Chemical Thermodynamics - I

BASICS Section - 1

Internal Energy :

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, U of the system, which may change, when

heat passes into or out of the system,
work is done on or by the system,
matter enters or leaves the system.

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as : $\Delta U = q + w$ ....(i)

For a given change in state, q and w can vary depending on how the change is carried out. However, $q + w = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if $w = 0$ and $q = 0$, then $\Delta U = 0$.

The equation, $\Delta U = q + w$ is mathematical statement of the first law of thermodynamics, which states that *the energy of an isolated system is constant*.

Many chemical reactions involve the generation of gases capable of doing mechanical work or the generation of heat. It is important for us to quantify these changes and relate them to the changes in the internal energy. Let us see how!

Pressure-Volume work :

For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. If external pressure is p_{ex} which is greater than p, piston is moved inward till the pressure inside becomes equal to p_{ex}. Let this change be achieved in a single step and the final volume be V_f . During this compression, suppose piston moves a distance, l and is cross-sectional area of the piston is A (figure shown).

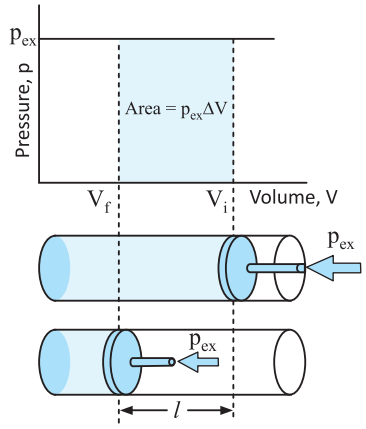

Figure : Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure, p_{ex} (in single step) is equal to the shaded area.

We also know, pressure $= \dfrac{\text{force}}{\text{area}}$ Therefore, force on the piston $= p_{ex} \cdot A$

If w is the work done on the system by movement of the piston then

$$w = \text{force} \times \text{distance} = p_{ex} \cdot A \cdot l = p_{ex} \cdot (-\Delta V) = -p_{ex}\,\Delta V = -p_{ex}\,(V_f - V_i) \quad \text{....(ii)}$$

The negative sign of this expression is required to obtain conventional sign for w, which will be positive. It indicates that in case of compression work is done on the system. Here $(V_f - V_i)$ will be negative and negative multiplied by negative will be positive.

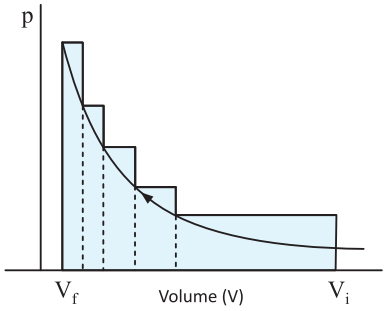

Figure : pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.

If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\sum p\Delta V$.

If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

$$w = -\int_{V_i}^{V_f} p_{ex}\,dV \qquad \ldots.(iii)$$

Here, p_{ex} at each stage is equal to $(p_{in} + dp)$ in case of compression. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., $p_{ex} = (p_{in} - dp)$. In general case we can write, $p_{ex} = (p_{in} \pm dp)$. Such processes are called reversible processes.

A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium state such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible are known as irreversible processes.

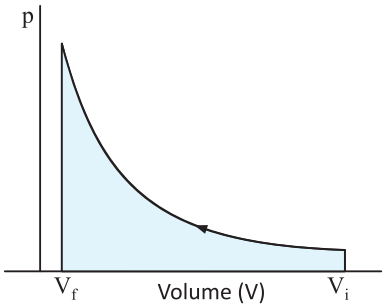

Figure : pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.

In chemistry, we face problems that can be solved if we relate the work term to the internal pressure of the system. We can relate work to internal pressure of the system under reversible conditions by writing equation (iii) as follows:

$$w_{rev} = -\int_{V_i}^{V_f} p_{ex}\,dV$$

Since dpxdV is very small we can write

$$w_{rev} = -\int_{V_i}^{V_f} p_{in}\,dV$$

Now, the pressure of the gas (p_{in} which we can write as p now) can be expressed in terms of its volume through ideal gas equation. For n mol of an ideal gas i.e., pV = nRT

$$\Rightarrow \qquad p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$w_{rev} = -\int_{V_i}^{V_f} nRT\frac{dV}{V} = -2.303\,nRT\log\frac{V_f}{V_i}$$

Free Expansion: Expansion of a gas in vacuum (p_{ex} = 0) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible (equation (ii) and (iii)).

Now, we can write equation (i) in number of ways depending on the type of processes.

Let us substitute $w = -p_{ex}\,\Delta V$ from equation (ii) in equation (i), and we get :

$$\Delta U = q - p_{ex}\,\Delta V$$

If a process is carried out at constant volume ($\Delta V = 0$), then

$$\Delta U = q_v$$

the subscript v in q_v denotes that heat is supplied at constant volume.

Isothermal and free expansion of an ideal gas :

For isothermal (T = constant) expansion of an ideal gas into vacuum : w = 0 since p_{ex} = 0. Also, Joule determined experimentally that q = 0 ; therefore, $\Delta U = 0$.

Equation $\Delta U = q + w$ can be expressed for isothermal irreversible and reversible changes as follows :

1. For isothermal irreversible change $q = -w = p_{ex}(V_f - V_i)$
2. For isothermal reversible change $q = -w = nRT\ln\frac{V_f}{V_i} = 2.303\,nRT\log\frac{V_f}{V_i}$
3. For adiabatic change, $q = 0$, $\Delta U = w_{ad}$
4. For isochoric process : $-w = 0$
5. For isobaric process : $-w = P_{gas}\,\Delta V$

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

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 :

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

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

Determination of 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 :

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

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

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

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 :

Illustration - 1 *Calculate w, q, ΔH and ΔU for an ideal gas expanding in vaccum (i) isothermally (ii) adiabatically.*

SOLUTION :

(i)
$w = 0$ [As $P_{Ext.} = 0$]
$\Delta H = \Delta U = 0$ [As T = constant for isothermal process]
$q = 0$ [Using First law of Thermodynamics]

(ii)
$q = 0$ [Adiabatic Process]
$w = 0$ [As $P_{Ext.} = 0$]
$\Delta U = 0$ [Using First law of Thermodynamics] $\Rightarrow$ T is constant
$\Delta H = 0$ [As T = constant]

Note : For an ideal gas, U = U(T) and H = H (T) but for real gas, U = U(T,V) and H = H (T, P)

Illustration - 2 *Five mole of an ideal gas at 293 K are expanded isothermally from an initial pressure 0.4 kPa to a final pressure of 0.1 kPa against a constant external pressure of 0.1 kPa.* ***(a)*** *Calculate q, w, ΔU and ΔH.* ***(b)*** *Calculate the corresponding value of q, w, ΔU and ΔH if the above process is carried out reversibly.*

SOLUTION :

(a) For an isothermal expansion against a constant pressure, we have:

$$-w = P_{Ext}(V_2 - V_1)$$

$$= P_{Ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right) = P_{Ext} nRT\left(\frac{1}{P_1} - \frac{1}{P_2}\right) \Rightarrow w = -9135\ J$$

Since temperature is constant: $\Delta U = 0, \Delta H = 0$
$q = -w = 9135\ J$ [Using First law of Thermodynamics]

(b) For isothermal reversible expansion :

$$-w = 2.303\ nRT \log_{10}\frac{P_1}{P_2} = 2.303 \times 5 \times 8.314 \times 293 \log_{10}\frac{0.4}{0.1} \Rightarrow w = -16888\ J$$

Since temperature is constant: $\Delta U = 0;\ \Delta H = 0,$
$q = -w = 16888\ J$ [Using First Law of Thermodynamics]

Illustration - 3 *The magnitude of enthalpy changes for reversible adiabatic expansion of a gas from volume V_1 to V_2 (in L) is ΔH_1 and for irreversible adiabatic expansion for the same expansion is ΔH_2. Then :*
(A) $\Delta H_1 > \Delta H_2$ ***(B)*** $\Delta H_1 < \Delta H_2$ ***(C)*** $\Delta H_1 = \Delta H_2$ ***(D)*** $\Delta H_1 = \Delta U_1$ *and* $\Delta H_2 = \Delta U_2$
where ΔU_1 and ΔU_2 are the changes in magnitudes for internal energy of gas in the two expansions.

SOLUTION : (A)

We know that work done in a reversible expansion process is always greater than in an irreversible

Using First Law of Therodynamics : $q = 0 = \Delta U + (-w)$

Thus, decrease in U will be larger in reversible adiabatic than irreversible adiabatic expansion and sin

conclude that ΔT in reversible adiabatic expansion will be greater than in irreversible adiabatic expa

Now, $\Delta H_1 = nC_p\Delta T_1$, and $\Delta H_2 = nC_P\Delta T_2$ $\Rightarrow$ $\Delta H_1 > \Delta H_2$

SPONTANEITY

Second Law of Thermodynamics :

It is impossible to construct a machine that is