Introduction

equilibrium. The thermal equilibrium can be checked by measuring the temperature of the bodies. If the two bodies have the same temperatures then they are in thermal equilibrium. If several bodies are in thermal contact with each other, they will be in thermal equilibrium if they have the same temperature.

We should also consider the internal thermal equilibrium of a thermodynamic system. In this case it is useful to understand the system as consisting of several parts that make up a set of multiple bodies in contact. The internal equilibrium means that there is no heat flows between the various parts of the system so that they all must have the same temperature. In summary, all parts of a system in thermal equilibrium have the same temperature. If the object of study is a mechanical system, the thermodynamic equilibrium will also comprise mechanical equilibrium. For example, two gases in a closed vessel and separated by a movable wall will be in mechanical equilibrium if the wall is at rest. In this situation, the pressure is the same on both sides of the wall. Generally speaking, the mechanical equilibriumof a fluid, in the absence of external forces, requires no pressure gradient inside the fluid. Thus all parts of a system in mechanical equilibrium have the same pressure, in the absence of external forces.

First Law of Thermodynamics

The Joule principle, or principle of conservation of energy, is the first law of thermodynamics. It was established by several scientists, but mostly by Mayer and Joule, who assumed that the various forms of work could be converted into one another and, moreover, that all of them could be dissipated as heat. Although it seems quite obvious that the work can be transformed into heat, for example, by friction, one can not conclude that the work dissipated always produce the same amount of heat. It is necessary to experimentally verify such a law, which is summarized in the determination of the mechanical equivalent of heat. This determination was in fact performed by Mayer and exhaustively by Joule by numerous experiments. By assuming that a certain amount of work always turns into the same amount of heat, they were adopting the conservation of energy.

The second law of thermodynamics

The second law of thermodynamics must be understood as consisting of three parts. The first one leads to the definition of absolute temperature and entropy. Combined with the principle of conservation of energy, it allows us to set up the thermodynamic space and introduce the fundamental relation of systems in equilibrium. The second part consists of the form postulated by Gibbs for the principle of maximum entropy. It leads us to the property of convexity of the entropy and the conditions of stability of thermodynamic systems in equilibrium. These two parts refer only to equilibriumstates and are represented by the Carnot principle and by the Clausius-Gibbs principle, respectively. These two principles altogether form the second law of thermodynamics for equilibrium systems. The third part of the second law of thermodynamics refers to the time evolution of thermodynamic systems and has to do with the growth of entropy in spontaneous and irreversible processes. It therefore corresponds to the dynamic aspect of the principle of maximum entropy.We emphasize, however, that this aspect is not used explicitly, since we treat only systems in thermodynamic equilibrium. In contrast, the static aspect of the maximum entropy principle is used explicitly in the form given by the Clausius-Gibbs principle. When the initial and final states of an irreversible process are made up of equilibrium states a close relationship exists between the two aspects, which we analyze below.

Third law of thermodynamics

the Nernst postulate together with the Planck postulate, which we call the Nernst- Planck principle or the third law of thermodynamics, tells us that S (T) pass to be null when the temperature pass to be null.

Heat capacity

$$\Delta u = c_v dT \quad \Rightarrow \left(\frac{\partial u}{\partial T}\right)_v = c_v$$

$$\Delta H = c_p dT \quad \Rightarrow \left(\frac{\partial H}{\partial T}\right)_p = c_p$$

Mathematical reminder:

$$c = c(x, y, z)$$

$$dc = \left(\frac{\partial c}{\partial x}\right) dx + \left(\frac{\partial c}{\partial y}\right) dy + \left(\frac{\partial c}{\partial z}\right) dz$$

The differential of internal energy heat and entropy

$$u = Q + W$$

$$du = dQ + dW$$

$ds = d_i s + d_e s$

$$ds = \frac{\partial Q}{T}$$

$\partial Q = Tds = Td_i s + Td_e s$

$$du = Tds + dW$$

$$dw = -pdv$$

$du = Tds - pdv$

$\left(\frac{\partial u}{\partial s}\right)_v = T$; $\left(\frac{\partial u}{\partial v}\right)_s = p$ and $\left(\frac{\partial T}{\partial v}\right)_p = -\left(\frac{\partial p}{\partial s}\right)_T$

$$-\left(\frac{\partial T}{\partial v}\right)_s = \left(\frac{\partial p}{\partial s}\right)_v$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P$$

- The differential of heat (Q):

$du = \partial \mathrm{Q} + \partial \mathrm{w}$

$\partial \mathrm{Q} = \mathrm{du} + \partial \mathrm{w}$

$$\partial \mathrm{Q} = \mathrm{CvdT} + \mathrm{pdv}$$

$$\partial \mathrm{Q} = \mathrm{CvdT} + \left(\frac{\mathrm{RT}}{\mathrm{V}}\right)\mathrm{dv}$$

The differential of entropy

$$ds = \left(\frac{\partial \mathrm{Q}}{T}\right)$$

$$ds = Cv\left(\frac{dT}{T}\right) + \frac{R}{V}dv$$

The differential of enthalpie

$$H = u + pv$$

$$dH = du + dpv$$

$$dH = du + vdp + pdv$$

$$dH = Tds - \cancel{pdv} + vdp + \cancel{pdv}$$

$$dH = Tds + vdp$$

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{s}}\right)_{\mathrm{p}} = \mathrm{T}; \left(\frac{\partial \mathrm{H}}{\partial \mathrm{p}}\right)_{\mathrm{s}} = \mathrm{v} \text{ and } \left(\frac{\partial \mathrm{T}}{\partial \mathrm{p}}\right)_{\mathrm{s}} = \left(\frac{\partial \mathrm{v}}{\partial \mathrm{s}}\right)_{\mathrm{p}}$$

The differential of Gibbs free energy (free enthalpy)

$$G = H - TS$$

$$dG = \cancel{Tds} + vdp - \cancel{Tds} - sdT$$

$$dG = vdp - sdT$$

$$\left(\frac{\partial G}{\partial p}\right)_T = v; \ \left(\frac{\partial G}{\partial T}\right)_p = -s \ and \ \left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

Free energy of helmoholtz (F=A)

$$A = U - TS$$

$A = \cancel{Tds} - pdv - \cancel{Tds} - sdT$

$dA = -pdv - sdT$

$\Rightarrow \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

A- Thermodynamics functions for closed systems with irreversible transformation and variable composition:

In this case we should take the entropy production Tds into consideration and this for chemical reaction

$$du = Tds - pdv + \sum \mathcal{U}_i dn_i - Td_is$$

$$dH = Tds + Vdp + \sum \mathcal{U}_i dn_i - Td_is$$

$$dA = -sdT - pdV + \sum \mathcal{U}_i dn_i - Td_is$$

$$dG = -sdT + Vdp + \sum \mathcal{U}_i dn_i - Td_is$$

B- thermodynamic functions for closed system with reversible transformation and heterogenous composition :

$$du = Tds - pdv + \sum_{i=1}^{n} \mu_i dn_i$$

$$dH = Tds + vdp + \sum_{i=1}^{n} \mu_i dn_i$$

$$dA = -sdT - pdv + \sum_{i=1}^{n} \mu_i dn_i$$

$$dG = -sdT + vdp + \sum_{i=1}^{n} \mu_i dn_i$$

Where :

μ_i : is the chemical potential ;

n_i : is the mole number of the constant i.

Chemical potential

For pure ideal systems, the chemical potential is expressed by :

$\mu_i = \mu°_i(T_0, p_0) + RTln\, x_i$

Where T_0 and p_0 are the reference temperature and pressure, and X_i is the mole fraction.

It can also be defined in terms of the concentration of species i :

$$c_i = \frac{N_i}{v}$$

$$\mu_i = \mu°_i(T_0, v_0) + RTlnc_i$$

For non ideal systems, we use an activity

$$\mu_i = \mu°_i(T_0, p_0) + RTln\gamma_i X_i$$

$\mu_i = \mu°_i + RTlna_i$

c- Thermodynamic functions for closed systems with irreversible transformation and variable composition

in this case we should take the entropy production into consideration and this for the chemical reactions :

$$du = Tds - pdv + \sum_{i=1}^{n} \mu_i dn_i - Td_i s$$

$$dH = Tds + vdp + \sum_{i=1}^{n} \mu_i dn_i - Td_i s$$

$$dA = -sdt + vdp + \sum_{i=1}^{n} \mu_i dn_i - Td_i s$$

$$dG = -sdT + vdp + \sum_{i=1}^{n} \mu_i dn_i - Td_i s$$

Suite: potential

Chemical potential of Gibbs free energy (G) is the partial molar free energy (G_i)

$$\mu_i = G_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

$$G = \sum \mu_i n_i$$

Chemical potential of Helmholtz free energy (A) is

$\mu_i = A_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,v}$ is the partial molar free energy

The chemical potential of internal energy (u) is the partial molar internal energy u_i

$$\mu_i = u_i = \left(\frac{\partial u}{\partial n_i}\right)_{s,v}$$

The chemical of enthalpy H is the partial molar enthalpy H_i

$$\mu_i = H_i = \left(\frac{\partial H}{\partial n_i}\right)_{s,p}$$

Usually A and G are used to calculate $\mathcal{U}_i$ because it is possible to control the temperature and the pressure $(G = G(p,T) \; and \; A = A(v,T)$

Chapter 02: Thermodynamic of pure species

Pure substance: is a substance with homogenous and stable chemical composition. For example liquid water, a mixter of ice/water or water/vapor. Also, the air is a pure substance.

All pure substances can be a solid, liquid or gas. A solid substance has different allotropic forms. For example, carbon and diamant.

Variance of a system (φ): is it defined with the following equation:

$\varphi = c + 2 - F$

Where:

C: is number of constituent;

F: is number of phases

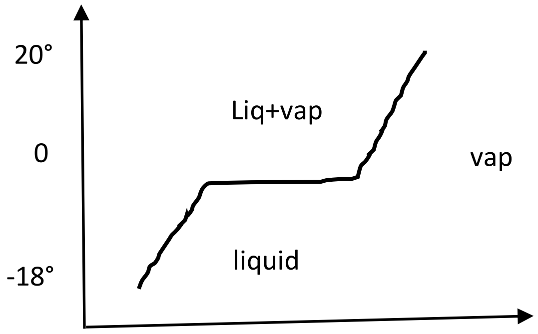
If $c = 1, F = 1 \Rightarrow \varphi = 2$; so we need two variables to describe the system

If $c = 1, F = 2 \Rightarrow \varphi = 1$; so we need just one variable to describe the system

If $c = 1, F = 3 \Rightarrow \varphi = 0$; all variables are constants

Example heating ice from (-18°c to 20°c) the temperature increase from 18°c the ice begin to melt and the temperature remains constant. At this point the liquid temperature begin to rise.

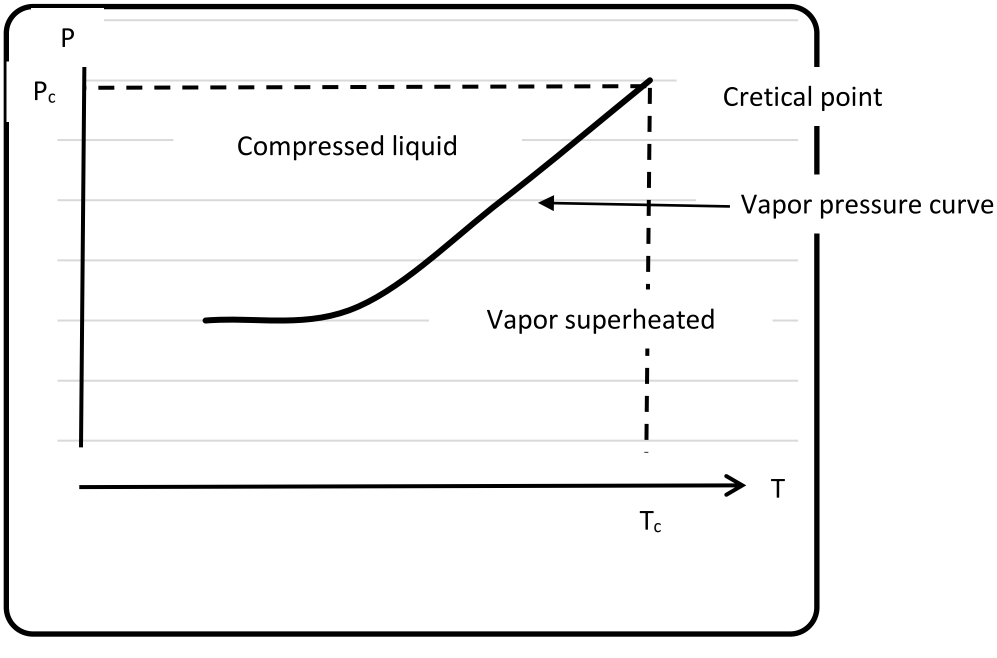
In this case, we have two phases and one constant (water), in this case $c = 1, F = 2$, $\varphi = 1$ we can describe the system using only one variable (temperature)



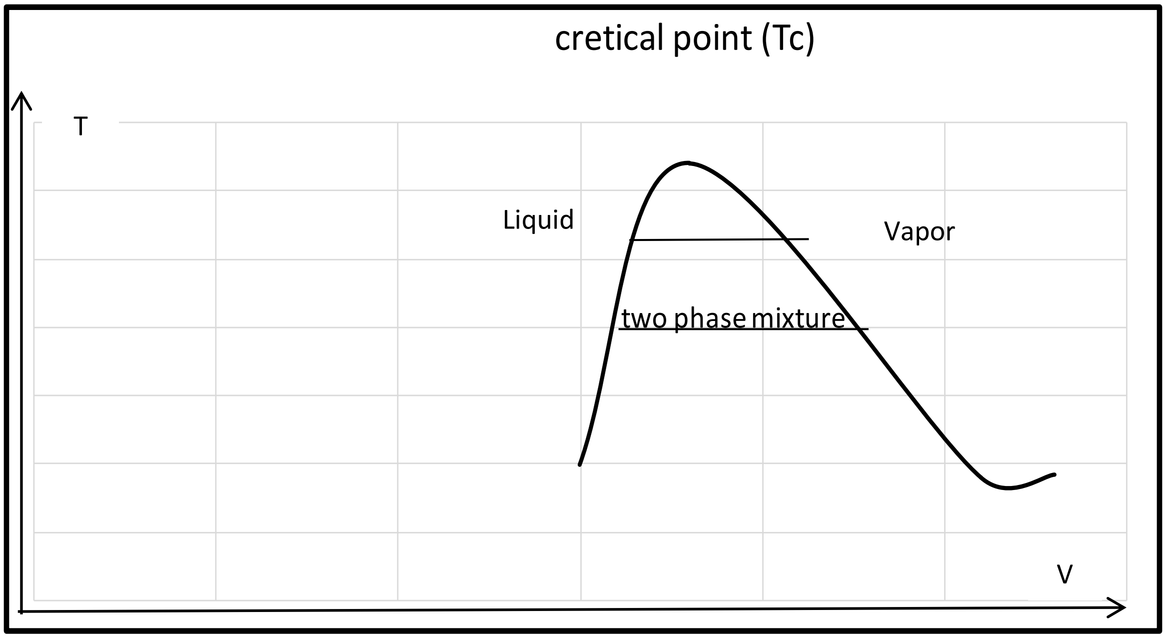
The saturated temperature (the boiling point)

It increases as pressure increases

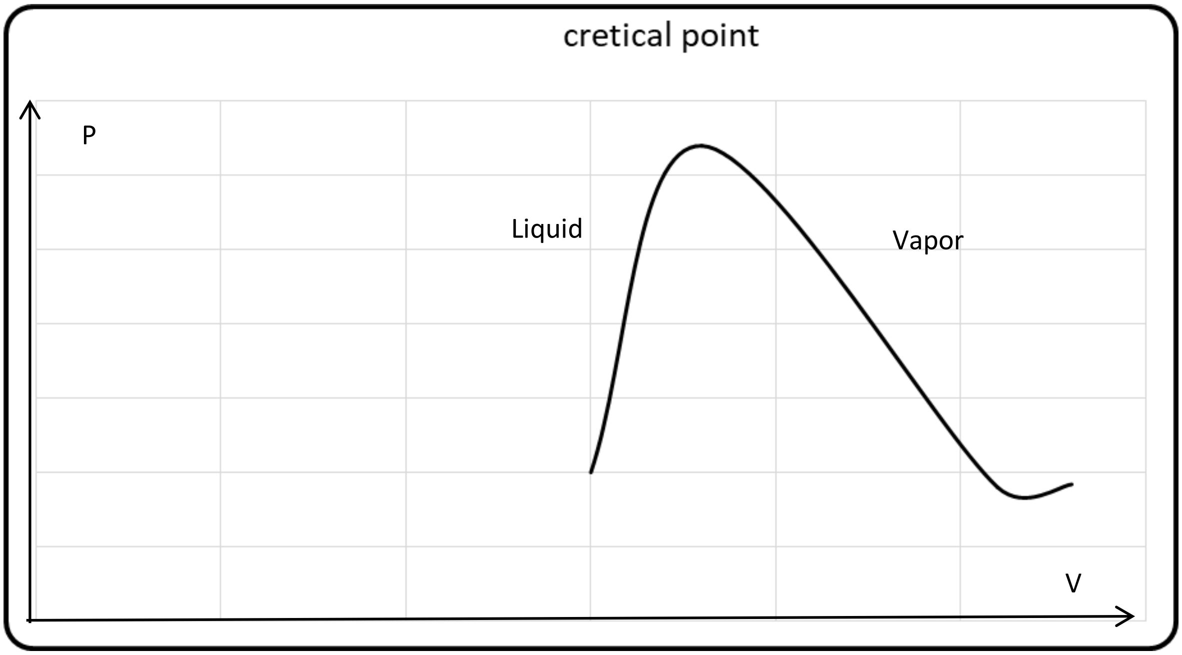
Platting the saturation pressure as a function of saturation temperature in the T-p plane. This is the S$_0$-called vapor pressure curve.



Sketch of T-V plane:



Sketch of p-v plan:



Ideal gas: for ideal gases, we have $PV = nRT$

The calorie equation is given on form: $u = u(T)$

We can specify h for ideal gas

$$H = u + PV \Longrightarrow H = u(T) + RT \qquad (1)$$

Thus the enthalpy of an ideal gas is a function of T only

$$\Delta H = \left(C_p \Delta T\right)_p \Longrightarrow \left(\frac{\partial H}{\partial T}\right)_p = C_p(T)$$

$$dH = C_p dT$$

$$\Delta u = (C_v \Delta T)_v \Longrightarrow \left(\frac{\partial u}{\partial T}\right)_v = C_v(T)$$

$$du = C_v dT$$

$$(1) \Longrightarrow H = u(T) + RT$$

$$dH = du(T) + RdT$$

$$C_p(T)\cancel{dT} = C_V(T)\cancel{dT} + R\cancel{dT}$$

$$C_p(T) - C_V(T) = R$$

If we have a mixture of two ideal gases A and B

The pressure of the mixture equal to P, where $P = P_A + P_B$

$P_A = \left(\frac{n_A}{n_A+n_B}\right).P$ and $P_B = \left(\frac{n_B}{n_A+n_B}\right).P$

$$X_A = \left(\frac{n_A}{n_A+n_B}\right)$$

X_A is the molar ratio of A in the mixture

Calorically perfect:

A calorically perfect gas has constant specific heat

$$\frac{du}{dT} = C_V \Rightarrow u = \int_{T_0}^{T} C_v dt$$

$u = u_0 + C_v(T - T_0)$…………..(2)

$$(2) \Longrightarrow u + PV = u_0 + C_v T_0 + PV$$

$u + PV = H; PV = RT$

$H = u_0 + C_v T - C_v T_0 + RT + RT_0 - RT_0$

$H = u_0 + RT_0 + (C_v + R)T - (C_v T_0 + RT_0)$

$u_0 + RT_0 = H_0$; $(C_v + R) = C_p$; $(C_v T_0 + RT_0) = C_P T_0$

$H = H_0 + C_p T - C_p T_0$

$H(T) = H_0 + C_p(T - T_0)$

Calorically imperfect gas:

$u = u(T)$

$C_v = C_v(T)$

$H = H(T)$

$$C_p = C_p(T)$$

$$u(T) = u_0 + \int_{T_0}^{T} C_v(T)dT$$

And

$$H(T) = H_0 + \int_{T_0}^{T} Cp(T)dT$$

Real gases:

A real gases have repulsive and attractive forces between molecules at low molecular volume and intermolecular forces can often be neglected

$$PV = RT\left[1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \cdots\right]$$

$$\bar{V} = V_m = \frac{V}{n}$$

$$P\bar{V} = RT\left[1 + \grave{B}P\grave{C}P^2 + \cdots\right]$$

C and B are coefficients

Vander Waals equation:

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

$$\bar{V} = V_m\ moleculor\ volume$$

$P + \frac{a}{\bar{V}^2}$ Internal pressure

$(\bar{V} - b)$ Excluded volume

Fugality: the fugality function can define phase equilibrium. For an ideal gas, the fugality of a species in an ideal gas mixture is equal to its partial pressure

$\frac{f_i}{P} = 1$ (For pure species i);

$\frac{f_i}{y_i p} = 1$ (For species i in mixtures)

Where Fi represent the fugality of species i in a mixture and y_i is the gas phase fraction of species i.

$\frac{PV_i}{nRT} = 1$ and $\frac{F_i}{p} = 1$

$$\frac{PV_i}{nRT} = \frac{F_i}{p} \Rightarrow \left(\frac{\partial F}{\partial P}\right)_{T,y_i} = \frac{V_i}{nRT}$$

For a mixture, the departure function of Gibbs energy, which is the difference between the partial Gibbs energy in the real state and in an ideal gas state, is related to the fugality function by $u_i - u_{iideal} = \Delta u(real - ideal)$

$$G_i - G°_i = u_{ireal} = u_{iideal} = RTln\ \frac{F_i}{y_i p°}$$

From the equation above, we define the fugality coefficient of species i, $\mathcal{L}_i$ in a mixture by:

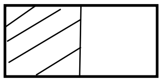
$$\mathcal{L}_i = \frac{F_i}{y_i p}, \begin{cases} y_i = 1\ if\ we\ have\ one\ species \\ y_i \neq 1\ if\ we\ have\ a\ mixture \end{cases}$$

$\mathcal{L}_i$ is a measure of deviation from the ideal gas mixture behavior, and unity an ideal gas mixture.

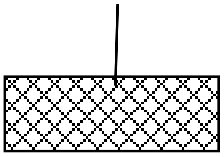
The fugality coefficient may be determined from compressibility factor $\mathcal{Z} = \left(\frac{PV}{RT}\right)$ data at constant temperature and composition chemical potential for ideal gas:

$$u_i = u^{\circ} + RTln\,(\frac{P}{y_i p^{\circ}})$$

The joule expansion



(a)



(b)

(a) A gas is kept to one part of vessel by a partition, the other part being evacuated.

(b) The partition is removed and the gas expands irreversibly to fill the whole vessel of complete isolation.

Joule expansion is also called a "free expansion".

Since $dQ = dw = 0$; we have $du = 0$ or $u = constant.$

$$du = Tds - pdv$$

$$\left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v = C_v$$

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

$$du = Tds - pdv = 0$$

$$Tds = pdv$$

$$\Delta s = \frac{P}{T}\Delta v$$

$$\Delta s = \int_{V1}^{V2} \frac{p}{T} dv$$

For the perfect gas this becomes $PV = nRT$

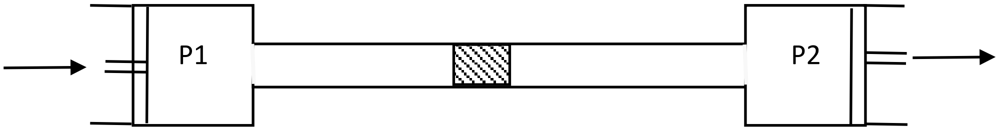
$$\frac{p}{T} = \frac{R}{V}$$

$$\Delta s = \int_{V_1}^{V_2} \frac{R}{V} dv = R\, ln \frac{V_2}{V_1}$$

$$\Delta s = Rlog \frac{V_2}{V_1}$$

The joule – Kelvin expansion (Joule-Thomson)

A gas is forced through a porous plug or a throttle valve under conditions of thermal isolation from the surround dings



In passing through the plug, the gas expands and the pressure drops from P1 to P2.

The pressure on either side are kept constant

BUT:

$dh = Tds + vdp$

$\left(\frac{\partial h}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = C_P$

$\left(\frac{\partial h}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \dots\dots\dots\dots\dots\dots\dots\dots (1)$

$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots . (2)$

$\left(\frac{\partial h}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_P + V$

Thermodynamic properties of condensed phases

A condensed phase consists of a liquid (very poorly compressible fluid) or a solid (quasi-incompressible) under the usual conditions of temperature and pressure and taking into account the quasi-constant V_0 nature of the condensed phase.

The thermo-elastic coefficient can be written isobaric.Expansion.Coefficient:

$$\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_p$$

Isothermal compressibility coefficient

$$B = \frac{-1}{V_0}\left(\frac{\partial V}{\partial p}\right)_T$$

A condensed phase is slightly expandable ($\alpha \approx 0$) and not very compressible ($\beta \approx 0$)

$$dv = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp$$

$$dv = \alpha v_0 dT - \beta v_0 dp$$

$$dv = v_0(\alpha dT - \beta dp) \approx 0$$

Chapter 03 Physical equilibrium

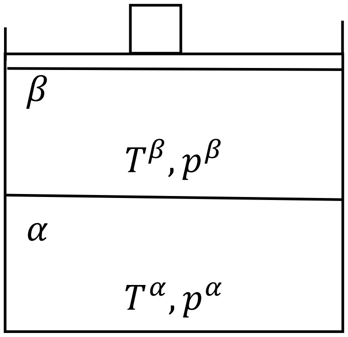
Phase equilibrium

A system of two phases is in equilibrium, if it has the following conditions:

$$T^{\alpha} = T^{\beta} = T; \qquad ethermal\ equilibrium$$

$$P^{\alpha} = P^{\beta} = P; \qquad dynamic\ equilibrium$$

$${G_m}^{\alpha} = G_m; \qquad chemical\ equilibrium$$



T: Temperature

P: Pressure

G: Free enthalpy

Taking this reaction $\alpha \rightleftharpoons \beta$

$$\Delta G = G^{\beta}_{m_{(p,T)}} - G^{T}_{m_{(p,T)}} = 0\ in\ the\ equilibrium\ where\ p = \mathcal{F}(T)$$

The clapeyron equation:

- Under isothermal and isotonic conditions various phases of a compound can coexist at phase equilibrium.
- A compound can be at various phases under suitable pressure and temperature.
- Chemical potentials of a species in vapor and liquid phases are equal at phase equilibrium must be zero.

$$u_{vap}(T,p) = u_{liq}(T,p)$$

$$vap: \alpha$$

$$liq: \beta$$

$$u_{\alpha}(T,p) = u_{\beta}(T,p)$$

$$\left(\frac{\partial u_{\alpha}}{\partial T}\right)_{T} dT + \left(\frac{\partial u_{\alpha}}{\partial p}\right)_{p} dp = \left(\frac{\partial u_{\beta}}{\partial T}\right)_{p} dT + \left(\frac{\partial u_{\beta}}{\partial p}\right)_{T} dp$$

$$u_{\alpha} = \overline{G_{\alpha}}$$

$$dG = vdp - Sdt$$

$$\left(\frac{\partial G}{\partial T}\right)_{p} = -S \;\Rightarrow \left(\frac{\partial \bar{G}}{\partial T}\right)_{p} = -\overline{S_{\alpha}} \;\Rightarrow\; \left(\frac{\partial \bar{G}}{\partial p}\right)_{T} = \bar{V}_{\alpha}$$

$$\overline{G_{\alpha}} = \overline{G_{B}}$$

$$-\overline{S_{\alpha}}dT + \bar{V}_{\alpha}dp = -\overline{S_{\alpha}}dT + \overline{V_{B}}dp$$

$$-\overline{S_{\alpha}}dT + \overline{S_{\beta}}dT = \overline{V_{\beta}}dp - \bar{V}_{\alpha}dp$$

$$(\overline{S_{B}} - \overline{S_{\alpha})}dT = (\overline{V_{\beta}} - \bar{V}_{\alpha})dp$$

$$\frac{dp}{dT} = \frac{(\overline{S_\beta} - \overline{S_\alpha})}{\left(\overline{V_\beta} - \overline{V_\alpha}\right)} = \frac{\overline{\Delta S}}{\overline{\Delta V}}$$

$\overline{\Delta G} = \overline{\Delta H} - T\overline{\Delta S} = 0$ at equilibrium

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

$\frac{dP}{dT} = \frac{\overline{\Delta H}}{T\overline{\Delta V}}$ *clapeyron equation*

$$\left.\begin{array}{r} \overline{\Delta\, H}_{fusion} > 0 \\ \overline{\Delta\, H}_{Vap} > 0 \\ \overline{\Delta\, H}_{sub} > 0 \end{array}\right\} always$$

Clausius-clapeyron equation

Solid-Vapor equilibrium

$\frac{dP}{dT} = \frac{\overline{\Delta H}_{s-g}}{T(v_g - V_S)}$ $\int x^n dx = \frac{x^{n+1}}{n+1} + \varepsilon$ $T^{-2}dt = \frac{T^{-2+1}}{-2+1} = -\frac{1}{T}$

Solid-Liquid equilibrium

$$\frac{dP}{dT} = \frac{\overline{\Delta H}_{ts}}{T(v_t - V_s)}$$

Liquid-Vapor equilibrium n=1 mole

$\frac{dP}{dT} = \frac{\overline{\Delta H}_{Lg}}{T(V_g - V_L)}$ $V_g \gg V_2$

$V_g = \frac{RT}{P}$ $V_g \ggg V_s$ $1V \approx V_g$

$\frac{dP}{dT} = \frac{\overline{\Delta H}}{RT^2} . P$ $\int \frac{dT}{T^2} = \left[-\frac{1}{T} \right]$

$$\frac{dP}{P} = \frac{\overline{\Delta H}}{RT^2} . dT \Rightarrow \ln \frac{P2}{P1} = \frac{- \overline{\Delta\ H}}{R} (\frac{1}{T_2} - \frac{1}{T_1})$$

Claussuis-clapeyron equation

Phase equilibration of binary mixtures:

- Many minerals are homogenous solid binary mixtures such as mercury and silver;
- Alocohol is usually found in association with water, forming a homogenous binary mixture.

Dilutes mixture:

The chemical potential of a solute is given by the following expression:

$$u_1 = u°_1 + RTln\ (1 - x)$$

$$u_2 = u°_2 + RTln\ x$$

The coexistence of two phases in binary mixture is described by a linear segment of $g(p, x)$or $g'(T, x)$.

Thermodynamic equilibrium:

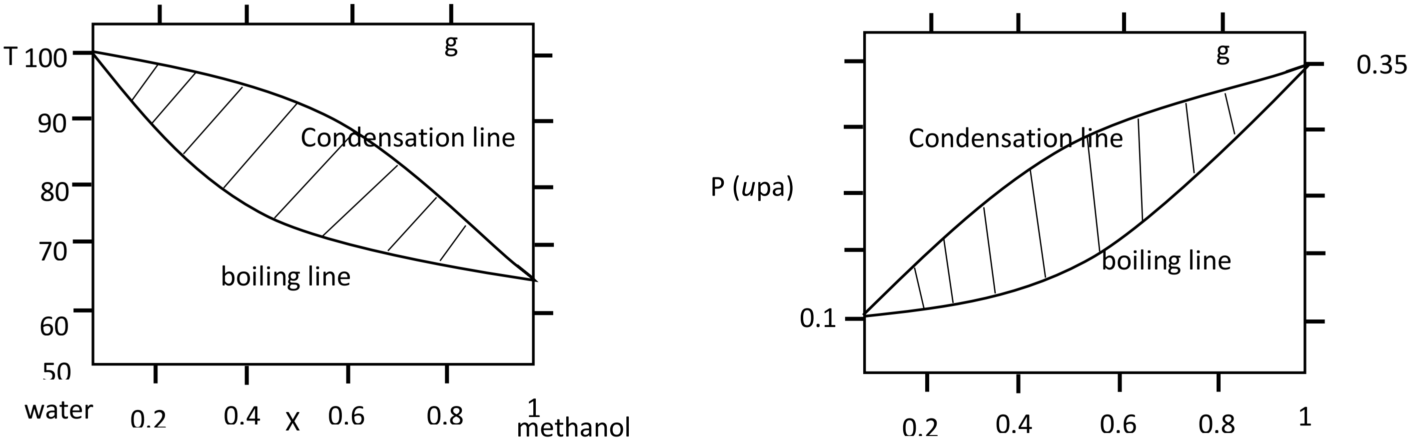
For a mixture of two components, the condition of thermodynamic equilibrium is:

$$\begin{cases} T_A = T_B \\ P_A = P_B \\ u1_A = u1_B \\ u2_A u2_B \end{cases}$$

$\Rightarrow u1\ and\ u2\ are\ chemical\ potentials\ of\ components\ 1\ and\ 2$

A and B are two phases for example (liquiduap)

Condensation and boiling lines:



Water and methol mixture

$$dG = Tds - pdv + u_1 dN_1 + u_2 dN_2$$

N_1 and N_2 are numbers of moles of components 1 and 2

$$S = \frac{\partial G}{\partial T}; \qquad v = \frac{\partial G}{\partial P}; \qquad u_1 = \frac{\partial G}{\partial N_1}; u_2 = \frac{\partial G}{\partial N_2}$$

Application of thermodynamic equilibration for distillation process

It is used for determining the number of theorical plates in distillation columns

Chapter 04 Chemical equilibrium

The condition of chemical equilibration is dG=0

$$dG = -SdT + vdp + \sum_{i=1}^{k} u_i dn_i = 0$$

$$\Rightarrow \sum u_i dn_i = 0$$

$u_i = u°_i + RTlog\varphi$

$\varphi_i = \frac{\mathcal{L}_i}{p_0}$

$\mathcal{L}_i$ is fugalitycoefficient

The standard chemical potential of Gibbs is given by the following equation :

$\Delta\mu° = \Delta G°_R = RT \ln K_a$

$where$:

K_a is the equilibrium constant.

$$k_a = \prod_{i=1}^{R} (\varphi)\, D_i$$

D_i is the stocheometric coefficient of component i

From the previous equations, we can deduce that :

$$\Delta G°_R = -RT \ln k_a = \Delta H°_R - T\Delta S°_R$$

$$\ln k_a = \frac{\Delta S°_R}{R} - \frac{\Delta H°_R}{RT}$$

Example ;

$$\frac{3}{2} H_2 + \frac{1}{2} N_2 = NH_3$$

$$aA + bB \rightarrow cC$$

$$K_a = \frac{\ell_C^c . \ell_D^d}{\ell_A^a . \ell_B^b}$$