3.4. Second Law of Thermodynamics

The first law enable us to compute and for different chemical reaction and physical transformations. It **is not capable of predicting the direction of a process.** So the second law was developed for prediction of the direction of the process (reaction). The important term of indicating the direction of the in the 2nd law of thermodynamics is **Spontaneous process** which is a process that takes place without the intervention of external force. **All process take place in nature are spontaneous in character.** This means they only proceed in one direction and therefore **they are thermodynamically irreversible.**

Some of the statements of the 2nd law are;

1) Entropy increases in irreversible process.

2) Heat cannot pass from a colder body to a warmer body.

3) Heat cannot be cannot be completely converted in to work without leaving changes either in the system or in the surrounding.

4) It is impossible to construct a machine working in a cycle which will transfer heat from a lower temperature to a higher temperature without the aid of external force. Such a machine is called perpetual motion machine of second order.

The first law of thermodynamics tells us that energy can be changed from one to another but can be neither created nor destroyed in any process. This law however, tells us nothing about the direction a process will take, yet we know that there are particular directions in which natural processes occur. The purpose of this topic is to explain the origin of the driving force and direction of physical and chemical changes (processes). If we wish to understand the direction of physical and chemical processes, we must have a thermodynamic function that allows us to predict the direction of the change that can be expected if we specify the initial conditions of a system and the constraints imposed on it. The energy function cannot help us, since it always remains constant in any isolated system or in the universe as a whole. Isolated systems change spontaneously from nonequilibrium state toward equilibrium states. We want a function that changes and stays constant when the system rests at equilibrium.

3.4.1. The Carnot cycle

It is reversible cycle (an ideal hypothetical cycle) in which all the processes constituting the cycle are reversible.The extent to which work can be obtained heat and its dependence on the temperature of the

source and sink is given by carnot cycle. The Carnot heat engine consists of a cylinder fitted with an ideal piston and contains a mole of an ideal gas as a working substance (system).
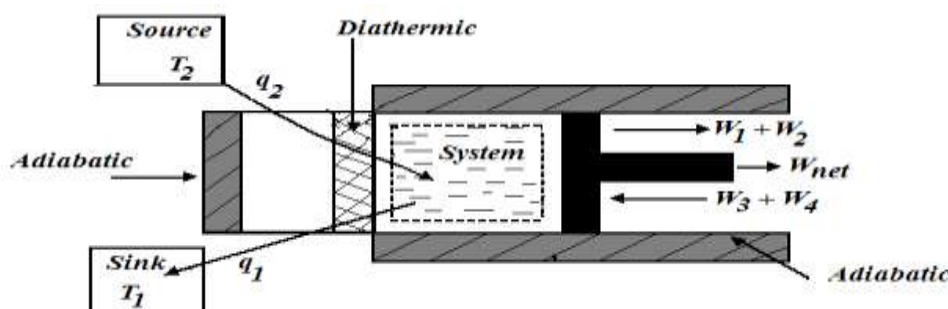

Figure 4.5. The Carnot heat engine system

The cycle consists of the following successive processes

   a) A reversible isothermal process (expansion)

   b) A reversible adiabatic process (expansion)

   c) A reversible isothermal process (compression)
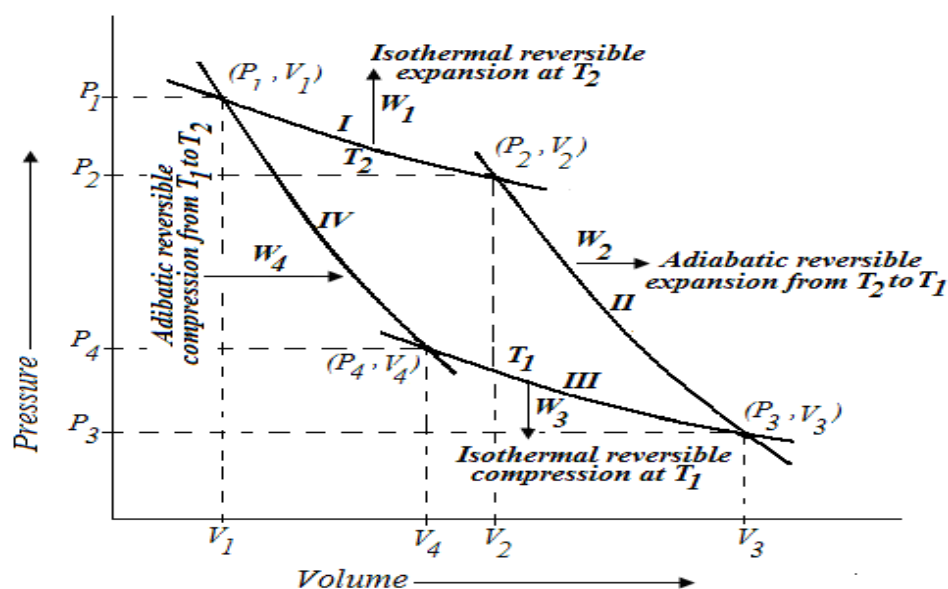
   d) A reversible adiabatic process (compression)

Figure 4.6. The PV diagram of Carnot heat engine system

a) **A reversible isothermal process:** The cylinder containing the gas is placed in contact with the reservoir at T_2. It absorbs a certain quantity of heat Q_2 and the gas is allowed to expand isothermally and reversibly at a temperature T_2 of the source.

    The volume of the gas changes from V_1 to V_2 . Since $dT = O \Rightarrow dE_1 = O \Rightarrow \Delta E_1 = O$

$$-q_2 = W_1 = -nRT_2 ln\left(\frac{V_2}{V_1}\right) \qquad \text{but n} = 1$$

b) **A reversible adiabatic process:** The cylinder is removed from the source, it is surrounded by an adiabatic cover and the gas is allowed to expand reversibly and adiabatically from V_2 to V_3 until the temperature drops to T_1 (the temperature of the sink)

   $q_2 = O$ because adiabatic

$$W_2 = \Delta E_2 = \int_{T_2}^{T_1} C_V dT = C_V(T_1 - T_2) \qquad \text{where W = negative because } T_2 > T_1 \text{ expansion.}$$

c) **A reversible isothermal process:** The termal insulation is removed and the cylinder is kept in contact with the sink at T_1. The gas is compressed isothermally and reversibly at a temperature of T_1 (sink). The volume changes from V_3 to V_4 as shown by the isotherm.

$$\Delta E_3 = O$$

$$\Rightarrow W_3 = -q_3 = -nRT ln\left(\frac{V_4}{V_3}\right)$$

d) **A reversible adiabatic compression process**: The cylinder is removed from the sink, and surrounded by an adiabatic cover and the gas is compressed adiabatically and reversibly until its temperature rises to that of the source and the volume decreases from V_4 to V_1.

$$Q = O$$

$$W_4 = \Delta E_4 = \int_{T_1}^{T_2} C_V dT = C_V(T_2 - T_1)$$

The network done during the complete cycle is given by

$$W_{net} = W_1 + W_2 + W_3 + W_4$$

$$= -RT_2 ln\left(\frac{V_2}{V_1}\right) + C_V(T_1 - T_2) - RT_1 ln\frac{V_4}{V_3} + C_V(T_2 - T_1)$$

$$= -RT_2 ln\left(\frac{V_2}{V_1}\right) - RT_1 ln\left(\frac{V_4}{V_3}\right) + C_V(T_2 - T_1) - C_V(T_2 - T_1) \quad W_T = -RT_2 ln\frac{V_2}{V_1} - RT_1 ln\frac{V_4}{V_3}$$

Since for adiabatic expansion or compression relationship between temperature & volume is

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

Based on this V_2 and V_3 lie on the adiabatic I and V_1 and V_4 lie on adiabatic II therefore.

$$\Rightarrow T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1} \text{ and } T_2 V_1^{\gamma-1} = T_1 V_4^{\gamma-1}$$

$$\Rightarrow \frac{T_2 V_2^{\gamma-1}}{T_2 V_1^{\gamma-1}} = \frac{T_1 V_3^{\gamma-1}}{T_1 V_4^{\gamma-1}} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$W_T = -RT_2 ln \frac{V_2}{V_1} + RT_1 ln \frac{V_3}{V_4} \text{ , Since } -ln \frac{V_4}{V_3} = ln \frac{V_3}{V_4}$$

$$= -RT_2 ln \frac{V_2}{V_1} + RT_1 ln \frac{V_2}{V_1} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$W_T = (T_1 - T_2) R ln \frac{V_2}{V_1} = -R ln \frac{V_2}{V_1} (T_2 - T_1)$$

Efficiency of the heat engine $\dfrac{(-W_{output})}{q_{input}} = \dfrac{(-W_T)}{q_2}$

$$\eta = \frac{(-W_T)}{q_2} = R \frac{(T_2 - T1) \ln \frac{V_2}{V_1}}{RT_2 \ln \ln \frac{V_2}{V_1}} \qquad W_1 = q_2 \text{ ,but opposit in direction}$$

$$\eta = \frac{(-W_T)}{q_2} = \frac{R(T_2 - T_1)}{RT_2} = \frac{T_2 - T_1}{T_2}$$

$$\eta = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

This equation gives the efficiency of any reversible engine working between the temperatures of the source and the sink and it depends only on the temperature difference of the two and is independent of the nature of the working system or substance.

For complete conversion $\eta = 1 \Rightarrow$ either T_2 = W or T_1 = O but both these temperatures can not be realized in actual practice "Heat can not be transformed completely in to work"

Carnot's Theorem

- ► It states that of all heat engines operating between a given constant temperature source and a given constant temperature sink, none has a higher efficiency than a reversible engine. or

- ► All reversible engines operating between the same two temperatures of the source and sink are equally efficient.

Example 4.1. A reversible heat engine working between 273K and 373K absorbs 764J of heat from the source. Calculate a) the work done b) the heat given of to the sink c) the η, and what would have been the efficiency if the temperature of the source were 573K.

Solution

$$\text{a) } \eta = \frac{W}{q_1} = \frac{T_2 - T_1}{T_1} \Rightarrow W = q\left(\frac{T_2 - T_1}{T_2}\right)$$

$$= 746J\left(\frac{100K}{373K}\right)$$

$$W = \underline{200J}$$

b) heat given to the sink = 746-200J = <u>546J</u>

c) $= \eta = \dfrac{W}{q} = \dfrac{T_2 - T_1}{T_2} = \dfrac{100K}{373K} = \underline{\underline{0.268}}$

If the temperature of the source raised to 573K

$\eta = \dfrac{573K - 273K}{373K} = \underline{\underline{0.349}}$

Example 4.2. Liquid helium boils at about 4K and liquid hydrogen boils at about 20K. What is the efficiency of a reversible engine operating between heat reservoirs at these temperatures? For the same efficiency calculate the temperature of the hot reservoir if the temperature of cold reservoir is 350K.

Solution

$a) \; \eta = \dfrac{20 - 4}{20} = 0.8 = 80\%$ $\qquad b) \; 0.8 = \dfrac{T - 350}{T} \Rightarrow T = 1750K$

3.4.2. Entropy

Entropy is a measure of the randomness or disorderness in a molecular system. Sometimes, it is a measure of unavailable energy. Random motion is considered as unavailable energy. For any substance

$$S_{gas} > S_{liquid} > S_{solid}$$

In calculation of entropy changes we must take in to consideration the entropy of system and the surroundings. The total entropy change of the isolated system ($\triangle S_{universe}$) is taken as

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surrounding}$$

3.4.2.1. Entropy change of system ($\triangle S_{system}$) and the surrounding ($\triangle S_{surrounding}$)

Entropy change of a system in a reversible isothermal change can be calculated using the relation

$dS = \dfrac{dq_{rev}}{T}$, but this equation can't be used to as such to calculate the entropy of irreversible changes.

For the surrounding entropy can be calculated if we know the gain or lose in the heat of the surrounding using the relation

$$dS = \dfrac{dq_{rev}}{T}$$

$$\Delta S_{surrounding} = -\dfrac{q_{system}}{T} = \dfrac{q_{surr}}{T}$$

3.4.2.2.Entropy changes for isolated system

For a reversible isolated process the change of entropy is zero, where as for irreversible isolated process the entropy change is greater than zero.this is shown as follows;

Let us suppose that the same small changes are made in the system reversibly and irreversibly. Since energy of a system is a state function and dE is an exact differential it must be the same for a given change whether it is performed reversibely or irrversibely. That is

$$dE = dE_{rev} = dE_{irr} \ .$$

Work done by the system reversible is greater than the irreversible one that is

$$dW_{rev(\exp)} > dW_{irr(\exp.)}$$

From the first law we have

$$dE = dq_{rev} + dW_{rev} \ \text{and} \ \ dE = dq_{irr} + dW_{irr}$$

$$\Rightarrow dq_{rev} + dW_{irr} = dq_{irr} + dW_{irr}$$

$$dq_{rev} - dq_{irr} = dW_{irr} - dW_{rev} = (-dW_{rev}) - (-dW_{irr})$$

Since $((-dW_{rev}) > (-dW_{irr})$, the right hand side of equation (4.) is positive therefore

$$\Rightarrow dq_{rev} > dq_{irr}$$

That means in any small change in a system absorb more heat under reversible condition than irreversible condition. On dividing both sides of equation (4.30) by T, we get

$$\Rightarrow \frac{dq_{rev}}{T} > \frac{dq_{irr}}{T}$$

But from second law $\quad \dfrac{dq_{rev}}{T} = dS$

$$\Rightarrow dS > \frac{dq_{irr}}{T}, \Rightarrow dS > \frac{dE - dW_{irr}}{T}$$

$dS = \dfrac{dE - dW_{rev}}{T}$ for a reversible process. Since entropy is a state function the value of dS is independent of the path.

$$\Rightarrow dS = \frac{dE - dW_{rev}}{T} > \frac{dE - dW_{irr}}{T}$$

In an isolated system, $dq = 0, dW = 0$ and $dE = 0$ introducing these conditions to equations, we get

$$\Rightarrow dS_{rev} = 0 \ and \ \Delta S_{rev} = 0$$

$$\Rightarrow dS_{irr} > 0 \ and \ \Delta S_{irr} > 0$$

The equality refers to a reversible change while the inequality applies to the irreversible change. Thus for a spontaneous transformation in an isolated system (universe) the essential requirement interims of entropy is that it must increase. All natural processes are attended by an increase in the entropy of the universe and continue until the system attains an equilibrium state where entropy had maximum state. The universe is therefore moving for a state of maximum entropy.

For a system $\Delta S_{rev}^{Sys} = \Delta S_{irr}^{Sys}$, It is the Δs_{surr} which is different for a reversible and irreversible process.

3.4.2.3. Entropy changes during Phases changes

During phase changes it is known that two phases are at equilibrium and the process is reversible. If we take melting of a solid. At melting point the liquid & solid coexist

$$\Rightarrow q = q_{rev}$$

$$\Rightarrow \Delta S_f = \int_1^2 \frac{dq_{rev}}{T_f} = \frac{1}{T_f} \int_1^2 \frac{dq_{rev}}{T}, \text{ because } T_f \text{ is constant}$$

q_{rev} for the constant pressure process is **enthalpy of fusion** $\Rightarrow \Delta S_f = \frac{1}{T_f} \int_1^2 dH_f \Rightarrow \Delta S_f = \frac{\Delta H_f}{T_f}$

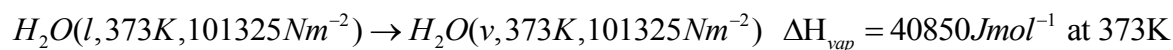In general for any transformation taking place at constant temperature and pressure such as

Solid ⬚   ⬚   ⬚

and solid$_\alpha$ ⬚ $_r$ (*transition*), it must be true that ;

$$\Delta S_t = \frac{\Delta H_t}{T_t}$$

Example 3.4.3.

a) Calculate the entropy change involved in the conversion of 1 mole of ice at 0^0C and 1 atm to liquid at 0^0C and 1 atm to. $\left(\Delta H_f = 6008 \frac{J}{mol^{-1}} \right)$

b) Calculate the change of entropy for the processes

$H_2O(l, 373K, 101325Nm^{-2}) \rightarrow H_2O(v, 373K, 101325Nm^{-2})$ $\Delta H_{vap} = 40850 Jmol^{-1}$ at 373K

c) Compare ςS in (a) with (b)

Solution

a) $\Delta S = \frac{\Delta H_{fus}}{T_m} = \frac{6008 \frac{J}{mol}}{273K} = \underline{\underline{22 JK^{-1}mol^{-1}}}$

b) $\Delta S_{vap} = \frac{40850 Jmol^{-1}}{373K} = \underline{\underline{109.5 JK^{-1}mol^{-1}}}$

c) $ςS_a < ςS_b ==>$ randomness increases as we go to vapour phase.

3.4.2.4. Entropy change for isothermal reversible process.

Since $\Delta E = 0, because\ dT = 0$

$$q_{rev} = -dW = (PdV) = nRTln\frac{V_2}{V_1}$$

$$\Rightarrow \Delta s_{syt} = \frac{q_{rev}}{T} = \frac{nR\cancel{T}ln\left(\frac{V_2}{V_1}\right)}{\cancel{T}} = nR\ln\frac{V_2}{V_1} = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right)$$

$$\Rightarrow \Delta s_{syt} = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right) = -nR\ln\left(\frac{P_2}{P_1}\right) = -2.303nR\log\left(\frac{P_2}{P_1}\right)$$

$$\Rightarrow \Delta s_{surr} = -\frac{q_{rev}}{T} = -nR\ln\left(\frac{V_2}{V_1}\right) = -nR\ln\left(\frac{P_1}{P_2}\right) = nR\ln\left(\frac{P_2}{P_1}\right) = 2.303nR\log\left(\frac{P_2}{P_1}\right)$$

Example 3.4.5. Calculate the entropy change when l mole of an ideal gas expends reversibly from an initial volume of $1dm^3$ to a final volume of $10dm^3$ at a constant temperature of 298k.

Solution

$$\Delta s_{sys} = nRln\left(\frac{V_2}{V_1}\right) = 2.303nR\log\left(\frac{V_2}{V_1}\right)$$
$$= 2.303(lmol)(8.314JK^{-1}mol^{-1})\log^{10}$$
$$= \underline{\underline{19.15k^{-1}gmol^{-1}}}$$

$$\Rightarrow \Delta S_{surr} = -\Delta S_{system} = \underline{-19.15Jk^{-1}mol^{-1}}$$

3.4.2.5. Entropy change for adiabatic reversible process

For adiabatic process $\qquad q_{rev} = 0 \quad \Rightarrow \Delta S = \left(\frac{q_{rev}}{T}\right) = 0$

$\Rightarrow$ The process is isoentropic but for Adiabatic irreversible process even though $q_{irr} = 0$

$\Delta S \neq \frac{q_{irr}}{T}$, so it çS is not zero

3.4.2.6. Entropy change on heating or cooling of a substance

For n mole of substances at a temperature of T_1. If its temperature is changed to T_2 keeping

i) The volume constant (ischoric) and if the change is brought about reversibly then we can use the defining equation of entropy. Heat change for this process is, at constant volume

$$dq_{rev} = C_V dT, \text{ where } C_V = \text{heat capacity at constant volume}$$

$$\Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T} = C_V ln\frac{T_2}{T_1} = n\overline{C}_V ln\left(\frac{T_2}{T_1}\right)$$

ii) For temperature changes T_1 to T_2 at constant pressure(isobaric)

$$\Delta S = \int_{T_1}^{T_2} C_P\left(\frac{dT}{T}\right) = n\overline{C}_P ln\left(\frac{T_2}{T_1}\right)$$

3.4.2.7. Adiabatic irreversible process

If an ideal gas is heated or cooled from T_1 to T_2 and expanding from V_1 to V_2 the entropy is given by

$$\Delta s = C_v ln\left(\frac{T_2}{T_1}\right) + nRln\left(\frac{V_2}{V_1}\right)$$

For adiabatic reversible change e $\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{nR/CV}$, for an ideal gas. Equation (4.41) gives

$$\Delta S_{sy} = -\frac{nR}{C_V}.C_V ln\left(\frac{V_2}{V_1}\right) + nRln\left(\frac{V_2}{V_1}\right) = 0$$

Any increase in entropy due to expansion is exactly balanced by an equal decrease in entropy due to lowered temperature in an adiabatic reversible expansion of an ideal gas.

For adiabatic irreversible change it is

$$-P_2 dV = P(V_2 - V_1)$$

$$= P_2\left(\frac{nRT_1}{P1} - \frac{nRT_2}{P_2}\right)$$

$$C_V(T_2 - T_1) = RT_1\left(\frac{P_2}{P_1}\right) - RT_2$$

$$\text{Shown that } \frac{T_2}{T_1} = \frac{C_v + \left(\frac{P_2}{p_1}\right)nR}{CP}$$

Therefore, ΔS for irreversible adiabatic change is not zero. This is because the final temperature (T_2) in adiabatic irreversible change and adiabatic reversible change are different.

Generally Entropy changes in adiabatic irreversible expansion of an ideal gas the entropy change for a reversible adiabatic expansion is zero but for irreversible process $\Delta s_{univ} > 0$.

If the system is thermally insulated it exchanges no heat with the system thus suffers no change in entropy i.e $\Delta s_{surr} = 0$.

$$\Delta s_{sys} + \Delta s_{urr} = \Delta s_{uir} > 0. i.e(\Delta s_{sys})_{adia} > 0.$$

Example3.4.6. 0.1 kg of Nitrogen gas at 298K are held by a piston under 30 atmosphere pressure. The pressure is suddenly released to 10 atm. and the gas expands a adiabetically. It $C_{r, m}$ is $= 20.8$ Jk^{-1} mol^{-1}, what is the find temperature and volume? Calculate Δs system for this expansion. What would be the value of ΔS (surrounding)

Solution

The change is adiabatic $\Rightarrow q = 0$

$$W = C_V(T_2 - T_1) = W - P_2(V_2 - V_1), \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = nR$$

$$\Rightarrow T_2 = \left(\frac{nC_{Vm} + nR\left(\frac{P_2}{P_1}\right)}{nC_{P.m}} \right) T_1 = 241k$$

$$V_2 = \left(\frac{P_1 V_1 T_2}{T_1 P_2} \right) = \frac{30 \times V_1 \times 241}{298 \times 10} = 2.42 V_1$$

$$\Delta s_{system} = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = 10.47 JK^{-1}$$

$$\Delta s_{sur} = \frac{q_{sur}}{T} = 0$$

Exercise 3.2. Evaluate the change in entropy when 3 moles of a gas is heated from 27^0_C to 727^0_C at constant pressure of 1atm, the molar heat capacity of the gas is 23.7 Jk^{-1}mol^{-1}.

3.4.2.8. **Entropy change in isothermal irreversible expansion of an ideal gas**

☞ For an irreversible isthermal expansion from V_1 to V_2

$$\Delta S_{sys} = \frac{q_{rev}}{T} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2} \quad \text{Because} \quad \Delta s_{universe} = \Delta S_{sys} + \Delta S_{sur}$$

☞ The total entropy change $\Delta s_{univers}$ depends on the surrounding

i) Free expansion , $dW = 0, dE = 0 \Rightarrow q = 0 \Rightarrow \Delta S_{surr} = 0$

$$\Delta S_{univ} = \Delta_{sys} + \Delta_{surr} = \Delta_{sys} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$$

is a positive quantity

ii)   If it expands against P irreversibly $\Rightarrow W \neq 0, \Delta E = 0 \Rightarrow q_{irr} = W_{irr}$

$$q_{irr} = W_{irr} < W_{rev} = nRT \ln \frac{V_2}{V_1} \quad or \quad \frac{q_{irr}}{T} < nR \ln \frac{V_2}{V_1}$$

$$q_{irr} = W_{irr} < nRT \ln \frac{V_2}{V_1} \quad or \quad \frac{q_{irr}}{T} < nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{univ} = nR \ln \frac{V_2}{V_1} + \frac{q_{surr}}{T} = nR \ln \frac{V_2}{V_1} - \frac{q_{irr,sys}}{T} > 0$$

3.4.3. Free Energy Functions

In most chemical processes neither the energy nor the entropy are held constant. It becomes essential to introduce two new functions involving energy and entropy. These functions are

❖ Helmholtz free energy function (work function)(A)

❖ Gibbs free energy functions (thermodynamic potential)(G)

We know energy can be converted in to work .the portion of energy which can be converted in to useful work is termed as available energy while the remaining portion of energy which can't be converted in to useful work is known as unavailable energy.

Total energy = isothermally available energy + isothermally unavailable energy.

Since entropy is a measure of unavailable energy, when it is multiplied by temperature (TS) gives unavailable amount of heat or energy which can't be converted in to work.

Out of the total heat absorbed by the system (q) the amount less by (TS) will give the available amount of heat which can be converted in to useful work. Thus the available energy X can be written as

$$X = q - TS$$

i) When heat is absorbed at constant volume $q_V = E$, so if X is replaced by the isothermally available energy at constant volume A which is called the ***helmholtz free energy*** can be written as $A = E - TS$ or $\Delta A = \Delta E - T\Delta S$

ii) When heat is absorbed at constant pressure $q_P = H$,so if X is replaced by the isothermally available energy at constant pressure G which is called the ***Gibb's free energy*** can be written as
$$G = H - TS \quad or \quad \Delta G = \Delta H - T\Delta S$$

Generally none of $\Delta H, \Delta E$ or ΔS_{system} alone decide the direction of a spontaneous process if we focus our attention on the system only. But ΔS_{univ} is a quantity which certainly decides the direction of a process. In all spontaneous processes, it is a common observation that for endothermic change the entropy change is positive and high. If entropy change is negative then the process is highly exothermic. In selecting Entropy as a criterion of spontaneity, one must consider the entropy changes for both the system and surrounding together $(\Delta s_{universe})$. But it is always not convenient to do so. Hence it is desirable to use the new functions as criteria of spontaneity which a compromise between ΔE or ΔH and the entropy change of a system with out considering the surrounding. These functions are A and G which are a state functions and they are extensive properties of the system.

If the experiment is carried out under conditions of constant volume and temperature we have the function (ΔA) written as;

$$\Delta A = \Delta E - T\Delta S$$

If $\Delta A = 0$ the system the process is at equilibrium (reversible)

$\Delta A > 0$ the process is not spontaneous

$\Delta A < 0$ the process is spontaneous $\Rightarrow \left(\Delta s \right)_{uniy} > 0 \Big)$

If the experiment is carried out under conditions of constant pressure and temperature, the

$\Delta G = \Delta H - T\Delta S$: If $\Delta G = 0$ the system /the process is at equilibrium

$\Delta G > 0$ the process is not spontaneous

$\Delta G < 0$ the process is spontaneous.

3.4.3.1.   Helmholtz free energy (A)

$$A = E - TS$$

$$dA = dE - TdS - SdT, \quad \text{But} \quad dE = dq + dW$$

$$\Rightarrow dA = dq + dW - TdS - SdT$$

For reversible isothermal $dq = TdS$

$$\Rightarrow dA = Td\!\!\!/S + dW - Td\!\!\!/S - Sd$$

$$dA = dW - SdT$$

At constant temperature $dT = 0 \Rightarrow (dA)_T = dW$ or $-(dA) = -dW$

The decrease in Helmholtz free energy is equal to the maximum amount of work which a system can do isothermally. Because of this relation between A and W, A is called as work function.

3.4.3.2.   Gibbs free Energy (G)

It is defined $G = H - TS$ Where $H = E + PV$

$$\Rightarrow G = E + PV - TS$$

$$dG = dE + PdV + VdP - TdS - SdT, \qquad \text{Since } dE = TdS + dW_{rev}$$

$$\Rightarrow dG = Td\!\!\!/S + dW_{rev} + PdV + Sd\!\!\!/P - Td\!\!\!/S - Sd\!\!\!/T$$

$$(dG)_{P,T} = dW_{rev} - (PdV), \text{ here } dW \text{ is all types of work, and } -PdV = \text{ mechanical work}$$

$$(dG)_{P,T} = dW_{rev} - (-PdV) = W_{net}$$

$$\Rightarrow (dG)_{T,P} = W_{net} \Rightarrow -\Delta G = (-W_{net})$$

Thus, the decrease in Gibbs free energy is equal to the amount of maximum work which a system can do isothermally and isobarically over and above the mechanical work. The logic free energy can now be made clear. The difference $\Delta E - T\Delta S$ and $\Delta H - T\Delta S$ are the free energies in the sense that if all the processes are reversible and isothermal than the complete conversion of free energies to work is possible. ΔG or ΔA sometimes called the <u>available</u> work or <u>availability</u>.

3.4.3.3.   Relation between A and G

$$A = E - TS$$

$$G = H - TS \text{ , we know that } H = E + PV$$

$$\Rightarrow G = E + PV - TS = (E - TS) + PV$$

$$G = A + PV$$

For a system changed from G_1 to G_2

$$\Delta G = G_2 - G_1 = (A_2 + P_2V_2) + (A_1 + P_1V_1)$$

$$\Delta G = G_2 - G_1 = (A_2 - A_1) + (P_2V_2 - P_1V_1), PV = nRT$$

$$\Delta G = \Delta A + nR(T_2 - T_2)$$

$$\Delta G = \Delta A + nR\Delta T$$

For an isothermal change $\Delta T = O \Rightarrow \Delta G = \Delta A$

$$\Rightarrow \Delta G = \Delta H = -nRT \ ln\left[\frac{V_2}{V_1}\right]$$

3.4.3.5.   Gibb's- Helmholtz equation

Gibb's-Helmholtz equation related the free energy change to the enthalpy change and the rate of change of free energy with temperature.

$$G = H - TS$$

$$H = E + PV \Rightarrow G = E + PV - TS$$

$$dG = dE + PdV + VdP + -TdS - SdT$$

By 1st low $dE + PdV = dq$

$$\therefore dG = dq + VdP - TdS - SdT \text{ But for reversible change } dq = TdS$$

$$dG = T\cancel{dS} + VdP - T\cancel{dS} - SdT$$

$$dG = -SdT + VdP$$

For an isobaric change, $dP = 0$ and the above equation yields

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

By substitution of $-S$ in to $G = H + T\Delta S$

$$G = H + \left(\frac{\partial G}{\partial T}\right)_P T \quad \Rightarrow \quad G - T\left(\frac{\partial G}{\partial T}\right)_P = H \quad \text{This is Gibbs-Helmholtz equation.}$$

Using Gibbs-Helmholtz equation we can find the rate of change of EMF with temperature in electrochemical cells as follows. For electrical work $\Delta G = -nFE$

$$\Rightarrow -nFE = \Delta H + \left(\frac{\partial(-nFE)}{\partial T}\right)_P .T$$

$$-nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$\left(\frac{\partial E}{\partial T}\right)_P$ is the rate of change of EMF with temperature

Example 3.4.7. For a Daniell cell calculate $\Delta G, \Delta H$ and ΔS using the following data $E = 1.01462\ V$, at $25^0C, n = 2, F = 96500C,$ and $\left(\frac{\partial E}{\partial T}\right)_P = -5.0 \times 10^{-5} VK^{-1}$
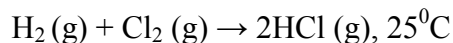
Solution

$$\Delta G = -nFE = -195815J$$

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P = nF\left(\frac{\partial E}{\partial T}\right)_P - 9.65 JK^{-1}$$

$$\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P = \underline{\underline{-19869J}}$$

Spontaneity and relative values of ΔH **and** $T\Delta S$

ΔH	ΔS	ΔG =ΔH-TΔS	Conclusion
- (exothermic)	+	At all T	Spontaneous
- (exothermic)	-	- at low T + at high T	Spontaneous Non-spontaneous
+ (endothermic)	+	+ at low T - at high T	Non spontaneous Spontaneous
+ (endothermic	-	At all T	Forbidden in the forward (non spontaneous)

Example 3.4.8. calculate the free energy change for the reaction

$$H_2\ (g) + Cl_2\ (g) \rightarrow 2HCl\ (g),\ 25^0C$$

Given , $\Delta H^0(H-H) = 435\ ^{KJ}/_{mol}, \Delta H^0(Cl-Cl) = 240\ ^{KJ}/_{mol}$

$\Delta H^0(H-HCl) = 430\ ^{KJ}/_{mol}\ S^0(H_2) = 130.59\ ^{K^{-1}J}/_{mol}$

$\Delta S^0(Cl_2) = 22.95 JK^{-1}mol^{-1}, S^0(HCl) = 186.68 JK^{-1}mol^{-1}$

Solution $\Delta G^0 = \Delta H^0 - T\Delta S^0$

ΔH^0 = energy absorbed – energy released

$$= \Delta H^0(H-H) + \Delta H^0(Cl-Cl) - 2 \times \Delta H^0(H-Cl)$$

$$= (435 + 240 - 2 \times 430)KJ = -185KJ$$

$\Delta S^0 = \sum S^0_{(products)} - \sum S^0_{(reac\tan ts)}$

$$= 2 \times S^0(HCl) - S^0(H_2) - S^0(Cl_2)$$

$$= (2 \times 186.68 - 130.59 - 222.95)JK^{-1} = 19.82 \times 10^{-3}\ KJK^{-1}$$

$\Delta G = \Delta H^0 - T\Delta S^0$

$$= -185KJ - (298 \cancel{K}) \times 19.82 \times 10^{-3}\ K\cancel{J}^{-1}$$

$\Rightarrow$ Spontaneous or exergonic

$$= \underline{\underline{-190.9KJ}}$$

3.4.4.   Maxwell relation

To this point, the state functions U, H, A, and G, all of which have the units of energy have been defined. The functions U and H are used to calculate changes in energy for processes, and A and G are used to calculate the direction in which processes evolve and the maximum work the reactions can produce. In this section, we discuss how these state functions depend on the macroscopic system variables. To do so, the differential forms dU, dH, dA, and dG are developed. As we will see, these differential forms are essential in calculating how U, H, A, and G vary with state variables such as P and T. Starting from the definitions

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS = U + PV - TS$$

the following total differentials can be formed:

$$dU = TdS - PdV$$

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$

$$dG = TdS + VdP - TdS - SdT = -SdT + VdP$$

These differential forms express the internal energy as $U(S,V)$, the enthalpy as $H(S,P)$, the Helmholtz energy as $A(T,V)$, and the Gibbs energy as $G(T,P)$. Although other combinations of variables can be used, these **natural variables** are used because the differential expressions are compact.

What information can be obtained from the differential expressions in Equations dU through Equations dG? Because U, H, A, and G are state functions, two different equivalent expressions such as those written for dU here can be formulated:

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

This Equation (6.21) to be valid, the coefficients of dS and dV on both sides of the equation must be equal. Applying this reasoning to Equations Du through dG, the following expressions are obtained:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

These expressions state how U, H, A, and G vary with their natural variables. For example, because T and V always have positive values, Equation H 1above states that H increases if either the entropy or the pressure of the system increases. There is also a second way in which the differential expressions in Equations dU through dG can be used. we know that because dU is an exact differential:

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U(S,V)}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U(S,V)}{\partial V}\right)_S\right)_V$$

The relations derived from the fundamental these equations, based on the criteria of exact differential (state function in physical chemistry) are called **Maxwell's Relation.**

$$dU = TdS - PdV \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dH = TdS + VdP \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$dA = -SdT - PdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dG = -SdT + VdP \Rightarrow -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

Example 3.6

Show that $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

Solution

Because U is a state function, $\left(\frac{\partial}{\partial V}\left(\frac{\partial U(S,V)}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U(S,V)}{\partial V}\right)_S\right)_V$.

Substituting $dU = TdS - PdV$ in the previous expression,

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial[TdS - PdV]}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial[TdS - PdV]}{\partial V}\right)_S\right)_V$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

3.5. The third law of thermodynamics

The variation of entropy of a substance with temperature at constant pressure is given by

$$dS = \frac{C_P}{T}dT$$

$$\int_{T_1}^{T_2} dS = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P}{T}dT$$

$$\Rightarrow S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_P}{T}dT$$

$\Rightarrow S(T_2)$ can be evaluated provided the quantities on the right hand side of this equation are known. C_P can be measured experimentally over a range of temperature but the problem remains to find the value of $S(T_1)$. This problem is solved by assigning a zero value to $S(T_1)$ at absolute zero as stated below by the third law of thermodynamics.

Statement of third law of thermodynamics:

*"**Every substance has finite positive entropy, but at absolute zero (0K) the entropy may become zero and does so in case of a perfectly crystalline substance.**"*

The statement is confined to pure crystalline solids because theoretical arguments and evidence have shown that the entropy of solutions and super cooled liquids is not zero. For pure crystalline solids the law has been varied repeatedly.

$$\text{Thus as } T \rightarrow 0, \ S(T) \rightarrow 0$$

$$\Rightarrow S^0(T) = \int_0^T \frac{C_P}{T} dT$$

Where $S^0(T)$ is the absolute entropy of a substance at a temperature $T \ K$ and it is appositive quantity. Its value can be calculated if we integrate the right hand side of the equation (4.45) from $T = 0$ to any desired temperature T. To be able to integrate we must know the value of right from $T = 0$ to the desired temperature T.

PROBLEMS

1. An electric battery is charged by supplying 250 kJ of energy to it as electrical work(by driving an electric current through it), but in the process it loses 25 kJ of energy as heat to the surroundings. What is the change in internal energy of the battery?   Ans: +225 kJ

2. The heat capacity of a beaker of water is 0.50 kJ/K with the observed temperature rise of 4.0 K. How much amount of heat transferred to the water?   Ans: 2kJ

CHAPTER FOUR

4. Chemical Equilibrium And Phase Equilibrium

4.1. Chemical Equilibrium

4.1.1. Introduction

It is well established fact that reversible reactions do not go to completion even if favorable conditions are maintained. The reactions proceed to some extent and supposed to stop often leaving considerable amounts of unreacted reactants. When such a stage is reached in the course of a reaction that no further reaction occur, it is said to have attained a state of equilibrium at that temperature and observable properties of the system do not change with time.

Equilibrium is a state in which there are no observable changes as time goes.

Chemical equilibrium is defined as a chemical system where the concentrations of reactants and products remain constant over time. On the molecular level, the system is dynamic: *The rate of change is the same in either the forward or reverse directions.* At this equilibrium condition the reaction proceeds in both directions at equal rates so that the rate of formation of products is exactly equal to the rate of disappearance of the reactants. There are two types of equilibrium: Physical and Chemical equilibrium.

Physical equilibrium occurs between two phases of the same substance. Changes that occur are physical which mean has the same chemical composition.

Chemical equilibrium occurs in between the chemical species of the reactionchemists are more interested in this because the progress of the reaction can be easily monitored.

The Equilibrium Constant (K) - A number equal to the ratio of the equilibrium concentrations of the products to the equilibrium concentrations of the reactants each raised to the power of its stoichiometric coefficient. For a general reaction:

$$aA + bB \rightleftharpoons cC + dD$$
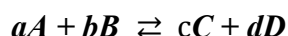
Equilibrium equation:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

coefficients
Products
Reactants
Equilibrium constant
Equilibrium constant expression or mass action expression

Equilibrium constants can be expressed using K_c or K_p. K_c uses the concentration of reactants and products to calculate the equilibrium constant. K_p uses the pressure of the gaseous reactants and products to calculate the equilibrium constant.

Law of Mass Action - For a reversible reaction at equilibrium and constant temperature, acertain ratio of reactant and product concentrations has a constant value (K).

**The relationships between chemical reaction and expression of its equilibrium constant**

► If a reaction is re-written where the reactants become products and products-reactants, the new Equilibrium Expression is the reciprocal of the old. i.e. ***K_{new} = 1/$K_{original}$***

► When the entire equation for a reaction is multiplied by n, ***K_{new} = $(K_{original})^n$***

► For a reaction which is the **sum** of two or more reactions, the overall *K* is the **product** of the expressions for *K* for the individual steps:

  o ***$K_{overall}$ = K1 × K2 × K3 • • •***

4.1.2. Standard Gibbs free energy of reaction and equilibrium

Let us consider the reaction

$$aA + bB \rightleftarrows cC + dD$$
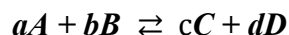
If all moles of the reactants as expressed by the balanced chemical equation have combined to form the products as expressed by the equation, then we can say that the progress of the reaction is 100%. But, when all the reactants are not consumed the progress of the reaction is less than 100%. Therefore, it is convenient to define a new variable to show the progress of the reaction called ***extent of reaction*** (ξ).

The value of the Gibbs free energy ΔG decreases until the extent of reaction ξ reaches its equilibrium $\xi(eq)$. At $\xi(eq)$, the reaction has no longer energy i.e. $\Delta G = 0$, at $\xi = 0$ there is no reaction and $\xi = 1$ mol represents complete reaction.

► Let the reaction advances with an infinitesimal amount $d\xi$, then the reactants and products are changed as follows

Change in amount of A $= dn_A = -ad\xi$, Change in amount of B $= dn_B = -bd\xi$, Change in amount of C $= dn_C = cd\xi$ and Change in amount of D $= dn_d = dd\xi$

➢ The negative indicates the decrease in the reactants because they are consumed in the reaction. Hence, we can express the differential extent of reaction as

As the reaction takes place the free energy also changes. The change in Gibb's free energy can be expressed in terms of the chemical potential of the species as

$$dG = -SdT + PdV + \sum \mu_i dn_i$$

$$dG = -SdT + PdV + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

$$dG = -SdT + PdV - \mu_A a d\xi - \mu_B b d\xi + \mu_C c d\xi + \mu_D d d\xi$$

Since the reaction is carried out at constant temperature and pressure (volume is also constant) can be written as

$$dG = \sum \mu_i dn_i$$

Substituting the values of dn_is , we have

$$(dG)_{P,T} = \left[d\mu_D + c\mu_C - (b\mu_B + a\mu_A) \right] d\xi$$

$$\Rightarrow \left[\frac{\partial G}{\partial \xi} \right]_{P,T} = \left[d\mu_D + c\mu_C - (b\mu_B + a\mu_A) \right] = \Delta G$$

Then, $\left[d\mu_D + c\mu_C - (b\mu_B + a\mu_A) \right] = \Delta G$ from the definition of chemical potential

Chemical potential is the change of Gibbs energy with the change of amount of one component of the system by keeping the T, P and the other amounts of components constant.

The sign of ΔG and $\left[\frac{\partial G}{\partial \xi} \right]_{P,T}$ are a measure of the nature of the chemical reaction. The decrease in the free energy of the reaction is defined as the ***chemical affinity*** (A_f):

$$\Rightarrow A_f = -\left[\frac{\partial G}{\partial \xi} \right]_{P,T} = -\Delta G$$

The affinity A_f and the reaction free energy ΔG are numerically exactly equal and opposite in sign but represent different ways of viewing at the same situation. When ΔG is used the system is thought of as large enough to allow a moles of A and b moles of B to react: When A_f is used it implies that only $a d\xi$ moles of A and $b d\xi$ moles of B react.

▶ When the derivative $\left[\frac{\partial G}{\partial \xi} \right]_{P,T} = -ve \Rightarrow A_f = +ve$, the free energy of the system decreases as the reaction proceeds in the forward direction i.e $d\xi$ is positive but ΔG is negative and the reaction is spontaneous.

▶ When the derivative $\left[\dfrac{\partial G}{\partial \xi}\right]_{P,T} = +ve \Rightarrow A_f = -ve$, the reaction is spontaneous in the reverse direction

▶ When the derivative $\left[\dfrac{\partial G}{\partial \xi}\right]_{P,T} = 0 \Rightarrow A_f = 0$, the free energy has the minimum value and reaction is at

equilibrium. This equilibrium condition is applicable for all reactions.

Relationships between K and ΔG^o

The standard Gibbs free energy change for reaction is ΔG^o and represents the energy available for reaction of one mole of reactants reacts until it reaches its equilibrium. Figure 2.1 relates ΔG and ξ, and clearly shows how the amount of energy available for reaction ΔG decreases during reaction (i.e. in going from left to right as ξ increases). Stated another way, the gradient of the curve is always negative before the position of equilibrium, so any increases in ξ cause the value of ΔG to become more negative.
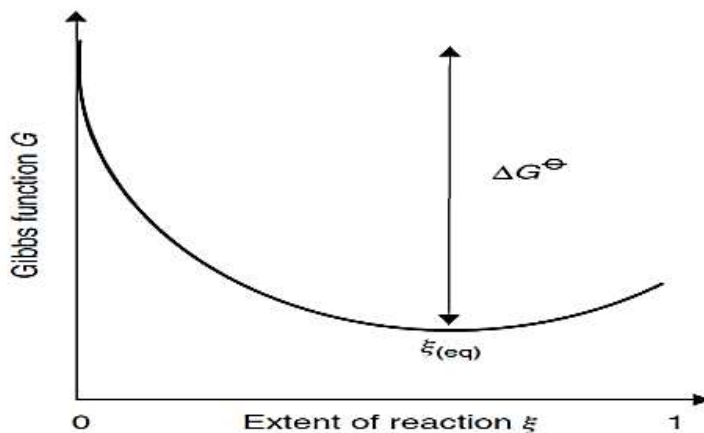

Figure 4.1. The value of Gibbs free energy as a function of an extent of reaction

The amount of energy liberated per incremental increase in reaction extent is quite larger at the beginning of reaction but decreases until the equilibrium; a tiny increase in the extent of reaction would not change the total ΔG. The minimum value of ξ *on the G* versus ξ *graph* is the reaction's position of equilibrium $\xi(eq)$ at which maximum amount of energy has already been expended at equilibrium, so ΔG is zero.

The relationship between the energy available for reaction ΔG and the extent of reaction (expressed in terms of the reaction quotient Q) is given by

$$\Delta G = \Delta G^o + RT \ln Q$$

Where ΔG is the energy available for reaction during chemical changes, Q is reaction quotient and ΔG^o is the standard change in Gibbs function.

Before we look at this Equation in any quantitative sense, we note that if $RT \ln Q$ is smaller than ΔG_o, then ΔG is positive. The value of ΔG only reaches zero when ΔG_o is exactly the same as $RT \ln Q$. In other words, there is no energy available for reaction when $\Delta G = 0$: we say the system has 'reached equilibrium'. In fact, $\Delta G = 0$ is one of the best definitions of equilibrium.

Justification

Consider again the simple reaction of Equation

$$aA + bB \rightleftarrows cC + dD$$
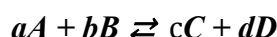
We ascertain the Gibbs energy change for this reaction. We start by saying

$$\Delta G = \sum vG_{products} - \sum vG_{reactants}$$

Where v is the respective stoichiometric number; so

$$G = cG_C + dG_D - aG_A - bG_B \qquad\qquad 2.7$$

And $G = G^0 + RT \ln \frac{P}{P^0}$, so each G term in Equation (2.7) may be converted to a *standard* Gibbs function.

$$\Delta G = cG_C{}^0 + RT\ln\left(\frac{P_C}{P^0}\right)^C + dG_D{}^0 + RT\ln\left(\frac{P_D}{P^0}\right)^d - aG_A{}^0 + RT\ln\left(\frac{P_A}{P^0}\right)^a - bG_B{}^0 + RT\ln\left(\frac{P_B}{P^0}\right)^b$$

We can combine the G_o terms as ΔG^o by saying

$$\Delta G^0 = cG_C{}^0 + dG_D{}^0 - aG_A{}^0 - bG_B{}^0$$

So the ΔG equation simplifies to become:

$$\Delta G = \Delta G^0 + RT\ln\left(\frac{P_C}{P^0}\right)^C + RT\ln\left(\frac{P_D}{P^0}\right)^d - RT\ln\left(\frac{P_A}{P^0}\right)^a - RT\ln\left(\frac{P_B}{P^0}\right)^b$$

Then, using the laws of logarithms, we can simplify further:

$$\Delta G = \Delta G^0 + RT\left[\ln\frac{\left(\frac{P_C}{P^0}\right)^C\left(\frac{P_D}{P^0}\right)^d}{\left(\frac{P_A}{P^0}\right)^a\left(\frac{P_B}{P^0}\right)^b}\right]$$

The bracketed term is the reaction quotient, expressed in terms of pressure; a similar proof may be used to derive an expression relating to ΔG_o and K_c. In the case of equilibrium, Q = Kp and $\Delta G = 0$

$$0 = \Delta G^0 + RT\left[\ln\frac{\left(\frac{P_C}{P^0}\right)^C\left(\frac{P_D}{P^0}\right)^d}{\left(\frac{P_A}{P^0}\right)^a\left(\frac{P_B}{P^0}\right)^b}\right] \qquad \text{Then,} \qquad \Delta G^0 = -RT\left[\ln\frac{\left(\frac{P_C}{P^0}\right)^C\left(\frac{P_D}{P^0}\right)^d}{\left(\frac{P_A}{P^0}\right)^a\left(\frac{P_B}{P^0}\right)^b}\right]$$

$$\text{Since, } Q = Kp = \frac{\left(\frac{P_C}{P^0}\right)^C \left(\frac{P_D}{P^0}\right)^d}{\left(\frac{P_A}{P^0}\right)^a \left(\frac{P_B}{P^0}\right)^b}$$

$$\Delta G^0 = -RTlnQ = -RTlnKp$$

The derivation of this equation is a thermodynamic proof the existence of equilibrium constant Since ΔG^o is a function of temperature alone, it cannot depend on the partial pressure

☙ As known *Kp* at certain temperature is constant.

☙ $\Delta G^0 = -RTlnKp$ not only proves the existence of an equilibrium constant, *Kp*, but also give us an explicit formula for calculating *Kp* from ΔG^o data.

This allows us to develop a set of criteria to determine in which direction a reaction will proceed under non-standard conditions. This is because Q/K will determine the sign of ΔG:

        1. If *Q/K < 1*, then ΔG is negative, and the reaction is spontaneous as written

        2. If *Q/K = 1*, then ΔG = 0 and the system is at equilibrium,

        3. If *Q/K > 1*, then ΔG is positive, and the reaction is spontaneous in the opposite direction as written

Example. Consider the dissolution of CaCO3 (calcite) in aqueous solution:

        $CaCO_3 \rightarrow Ca^{2+} + CO_3{}^{2-}$

        Does the reaction proceed spontaneously as written?

Calculate the free energy of reaction at standard state and equilibrium constant (products and reactants at activity = 1, P = 1 atm, T = 25°C): free energy of $CaCO_3$, Ca^{2+} and $CO_3{}^{2-}$ are -270,-132, and -126 kcalmol^{-1} respectively.

$$\Delta G^0 = \sum vG_{products} - \sum vG_{reactants}$$

$$\Delta G° = (1(-132) + 1(-126) - (1(-270)) \text{ kcal/mole}$$

$$= (-258 + 270) \text{ kcal/mole}$$

$$= +12 \text{ kcal/mole}$$

Therefore, at standard state, the reaction spontaneously proceeds in the opposite direction to what is written *(i.e.*, calcite precipitates).

From Sample Calculation of above, we know: ΔG° = +12 kcal/mole

Thus:

$$12\frac{kcal}{mol} = -\left(\frac{1.9987cal}{mol}\right)\left(\frac{1kcal}{1000ca}\right)(298K)lnK \qquad \text{All units cancel out}$$

$$lnK= -20.27$$

$$K = 1.58 \times 10^{-9} \quad \textbf{equilibrium constant}$$

Example. The equilibrium constant for the reaction $A \rightarrow M$ is 0.1 at 300K. Calculate ΔG and ΔG^0 for the production of 1 mol of M at a pressure of 1 atm from A at a pressure of 20 atm and predict the nature of the reaction under this condition.

Solution

$$\Delta G^0 = -RT \ln K_P$$

$$\Delta G^0 = -2.303 \times 8.314 JK^{-1}mol^{-1} \times 300K \log 0.1$$

$$\Delta G^0 = 5744 Jmol^{-1}$$

$$Q_P = \frac{1.0\ atm}{20.0\ atm} = \frac{1}{20}$$

$$\Delta G = \Delta G^0 + RT\ \ln Q_P = -RT \ln K_P + RT\ \ln Q_P$$

$$\Delta G = 2.303 \times 8.314 JK^{-1}mol^{-1} \times 300K[-\log 0.1 + \log \frac{1}{20}]$$

$$\Delta G = -1729 Jmol^{-1}$$

❖ Since the free energy change ΔG is negative for the given reaction it should precede forward spontaneously.

4.1. **Relationship between K_P and K_C**

Kp and Kc for a given reaction are not the same numerically. Since for ideal gases the pressure is given by

$$P = \left(\frac{n}{v}\right)RT \qquad \text{Where V is the volume occupied by } \boldsymbol{n} \text{ moles of a gas at a temperature T}$$

But from the expression in the above equation $\frac{n}{V}$ is equal to the molar concentration C therefore

$$P = \left(\frac{n}{V}\right)RT \Rightarrow P = CRT$$

Substitute the value of P in the Kp equation give

$$K_P = \frac{C_C^c(RT)^c \cdot C_D^d(RT)^d}{C_A^a(RT)^a \cdot C_B^b(RT)^b}$$

$$K_P = \frac{C_C^c \cdot C_D^d}{C_A^a C_B^b} \cdot \frac{(RT)^C \cdot (RT)^d}{(RT)^a \cdot (RT)^b} = \frac{C_C^c C_D^d}{C_A^a C_B^b} \cdot \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

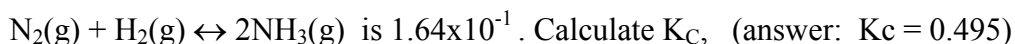$$K_P = K_C.(RT)^{(c+d-a+b)} \qquad \text{But } (c + d) - (a + b) = \Delta n$$

$$K_P = K_C (RT)^{\Delta n}$$

If $\Delta n > O$ => number moles reactants < number moles of prod => $K_P > K_C$

If $\Delta n > O$ => number moles reactants < number moles of prod => $K_P < K_C$

If $\Delta n > O$ => number moles reactants < number moles of prod => $K_P = K_C$

Problem. At 2 atmosphere and 673 k, the equilibrium constant K_P for the given reaction.

$N_2(g) + H_2(g) \leftrightarrow 2NH_3(g)$ is 1.64×10^{-1}. Calculate K_C, (answer: $Kc = 0.495$)

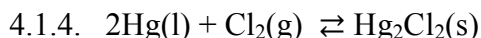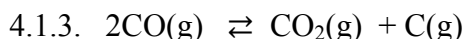## Properties of equilibrium constants (Kc and K_P)

i.   The expressions for K_P and K_C are valid only at equilibrium

ii.   The equilibrium varies only with T of the reaction and is constant at a constant temperature

iii.   The values of K_P and K_C can determine the extent to which a particular reaction which take place under the given conditions. Large value of K_P and K_C imply that the formation of more products & the reaction is more on the right side. Small value of K_P and K_C shows little product and the reaction is more on the left side.

iv.   It is possible to predict quantitatively the effect of changing concentrations of reactants and products on the extent of reaction.

4.2. Heterogeneous Equilibria

Homogeneous equilibrium is an equilibrium at which all reactants and products of the reaction system are in the same phase. On the other hand, *Heterogeneous* equilibrium is an condition in which more than one phase exists in a reaction mixture. (One or more of the components is a liquid or solid.)

A pure solid always has the same concentration at a given temperature, and its volume does not change much. Since, we're only concerned with quantities that are changing, we eliminate the terms for pure liquids and solids from the reaction quotient:

Problem: Write equilibrium laws for the following heterogeneous reactions.

4.1.3. $2CO(g) \rightleftarrows CO_2(g) + C(g)$

4.1.4. $2Hg(l) + Cl_2(g) \rightleftarrows Hg_2Cl_2(s)$

4.1.5. $NH_3(g) + HCl(g) \rightleftarrows NH_4Cl(s)$

4.3. Factors which influence the equilibrium: Lechateliers principle

Lechatelier's principle states *''If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change''*. When a chemical system in a state of equilibrium is disturbed, it retains the equilibrium by undergoing a net reaction that reduces the effect of the disturbance Such common disturbances are the change in the factors that affect the equilibrium are *concentration, pressure and temperature*

- If the concentration of a solute reactant is increased, the equilibrium position shifts to use up the added reactants by producing more products.
- If the pressure on an equilibrium system is increased, then the equilibrium position shifts to reduce the pressure.
- If the volume of a gaseous equilibrium system is reduced (equivalent to an increase in pressure) then the equilibrium position shifts to increase the volume (equivalent to a decrease in pressure).
- If the temperature of an endothermic equilibrium system is increased, the equilibrium position shifts to use up the heat by producing more products.
- If the temperature of an exothermic equilibrium system is increased, the equilibrium position shifts to use up the heat by producing more reactants.

Quantitative Effects in Temperature and Pressure

The equilibrium constant of a chemical reaction is constant at a given temperature, but its magnitude varies considerably with changes in temperature. The Lech atelier's principle gives only a qualitative idea of the shift of equilibrium when temperature changes. However, Quantitative expression for the variation of equilibrium constant with temperature can be derived thermodynamically as follows :

From the relation of equilibrium constant and Gibbs function, we have

$$\Delta G^\circ = -RT \ln Kp \quad \text{then} \quad \ln Kp = -\frac{\Delta G^\circ}{RT}$$

The differentiation of this equation with respect to T at constant pressure gives,

$$\frac{d\ln Kp}{dT} = -\frac{1}{R}\left[\frac{d(\Delta G^\circ)/T}{dT}\right]$$

Where $\Delta G^\circ = \Delta H^o - T\Delta S$ then $\left[\frac{d(\Delta G^\circ)/T}{dT}\right]_P = -\frac{\Delta H^o}{T^2}$ and the above diferention becomes

$$\frac{d\ln Kp}{dT} = -\frac{1}{R}\left[-\frac{\Delta H^o}{T^2}\right]$$

$$\text{Then} \quad \frac{d\ln Kp}{dT} = \frac{\Delta H^o}{RT^2}$$

This result, which is fundamentally important in chemistry, it represents the variation of equilibrium constant with temperature. In order to integrate this equation; it must be known as function of temperature. Assuming to be constant over a small range of temperature, integration of the above equation yields

$$log \frac{Kp_2}{Kp_1} = \frac{\Delta H^o}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$ This equation is known as ***Van't Hoff's equation.***

4.2. Phase Equilibrium

4.2.1. Introduction

The main idea of this chapter is to establish the thermodynamic relations obeyed by two or more phases that are at equilibrium with each other. A phase is a portion of a system (or an entire system) inside which intensive properties do not change abruptly as a function of position. The principal kinds of phases are solids, liquids, and gases, also plasmas (ionized gases), liquid crystals, and glasses are sometimes considered to be separate types of phases. Solid and liquid phases are called condensed phases and a gas phase is often called a vapor phase. Several elements such as carbon exhibit solid-phase allotropy because there is more than one kind of solid phase of the element. For example, diamond and graphite are both solid carbon but have different crystal structures and physical properties. This phenomenon is called **polymorphism**

Phase equilibrium describes the condition at which phases (such as solid, liquid and/or gas) co-exist at some temperatures and pressure, but interchange at others.

4.2.2. Definitions

1. *Phase* (P)

A phase is defined as part of the system which is homogenous throughout and separated from other homogenous part of the system by a means of definite boundary.

Example 4.2.1.

i. A gaseous mixture constitute one phases

ii. In case of liquids depending up on their mutual solubility one or more phases can arise.

a) Water – $CCl_4 \rightarrow$ two phases   d) Water – ethanol $\rightarrow$ one phase

b) Liquid – its vapour $\rightarrow$ two phases   e) Aqueous solutions, NaCl in $H_2O \rightarrow$ one phase

c) $CaCO_3$ (s) $\rightarrow$ CaO (s) + CO_2 (g) $\rightarrow$ three phases   f) $S_{rho} \rightarrow S_{mono} \rightarrow$ two phases

2. *Number of components* (C)

The minimum number of independent chemical species necessary to describe the composition of each and every phase of the system in equilibrium is called the number of components.

Example 4.2.2.

a. Equilibria between phases of water. C is *one* because each phase is represented by H_2O

b. Aqueous sugar solution (sugar + H_2O (l)) number of components is 2.

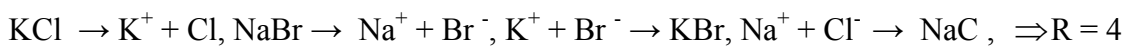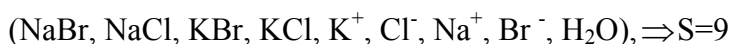For chemically reactive systems the number of components can be calculated as $C = S - R$

Where S is number of chemical species and R is number of independent chemical reactions

If ions are also present in the system then for the condition of neutrality (No, positive ions = n negative ions) one is added to the value of R and the equation modified as

$$C = S - (R + 1)$$

Example 4.2.3

a. For Aqueous NaCl solution, $C = S - (1 + 1) = 4\text{-}2 = \underline{2}$
b. For PCl_5 (s) $\rightarrow$ PCl_3 (s) + Cl_2 (g), $C = S - (1 + 0) = 3\text{-}1 = \underline{2}$
c. $CaCO_3$ (s) $\rightarrow$ CaO (s) + CO_2 (g), $C = S - (1 + 0) = 3\text{-}1 = \underline{2}$
d. $KCl - NaCl\text{-}H_2O$ system, $C = 6 - (2 + 1) = \underline{3}$

e. $KCl - NaBr - H_2O$ system , $C = 9 - (4 + 1) = \underline{4}$ (Condition of neutrality = 1)

    (NaBr, NaCl, KBr, KCl, K^+, Cl^-, Na^+, Br^-, H_2O), $\Rightarrow$S=9

    $KCl \rightarrow K^+ + Cl$, NaBr $\rightarrow$ $Na^+ + Br^-$, $K^+ + Br^- \rightarrow$ KBr, $Na^+ + Cl^- \rightarrow$ NaC , $\Rightarrow R = 4$

3. *Number of degrees of freedom* (F)

Number of degrees of freedom is defined as the minimum number of independent intensive variables such as pressure, temperature and concentration that must be specified in order to know all the remaining intensive variables and describe the state of a system completely. If we consider a one phase, one component system, it will have a number of intensive properties like density, refractive index, surface tension, viscosity etc. If the temperature and pressure are given, then the substance will have a fixed value of other intensive properties at this given temperature and pressure. Degree of freedom is sometimes known as variance of the system.

Example 4.2.4.

a) For a gaseous system, to describe completely only two of the three variables (T and P) are essential because the third can be obtained from the two using the equation of state.

$\Rightarrow$ Number degrees of freedom = 2 for pure gaseous systems.

b) For one component system F + P = 3

c) If there is a single phase F = 3 –1 = 2 for pure gas specify P & T

d) If there are two phase F = 3 – 2 = 1 specifying T or P

e) If there are three phases F = 3 – 3 = O   no need of fixing because any variable will not be altered without losing one of the phases. For example the three phases of water coexist at 0.0099 ^{0}C and 4.579 mmHg. This point is called the triple point. If change one of the variable we will lose the triple point. this if

F = 0, invariant system, F = 1, univeriant system and F = 2, bi-variant system

4.2.3. Phase rule

The ***phase rule*** is an important and versatile tool in the study of heterogeneous equilibria. It relates the conditions which must be specified to describe the state of a system at equilibrium. If the *p* phases in a multiphase simple system and *c* components are separated from each other so that they cannot equilibrate with *c* + 1 independent intensive variables for each phase, a total of *p(c* + 1) variables. Now place the phases in contact with each other, open them to each other, and allow them to equilibrate. There are three aspects of equilibrium. *Thermal equilibrium* implies that all phases have the same temperature; mechanical *equilibrium* implies that all phases have the same pressure, and *phase equilibrium* implies that the chemical potential of every substance has the same value in every phase.

The phase rule states that ''***for systems in complete internal equilibrium in which the phases can exchange material, heat and P-V work''***.

4.2.4. Derivation of the phase rule

Consider a system of C components containing P phases.

- The composition of each phase can be specified if the amount of each component is known. All we need here is to describe the mole fraction of each component.

- If C is the number of components required to describe the composition of a phase, then the total number of composition variables for P phases are PC.

- Besides these there are two variables temperature and pressure which have to be considered. Then the total number of independent variables is PC + 2.

- For each phase there is one equation and for phases there are P equation similar to the above equation and the total numbers of independent variables are to be specified are

$$CP + 2 - P \text{ or } P(C-1) + 2$$

When a heterogeneous system is in equilibrium at a constant temperature and pressure, the chemical potential of a particular component must be the same in all the phases in which it appears. For one component system having two phases α and β, the equality of chemical potential implies $\mu(\alpha) = \mu(\beta)$. Similarly for one component system having three $\alpha, \beta \& \delta$

$$\mu(\alpha) = \mu(\beta) = \mu(\delta) = \mu(\alpha)$$

- For each component in P phases, (P-1) relations are possible. Since three are C components, the total number of relations restricting the variations will be

$$C(P-1)$$

- Therefore, the degree of freedom or the number of independent variables F is given by

F = Total number of variables – Total number of relations restricting the variation among the variables
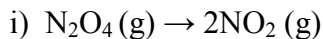
$$F = PC + 2 - P - C(P-1)$$

$$F + P = C + 2$$

This equation is given by Willard Gibbs and it is called the ***Gibbs phase rule***, the fundamental relation controlling the equilibria in heterogeneous systems.
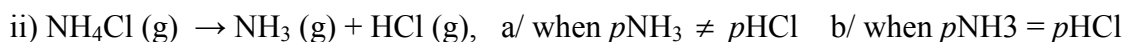
- For condensed systems pressure is not a significant variable and the phase rule takes the form $F + P = C + 1$.

Example 4.2.5. Write down the number of components, number of phases and evaluate the degrees of freedom for the following equilibria**.**

i) N_2O_4 (g) $\rightarrow$ 2NO$_2$ (g)

$$C = S - (R) = 2\text{-}1 = 1 \text{ and } P = 1, F = C + 2 - P = 1 + 2 - 1 = 2$$

ii) NH$_4$Cl (g) $\rightarrow$ NH$_3$ (g) + HCl (g),   a/ when pNH$_3 \neq p$HCl   b/ when pNH3 $= p$HCl
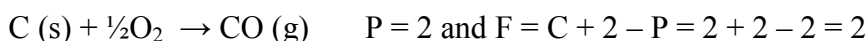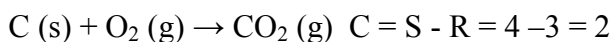
a/ $C = S - (R) = 3 - 1 = 2$, $P = 1$ and $F = C + 2 - P = 2 + 2 - 1 = 3$

b/ $C = S - (R + 1) = 3 - 2 = 1$, $P = 1$ and $F = C + 2 - P = 1 + 2 - 1 = 2$
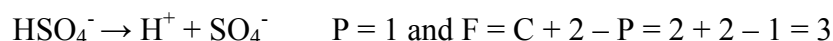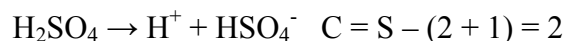
iii) Pure partly frozen acetic acid CH_3COOH (l) $\rightarrow$ CH_3COOH (s)

$C = S - R = 1 - 0 = 1$, $P = 2$ and $F = C + 2 - P = 1 + 2 - 2 = 1$

iv) Solid carbon in equilibrium with gaseous CO, CO_2, and O_2, at 100^0C.

C (s) $+ O_2$ (g) $\rightarrow CO_2$ (g) $C = S - R = 4 - 3 = 2$

C (s) $+ \frac{1}{2}O_2 \rightarrow CO$ (g) $P = 2$ and $F = C + 2 - P = 2 + 2 - 2 = 2$

v) A dilute solution of sulphuric acid in water

$H_2SO_4 \rightarrow H^+ + HSO_4^-$ $C = S - (2 + 1) = 2$

$HSO_4^- \rightarrow H^+ + SO_4^-$ $P = 1$ and $F = C + 2 - P = 2 + 2 - 1 = 3$

Exercise 4.2.1. Write down the number of components, number of phases and evaluate the degrees of freedom for the following equilibria**.**

a) An aqueous solution saturated with respect to both NaCl and KBr and in equilibrium with the vapour phase

b) Reduction of Fe_2O_3 in the presence of i) air ,and ii) oxygen alone

c) N_2 (g) $+ 3H_2$(g) $\rightarrow 2NH_3$(g)

4.2.5.   Phase diagrams

A *phase* of a substance is a form of matter that is uniform throughout in chemical composition and physical state. Thus, we speak of solid, liquid, and gas phases of a substance, and of its various solid phases, such as the white and black allotropes of phosphorus. A *phase transition* is the spontaneous conversion of one phase into another phase which occurs at a characteristic temperature for a given pressure. *A phase diagram* is a map that shows which phase is the most stable at different pressures and temperatures. The lines separating the regions in a phase diagram are called *phase boundaries*. At this curve the values of *p* and *T* at which two phases coexist in equilibrium and their chemical potentials are equal. A **triple point** is a point where three phase boundaries meet on a phase diagram.

Characteristic points

As we have seen, as the temperature of a liquid is raised, its vapour pressure increases. First, consider what we would observe when we heat a liquid in an open vessel. At a certain temperature, the vapour pressure becomes equal to the external pressure. At this temperature, the vapour can drive back the surrounding atmosphere and expand indefinitely. Moreover, there is no constraint on expansion; bubbles of vapour can form throughout the body of the liquid, a condition known as boiling.
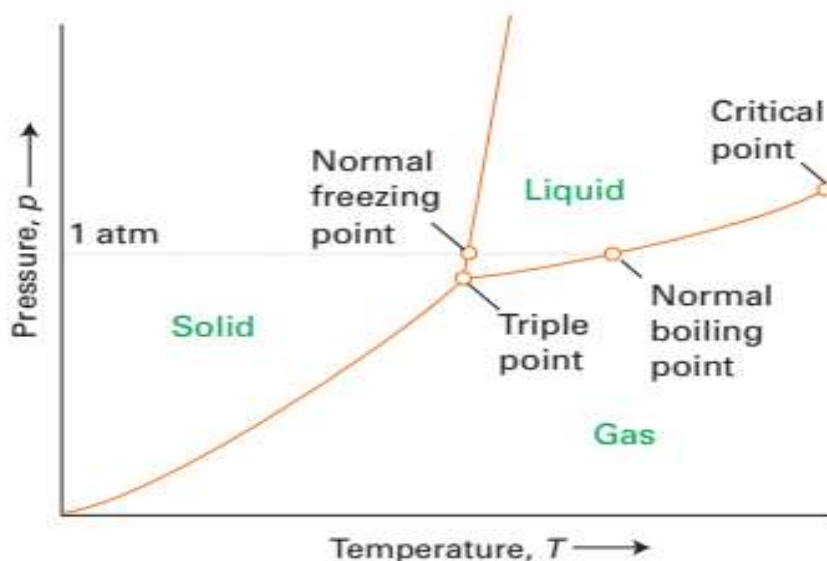
Figure 4.2. A typical phase diagram showing the regions of pressure and temperature at which each phase is the most stable.

The temperature at which the vapour pressure of a liquid is equal to the external pressure is called the boiling temperature. When the external pressure is 1 atm, the boiling temperature is called the normal boiling point, Tb.

Now consider what happens when we heat the liquid in a closed vessel. Because the vapour cannot escape, its density increases as the vapour pressure rises and in due course the density of the vapour becomes equal to that of the remaining liquid. At this stage the surface between the two phases disappears, as was depicted in Fig. 4.1. The temperature at which the surface disappears is the critical temperature, Tc. The vapour pressure at the critical temperature is called the critical pressure, pc, and the critical temperature and critical pressure together identify the critical point of the substance.

Table 4.1. Summary of terms used to describe phase changes

Phase transition	Name of transition	Everyday examples
Solid → gas	sublimation	Smoke forming from dry ice
Solid →liquid	Melting	Melting of snow or ice
Liquid → gas	Boiling or vaporization	Steam formed by a kettle
Liquid → solid	Freezing, solidification or fusion	Ice cubes formed in a fridge; hail
Gas → liquid	Condensation or liquefaction	Formation of dew or rain
Gas → solid	Deposition or condensation	Formation of frost

The temperature at which the liquid and solid phases of a substance coexist in equilibrium at a specified pressure is called the melting temperature of the substance. Because a substance melts at the same temperature as it freezes, 'melting temperature' is similar with freezing temperature. The solid–liquid boundary therefore shows how the melting temperature of a solid varies with pressure. The melting temperature when the pressure on the sample is 1 atm is called the normal melting point or normal freezing point, Tf

There is a set of conditions under which three different phases (typically solid, liquid, and vapour) all simultaneously coexist in equilibrium. It is represented by the triple point, where the three phase boundaries meet. The triple point of a pure substance is a characteristic, unchangeable physical property of the substance. For water the triple point lies at ice, liquid water, and water vapour coexist in equilibrium at no other combination of pressure and temperature. At the triple point, the rates of each forward and reverse process are equal (but the three individual rates are not necessarily the same).

4.2.6. Phase Diagrams for Simple Systems

1. One component system

The composition of a one-component system is fixed so that the state of the system may therefore be defined by specifying the value of any two of the pressure, volume and temperature. The state of the system may therefore be represented as a surface on a three dimensional pressure, volume and temperature plot. *Areas* on the surface represent regions where only one phase is stable. The *lines* drawn between the regions represent the values of these variables at which *two phases* coexist in equilibrium. *Triple Points* at the intersection between two lines represent the values at which *three phases* coexist in equilibrium.
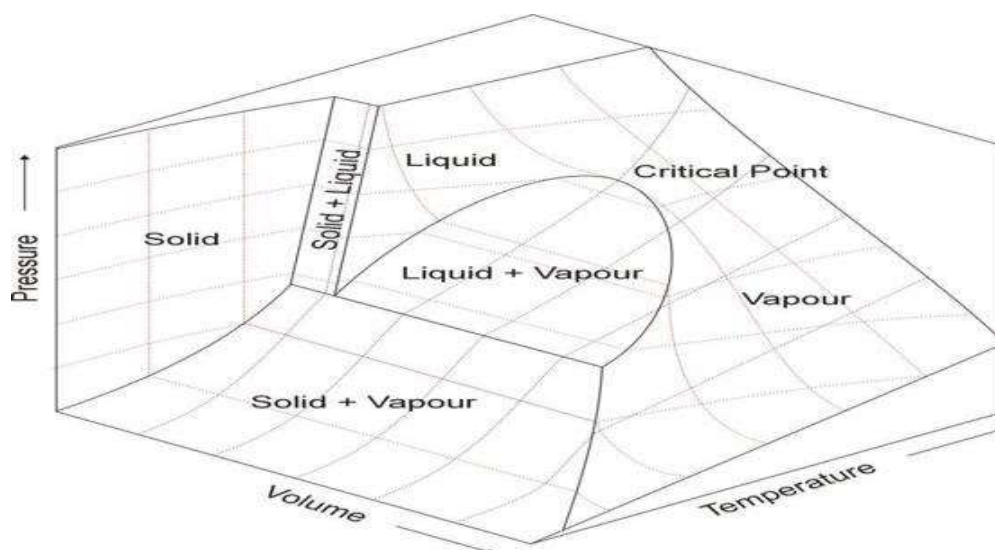

Figure 4.3. Pressure-volume-temperature phase diagram for a typical single component system

In practice it is usually easier to represent the phase diagram as two-dimensional projections of the three-dimensional surface. Phase diagrams of one-component systems are therefore usually drawn as pressure-temperature, pressure-volume and, occasionally, volume-temperature plots.

Pressure-Temperature Phase Diagrams

If pressure and temperature are taken as the independent variables that define the state of the system, then the volume must be a dependent variable and its value may therefore be determined for any point on the diagram.

Pressure-Volume Phase Diagrams

Less commonly seen are pressure-volume phase diagrams in which the pressure and volume are taken as the independent variable and temperature as the dependent variable.
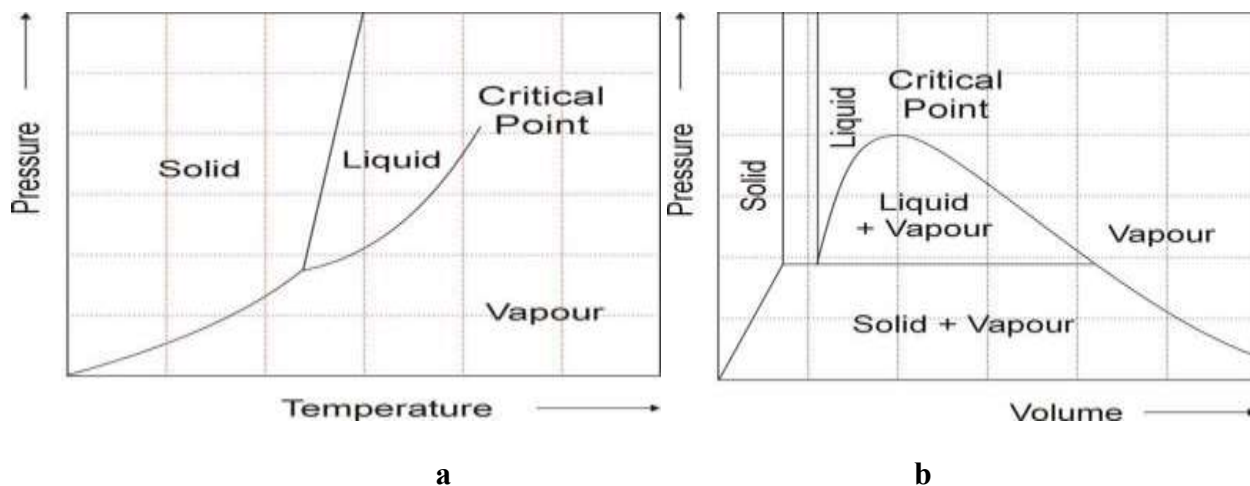

a   **b**

Figure 4.4. Projection of the pressure-volume-temperature surface to form a pressure- temperature (a) and pressure-volume (b) phase diagram

The Critical Point and Supercritical Behaviour

A critical point marks the conditions at which two phases become identical. Single component systems exhibit a critical point at which liquid and vapour phases become indistinguishable. Consider the behaviour of a one-component system in which liquid and vapour are in equilibrium. As the temperature increases, the pressure also increases, as the system follows the liquid-vapour equilibrium line on the phase diagram. This causes an increase in the density of the vapour phase and a slight decrease in the density of the liquid phase. Eventually, at the critical point, the densities of the two phases become equal and the two phases cannot be distinguished.

Invariant, Univariant and Bivariant Systems

Invariant states are represented by points on phase diagrams. Systems with one degree of freedom, $F = 1$, are univariant and are represented by lines and those with two degrees of freedom, $F = 2$, are bivariant and correspond to areas on phase diagrams.

For a one-component system, the coexistence of three phases in equilibrium corresponds to an invariant state since variant

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

This state is usually called *a triple point.* The three phases may only exist at a particular temperature and particular pressure. A single-component phase diagram may have several triple points. The most obvious triple point corresponds to the coexistence of solid, liquid and vapour phases. For water, this triple point occurs at a temperature of 273.16 K and a pressure of 608 Pa, at a temperature close to the normal freezing point, but at a much lower pressure. In contrast, for carbon dioxide, the triple point occurs at a much higher temperature and pressure than ambient conditions.

2. The phase diagram of the water system

Water exists in three forms as solid (ice), liquid (*l*) and vapour. The application of phase rule reveals that we can have the following types of equilibria. As the maximum number of degrees of freedom is two, water system can be represented by a two dimensional phase diagram using temperature and pressure as a variable, as shown in figure 3.4
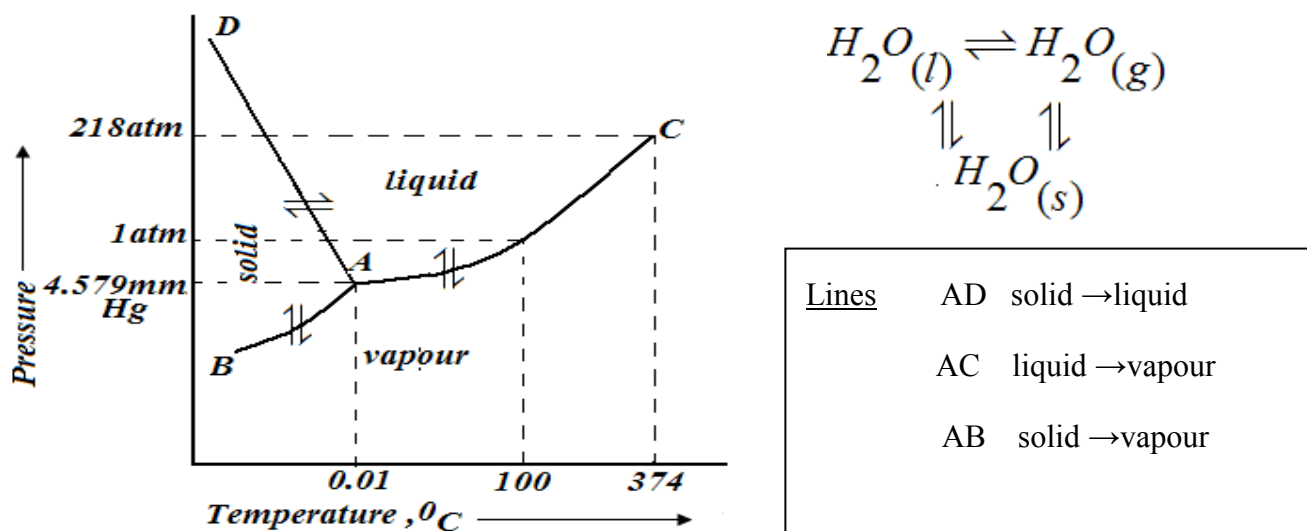

Figure 4.5 Phase diagram of water

Point A – is triple point where solid , liuid and vapour phases are at equilibrium

Point C – is critical point where the vapour & liquid are indistinguishable above that point.

➤ Within the single phase (areas) the system is bivariant, so the pressure and temperature can be varied independently.

➤ Separating the areas are lines connecting the point at which two phases coexist at equilibrium. The system is univariant (having one degree of freedom) i.e for each value of temperature there is only one value of the pressure within the lines at which both phases coexist.

➤ At the triple point the system is invariant (invariant) i.e if we change he values of the variables one of the phases will disappear.

3. The Clapeyron Equation

The slopes of the lines on a one-component pressure-temperature phase diagram may be derived from the Clapeyron equation. For any two phases we can write

$$dG\alpha = V\alpha dP - S\alpha dT \ and \ dG\beta = V\beta dP - S\beta dT$$

Where $V\alpha$ is the molar volume of phase α and $S\beta$ is the molar entropy of phase β.we need not label the pressure and temperature since at equilibrium these properties are the same for all phase within the system.

At equilibrium, $dG\alpha = dG\beta$ so, that

$$V\alpha dP - S\alpha dT = V\beta dP - S\beta dT$$

$$(V\alpha - V\beta)dP = (S\alpha - S\beta)dT,$$

We can write the differences as $V\alpha - V\beta = \Delta V \ and \ S\alpha - S\beta = \Delta S$. then

$$\Delta VdP = \Delta SdT \quad \text{this implies} \quad \frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

But

$$\Delta G = \Delta H - T\Delta S = 0$$

since at equilibrium

$$\Delta G = G_\alpha - G_\beta = 0$$

and therefore

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

which is the basis of Trouton's Rule.

Substituting gives

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

For one mole of ideal gas $\Delta V = RT/P$

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} = \frac{P \Delta H}{R T^2}$$

which is the differential form of the Clausius-Clapeyron equation. Rearranging gives

$$\frac{dp}{P} = \frac{\Delta H}{R} \frac{dT}{T^2}$$

The integrated form of this equation is

$$lnP_2 - lnP_1 = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad Clausius\text{-}Clapeyron\ equation$$

4. Two component systems

For a two component system, C =2, the phase rule can be written as

F = C – P + 2 or F + P = C + 2   ⇒ F = 4 – P

⇨ For a system having one phase the number degrees of freedom would be three

⇨ Three variables temperature, pressure & composition must be specified in order to describe a two component system completely.

To represent such a system graphically we must have the coordinates temperature, pressure and composition at right angles. This is a three dimensional figure which is rather difficult to construct. It is therefore customary to represent such a system by any two of the three variables keeping the third constant in this way one can represent the various relations in two component systems. In a two component system, the possible phase equilibria are;

Liquid → Vapour, Liquid → Liquid, Solid → Vapour , Liquid → Solid and Solid → Solid

Among the above listed equilibria those without the vapour phase are relatively unaffected by changes in pressure and such systems are often called condensed systems and are studied at constant pressure, usually (1 atmosphere).

⇨   When pressure is constant the phase rule become $F + P = C + 1$

 The equation is known as the reduced phase rule. F + P = 3   for a two component system

⇨ The equilibria taken is the liquid → solid equilibria the variables are temperature, and composition.

⇨ The phase diagram is represented on a temperature composition diagram

Experimental techniques to determine the equilibrium conditions

To determine the equilibrium conditions for solid-liquid systems, it is necessary to determine the composition of the mixture at different temperatures. This can be done in two general ways

      a. Thermal analysis method

      b. The solubility (saturation) method

a. Thermal analysis method

In this technique a mixture of two components of known composition is heated until a homogenous melt or liquid phase is obtained (inert atmosphere is used to avoid oxidation). The melt is then cooled at a slow rate during which the melt is thoroughly stirred to avoid super cooling. The temperature of the melt is recorded at regular intervals until it completely solidifies. The process is repeated for other mixtures covering the entire range of composition (0-100%).

The temperature time plots (cooling curves) for each composition are then constructed. From such a diagram (figure 3.5.) it is possible to detect the various transformations and phase transitions that occur during cooling.
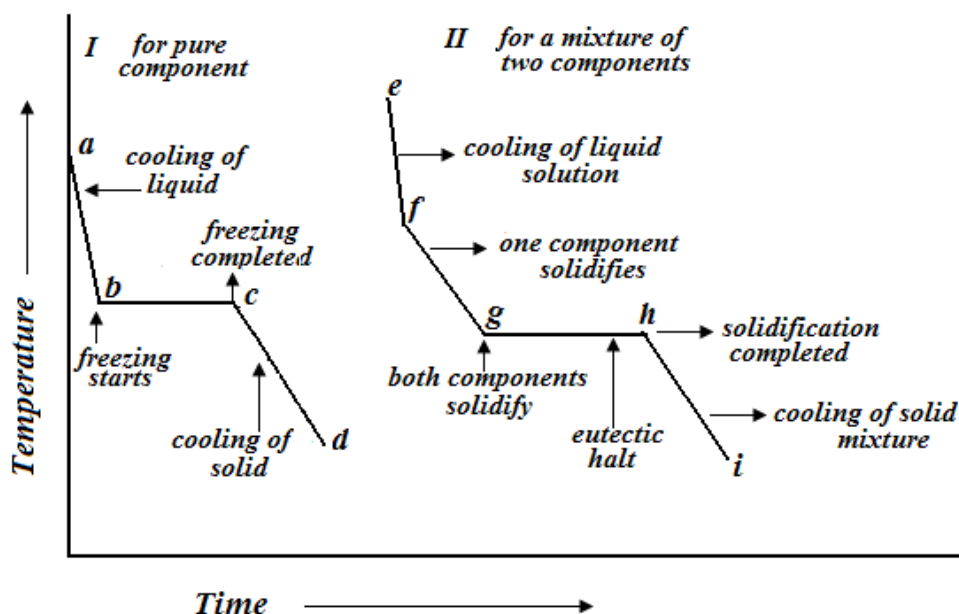

Figure 3.5. Cooling curves for a binary system with eutectic point **I)** for a pure component **II)** for a mixture of two components

When a melt containing only the pure component (a) is cooled slowly the cooling curve reveals that the slop of the curve is constant up to (b) which represents cooling of the melt at (b) the temperature is

constant with time up to (c) which is called the <u>Halt,</u> is due to the heat evolved when the liquid solidifies. When solidification is complete the curve cd is obtained which represents the progressive cooling of the pure solid. But when a melt of two components is cooled slowly, a typical cooling curve of type shown in figure 3.5 (II) is obtained. The system becomes univariant (F = 3-2 = 1). On further cooling more and more of the pure components separate out. At point g, the 2nd component also begins to crystallize from the melt and three phases are in equilibrium and the system becomes in variant (F = 3-3 = 0). The temperature remains constant. Finally when solidification is completed the system regains a degree of freedom (F = 1), and the temperature drops (hi) of the curve with a uniform cooling of the solid mass.

The experiments is repeated for different compositions of the substances (a and b), the temperature of the breaks and the halts for each cooling curve are recorded and plotted as functions of composition and a diagram of type figure 8.4 is obtained.
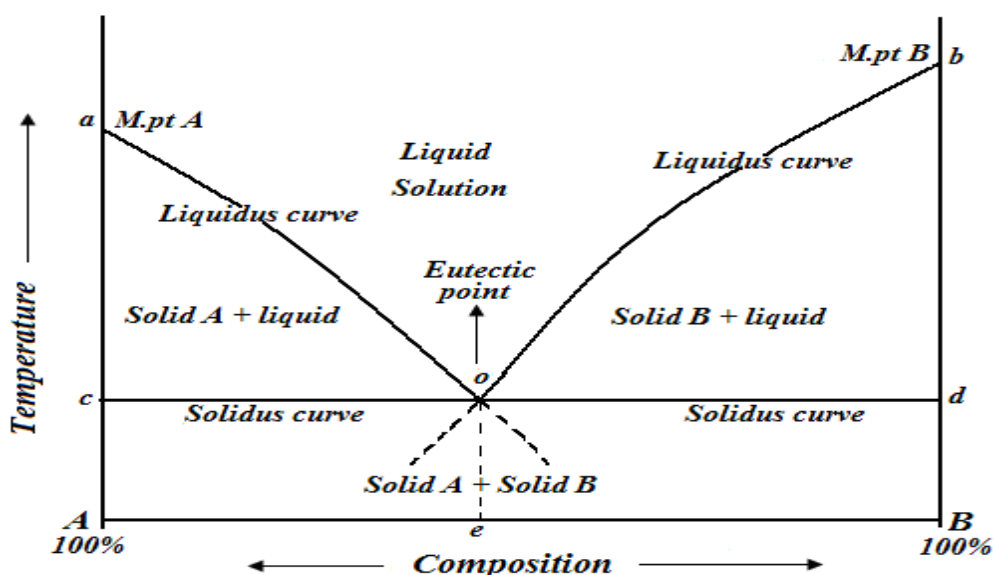

Figure 3.6.   Phase diagram for a binary system with eutectic point.

At the eutectic point three phases coexist (melt, solid $_A$ solid $_B$) the composition corresponding to this point has the lowest melting point. The temperature at this point is called the Eutectic temperature and the composition (e) is called the eutectic composition.

b. Solubility or saturation method

In this method solubility of one component is determined in the presence of the other at various temperatures. These measurements of solubility at different temperatures lead to the construction of phase diagram.