Chemical Thermodynamics - II

BASICS | Section - 1

1. Heat Capacity :

Heat Capacity (C) : Heat required to raise the temperature of a system by 1°C or 1 K.

Units : J/K; kJ/K

Specific Heat Capacity (c) : Heat required to raise the temperature of a 1gm of a system by 1°C or 1 K.

Units : J/g/K; kJ/Kg/K

Molar Heat Capacity (C_m) : Heat required to raise the temperature of a 1 mole of a system by 1°C or 1 K.

Units : J/mole/K; kJ/mole/K

Mathematically, the above quantities are defined as :

$$q = C \times \Delta T; \qquad q = n \times C_m \times \Delta T; \quad q = m \times c \times \Delta T$$

where q = amount of heat absorbed by the system; ΔT = Rise in the temperature; m = mass of the system; n = moles of the system

Note : Molar heat capacity has 2 forms : C_P (at constant pressure) and C_v (at constant volume) defined as :

$$C_P = \left(\frac{q}{\Delta T}\right)_P = \left(\frac{\Delta H}{\Delta T}\right)_P; \quad C_V = \left(\frac{q}{\Delta T}\right)_V = \left(\frac{\Delta U}{\Delta T}\right)_V \quad [\because \Delta H = q_P ; \Delta U = q_V]$$

The subscript after the brackets in the above equation denotes the parameter kept constant during the process.

i.e. $\left(\frac{\Delta H}{\Delta T}\right)_P$ denotes change in Enthalpy per unit change in Temperature keeping Pressure constant.

In terms of *differentials* :

$$C_P = \left(\frac{dq}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P; \quad C_V = \left(\frac{dq}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \quad [\because dH = dq_P ; dU = dq_V]$$

Also, $C_P - C_V = R$; $\quad \frac{C_P}{C_v} = \gamma$

Illustration - 1 *The molar heat capacity of water in equilibrium with ice at constant pressure is :*

(A) *zero* **(B)** *infinity* (∞) **(C)** 40.45 $kJ\ K^{-1}\ mol^{-1}$ **(D)** 75.48 $kJ\ K^{-1}\ mol^{-1}$

SOLUTION :

We know that heat capacity at constant pressure is given by

$$C_P = \left(\frac{\Delta H}{\Delta T}\right)_P$$

Since the phase transformation i.e., ice ⇌ water, takes place at a fixed temperature so $\Delta T = 0$.

$\therefore \quad C_P = \frac{\Delta H}{0} = \infty \quad \therefore$ (B)

2. Reversible and Irreversible process :

Reversible process : Process which is carried out in such a manner that it could be reversed by an infinitesimal change. A reversible process takes infinitesimally small, infinite steps to complete and time taken to complete the process is infinite. So, it is a theoretical process and it sets a ceiling on the processes carried out practically.

Irreversible process : Process which doesn't satisfy the reversible criteria.

Examples of irreversible process :

1. Free expansion of gas
2. Melting of ice in warmer liquid
3. Anything that is real.

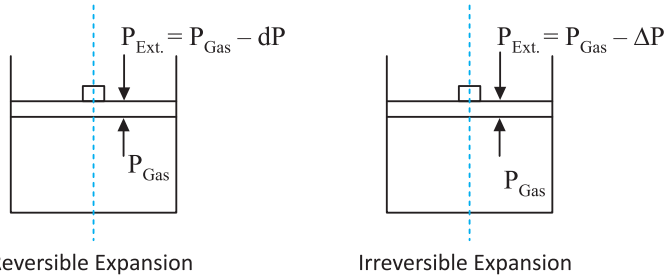
We can also define the reversible and irreversible process in a more of mathematical sense as follows :

Reversible process : Process in which there is an infinitesimally small difference between the driving force and opposing force.

Irreversible process : Process in which there is a finite difference between the driving force and opposing force.

For example :

(i) Consider the following two diagrams showing reversible and irreversible expansions :

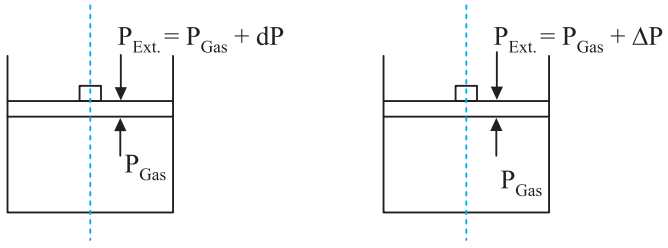


Reversible Expansion Irreversible Expansion

Here, Opposing force is $P_{Ext.}$ and Driving force is P_{Gas}.

(ii) Consider the following two diagrams showing reversible and irreversible compressions :

Here, Driving force is $P_{Ext.}$ and Opposing force is P_{Gas}.



Reversible Compression Irreversible Compression

Note : ➤ In many cases, an irreversible process can be easily recognized by using the fact that the process involving constant external pressure is an irreversible process.

➤ In a reversible process, an equilibrium exists (known as quasi-equilibrium) at every stage of the process.

3. Calculating Work (w) for Reversible and Irreversible process :

To calculate work, use the formula : $-w = \int P_{Ext.} dV$

(i) For an irreversible process, P_{Ext} is constant, thus $-w = P_{Ext.}\Delta V$ .... (iv)

(ii) For a reversible process, $P_{Ext.} = P_{Gas} \pm dP \Rightarrow -w = \int P_{Gas} dV \pm \int dP dV \approx \int P_{Gas} dV$

Thus, work (w) depends on the process equation i.e. how P_{Gas} and V varies in the process :

I. For Isothermal process : $-w = 2.303nRT\log_{10}\left(\frac{V_2}{V_1}\right) = 2.303nRT\log_{10}\left(\frac{P_1}{P_2}\right)$ $[\because P_1V_1 = P_2V_2]$

II. For Adiabatic process : $-w = \frac{(P_1V_1 - P_2V_2)}{(\gamma - 1)} = -\Delta U = -nC_v(T_2 - T_1)$

where $\gamma = \frac{C_p}{C_v}$ (ratio of molar heat capacities at constant P and constant V)

(a) Monoatomic gas: $C_p = \frac{5}{2}R, C_v = \frac{3}{2}R, \gamma = 1.66$

(b) Diatomic gas : $C_p = \frac{7}{2}R, C_v = \frac{5}{2}R, \gamma = 1.40$

(c) Polyatomic gas : $C_p = 4R, C_V = 3R, \gamma = 1.33$

III. For Isochoric process : $-w = 0$

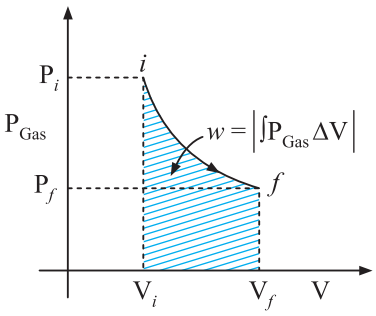
IV. For Isobaric process : $-w = P_{Gas}\Delta V$

Note : Work done by system in a reversible expansion process will always be greater than that in irreversible expansion process.

4. Graphical interpretation of Work :

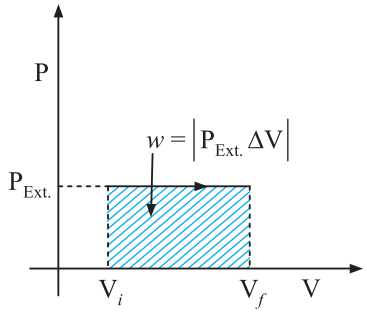
(i) For a reversible process :

Work can also be graphically calculated for a reversible process.
It is the area under Pressure vs. Volume diagram as shown:



(ii) For an irreversible process :

For an irreversible process, Pressure vs. Volume graph cannot be plotted.
However, we can represent the irreversible work ($P_{Ext.}\Delta V$) on a
Pressure vs. Volume diagram as shown :



5. Types of Irreversible expansion :

(i) **Free expansion** : Expansion of a gas against vaccum (i.e. $P_{Ext.} = 0$)

(ii) **Intermediate expansion** : Expansion of a gas when $P_{Ext.} \neq 0$

6. Calculate w, q, ΔH and ΔU for a process and a reaction :

Clearly, we need to create 4 equations to solve 4 variables (w, q, ΔH and ΔU) as follows :

Whether it is a process or a reaction, the first equation will always be applicable :

$q = \Delta U + (-w)$ .... (i) [From First law of Thermodynamics]

Calculating ΔH and ΔU will be different in case of a process and a reaction and explained as follows :

(i) **For a process :**

$\Delta H = nC_P\Delta T$ .... (ii) [From definition of C_P]

or $\Delta H = \int_{T_1}^{T_2} nC_P dT$ [When C_P is also a function of Temperature]

$\Delta U = nC_V\Delta T$ .... (iii) [From definition of C_V]

or $\Delta U = \int_{T_1}^{T_2} nC_V dT$ [When C_V is also a function of Temperature]

Also, $\Delta H = \Delta U + \Delta(PV)$ or $dH = dU + dPV + VdP$ [$\because$ $H = U + PV$]

Many a times, we also write : $\Delta(PV) = P_2V_2 - P_1V_1 = \Delta(nRT) = nR\Delta T$

(ii) **For a reaction :**

For a reaction, ΔH is the most important parameter and can be calculated as :

$\Delta_r H = \sum H_{Products} - \sum H_{Reactants}$ .... (ii)

Also, $\Delta_r H = \Delta_r U + P\Delta V$ [As Chemical reactions occur at constant pressure and constant temperature]

or $\Delta_r H = \Delta_r U + \Delta n_g RT$ .... (iii)

Thus, to get the interconversion between $\Delta_r H$ and $\Delta_r U$,we must need to write down the balanced chemical reaction with states of all the reactants and products and then calculate the change in the number of gaseous moles.

The fourth variable can be calculated based on the process / situation as explained in the illustrations below :

7. Calculating final temperature T_2 in a reversible and irreversible adiabatic expansion processes :

(i) For a reversible adiabatic expansion process, use : $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ or $P_1^{1-\gamma} T_1^{\gamma} = P_2^{1-\gamma} T_2^{\gamma}$

(ii) For an irreversible adiabatic expansion process, we cannot use the equation : $TV^{\gamma-1} = \text{const.}$ or $P^{1-\gamma}T^{\gamma} = \text{const.}$ We have to find another way out (use first law of thermodynamics).

Proceed as follows : $q = 0 = \Delta U + (-w)$ [$\because$ Adiabatic process and using First Law of Thermodynamics]

$\Rightarrow$ $0 = nC_V(T_2 - T_1) + P_{Ext.}\Delta V$ [$\because$ $-w = P_{Ext.}\Delta V$]

$\Rightarrow$ $0 = nC_V(T_2 - T_1) + P_{Ext.}(V_2 - V_1)$

$$\Rightarrow \qquad 0 = nC_V\left(T_2 - T_1\right) + P_{Ext.}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right) \Rightarrow \qquad T_2 = \left[\frac{C_V + \left(\frac{P_{Ext.}}{P_1}\right).R}{C_V + \left(\frac{P_{Ext.}}{P_2}\right).R}\right] T_1$$

where $P_{Ext.}$ is the constant pressure against which system is doing work.

If $P_2 = P_{Ext.}$ (i.e. system expands to external pressure) $\Rightarrow \qquad T_2 = \left[\frac{C_V + \left(\frac{P_{Ext.}}{P_1}\right).R}{C_V + R}\right] T_1$

Illustration - 2 *1 mole of an ideal gas at 400 K and 10 atm is allowed to expand, adiabatically, against 2.0 atm external pressure. Find the final temperature of the gas.* $\left[Use : C_V = \frac{5}{2}R\right]$

SOLUTION : Finally $P_2 = P_{Ext.}$ and $\because \quad \Delta U = -P_{ext}\,\Delta V \quad (as\ \Delta q = 0)$

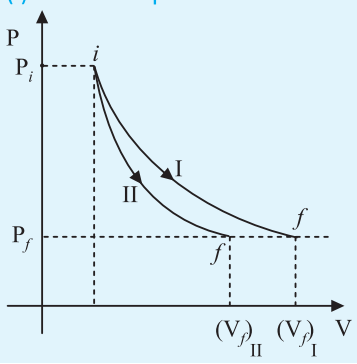
$$n\,C_V\,(T_2 - T_1) = -2\left(\frac{nRT_2}{2} - \frac{nRT_1}{10}\right)$$

$$\Rightarrow \qquad T_2 = \left[\frac{\frac{5}{2}R + \frac{2}{10}R}{\frac{5}{2}R + R}\right] \times 400\,K = \left[\frac{2.7\,R}{3.5\,R}\right] \times 400\,K = 308.6\,K$$

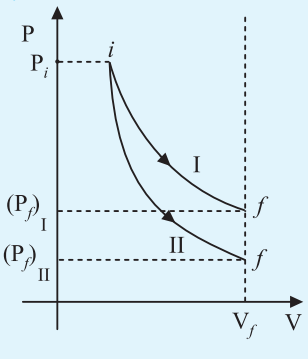
8. Comparison between reversible isothermal and reversible adiabatic process :

We can compare reversible isothermal (I) and reversible adiabatic (II) process for two cases through P–V diagram as follows :

(i) same final pressure



(ii) same final volume



Clearly, work done in reversible isothermal process is greater than in reversible adiabatic process.

Also, we can see that in case (i), final volume is greater in reversible isothermal process and in case (ii) final pressure is greater in reversible isothermal process.

Note : ➤ Sometimes P–V diagrams come as a handy tool to calculate the final conditions rather than doing rigorous calculations.

➤ Adiabatic curves are steeper than isothermal curves [$m_{adiabatic} = \gamma\, m_{isothermal}$ where 'm' denotes slope].

Illustration - 3 $1m^3$ *of neon gas* $\left(C_v = \frac{3}{2}R\right)$ *at* 273.2 *K and* 10 *atm undergoes three different expansions to a final pressure of* 1 *atm. Calculated the final volume and the work done in three different expansions.*

(i) *Isothermal reversible expansion* **(ii)** *Adiabatic reversible expansion*

(iii) *Irreversible adiabatic expansion*

SOLUTION :

(i) Final volume, $V_2 = \frac{P_1V_1}{P_2} = \frac{(1)(10)}{(1)} = 10\,m^3$

The work done by the gas in expanding equals the heat absorbed by the gas from its surrounding.

$\therefore \quad -w = q = nRT\ln\frac{V_2}{V_1}$

$$n = \frac{10\times10^3}{0.0821\times273.2} = 446.1\,mol$$

$-w = (446.1)(8.314)(273.2)(2.303)\log_{10}10$

$= 232.85$ kJ

(ii) For adiabatic reversible expansion,

$$V_2 = \left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}}\cdot V_1$$

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{3}{2}R+R}{\frac{3}{2}R} = \frac{5}{3}$$

$\therefore \quad V_2 = (10)^{3/5}(1) = 3.981\,m^3$

The final temperature is obtained from $P_2V_2 = nRT_2$

$$T_2 = \frac{P_2V_2}{nR} = \frac{(1)\left(3.981\times10^3\right)}{(446.1)0.0821} = 108.8\,K$$

For an adiabatic process, $q = 0$ & $\Delta E = w$

$$w = nC_V\left(T_2-T_1\right) = \left(n\frac{3}{2}R\right)\left(T_2-T_1\right)$$

$$= (446.1)\left(\frac{3}{2}R\right)(108.8-273.2) = -914.1\,kJ$$

(iii) For irreversible adiabatic expansion,

$$-C_V\left(T_2-T_1\right) = nR\,P_2\left(\frac{T_2}{P_2}-\frac{T_1}{P_1}\right)$$

$$-\frac{3}{2}\left(T_2-273.2\right) = nR\,(1)\left(\frac{T_2}{1}-\frac{273.2}{10}\right)$$

$\therefore \quad T_2 = 174.8\,K$

$\therefore \quad \Delta E = w = \frac{3}{2}nR\,(174.8-273.2) = -547.4\,kJ$

Note that there is considerable less cooling of the gas and less work is done by the gas in the irrevarsible adiabatic expansion than in the reversible adiabatic expansion.

Illustration - 4 A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in process ?

SOLUTION :

$$n = \frac{PV}{RT} = \frac{1.25\times1}{0.0821\times300} = 0.05$$

$TV^{\gamma-1}$ = constant for adiabatic process

$\therefore \quad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

On solving, $T_2 = 188.55\,K$

$\Delta H = nC_P\Delta T = -0.05\times20.794\times111.45 = -115.87\,J$

Illustration - 5 *An ideal gas having initial pressure P, volume V and temperature T is allowed to expand adiabatically until volume becomes 5.66 V while its temperature falls to T/2.*

(i) *What is the atomicity of gas molecules.*

(ii) *Obtain an expression for the work done by the gas during the expansion as a function of the initial pressure P and volume V.*

SOLUTION :

For a adiabatic process,

$$TV^{\gamma-1} = \text{constant}$$

$$\therefore \quad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} = \frac{T_1}{2}(5.66\,V_1)^{\gamma-1}$$

Hence, $2 = (5.66)^{\gamma-1}$ or $\log 2 = (\gamma-1)\log 5.66$ $\quad\therefore\quad$ $\gamma = 1.4$

The gas is, therefore a diatomic gas.

The work done by a gas during an adiabatic process is $W = \dfrac{P_2V_2 - P_1V_1}{\gamma-1}$

Since $P_1V_1^{\gamma} = P_2V_2^{\gamma} = P_2(5.66\,V_1)^{\gamma}$

$$P_2 = \frac{P_1}{(5.66)\gamma} \qquad \therefore \qquad W = \left[\frac{P_1(5.66\,V_1)^{\gamma}}{(5.66)^{\gamma}} - P_1V_1\right]\frac{1}{0.4} = 1.25\,P_1V_1 \text{ or } W = 1.25\,PV$$

9. Second Law of Thermodynamics :

It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done the machine by some outside agency.

Second law of Thermodynamics also helps in predicting the spontaneity of a reaction/process.

A process which proceeds of its own accord without any outside help is termed as a spontaneous process. To understand the concept of spontaneity, we first need to understand the most important factor involved which is Entropy (S) and is explained below :

(i) Entropy (S) :

Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the system. More is the randomness in the system, more is the entropy of the system.

(i) Entropy is a state function and depends only on initial and final states of the system.

(ii) Entropy change of the system for a reversible process is mathematically defined as :

$$dS = \frac{dq_{Rev}}{T} \quad \text{or} \quad \Delta S = \int\frac{dq_{Rev}}{T} = \left(\frac{q_{Rev}}{T}\right) \text{ [when the heat is absorbed reversibly at constant T]}$$

If heat is absorbed, then ΔS is positive (increase in entropy). If heat is released, then ΔS is negative (decrease in entropy). Also, for the same amount of heat absorbed, increase in entropy will be more at lower temperature than at higher temperature.

(iii) If the temperature of a system increases, entropy increases. If the temperature of a system decreases, entropy decreases.

(ii) Criteria for Spontaneity :

First law of thermodynamics is basically the law of conservation of energy. It has no restriction on the way energy can flow. Thus, energy can flow from higher to lower temperature or lower to higher temperature, as per first law of thermodynamics. But, natural processes tend to flow only in one direction (known as direction of spontaneity).

A chemical reaction or process tends to follow the direction of minimum energy and maximum randomness, i.e. reaction will be more probable to occur if it is exothermic or there is an increase in entropy. A reaction will occur if the value of ΔH is negative and the value of ΔS is positive. But the endothermic reactions in which ΔH is positive, also take place. There are also reactions in which there is decrease in entropy, i.e., ΔS is negative but still they occur. It is, thus, clear that for the spontaneity of a reaction both ΔH and ΔS should be considered simultaneously.

Thus, for processes which do not involve a heat change, increase in entropy is the only criteria. It should be noted that the criterias for the prediction of direction of spontaneity have been derived through mere observations. No process/reaction has been found to violate these.

Illustrating the Concept:

Consider the adiabatic expansion of an ideal gas in vaccum. This system is an isolated system (as no exchange of energy and mass between system and surroundings). So, direction of spontaneity is expansion process because expansion will cause an increase in the entropy of the system.

(iii) Finding the direction of spontaneity :

For spontaneity, Second Law of Thermodyamics defines the following statements:

(i) In an isolated system, direction of increase in entropy of the system is the direction of spontaneity.

(ii) In a non-isolated system, direction of increase in total entropy i.e. $\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surroundings}$, is the direction of spontaneity.

$\Rightarrow$ For a reaction/process to be spontaneous: $\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surroundings} > 0$

To focus on the system for thermodynamic analysis, $\Delta S_{Surroundings}$ is defined and eliminated as :

(a) For a reaction :

$$\Delta S_{Surroundings} = \frac{q_{Surroundings}}{T} = \frac{-q_{System}}{T}$$

$$\Delta S_{Surroundings} = \frac{-\Delta H_{System}}{T} \qquad \text{[Chemical reactions occur at constant T and P]}$$

$$\Rightarrow \quad \Delta S_{Total} = \Delta S_{System} - \frac{\Delta H_{System}}{T} \quad \Rightarrow \quad -T\Delta S_{Total} = \Delta H_{System} - T\Delta S_{System}$$

(b) For a process :

$$\Delta S_{Surroundings} = \frac{q_{Surroundings}}{T} = \frac{-q_{System}}{T}$$

$$\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surroundings} \qquad \text{[In a short while, we will learn to calculate } \Delta S_{System}\text{]}$$

Also, a new thermodynamic function, Gibbs energy 'G' is introduced to check the spontaneity of the reaction directly and is defined as :

$$G = H - TS$$

$\Rightarrow \quad \Delta G = \Delta H - \Delta(TS) \quad$ or $\quad dG = dH - TdS - SdT$

Thus, for a reaction taking place at a certain temperature, we can also define spontaineity of a reaction in terms of change in Gibbs energy as : $\Delta G_{System} = -T\Delta S_{Total} = \Delta H_{System} - T\Delta S_{System}$

(i) If $\Delta S_{Total} > 0 \Rightarrow \Delta G_{System} < 0$ [Spontaneous]

(ii) If $\Delta S_{Total} < 0 \Rightarrow \Delta G_{System} > 0$ [Non- spontaneous]

(iii) If $\Delta S_{Total} = 0 \Rightarrow \Delta G_{System} = 0$ [At Equilibrium]

The free energy of a reaction is the chemical analogue of 'potential energy' of mechanical systems. A body moves in the direction in which there is decrease in potential energy. Similarly, in chemical system, the substance moves in a direction in which there is decrease in free enrgy, i.e., ΔG is negative.

For any system in which a reaction/process taking place, $\Delta G = 0$ denotes the attainment of equilibrium. In other words, a reaction/process proceeds till its entropy has become maximum i.e. no furthur change in entropy is possible. A very famous example is the mixing of two ideal gases which happens till the new system has become homogenous (because in that state only it will have maximum entropy).

(iv) Calculating entropy change in phase change :

When a substance changes phase (e.g., solid to liquid), there is a change in entropy associated with it (even though temperature is constant at phase change).

(a) Melting : $\Delta S_{melting} = \dfrac{\Delta H_{melting}}{T_{melting}}$ = Entropy change due to melting (takes place at constant temperature)

e.g. Entropy change for 1 kg ice at its melting point :

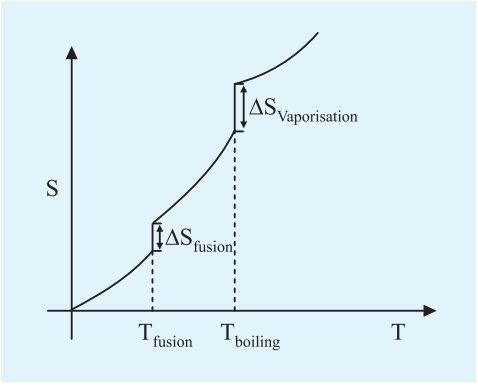
$\Rightarrow \quad \Delta S_{melting} = \dfrac{\left(\frac{1000}{18}\right) \times 6 \times 1000}{273} = 1220.8 \text{ J/K}$ [Enthalpy of fusion of water = 6 kJ/mole]

(b) Vaporisation : $\Delta S_{vaporisation} = \dfrac{\Delta H_{vaporisation}}{T_{boiling}}$

e.g. Entropy change for 1 kg water at its boiling point :

$\Delta S_{vaporisation} = \dfrac{\left(\frac{1000}{18}\right) \times 44 \times 1000}{373} = 6552.8 \text{ J/K}$

[Enthalpy of vaporisation of water = 44 kJ/mole]



(c) Allotropic Transition : $\Delta S_{Transition} = \dfrac{\Delta H_{Transition}}{T_{Transition}}$

e.g. Transition of 1 mole of Sulphur from Rhombic to Monoclinic :

$\Delta S_{transition} = \dfrac{402}{368.5} = 1.09 \text{ JK}^{-1} \text{ mol}^{-1}$

[Enthalpy of transition from rhombic to monoclinic Sulphur = 402 J mole^{-1} and $T_{transition} = 368.5$ K]

Illustration - 6 *A mole of steam is condensed at 100°C, the water is cooled to 0°C and frozen to ice. What is the difference in entropies of the steam and ice? The heats of vaporization and fusion are 540 cal gm^{-1} and 80 cal gm^{-1} respectively. Use the average heat capacity of liquid water as 1 cal gm^{-1} degree^{-1}.*

SOLUTION :

Entropy change during condensation of steam

$$\Delta S_1 = \frac{18\times540}{373}\text{cal}/^\circ = -26.06\,\text{cal}/^\circ$$

Entropy change during cooling of water from 100°C to 0°C

$$\Delta S_2 = 18\times11\text{n}\frac{273}{373}\text{cal}/^\circ = -5.62\,\text{cal}/^\circ$$

Entropy change during freezing of water at 0°C

$$\Delta S_3 = -\frac{18\times80}{273}\text{cal}/^\circ = -5.27\,\text{cal}/^\circ$$

So total entropy change $= -26.06 - 5.62 - 5.27 = -36.95\,\text{cal}/^\circ$

Hence differece in entropy between steam and ice $= 36.95\,\text{cal}/^\circ$

(v) Calculating ΔS for a process :

To calculate ΔS_{system} for a reversible process, proceed as follows :

As per the definition : $dS = \frac{dq_{rev}}{T}$

$\Rightarrow$ $TdS = q_{rev} = dU + (-dw)$ [From First Law of Thermodynamics]

or $TdS = n\,C_v\,dT + P\,dV$ [$dU = nC_vdT$ and $dw = -PdV$]

or $TdS = n\,C_v\,dT + \frac{nRT}{V}\,dV \Rightarrow dS = \frac{nC_vdT}{T} + \frac{nR}{V}dV$

Integrating the above equation with appropriate limits, we get :

$$\Delta S_{System} = n\,C_v\,\ln\left(\frac{T_2}{T_1}\right) + n\,R\,\ln\left(\frac{V_2}{V_1}\right) \quad \text{and} \quad \Delta S_{Surroundings} = \frac{q_{Surr.}}{T_{Surr.}} = \frac{-q_{Sys.}}{T_{Surr.}}$$

Note : Although the above relation has been derived assuming the process to be reversible but this relation can also be used for an irreversible process as well since Entropy change is a state function.

Illustration - 7 *Calculate the total entropy change for the following reversible processes :*
(a) *Isothermal* **(b)** *Adiabatic.*

SOLUTION :

Entropy change for a process is given by : $\Delta S_{system} = n\,C_V\,\ell n\frac{T_2}{T_1} + nR\,\ell n\frac{V_2}{V_1}$; $\Delta S_{surrounding} = \frac{-q_{system}}{T_{surr.}}$

(a) For isothermal process : $T_2 = T_1$

$\Rightarrow$ $\Delta S_{system} = n\,R\,\ell n\frac{V_2}{V_1}$ and $\Delta S_{surroundings} = \frac{-q_{system}}{T_{surr}} = \frac{-n\,R\,T\,\ell n\frac{V_2}{V_1}}{T} = -n\,R\,\ell n\frac{V_2}{V_1}$

[$\because$ $q_{system} = nRT\ell n\frac{V_2}{V_1}$ for isothermal process]

$\Rightarrow$ $\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings} = 0$

(b) For adiabatic process : $\Delta S_{system} = n C_V \ell n \frac{T_2}{T_1} + n R \ell n \frac{V_2}{V_1}$

$$= \frac{nR}{(\gamma - 1)} \ell n \frac{T_2}{T_1} + n R \ell n \frac{V_2}{V_1}$$

Also, $TV^{\gamma-1} = \text{const.} \Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

$\Rightarrow \Delta S_{system} = \frac{nR}{(\gamma-1)} \ell n \left[\left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] + n R \ell n \frac{V_2}{V_1} = 0$ and $\Delta S_{surroundings} = \frac{-q_{system}}{T_{surr.}} = 0$

[$\because$ $q = 0$ in adiabatic process]

$\Rightarrow \Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings} = 0$

Note :
- $\Delta S_{system} = n C_V \ell n \frac{T_2}{T_1} + n R \ell n \frac{V_2}{V_1}$ for both reversible and irreversible process since ΔS is a state function.
- ΔS_{system} for irreversible adiabatic process is > 0. This is because $(T_2)_{\text{Reversible adiabatic}} \neq (T_2)_{\text{Irreversible adiabatic}}$
- $\Delta S_{Total} = 0$ for any reversible process and $\Delta S_{Total} > 0$ for any irreversible (i.e. spontaneous) process.

The table below shows the ΔS_{system} and $\Delta S_{surroundings}$ for some of the famous type of processes in thermodynamics :

Process	ΔS_{System}	$\Delta S_{Surrounding}$	Sign of ΔS_{Total}
Reversible Isothermal	$n R \ln \left(\frac{V_2}{V_1}\right)$	$-n R \ell n \left(\frac{V_2}{V_1}\right)$	$=0$
Irreversible Isothermal	$n R \ell n \left(\frac{V_2}{V_1}\right)$	$\frac{-P_{Ext.}\Delta V}{T}$	>0
Reversible Adiabatic	0	0	$=0$
Irreversible Adiabatic	$n C_v \ell n \left(\frac{T_2}{T_1}\right) + n R \ell n \left(\frac{V_2}{V_1}\right)$	0	>0
Reversible Isobaric	$n C_P \ell n \left(\frac{T_2}{T_1}\right)$	$-n C_P \ell n \left(\frac{T_2}{T_1}\right)$	$=0$
Reversible Isochoric	$n C_v \ell n \left(\frac{T_2}{T_1}\right)$	$-n C_v \ell n \left(\frac{T_2}{T_1}\right)$	$=0$

(vi) Entropy change due to isothermal mixing of two gases (at constant P) :

Consider the following diagram which shows two gases before and after mixing :

To find the change in entropy of the system due to mixing, proceed as follows :

$$\Delta S_{\text{Gas1 due to mixing}} = n_1 R\,\ell n\,\frac{V_1+V_2}{V_1} = n_1 R\,\ell n\left(\frac{1}{\chi_1}\right) \qquad \text{[For ideal gases : n } \alpha \text{ V at const T and P]}$$

$$\Delta S_{\text{Gas2 due to mixing}} = n_2 R\,\ell n\,\frac{V_1+V_2}{V_2} = n_1 R\,\ell n\left(\frac{1}{\chi_2}\right) \qquad \text{[For ideal gases : n } \alpha \text{ V at const T and P]}$$

Total change in entropy of the system :

$$\Delta S_{\text{system (mixing)}} = \Delta S_{\text{Gas1due to mixing}} + \Delta S_{\text{Gas2 due to mixing}}$$
$$= -n_1 R\,\ell n\,\chi_1 - n_2 R\,\ell n\chi_2 = -R\,[n_1\,\ell n\,\chi_1 + n_2\,\ell n\,\chi_2]$$

Thus, in general, $\Delta S_{\text{system (mixing)}} = -R\sum n_i\,\ell n\,\chi_i$

The above expression can also be expressed as :

$$\Delta S_{\text{system (mixing)}} = -R\,(n_1+n_2)\left[\frac{n_1}{(n_1+n_2)}\ell n\,\chi_1 + \frac{n_2}{(n_1+n_2)}\ell n\,\chi_2\right] = -R\left(\sum n_i\right)\left[\chi_1\,\ell n\,\chi_1 + \chi_2\,\ell n\,\chi_2\right]$$

$$\Delta S_{\text{system (mixing)}} = -R\left(\sum n_i\right)\left(\sum \chi_i\,\ell n\,\chi_i\right)$$

Illustration - 8 *Two vessels divided by a partition contain one mole of N_2 and two moles of O_2 gas. If partition is removed and gases mixed isothermally, find the change in entropy due to mixing assuming initial and final pressure are same.*

SOLUTION : Using $\Delta S_{\text{system (mixing)}} = -R\sum n_i\,\ell n\,\chi_i$

$$= -R\left(1\times \ell n\left(\frac{1}{3}\right) + 2\times \ell n\left(\frac{2}{3}\right)\right) = -R\left(\ell n 3 + 2\,\ell n\left(\frac{3}{2}\right)\right) = 8.314(1.0+2\times 0.4) = 15.9\ \text{JK}^{-1}$$

(vii) Calculating entropy for a substance :

First of all, we need to know an important law helpful in finding the entropy of a substance i.e. Third Law of Thermodynamics. As per Third Law of Thermodynamics (also knows as Nernst heat theorem) :

(a) All substance have same heat capacities at 0 K.

(b) Heat capacity of every substance is zero at 0 K.

(c) Entropy of a perfectly crystalline substance is zero at 0 K.

This law provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is the absolute entropy.

Illustration - 9 *A sample of an ideal gas is expanded to twice its original volume of $1m^3$ in a reversible process for which $P = \alpha V^2$ where $\alpha = 5atm/m^6$. If $C_{V,m} = 20\ J\ mol^{-1}\ K^{-1}$, determine molar change in entropy (ΔS_m) for the process.*

SOLUTION :

Using : $\Delta S = nC_V \ell n \frac{T_2}{T_1} + nR \ell n \frac{V_2}{V_1}$ $(n = 1)$

and $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{T_2}{T_1} = \frac{P_2}{P_1} \cdot \frac{V_2}{V_1} = \frac{V_2^3}{V_1^3}$ $(\because P = \alpha V^2) = 8\ (\because V_2 = 2V_1)$

$\Rightarrow$ $\Delta S = 1 \times 20 \times \ell n\ 8 + 8.314\ \ell n\ 2 = 45.8\ J\ mol^{-1}\ K^{-1}$

(viii) Calculating $\Delta_r G$ for a process :

By definition : $G = H - TS \Rightarrow dG = dH - TdS - SdT$ .... (i)

Also, $H = U + PV \Rightarrow dH = dU + PdV + VdP$ .... (ii) and $dq = dU + (-dw)$ .... (iii)

and $TdS = dq$ .... (iv)

Using (i), (ii) (iii) and (iv), we have : $dG = VdP - SdT$

(a) **For a process at constant pressure :** $dP = 0 \Rightarrow dG = -SdT \Rightarrow \left(\frac{dG}{dT}\right)_P = -S$

Since 'S' is always positive, above equation tells us that as temperature increases keeping pressure constant, Gibbs energy decreases with rise in temperature.

(b) **For a process at constant temperature :** $dT = 0 \Rightarrow dG = VdP \Rightarrow \left(\frac{dG}{dP}\right)_T = V$

Thus, at constant temperature, Gibbs energy increases with a rise in pressure since 'V' is always positive.

Illustration - 10 *1.0 mol of an ideal gas, initially present in a 2.0 L insulated cylinder at 300 K is allowed to expand against vacuum to 8.0 L. Determine, w, ΔU, ΔH, ΔS_{Total} and ΔG.*

SOLUTION :

$w = -P_{ext}\Delta V = 0;\ q = 0$ (Insulated Cylinder) $\Rightarrow$ $\Delta U = 0 = \Delta H$

$\Rightarrow$ $T_f = 300\ K$

$\Delta S_{sys} = nR \ln \frac{V_2}{V_1} = 2R \ln 2 = 11.52\ JK^{-1}$

and $\Delta S_{surr} = 0$ $\because q_{sys} = q_{surr} = 0$

$\Rightarrow$ $\Delta S_{Total} = 11.52\ JK^{-1} \Rightarrow \Delta G = -T\Delta S_{Total} = -300 \times 11.52 = -3456\ J.$

Illustration - 11 *Which of the following processes thermodynamic relation(s) is (are) correct?*

(A) *In a cyclic process,* $\oint dS = 0$ **(B)** $\Delta G = \Delta H - T\Delta S$

(C) $\left(\frac{\partial G}{\partial T}\right)_P = -S$ **(D)** $\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$, Q = Reaction quotient

SOLUTION :

As we know for a cyclic process

$$\oint dS = 0$$

Also $dG = Vdp - SdT$

$$\Rightarrow \quad \frac{dG}{dT} = \frac{VdP}{dT} - S$$

For constant pressure

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$\Delta G = \Delta H - T\Delta S$ true for a reaction only.

$\Delta G = \Delta G^\circ + RT\,\ell n\, Q$ true for a reaction only.

Illustration - 12 *Calculate the entropy change per mole of substance in each of the following cases.*

(i) *The freezing of isobutane at* $-160^\circ C$. $\Delta H(Solid \longrightarrow Liquid) = 4540\ J\ mol^{-1}$.

(ii) *The vaporization of water at its boiling point,* $100^\circ C$. $\Delta H(Liquid \longrightarrow Vapour) = 407\ kJ\ mol^{-1}$.

(iii) *Expansion reversibly and isothermally of an ideal gas from a volume of* $2\ dm^3$ *to* $10\ dm^3$ *at* $27^\circ C$. *Also calculate entropy change of surroundings due to the process.*

(iv) *Expansion irreversibly and isothermally of an ideal gas from* $2\ dm^3$ *to* $10\ dm^3$ *against a constant pressure of* $1\ atm$, *at* $27^\circ C$. *Also calculate entropy change of surrounding due to the process.*

SOLUTION :

(i) Freezing temperature of isobutane $= -160^\circ C = (-160 + 273)\,K = 113\,K$

$$\Delta S = \frac{q_{rev}}{T}$$

Here $q_{rev} = -4540\,J\,mol^{-1}$ $\quad\therefore\quad$ $\Delta S = \dfrac{-4540}{113} = -40.2\,JK^{-1}mol^{-1}$

Note that in freezing, the substance becomes more ordered. Hence, entropy is lost by the substance $(\Delta S$ is $-ve)$.

(ii) For the reversible vaporisation of water at $100^\circ C$,

$$\Delta S = \frac{q_{rev}}{T} = \frac{L}{T} = \frac{\Delta H_{vap}}{T} = \frac{407000}{373} = 1091.2\,JK^{-1}mol^{-1}$$

(iii) For an isothermal process, $\Delta S = R\ln\dfrac{P_1}{P_2}$

At constant temperature, $P_1V_1 = P_2V_2$

$$\therefore \quad \frac{P_1}{P_2} = \frac{V_2}{V_1} \quad\therefore\quad \Delta S = R\ln\frac{V_2}{V_1} = 8.314\times 2.303\log\frac{10}{2} = 13.4\,JK^{-1}mol$$

If we treat system and surroundings as an isolated system, entropy change of surrounding $= -\Delta S = -13.4\,J\,K^{-1}\,mol^{-1}$.

$\therefore$ For a reversible process entropy of universe remains constant. Total entropy change for isolated system = 0

(iv) Total entropy change of the system, has to be calculated assuming a reversible path,

$$\Delta S_{system} = \int\frac{dq_{rev}}{T} = R\ln\frac{V_2}{V_1} = 13.4\,J\,k^{-1}mol^{-1} \qquad \text{[Same as in (iii)]}$$

If we consider system and surrounding as an isolated system, entropy change of surrounding,

$$\Delta S_{surrounding} = \frac{\text{Heat exchanged by surrounding}}{T} = \frac{q}{T}$$

*7.★★ *The mixing of gases in always accompanied by an increase in entropy. In the formation of a binary mixture of two ideal gases the maximum entropy increases when the ratio of moles of gases is :*

(A) 1 : 2 **(B)** 1 : 3 **(C)** 2 : 3 **(D)** 1 : 1

8.★★ *The change in Gibbs energy accompanied by the isothermal reversible expansion of* 1 *mol of an ideal gas when it doubles it volume is* ΔG_1. *The change in Gibbs energy accompained by sudden isothermal irreversible doubling volume of* 1 *mole of the same gas* ΔG_2 *Ratio of* ΔG_1 *and* ΔG_2 *is :*

(A) 1 **(B)** 1/2 **(C)** –1 **(D)** –1/2

9. *When one mole of a monoatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of* 1 *atm, volume changes from* 1 *L to* 2 *L. The final temperature in kelvin would be :*

(A) $\frac{T}{2^{2/3}}$ **(B)** $T + \frac{2}{3 \times 0.0821}$ **(C)** T **(D)** $T - \frac{2}{3 \times 0.0821}$

10. 2 *moles of an ideal gas are expanded isothermally and reversibly from* 1 *L to* 10 *L at* 300 *k. What is the enthalpy change?*

(A) 4.98 *kJ* **(B)** 11.47 *kJ* **(C)** –11.47 *kJ* **(D)** 0 *kJ*

SOLUTIONS TO IN-CHAPTER EXERCISE

1. Using $PV = nRT \Rightarrow P_A = \frac{n_A RT_A}{V_A} = \frac{1 \times 0.082 \times 300}{24} = 1.02\,\text{atm}$

and $P_B = \frac{1 \times 0.082 \times 600}{24} = 2.04\,\text{atm}$; $P_C = \frac{1 \times 0.082 \times 300}{12} = 2.04\ \text{atm}$

$-w_{A \to B} = 0$ (Isochoric) ; $-w_{B \to C} = P_B \Delta V = 2.04(12 - 24)\,\text{Latm} \Rightarrow w_{B \to C} = 24.48\ \text{Latm} = 2.48\ \text{kJ}$ (Isobaric)

$-w_{C \to A} = nRT \ell n \frac{V_2}{V_1} = 1 \times 8.314 \times 300\ \ell n \frac{24}{12} \Rightarrow w_{C \to A} = -1.73\,\text{kJ}$ (Isothermal)

$\Rightarrow w_{net} = 0 + 2.45 - 1.73 = 0.72\ \text{KJ}$

2. $800 = \Delta U + 1 \times (14 - 4) \times 101.3 \Rightarrow \Delta U = 800 - 1013 = -213\ \text{J}$

3.(BCD) For a reversible adiabatic process, $PV^{\gamma} = \text{const.}; TV^{\gamma-1} = \text{const.}; P^{1-\gamma}.T^{\gamma} = \text{const.}$

4.(AB) $q = \Delta U + (-w) \Rightarrow 0 = 2 \times 1.5R\,(T_2 - 400) + 1 \times (10 - 1) \Rightarrow T_2 = 400 - \frac{9}{3R} = 363\,\text{K}$

If the process is under reversible conditions, work will be more $\Rightarrow$ T will be lesser

5.(ABD) Refer to theory

6.(ABCD) $2\text{Bar}, 300\text{K} \longrightarrow 4\text{Bar}$
$1\,\text{mole} \qquad\qquad 1\,\text{mole}$

$\frac{P}{V} = \text{const.} \Rightarrow P = V.\text{const.}$

$PV = nRT \Rightarrow P^2 = T.\text{ const.}$

$$\Rightarrow \frac{2^2}{300} = \frac{4^2}{T_2} \Rightarrow T_2 = 1200\text{K}$$

Now, $\Delta U = nC_V\Delta T = 1 \times 12.5 \times 900 = 11.25\text{ kJ}$

and $$-w = \int PdV = \int_{V_1}^{V_2} kV.dV = \frac{k}{2}\left[V_2^2 - V_1^2\right] = \frac{-1}{2}[P_1V_1 - P_2V_2] = \frac{1}{2}nR(T_2 - T_1) = 3.74\,\text{kJ}$$

$\Rightarrow$ $w = -3.74$ kJ and $q = 11.25 + 3.74 = 15$ kJ

7.(D) ΔS_{mixing} will be maximum when $\chi_{\text{gas}} = \frac{1}{2}$ (or equal) (Remember it as fact).

8.(A) ΔG is same because it is a state function.

9.(D) $$0 = 1 \times \frac{3}{2}R(T_2 - T) + 1 \times (2-1) \Rightarrow T_2 = T - \frac{2}{3 \times 0.082}$$

10.(D) $\Delta H = nC_P\Delta T = 0$

ANSWERS TO IN-CHAPTER EXERCISE

1.	$P_A = 1.02$ atm ; $P_B = 2.04$ atm ; $P_C = 2.04$; 0.72 kJ	**2.**	–213 J	**3.**	BCD	**4.** AB
5.	ABD	**6.**	ABCD	**7.**	D	**8.** A
9.	D	**10.**	D			