0$ in an adiabatic process.
$\bullet$



## Enthalpy Change ( $\Delta H$ ):

For a substance of fixed composition, the enthalpy change with change in temperature at constant pressure P can be calculated as follows:

$$
C_{P}=\frac{d H}{d T} \rightarrow d H=C_{P} d T
$$



Or integration from $T_{1}$ to $T_{2}$,

$$
\begin{gathered}
\Delta H=\int_{T_{1}}^{T_{2}} C_{P} d T \\
\Delta H=\int_{T_{1}}^{T_{2}}\left(a+b T+c T^{-2}\right) d T
\end{gathered}
$$

The enthalpy change associated with a chemical reaction or phase change at constant pressure and temperature can be calculated from the enthalpy of each species involved in the process. When species A undergoes the phase transformation from $\alpha$ to $\beta$.


The enthalpy changes due to chemical reaction $(\Delta H)$ is the difference between the sum of enthalpies of the products and the sum of enthalpies of the reactants:

$$
\Delta H=\sum H_{\text {products }}-\sum H_{\text {reactants }}
$$

Example:

$$
\mathrm{Fe}_{2} \mathrm{O}_{3}+2 \mathrm{Al}=\mathrm{Al}_{2} \mathrm{O}_{3}+2 \mathrm{Fe}: \Delta H=\left(H_{A l_{2} O_{3}}+2 \mathrm{H}_{\mathrm{Fe}}\right)-\left(H_{\mathrm{Fe}_{2} \mathrm{O}_{3}}+2 \mathrm{H}_{A l}\right)
$$

Because enthalpy is a state property, the enthalpy change depends on the initial and final states only, not on the path the process follows.

The additive properties of enthalpy is known as Hess 's Law. According to this law:

- the enthalpy change associated with a given chemical reaction is the same whether it takes place in one several states, or
- enthalpies or enthalpy changes may be added or subtracted in parallel with the same manipulations performed on their respective components or reactions.

The above is in fact a different expression of the state property of enthalpy.

## Thoughtful Example:

The specific heat $\left(C_{P}\right)$ of pure iron expressed in $\mathrm{J} /(\mathrm{mol} . \mathrm{K})$ as a function of temperature $T$ (in K ) is given as:

$$
C_{P}=17.49+24.77 \times 10^{-3} T
$$

What is the change in the enthalpy of pure iron (in $\mathrm{J} / \mathrm{mol}$ ) when it is heated from $25^{\circ} \mathrm{C}$ to $700^{\circ} \mathrm{C}$ $\qquad$ .?

## Solution:

Given: $C_{P}=17.49+24.77 \times 10^{-3} T$
As we know that:

$$
\Delta H=\int_{T_{1}}^{T_{2}} C_{P} d T
$$

Where, $\quad T_{1}=298 \mathrm{~K}$ and $T_{2}=973 \mathrm{~K}$

$$
=\int_{T_{1}}^{T_{2}}\left(17.49+24.77 \times 10^{-3} T\right) d T
$$

$$
\Delta H=22431.15 \mathrm{~J} / \mathrm{mol}
$$

## Thoughtful Example:

Enthalpy of formation at $298 \mathrm{~K}, \Delta H^{0}$ of $\mathrm{CO}_{2}$ and PbO are $-393 \mathrm{~kJ} / \mathrm{mol}$ and $-220 \mathrm{~kJ} / \mathrm{mol}$, respectively. The enthalpy changes for the reaction is

$$
2 \mathrm{PbO}+C \rightarrow 2 \mathrm{~Pb}+\mathrm{CO}_{2}
$$

## Solution:

The reaction will be

$$
\begin{aligned}
& \mathrm{C}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2} ; \Delta \mathrm{H}_{f}=-393 \mathrm{kJmole}^{-1} \\
& 2 \times\left[P b+\frac{1}{2} O_{2} \rightarrow P b_{O}\right] ; \Delta H_{f}=-220 \mathrm{kJmole}^{-1}
\end{aligned}
$$

The enthalpy of the given below reaction will be

$$
2 \mathrm{PbO}+\mathrm{C} \rightarrow 2 \mathrm{~Pb}+\mathrm{O}_{2} ; \Delta \mathrm{H}_{f}=2 \times 220 \mathrm{kJmole}^{-1}
$$

After adding the reactions, we get,

$$
2 \mathrm{PbO}+\mathrm{C} \rightarrow 2 \mathrm{~Pb}+\mathrm{CO}_{2}
$$

$$
\Delta H_{f}=(-39+440) \mathrm{kJmole}^{-1}=47 \mathrm{kJmole}^{-1}
$$

## Second Law of Thermodynamics:

## Reversible and Irreversible Processes:

- Wood will burn spontaneously in air if ignited, but the reverse process, i.e., the spontaneous recombination of the combustion products to wood and oxygen in air, has never been observed in nature.
- Ice at 1 atm pressure and a temperature above $\mathbf{0}^{\mathbf{0}} \boldsymbol{C}$ always melts spontaneously, but water at 1 atm pressure and a temperature above $\mathbf{0}^{\mathbf{0}} \boldsymbol{C}$ never freezes spontaneously in nature.
- Heat always flows spontaneously from higher to lower temperature systems, and never the reverse.

A process, which involves the spontaneous change of a system from a state to some other state, is called spontaneous or natural process. As such a process cannot be reversed without help of an external agency, the process is called an irreversible process.


A process during which the system is never away from equilibrium is called a reversible process. This statement is obviously contradictory to the definition of equilibrium.

| Reversible Process | Irreversible Process |
| :---: | :--- |
| - The maximum work the system can do | - If the pressure drop, $d P$, is a finite amount, |
| occurs when $d P \rightarrow 0$. | i.e., $d P \neq 0$, in other words, the system <br> undergoes an irreversible process, then the |



## Entropy (s):

Let's us consider a system as given below:


- Heat $q$ is to flow from the hot body to the cold body.
- The flow may take place either
- directly from the hot to cold bodies, i.e., Path 1, or
- from the hot to warm to cold bodies, i.e., Path $2+$ Path 3 .
- Each of these processes is spontaneous and hence irreversible. Therefore, degradation occurs in each process.

$$
\text { Path } 1=\text { Path } 2+\text { Path } 3
$$

Therefore, Degradation in Path $1>$ Degradation in Path 2,

And, Degradation in Path $1>$ Degradation in Path 3.

Thus, Path 1 is more irreversible than either Path 2 or Path 3. Examination of these three paths clearly indicates that the degree of irreversibility is related to temperature T and the amount of heat q.

- The more the heat flow, the higher the degree of irreversibility.
- The lower the temperature of the body to which heat flows, the higher the degree of irreversibility.

Therefore,

$$
\text { Degree of irreversibility } \propto \frac{q}{T}
$$

Now we define a new thermodynamics function, $S$, called entropy, as

$$
\begin{gathered}
\text { Entropy change }=\frac{\text { Total heat input }}{\text { Temperature }} \\
\qquad \Delta S=\frac{q_{t o t a l}}{T}
\end{gathered}
$$

The entropy change $(\Delta S)$ is the measure of the degree of irreversibility of a process.

The total entropy change associated with the process consists of two terms:

- Entropy change of the system $: \Delta S_{s y s}$
- Entropy change of the surroundings : $\Delta S_{\text {sur }}$

$$
\Delta S_{t o t}=\Delta S_{s y s}+\Delta S_{s u r}
$$

Recall that the total heat appearing in the system is the sum of heat entering from the surroundings $(q)$ and heat produced by degradation due to irreversibility $\left(\boldsymbol{q}_{\boldsymbol{r}}-\boldsymbol{q}\right)$ :


The total heat leaving the surroundings is $q$ :


Negative sign is due to heat loss of the surroundings.

Graphical representation:


## Thoughtful Example:

The given below reaction:

$$
\begin{gathered}
\operatorname{Ag}(S)=\operatorname{Ag}(1) \text { at } T=1234 \mathrm{~K}, \Delta H_{f}=11300 \mathrm{~J} / \mathrm{mol} \\
\Delta C_{P}=C_{P}(1)-C_{P}(s)=0
\end{gathered}
$$

When 1 mol of super cooled liquid silver freezes at an ambient temperature of 1000 K , the total entropy changes of the system $(\mathrm{Ag})$ and the surrounding is $\qquad$ .

## Solution:

The change in entropy in the system will be

$$
\left(\Delta S^{L \rightarrow S}\right)_{\text {system }}=-\left(\frac{\Delta H_{f}}{T_{m}}\right)=\frac{-11300}{1234}=-9.16 \mathrm{Jmole}^{-1}
$$

The change in entropy in the surrounding will be

$$
\begin{gathered}
\Delta S_{\text {surr }}=-\left(\frac{\Delta H_{\text {system }}}{1000}\right) \\
\Delta H_{\text {system }}=\int_{1000}^{1234} C_{P}(l) d T-\Delta H_{f} \int_{1234}^{1000} C_{P}(s) d T
\end{gathered}
$$

But given that:

$$
\begin{gathered}
C_{P}(l)=C_{P}(s) \\
\Delta H_{\text {system }}=-\Delta H_{f}
\end{gathered}
$$

Thus,

$$
\Delta S_{\text {surr }}=\frac{11300}{1000}=11.300
$$

Hence total entropy change will be

$$
\begin{gathered}
\Delta S_{\text {total }}=\Delta S_{\text {system }}+\Delta S_{\text {surr }} \\
=-9.160+11.300=2.14 \mathrm{JK}^{-1}
\end{gathered}
$$

Note:

- Entropy, like energy, is a fundamental thermodynamic concept.
- Entropy is not directly measurable.

$$
\Delta S_{t o t}=\Delta S_{s y z}+\Delta S_{s u t r}=\frac{q_{r}}{T}+\frac{-q}{T}=\frac{q_{r}-q}{T}
$$

Corollary: Consider one mole of a perfect gas.


Therefore $S$ is a state function for a perfect gas
More general arguments of this type enable us to show that entropy is a state function for all substances

## Thoughtful Example:

A 1 mol piece of copper at 400 K is brought in contact with another 1 mol piece of copper at 300 K and allowed to reach thermal equilibrium. The entropy change for this process is $\qquad$ (in $J K^{-1}$ to three decimal places)

Given: Specific heat capacity of copper (between 250 K and 500 K ) is $22.6 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$. Assume that the system containing the two pieces of copper remains isolated during this process.

Solution:

| 1 mol Cu 400 K | 1 mol Cu 300 K |
| :---: | :---: |

$$
\Delta s=n C_{p} \ln \left(\frac{T_{e q}}{T_{1}}\right)
$$

Here,

$$
\begin{gathered}
T_{e q}=\left(\frac{T_{1}+T_{2}}{2}\right)=350 \\
\Delta S_{T}=\Delta S_{1}+\Delta S_{2}
\end{gathered}
$$

$$
\Delta S_{T}=22.6 \ln \left(\frac{350}{400}\right)+22.6 \ln \left(\frac{350}{300}\right)
$$

$$
\Delta S_{T}=0.466
$$

## Thoughtful Example:

Air of mass 1 kg , initially at 300 K and 10 bar , is allowed to expand isothermally till it reaches a pressure of 1 bar . Assuming air as an ideal gas with gas constant of $0.287 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$, the change in entropy of air (in $\mathrm{kJ} / \mathrm{kg} \mathrm{K}$, round off to two decimal place) is $\qquad$ .

## Solution:

Isothermal expansion takes place:

$$
\Delta s=C_{p} \ln \left(\frac{T_{2}}{T_{1}}\right)-R \ln \left(\frac{P_{2}}{P_{1}}\right)
$$

Here,

$$
\begin{gathered}
T_{2}=T_{1} \\
\Delta s=-0.87 \ln \frac{1}{10} \mathrm{~kJ} / \mathrm{kgK}=0.66 \mathrm{~kJ} / \mathrm{kgK}
\end{gathered}
$$

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