CHAPTER 4

Thermodynamics

Thermodynamics (from the Greek thermos meaning heat and dynamis meaning power). The term thermodynamics was coined by Lord Kelvin in 1849. Historically, thermodynamics developed out of the need to increase the efficiency of early steam engines. Roughly, heat means "energy in transit" and dynamics relates to "movement", thus, in essence thermodynamics studies the movement of energy and how energy instills movement. *Energy can be defined as the capacity of a body to do work.* Energy is available in various forms like potential energy (due to the position), kinetic energy (due to motion), heat energy, chemical energy, electrical energy.

Units of Energy = ergs (C.G.S)

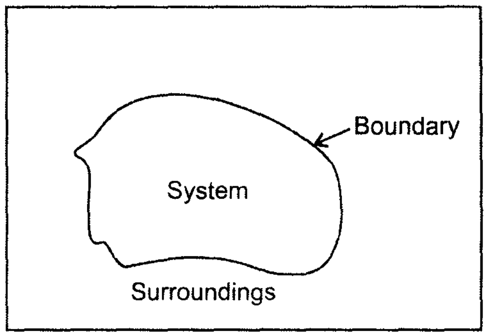
Joules (S.I. System)

1 Joule = 10^7 ergs.

Thermodynamics is a branch of science which deals with the heat changes accompanying a particular process.

An important concept in thermodynamics is the "System". A system is the region of universe under study. A system is separated from the remainder of universe by a boundary which may be imaginary or not, but which by convention delimits a finite volume. The possible exchange of work, heat, or matter between the system and surroundings take place across this boundary. Various types of systems are –

(a) Isolated System – matter and energy may not cross the boundary
(b) Adiabatic System – heat and matter may not cross the boundary
(c) Closed System – matter may not cross the boundary
(d) Open System – heat, work and matter may cross the boundary.



Law of Conservation of Energy or First law of Thermodynamics :

This can be stated in various forms

"*Energy can neither be created nor destroyed and may be conversed from one form to another*".

"When a quantity of one kind energy disappeares an exactly equivalent amount of other form must be produced".

Mathematically it can be expressed as,

$$\Delta E = Q - W \qquad .....(4.1)$$

In differential form

$$dE = dQ - dW \qquad .....(4.2)$$

or $$\Delta E = Q - P\Delta V$$

where,

$\Delta E \;=\; E_B - E_A$ = change in the internal energy

Q = heat (It is denoted by +Q when heat is input and – Q when heat is output).

W = Work done (It is denoted by +W when work is input and –W when work is output).

Since in thermodynamics it is difficult to find absolute value of energy, it is always expressed as the difference in the final and initial states of system.

i.e., $$\Delta E = E_2 - E_1$$

When the process is adiabatic (i.e., neither heat is absorbed nor given out), then eq. (4.1) can be written as

$$\Delta E = -W \quad (Q = 0)$$

and when work done is zero then,

$$\Delta E = Q$$

Applications of First Law of Thermodynamics

Reversible and irreversible Process

A reversible process may be defined as one which can be performed in forward and reverse directions, so that all changes occuring in any part of the direct process are exactly reversed in the corresponding part of the reverse process, and only infinitesimal changes are produced.

A simple illustration of reversible process can be made by considering hypothetical case of water at its boiling point in a cylinder placed in a constant temperature bath. The cylinder is closed by means of a frictionless piston as shown in Fig. 4.1.

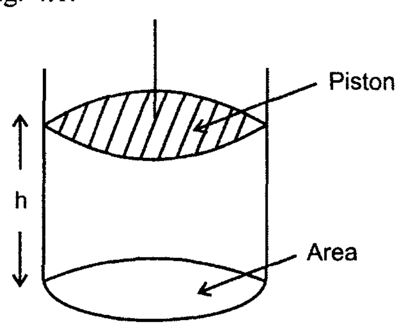


Fig. 4.1 Cylinder with weightless and frictionless piston.

If the external pressure is increased infinitesimally then small amount of vapour will condense, but this process will take place at such a slow rate that the system will not change and pressure above liquid remains unaltered. Although condensation is occuring, the system at every instant is in equilibrium. Similarly, if the external pressure is reduced slightly than the vapour pressure, the liquid will evaporate at an extremely slow rate, maintaining the system in equilibrium. The change may be regarded as a series of equilibrium states. Since, this process is always in a state of virtual thermodynamic equilibrium, being reversed by an infinitesimal change of pressure, it is said to be reversible. The work done by a system in an isothermal process is maximum when it is done reversibly.

A process is called irreversible if it cannot be reversed and if it is reversed, it cannot do so without leaving the surroundings permanently changed.

Reversible Isothermal Expansion of Gas at Constant Pressure

In this process the pressure remains constant throughout, since it is always equal to the equilibrium vapour pressure P of the liquid at the experimental temperature. Let ΔV be the change in volume. The work done by the system against opposing pressure is

$$W = P \times \Delta V \qquad .....(4.3)$$

or

$$P(V_2 - V_1)$$

Isothermal Work of Expansion against a Variable Pressure

As we have mentioned earlier the external pressure is only infinitesimally less than the pressure of an ideal gas in an isothermal expansion. So the external pressure can be replaced by gas equation $P = nRT/V$.

Substituting this in Eq. (4.3) we will get,

$$\int dw = nRT \int_{V_1}^{V_2} \frac{1}{V}\, dV.$$

$$W_{max} = nRT \left[ln V\right]_{1/1}^{V_2}$$

$$= nRT \left[ln \frac{V_2}{V_1}\right]$$

or

$$= 2.303\ nRT \left[\log \frac{V_2}{V_1}\right] \qquad .....(4.4)$$

According to Boyle's law, $P_1 V_1 = P_2 V_2$.

Replacing this in Eq. (4.4) gives

$$W_{max} = 2.303 \text{ nRT} \log \frac{P_1}{P_2}.$$

Heat Content : Consider a system at constant pressure or (enthalpy). By replacing ΔE by $E_B - E_A$. The Eq. (4.1) can be written as

$$(E_B - E_A) = Q_p - P(V_B - V_A)$$

$$\Rightarrow Q_p = (E_B + PV_B) - (E_A + PV_A)$$

By replacing E + PV with symbol H, we can write,

$$Q_P = H_B - H_A = \Delta H \qquad .....(4.5)$$

The symbol H is used to represent heat content of a system at constant pressure.

Substituting ΔH for Q_P we get

$$\Delta H = \Delta E + P \Delta V \qquad .....(4.6)$$

Heat Capacity

The heat capacity of a system is defined as quantity of heat required to raise the temperature of one mole of a substance by 1 degree. It is denoted by C. It is also known as molar heat capacity since we consider 1 mole of a pure substance.

$$C = \frac{q}{dT} \qquad .....(4.7)$$

The heat capacity varies with temperature, it is defined for infinitesimally small value dT at constant volume. Eq. (4.7) may be represented as

$$C_V = \frac{q_v}{dT} \qquad .....(4.8)$$

but at constant volume, d E = q_v (from first law) so Eq. (4.8) becomes

$$C_V = \left(\frac{\partial E}{\partial T}\right)_v \qquad .....(4.9)$$

At constant pressure, the heat capacity is

$$C_p = \frac{q_p}{dT} \qquad .....(4.10)$$

But $q_P = dH$ from Eq. (4.5), so

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \qquad .....(4.11)$$

Difference in Heat Capacities

By subtracting Eq. (4.9) from Eq. (4.11)

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_v$$

But H = E + PV.

$$C_P - C_V = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V \qquad .....(4.12)$$

Here dE is completely differential

$$\partial E = \left(\frac{\partial E}{\partial V}\right)_T^{dv} + \left(\frac{\partial E}{\partial T}\right)_T^{dT}$$

Upon dividing by ∂T and at constant pressure

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial E}{\partial T}\right)_V \qquad .....(4.13)$$

Addition of Eq. (4.12) and Eq. (4.13) gives

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad .....(4.14)$$

The Eq. (4.14) represents general form of equation for difference in heat capacities of ideal gas.

Thermochemistry

Heat changes in chemical Reactions

The aspect of physical chemistry which deals with the heat changes accompanying a chemical reaction is known as thermochemistry. To a great extent it is based on first law of thermodynamics. A chemical reaction may be either exothermic (heat evolved) or endothermic (heat absorbed).

Generally the reaction proceeds under constant pressure or constant volume. One of these must be specified so as to conclude whether the reaction is exothermic or endothermic.

In practice the reactions proceed under atmospheric conditions so pressure is considered to be constant and heat changes (Q_P) is equal to ΔH. This quantity is often referred to as *heat of reaction*. If the reaction proceeds at constant volume then Q_V is equal to ΔE.

The heat changes accompanying a reaction involving solid carbon and gaseous oxygen to yield carbon dioxide gas as given below

$$C \text{ (solid)} + O_2 \text{ (gas)} \rightarrow CO_2 \text{ (gas)}$$

$$\Delta H = -94.05 \text{ kcal}$$

The above reaction proceeds with evolution of heat which implies that reactants contain 94.05 kcal in excess compared to the product.

Heat of Formation

It is the increase in heat content ΔH when 1 mole of substance is formed from its constituents. From the above mentioned example the heat of formation of CO_2 (gas) is – 94.05 Kcal.

Heats of formation per mole in Kcal at 25 °C.

1. NO : 27.5
2. N_2O : 17.0
3. H I : 6.0
4. NH_3 : 11.0
5. CO : 26.4

Heat of Combustion

It is defined as the change in heat content accompanying when of 1 mole of a compound undergoes combustion process.

Heats of combustion per mole in kcal at 25 °C.

Substance	$-\Delta H$
1. Ethane	368.5
2. Toluene	936
3. Ethanol	327
4. Methanol	171

Heat of Hydrogenation

It is defined as the increase in heat content when 1 mole of unsaturated hydrocarbon is converted in to corresponding saturated compound by gaseous hydrogen.

E.g. : $C_6H_6\,(s) + 3\,H_2\,(g) \rightarrow C_6H_{12}\,(g)$

$\Delta H = -\,49.80$ Kcal

Thermochemical Laws

The quantity of heat required to decompose a compound into its elements is equal to the heat evolved when compound is formed from its element.

G. H. Hess in the year 1840 proposed second law. According to this law the heat changes in a chemical reaction is the same whether it takes place in one or several stages.

E.g. :

$$\begin{tikzcd} C\,(s) + 2\,S\,(s) \arrow[r, "\mathrm{I}"] \arrow[dr, "3O_2\ \mathrm{III}"'] & C\,S_2\,(l) \arrow[d, "\mathrm{II}\ 3O_2"] \\ & CO_2\,(g) + 2\,SO_2\,(g) \end{tikzcd}$$

If ΔH_I, ΔH_{II} and ΔH_{III} are the heat content changes in the respective processes marked I, II and III, then from Hess's Law

$$\Delta H_I + \Delta H_{II} = \Delta H_{III}$$

Second Law of Thermodynamics

There is no body in the universe that can convert the entire energy into work. According to second law, "*It is impossible to construct a machine functioning in cycles that can convert heat completely into the equivalent amount of work without producing changes elsewhere*".

This practical impossibility of converting entire energy into work led to the coining of term "efficiency". *The amount of energy utilized for doing useful work is called free energy.*

The Efficiency of a Heat Engine

It is the fraction of the heat Q at the source converted into work W.

The efficicency of the engine : efficiency $= \dfrac{W}{Q}$.

Imagine a hypothetical steam engine operating reversibly between an upper temperature T_2 and a lower temperature T_1. It absorbs heat Q_2 from source. It converts the quantity W into work and returns heat Q_1 to the cold reservior or sink. The efficiency of such an engine can be given by the expression (Carnot, 1824).

$$\frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} \qquad .....(4.15)$$

Lord Kelvin used the ratio of two heat quntities Q_2 and Q_1 of the Carnot cycle to establish the Kelvin temperature scale.

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \qquad .....(4.16)$$

By combining Eq. (4.15) and Eq. (4.16) we can write,

$$\text{Efficiency} = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}$$

Entropy

From Eq. (4.15) and (4.16) we can obtain

$$\frac{W}{Q_2} = \frac{T_2 - T_1}{T_2}$$

or

$$W = Q_2 - T_1 \frac{Q_2}{T_2} \qquad .....(4.17)$$

The term $\frac{Q_2}{T_2}$ is denoted as entropy change of reversible process at T_2

and $\frac{Q_2}{T_1}$ is the entropy change of T_1.

From Eq. (4.16) we obtain

$$\frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0 \qquad .....(4.18)$$

or

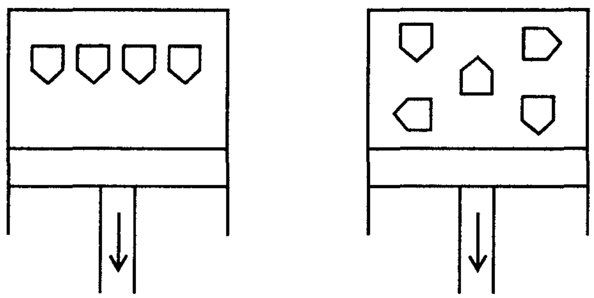
$$\sum \frac{q}{T} = 0$$

Eq. (4.18) implies that the total entropy change in a reversible cycle is zero. But if we consider an irreversible cycle then,

$$\sum \frac{q}{T} > 0$$

Entropy and Probability

R.Clausius suggested second law of thermodynamics in terms of entropy. According to him the total amount of entropy in nature is always increasing. Consider molecules of gas in a cylinder. The probability that all the gas molecules will be equally spaced and move in an ordered manner relative to each other is very small. This is due to irregular collisions of the gas molecules between themselves and with walls of container. This state has got more probability to occur than the ordered state in the Fig. 4.2.



(a) (b)

Fig. 4.2 Cyclinders containing gas molecules showing (a) low entropy; or orderliness, and (b) high entropy, or disorderliness.

Boltzmann Equation

$$S = k \ln W$$

where,

k = Boltzmann Constant = 1.38066×10^{-16} erg. deg^{-1}. $molecule^{-1}$.

W = Probability of system or number of configuration that system can assume.

Third Law of Thermodynamics

According to this law the probability of entropy of a pure crystalline substance is zero at absolute zero because the crystal arrangement must show the greatest orderliness at this temperature.

This is not applicable for supercooled liquids.

$$\Delta S = \int_0^T \frac{C_P}{T} dT$$

$$= 2.303 \int_0^T C_P \, d \log T. \qquad .....(4.19)$$

From $T = 0^{\circ}$ where $S = O$ to T where $S = S$.

Using this law one can calculate the absolute entropies of pure crystalline substance.

Eq. (4.19) can be calculated by plotting values of C_p against log T and determining the area under the curve by the use of planimeter.

Free Energy Functions and Applications

Helmholtz Free Energy

It is also known as total work function.

Mathematically,

$$A = E - TS$$

for small change

$$dA = dE - TdS - SdT. \quad .....(4.20)$$

But $$dS = \frac{dQ_{rev}}{T}$$

According to first law of thermodynamics

$$dQ = dE + PdV$$

$$\Rightarrow dS = \frac{dE + PdV}{T} \quad .....(4.21)$$

Substituting (4.21) into (4.20)

$$dA = -PdV - SdT$$

or $$dA = -dW.$$

So the change in Helmholtz free energy (A) denotes the total work that can be obtained

Gibb's Free Energy

It is denoted by G.

Mathematically,

$$\Delta G = E + PV - T\Delta S$$

But E + PV can be replaced by H.

$$\Delta G = H - T\Delta S$$

or We can replace $E - T\Delta S$ with A [see Eq. (4.20)]

$$\Delta G = A + PV \text{ (Gibbs – Helmholtz Equation)}$$

Pressure and Temperature Co-efficients of Free energy

The free energy change of an ideal gas which is undergoing isothermal reversible or irreversible change can be denoted by

$$\Delta G = n\,RT \ln \frac{P_2}{P_1} = 2.303\eta\,RT \log \frac{P_2}{P_1} \qquad .....(4.22)$$

Spontaneity of a Reaction

Gibb's free energy can be used to determine the nature of a reaction i.e., spontaneous or non-spontaneous

If $\Delta G < 0$ (The reaction is spontaneous)

$\Delta G > 0$ (The reaction is non-spontaneous)

$\Delta G = 0$ (The reaction is at equilibrium)

Clausius - Clapeyron Equation

The changes in pressure of a two phase system for a single component with temperature is given by equation.

$$\log \frac{P_2}{P_1} = \frac{\Delta H_V}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or $$\log \frac{P_2}{P_1} = \frac{\Delta H_v (T_2 - T_1)}{2.030\,RT_1T_2} \qquad .....(4.23)$$

where ΔH_V = Molar heat of vapourisation of liquid.

This equation is used to calculate the mean heat of vapourisation of a liquid if it's vapour pressure at two different temperatures is available. It is also helpful in the development of some colligative properties.

Problems

1. Calculate the maximum work done in ergs when one mole of an ideal gas expands from 10 liter to 20 liters at room temperature.

   Solution : Data given

   V_1 = 10 liters and V_2 = 20 liters.

   R = 1.98 cal. deg^{-1} $mole^{-1}$.

Equation for maximum work

$$W_{max} = 2.303 \text{ nRT} \log \frac{V_2}{V_1}$$

$$= 2.303 \times 1 \times 298 \times 1.98 \log \frac{20}{10}$$

$$= 409 \text{ calories.}$$

It can be converted to ergs.

$$W_{max} = JH = 4.2 \times 10^7 \times 409$$

$$= 1.72 \times 10^{10} \text{ ergs.}$$

2. Calculate the maximum work done in isothermal reversible expansion of 2 moles of an ideal gas from 1 to 5 liters at room temperature.

Solution : Data given

$$P_1 = 5 \text{ and } P_2 = 1$$

Equations for $W_{max} = 2.303 \text{ nRT} \log \frac{P_1}{P_2}$

$$= 2.303 \times 2 \times 1.98 \times 298 \times \log 5.$$

$$= 1908 \text{ cal.}$$

3. Calculate work done when 2 moles of H_2 expands from 15 to 50 liters at room temperature.

Solution : Data given

$$V_1 = 15, V_2 = 50.$$

Equation for $W_{max} = 2.303 \text{ nRT} \log \frac{V_2}{V_1}$

$$= 2.303 \times 2 \times 1.98 \times 298 \log \frac{50}{15}$$

$$= 1830 \text{ calories.}$$

4. Calculate the entropy change [ΔS] accompanying the vaporization of 1 mole of water in equilibrium with its vapour at 25 °C. In this reversible isothermal process, the heat of vaporization [ΔH_v] required to convert the liquid to vapour state is 12,500 cal/mole.

Solution : Data given

$$\Delta H_v = 12{,}500 \text{ cal/mole.}$$

Equation for entropy change

$$\Delta S = \frac{\Delta H_v}{T}$$

$$= \frac{12500}{298} = 41.94 \text{ cal/mole deg.}$$

5. A heat engine works between 130 °C and 42 °C. Calculate the efficiency of engine.

Solution : Data given

Temperature of hot reservoir = T_2 = 130 °C.

Temperature of cold reservoir = T_1 = 42 °C.

Equation of

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2}$$

$$T_2 = 130\ °C = 273 + 130 = 403\ °K$$

$$T_1 = 42\ °C = 273 + 42 = 315\ °K$$

$$\text{Efficiency} = \frac{403 - 315}{403} = \frac{88}{403}$$

$$= 0.2183 = 21.84\%$$

6. A steam engine operates between the temperature of 397 °K and 298 °K.

(a) What is theoretical efficiency of the engine ?

(b) If the engine supplied units 1000 cal of heat Q_2. What is the theoretical work in ergs ?

Solution : Data given

(a) $T_1 = 298\ ^oK$

$T_2 = 397\ ^oK.$

Equation for efficiency

$$= \frac{T_2 - T_1}{T_2}$$

$$= \frac{397 - 298}{397} = 0.2493 \text{ or } \cong 25\%$$

(b) $W = 1000 \times 0.25 = 250$ cal.

$= 250 \text{ cal} \times 4.184 \times 10^7 \text{erg/cal.}$

$= 10.46 \times 10^9$ ergs.

7. A gas expands by 2 liters against a constant pressure of 1.2 atm at 25 °C. What is work done by system in joules ?

(1 atm= 1.013×10^6 dyne/cm^2)

$W = P \Delta V$

$= 1.2 \times 1.013 \times 10^6 \times 2000$

$= 2.43 \times 10^9$ ergs or 243 joules.