Chapter 8　Review of Thermodynamics

§8-1: Why do we learn thermodynamics?

∗ 〝Materials thermodynamics〞 : What determines how matter behaves ?
∗ 〝Thermodynamics〞 : From the 〝energy〞 point of view to discuss the equilibrium of matter.
∗ Materials thermodynamics ⇔ 〝material〞 system.

§8-2. Original development of thermodynamics.

∗ 〝Heat〞 and 〝Work〞 relations of a system.

Ex1. Heat engine : How much work can be performed by the adsorbed heat?

Ex2. Refrigerator : How much heat can be attracted by the work done on the system?

§8-3. Scope of Material Thermodynamics.

∗ Why material behaves in a certain condition?
∗ Equilibrium state of a material system:

$$\Leftrightarrow \begin{cases} \text{Minimum Energy.} \\ \text{Maximum Entropy.} \end{cases}$$

Ex: 1. Pure metal is not stable.
2. Crystal defects : vacancy? Dislocation? G.B.?
3. Phase transformation : H_2O , Fe, and Diamond
4. Complex material system : Stability? Equilibrium state?

§8-4. Classical Thermodynamics vs Statistical Thermodynamics.

Classical Thermodynamics ⇒ Macroscopic phenomena.
Statistical Thermodynamics ⇒ Microscopic description.
Particles : electrons, atoms, molecules.
Probability : distribution, partition function.

§8-5. Thermodynamics vs. Kinetics

$$\begin{cases} \text{Thermodynamics : Equilibrium State?} \\ \qquad \text{Kinetics : Reaction Rate?} \end{cases}$$

§8-6. Laws of Thermodynamics

1. The 1st law : Energy conservation

$$\begin{cases} dU = \delta Q - \delta W \\ \Delta \mathbf{U} = \mathbf{Q} - \mathbf{W} \end{cases}$$

$$* \begin{cases} \mathbf{U : state\ function,\ indep.\ of\ path} \\ \mathbf{Q, W : process\ function,\ dep.\ on\ path} \end{cases}$$

$$* \ \delta\ \mathbf{W}_{\mathrm{Rev.}} = P\ dV \begin{cases} \mathbf{work\ done\ "By"\ system, \delta W} > 0 \\ \mathbf{work\ done\ "ON"\ system, \delta W} < 0 \end{cases}$$

2. The 2nd law : Entropy is created.

$$* \ \boxed{dS \equiv \frac{\boldsymbol{\delta} \mathbf{Q}_{\mathbf{rev.}}}{\mathbf{T}}}$$, S is a state function.

$$* \ \Delta \mathbf{S}_{\mathbf{adiabatic}} \geq 0, \quad \begin{cases} \Delta S_{adia.} = 0, & \mathrm{Re}\,versible\ \ process \\ \Delta S_{adia.} > 0, & Irreersible\ \ process \end{cases}$$

$$* \ \Delta \mathbf{S}_{\mathbf{univ.}} > 0 \quad \Leftrightarrow \quad \boxed{\Delta S_{U,V} > 0}$$

Universe $\Leftrightarrow$ Isolated System.
(No mass and energy transfer)

$$* \text{Reversible Process : } \begin{cases} No\ \ dissipation\ \ (\,friction) \\ No\ \ entropy\ \ production \\ No\ \ permanent\ \ change\ \ in \\ \quad the\ \ unreverse, \begin{cases} dS_{production} = 0 \\ dS_{U,V} = 0 \end{cases} \end{cases}$$

$\therefore$ A reversible process is imaginary.

All real processes are irreversible.
However , S is a state function.

Change of entropy , $\Delta \mathbf{S} = (\mathbf{S_B} - \mathbf{S_A})$, can be calculated via a reversible path.

$$\Delta \mathbf{S} = (\mathbf{S_B} - \mathbf{S_A}) = \int_A^B \frac{(\delta \mathbf{Q})_{rev.}}{\mathbf{T}}$$

∗ All spontaneous process is irreversible, Δ S>0 always!

∗ Statistical definition of entropy:

$$\boxed{S \equiv k \ln \Omega}$$

$$\begin{cases} \mathbf{k} = \textbf{Boltzmann constant} = 1.38 \times 10^{-23}\ \mathbf{J/K} \\ \Omega = \textbf{Number of available microstates for a specific macrostate}. \end{cases}$$

$$\mathbf{N_A} \cdot \mathbf{k} = \mathbf{R} = 8.314\ \mathbf{J/K \cdot mole}\ ,\ \mathbf{N_A} = 6.02 \times 10^{23} / \mathbf{mole}$$

∗ S : Distribution Randomness of a system

Thermal Entropy: $S_{therm} \Rightarrow$ Distribution in energy states (levels)

Configurational Entropy: $S_{conf.} \Rightarrow$ Distribution in space (arrangements)

3. The 3rd law : Entropy of substance at 0 **K**

∗ Entropy of all substance is the same at 0 **K**

∗ Nernst's theorem : all reaction involving substances in the condensed state , $\Delta \mathbf{S} = 0$ at 0 **K**

$\therefore$ A + B = AB

$$\Delta \mathbf{S} = \mathbf{S_{AB}} - \mathbf{S_A} - \mathbf{S_B}$$

If assigned, $\mathbf{S_A} = \mathbf{S_B} = 0$, **at** 0 **K**

then $\mathbf{S_{AB}} = 0$, **at** 0 **K**

∗ Plank : Entropy of any "homogeneous" substance, which is in "complete internal equilibrium" may be taken to be zero at 0 **K** .

Ex : Following substance at 0 **K** , $S_0 \neq 0$

(1) glass: supercooled liquid.

(2) disordered compound.

(3) mixture of isotopes : $\mathbf{Cl}^{35} - \mathbf{Cl}^{37}$

(4) non-equil. concentration of vacancy.

§8-7. Definitions of some important parameters and functions.

∗ Thermal expansion coeff. $\alpha \equiv +\frac{1}{V}(\frac{\partial V}{\partial T})_P$

∗ Isothermal compressibility $\beta \equiv -\frac{1}{V}(\frac{\partial V}{\partial P})_T$

∗ Heat capacity $C \equiv \frac{\delta Q_{rev}}{dT}$

$C_P = (\frac{\delta Q_{rev}}{dT})_P$, $\therefore (\delta Q_{rev})_P = C_P \cdot dT$

$C_v = (\frac{\delta Q_{rev}}{dT})_V$, $\therefore (\delta Q_{rev})_V = C_V \cdot dT$

Theoretically derived $C_V(T)$ is a complicated function.

Empirical : $C_P(T) = a + bT + \frac{c}{T^2}$ $(J/g-atom \cdot K)$

experimental a, b and c values can be obtained from Table A-2.

$$C_P - C_V = \frac{TV\alpha^2}{\beta}$$

∗ Defined energy functions : H≡U+PV (enthalpy, 焓)

F≡U-TS (Helmholtz Free Energy)

G≡H-TS (Gibbs Free Energy)

§8-8. Fundamental Thermodynamic Equations

∗ combination of 1st and 2nd laws :

$$\because \begin{cases} \delta Q_{rev} = TdS \\ \delta W_{rev} = PdV \ (\text{mechanical}) \end{cases} \qquad \therefore dU = TdS - PdV + \delta W'$$

$\delta W'$: other work, e.g. chemical work $\delta W'$=0 for pure substance.

$$\ast \begin{cases} dU = TdS - PdV \\ dH = TdS + VdP \\ dF = -SdT - PdV \\ dG = -SdT + VdP \end{cases}$$

∗ Coefficient Relations : $T=(\frac{\partial U}{\partial S})_V$, $-P=(\frac{\partial U}{\partial V})_S$

$T=(\frac{\partial H}{\partial S})_P$, $V=(\frac{\partial H}{\partial P})_S$

$-S=(\frac{\partial F}{\partial T})_V$, $-P=(\frac{\partial F}{\partial V})_T$

$-S=(\frac{\partial G}{\partial T})_P$, $V=(\frac{\partial G}{\partial P})_T$

∗ Maxwell Relations : $(\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V$

$(\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P$

$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V$

$(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$

∗ Gibbs-Helmholtz equation:

$$\left[\frac{\partial(G/T)}{\partial T}\right]_P = -\frac{H}{T^2} \quad , \qquad \left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$$

∗ Variation of V , S , H , G as a function of T, P.

(1) V=V(T,P)

$$dV=(\frac{\partial V}{\partial T})_P \cdot dT + (\frac{\partial V}{\partial P})_T \cdot dP$$

$$\boxed{dV=\alpha V\,dT - \beta V\,dP}$$

(2) S=S(T,P)

$$dS=(\frac{\partial S}{\partial T})_P \cdot dT + (\frac{\partial S}{\partial P})_T \cdot dP$$

$$\because C_P \equiv (\frac{\delta Q_{rev}}{dT})_P = (\frac{TdS}{dT})_P = T(\frac{\partial S}{\partial T})_P$$

Maxwell $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P = -\alpha V$

$$\therefore \boxed{dS = \frac{C_P}{T}dT - \alpha V dP}$$

(3) $H = H(T,P)$

$$dH = TdS + VdP = T\left[\frac{C_P}{T}dT - \alpha V dP\right] + VdP$$

$$\therefore \boxed{dH = C_P\,dT + V(1-\alpha T)\,dP}$$

(4) $G = G(T,P)$

$$\boxed{dG = -S\,dT + V\,dP}$$

For a constant pressure , P=1atm, process: $dP = 0$.

$$\begin{cases} dS = \dfrac{C_P}{T}dT \\ dH = C_P dT \\ dG = -SdT \end{cases}$$

when $C_P = a + bT + \dfrac{c}{T^2}$ is known , ΔS, ΔH, ΔG can be calculated

for $T_1 \to T_2$, e.g.

$$\Delta S = S_2 - S_1 = \int dS = \int_{T_1}^{T_2}\frac{C_P}{T}dT$$

$$\Delta H = \int_{T_1}^{T_2} C_P dT$$

$$\Delta G = -\int_{T_1}^{T_2} SdT$$

Ex: one mole H_2O , $\begin{cases} C_P(s) = 38\ J/K\cdot mole \\ C_P(l) = 75.44\ J/K\cdot mole \\ C_P(g) = 30 + 10.7\times 10^{-3}T + 0.33\times 10^{5}T^{-2}\ J/K\cdot mole \end{cases}$

, $\rho(s)=0.9\ g/cm^3$, $\rho(l)=1.0\ g/cm^3$

$S(s)_{,298K} = 44.77 J/K\cdot mole$, $1 atm\cdot cm^3 = 0.101 J$

$S(l)_{,298K} = 70.08 J/K\cdot mole$, $H(l)_{,298K} = 0$

$\Delta H_{s\to l} = \Delta H_m$ at 273K = 6008 J/mole

$\Delta H_{l\to g} = \Delta H_{evap.}$ at 373K = 41090 J/mole

Q1: $H_{(S),270K} = ?$

Q2: $G_{(s)}(T) = ?$ $G_{(l)}(T) = ?$ $T_m = ?$

Q3: When P=100 atm , $T_{m'} = ?$

Q4: Calculate the equilibrium vapor pressure of water, P(T)=?

sol.1 : Figure. 1

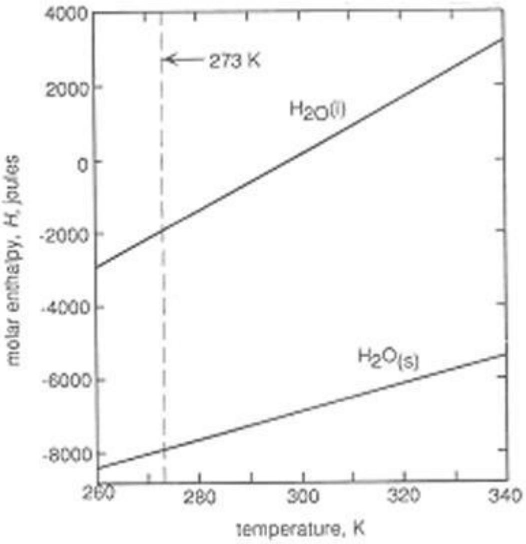

Figure 8.1 The variations, with temperature, of the molar enthalpies of solid and liquid water at 1 atm pressure. The molar enthalpy of liquid water at 298 K is arbitrarily assigned the value of zero.

$$H_{(s),270K} + \int_{270}^{273} C_{P(s)} \cdot dT + \Delta H_m + \int_{273}^{298} C_{P(l)} dT = H_{(l),298} = 0.$$

$$\therefore \quad H_{(s),270K} = -\left[C_{P(s)}(273-270) + \Delta H_m + C_{P(l)}(298-273)\right]$$

$$= -\left[(38\times 3) + 6008 + (75.44\times 25)\right]$$

$$= -8008(J)$$

sol.2 : G $\equiv$ H-TS

(1) For liquid H_2O :

$$H_{(l)}(T) = H_{(l),298K} + \int_{298}^{T} C_{P(l)} \cdot dT = 75.44\ (T-298)$$

$$S_{(l)}(T) = S_{(l),298K} + \int_{298}^{T} \frac{C_{P(l)}}{T} dT = 70.08 + 75.44 \ln\left(\frac{T}{298}\right)$$

(2) For solid H_2O :

$$S_{(s)}(T) = S_{(s),298K} + \int_{298}^{T} \frac{C_{P(s)}}{T} dT = 44.7 + 38 \ln\left(\frac{T}{298}\right)$$

$$H_{(s)}(T) = H_{(s),270K} + \int_{270}^{T} C_{P(s)} dT = -8008 + (T-270)\times 38$$

$$\therefore G_{(l)}(T) = H_{(l)}(T) - T \cdot S_{(l)}(T)$$

$$G_{(l)}(T) = 75.44(T-298)-70.08T-75.44T \cdot \ln\left(\frac{T}{298}\right)$$

$$G_{(s)}(T) = -8008 + 38\,(T-270) - 44.7T - 38T \cdot \ln\left(\frac{T}{298}\right)$$

$$\therefore \begin{cases} G_{(l)}(T) = -22481.12 + 435.15T - 75.44T\ln T \\ G_{(s)}(T) = -18268 + 209.79T - 38T\ln T \end{cases}$$

at T= T_m , $G_{(l)} = G_{(s)}$

$$\therefore -4213.12+225.36\,T_m - 37.44\,T_m \ln T_m = 0$$

T_m = 271.9 K (~—1.1°C)

sol.3 : $\because$Clapeyron Eq. $\boxed{\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta S_{\alpha\beta}}{\Delta V_{\alpha\beta}} = \frac{\Delta H_{\alpha\beta}}{T\Delta V_{\alpha\beta}}}$

$$\because \Delta V_m < 0 \qquad \therefore P \uparrow \Rightarrow T_m \downarrow$$

$$\Delta V_m = V_{(l)} - V_{(s)} = \frac{18}{1.0} - \frac{18}{0.9} \cong -2.0 \ \text{cm}^3/\text{mole}$$

$$\therefore dP = \frac{\Delta H_m}{T\Delta V_m} \cdot dT \cong \frac{\Delta H_m}{\Delta V_m} \cdot \frac{dT}{T} = \frac{-6008}{2.0} \cdot \frac{dT}{T} = -3004\frac{dT}{T} \quad (\text{J/cm}^3)$$

$$\therefore \int_{1}^{100} dP = -3004\int_{273}^{T_{m'}} \frac{dT}{T}$$

$$(100-1)\ \text{atm} = -3004(\text{J/cm}^3) \cdot \ln\left(\frac{T_{m'}}{273}\right)$$

$$\frac{99\times 0.101}{3004} = \cdot \ln\left(\frac{273}{T_{m'}}\right) \qquad \therefore T_{m'} \cong 272K = -1^\circ C$$

sol.4 : Assume that water vapor is ideal gas

$\therefore$PV=RT

$$\because \left(\frac{\mathbf{dP}}{\mathbf{dT}}\right)_{\mathbf{eq}} = \frac{\mathbf{\Delta H}}{\mathbf{T\Delta V}} \;,\; \mathbf{l} \rightarrow \mathbf{g}$$

$$\mathbf{\Delta V} = \mathbf{V}_{(\mathbf{g})} - \mathbf{V}_{(\mathbf{l})} \cong \mathbf{V}_{(\mathbf{g})}$$

$$\therefore \frac{\mathbf{dP}}{\mathbf{dT}} \cong \frac{\mathbf{P\Delta H}_{\mathbf{evap.}}}{\mathbf{RT}^2}$$

$$\therefore \boxed{\text{d ln P} = \frac{\mathbf{\Delta H}_{\mathbf{evap.}}}{\mathbf{RT}^2}\,\text{dT}}$$

, Clausius-Clapeyron Eq.

$$\because \mathbf{\Delta H}_{\mathbf{evap.}}(\mathbf{T}) = \mathbf{\Delta H}_{\mathbf{evap},373} + \int_{373}^{\mathbf{T}} \mathbf{\Delta C}_{\mathbf{P(l\rightarrow g)}}\,\text{dT}$$

$$\therefore \begin{cases} \mathbf{\Delta H}_{\mathbf{evap},373} = 41090 \;\; \mathbf{J/mole} \\ \mathbf{\Delta C}_{\mathbf{P(l\rightarrow g)}} = \mathbf{C}_{\mathbf{P(g)}} - \mathbf{C}_{\mathbf{P(l)}} = -45.44 + 10.7\times10^{-3}\mathbf{T} + 0.33\times10^{5}\mathbf{T}^{-2} \end{cases}$$

$$\therefore \quad \mathbf{\Delta H}_{\mathbf{evap.}}(\mathbf{T}) \;=\; 41090 \;-\; 45.44(\text{T-373}) \;+\; \frac{10.7\times10^{-3}}{2}(\mathbf{T}^2 - 373^2) \;-\; 0.33\times10^5\left(\frac{1}{\mathbf{T}} - \frac{1}{373}\right)$$

$$= 57383 \;-45.44\text{T} + 5.35\times10^{-3}\mathbf{T}^2 - \frac{0.33\times10^5}{\mathbf{T}}$$

$$\therefore \text{d ln P} = \left(\frac{57383}{\mathbf{RT}^2} - \frac{45.44}{\mathbf{RT}} + \frac{5.35\times10^{-3}}{\mathbf{R}} - \frac{0.33\times10^5}{\mathbf{RT}^3}\right)\text{dT}$$

$$\therefore \text{ln P} = -\frac{57383}{RT} - \frac{45.44\ln T}{R} + \frac{5.35\times10^{-3}T}{R} - \frac{0.33\times10^5}{2RT^2} + const.$$

when T=373 , P = 1 atm , $\therefore$ const.= 50.61 , R=8.314 J/K · mole

$$\therefore \text{ln P} = -\frac{6902}{\mathbf{T}} - 5.465\ln\mathbf{T} + 6.434\times10^{-4}\mathbf{T} + \frac{1985}{\mathbf{T}^2} + 50.61$$

§8-9. Free Energy as a function of T, P

i.e.
$$\begin{cases} 1.\ \mathbf{cons\,tan\,t\;\;P,G(T)\;\;curve} \\ 2.\ \mathbf{cons\,tan\,t\;\;T,G(P)\;\;curve} \end{cases}$$

1. G(T)

＊For single phase substance

$G = H - TS$

$dG = -SdT + VdP$

constant P , $\therefore d\mathbf{G_P} = -S\, d\mathbf{T_P}$

$$\left(\frac{\partial \mathbf{G}}{\partial \mathbf{T}}\right)_{\mathbf{P}} = -S \qquad (\because S > 0\,,\ \therefore \frac{\mathbf{dG}}{\mathbf{dT}} < 0)$$

$$\left(\frac{\partial^2 \mathbf{G}}{\partial \mathbf{T}^2}\right)_{\mathbf{P}} = -\left(\frac{\partial \mathbf{S}}{\partial \mathbf{T}}\right)_{\mathbf{P}} = \frac{-\mathbf{C_P}}{\mathbf{T}} < 0 \quad (\text{curvature} < 0)$$

Figure. 2

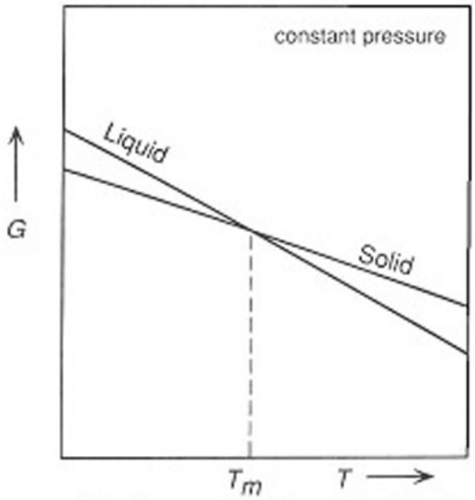

Figure 8.2 Schematic representation of the variations of the molar Gibbs free energies of solid and liquid water with temperature at constant pressure.

＊Two-phase equilibrium (e.g. melting)

$$\begin{cases} \mathbf{dG^s} = -\mathbf{S^s dT} + \mathbf{V^s dP} \\ \mathbf{dG^l} = -\mathbf{S^l dT} + \mathbf{V^l dP} \end{cases}$$

$$\therefore d(\Delta\mathbf{G^{sl}}) = -\Delta\mathbf{S^{sl}dT} + \Delta\mathbf{V^{sl}dP}$$

$$\therefore \left(\frac{\partial \Delta\mathbf{G^{sl}}}{\partial \mathbf{T}}\right)_{\mathbf{P}} = -\Delta\mathbf{S^{sl}}$$

$$\Delta\mathbf{S^{sl}} \quad = (\mathbf{S^l} - \mathbf{S^s}) > 0\,,\ \therefore \left(\frac{\partial \Delta\mathbf{G^{sl}}}{\partial \mathbf{T}}\right)_{\mathbf{P}} < 0$$

$$\left(\frac{\partial^2 \Delta \mathbf{G}^{\mathbf{sl}}}{\partial \mathbf{T}^2}\right)_{\mathbf{P}} = -\left(\frac{\partial \Delta \mathbf{S}^{\mathbf{sl}}}{\partial \mathbf{T}}\right)_{\mathbf{P}} \cong 0$$

$\because \Delta \mathbf{S}^{\mathbf{sl}} = \Delta \mathbf{S}^{\mathbf{m}} \cong 8.4$ J/K-mole. (Richard’s rule)

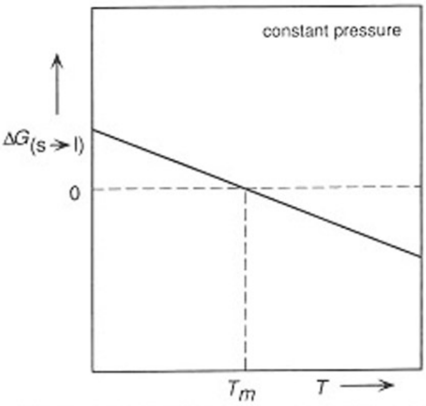

Figure. 3

Figure 8.3 Schematic representation of the variation of the molar Gibbs free energy of melting of water with temperature at constant pressure.

2. G(P)

∗For single phase substance

dG=－SdT+VdP

constant T , $\left(\frac{\partial \mathbf{G}}{\partial \mathbf{P}}\right)_{\mathbf{T}}$ =V > 0

$$\left(\frac{\partial^2 \mathbf{G}}{\partial \mathbf{P}^2}\right)_{\mathbf{T}} = \left(\frac{\partial \mathbf{V}}{\partial \mathbf{P}}\right)_{\mathbf{T}} = -\boldsymbol{\beta} V \; < 0 \; (\rightarrow 0)$$

because β is very small

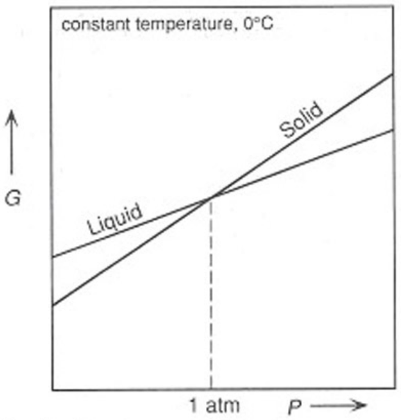

Figure. 4

Figure 8.4 Schematic representation of the variations of the molar Gibbs fee energies of solid and liquid water with pressure at constant temperature.

$\ast$ Two-phase equilibrium (e.g. melting)

$$\left(\frac{\partial \Delta \mathbf{G}^{\mathbf{sl}}}{\partial \mathbf{P}}\right)_{\mathbf{T}} = -\,\Delta \mathbf{V}^{\mathbf{sl}} \quad \begin{cases} > 0, \textbf{usually} \\ < 0, \mathbf{H_2O} \end{cases}$$

$$\left(\frac{\partial^2 \Delta \mathbf{G}^{\mathbf{sl}}}{\partial \mathbf{P}^2}\right)_{\mathbf{T}} = -\left(\frac{\partial \Delta \mathbf{V}^{\mathbf{sl}}}{\partial \mathbf{P}}\right)_{\mathbf{T}} \cong 0$$

Figure 8.5

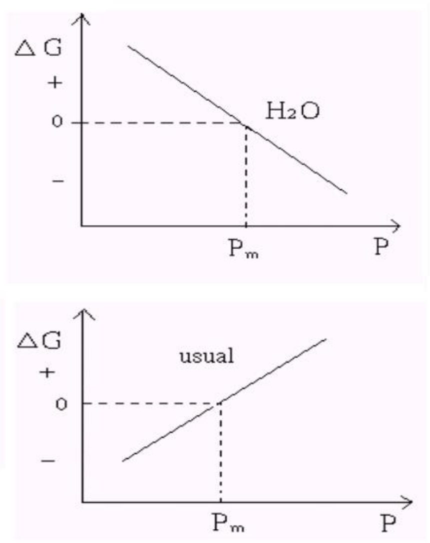

Figure. 5.

§8-10. Criterion for Thermodynamic Equilibrium

1. In an “isolated” system entropy is maximum.

$$\mathbf{S}_{\mathbf{U,V}} = \mathbf{S}_{\max} \quad \text{or} \quad \Delta S_{U,V} \geq 0$$

2. In a “constrained” system , energy is minimum.

$$\mathbf{U}_{\mathbf{S,V}} = \mathbf{U}_{\min} \quad \text{or} \quad \Delta U_{S,V} \leq 0$$

$$\mathbf{H}_{\mathbf{S,P}} = \mathbf{H}_{\min} \quad \text{or} \quad \Delta H_{S,P} \leq 0$$

$$\mathbf{F}_{\mathbf{T,V}} = \mathbf{F}_{\min} \quad \text{or} \quad \Delta F_{T,V} \le 0$$

$$\mathbf{G}_{\mathbf{T,P}} = \mathbf{G}_{\min} \quad \text{or} \quad \Delta G_{T,P} \le 0$$

§8-11. Thermodynamic Properties of Ideal Gas and Ideal Gas Mixture.

1. Isothermal G-P relationship, $dT=0$

$$dG = V\,dP = \frac{\mathbf{RT}}{\mathbf{P}}\mathbf{dP} = RT\, d\ln P$$

$\therefore$ <u>$dG = RT\, d\ln P$ (constant T)</u>

$$\Delta\mathbf{G} = \int_{\mathbf{P}_\circ}^{\mathbf{P}} \mathbf{dG} = G(P) - G(P_o) = RT\ln P - 0 = RT\ln P$$

$(P_o = 1\text{ atm}, \quad G=0)$

Standard State : P = 1 atm , 1 mole pure gas at T

$$G\,(P = 1\text{ atm}) = \mathbf{G}^\circ = 0$$

$\therefore\ \Delta\mathbf{G} = \mathbf{G} - \mathbf{G}^\circ = \mathbf{RT}\ln P$ (constant T)

2. Mixture of Ideal Gases

$$\text{consider:}\begin{cases}\textbf{Fixed total volume}: \mathbf{V}' \\ \textbf{Fixed temperature}: \mathbf{T} \\ \mathbf{n_A} + \mathbf{n_B} + \mathbf{n_c}\end{cases}$$

total pressure : P

(or initial pressure) $\mathbf{P}_\mathbf{A}^\circ = \mathbf{P}_\mathbf{B}^\circ = \mathbf{P}_\mathbf{C}^\circ = P$

$\ast$ mole fraction : $\mathbf{X_A} = \dfrac{\mathbf{n_A}}{\mathbf{n_A} + \mathbf{n_B} + \mathbf{n_C}} = \dfrac{\mathbf{n_A}}{\sum \mathbf{n_i}}$

$\therefore \sum \mathbf{X_i} = \mathbf{X_A} + \mathbf{X_B} + \mathbf{X_C} = 1$

$P = \mathbf{p_A} + \mathbf{p_B} + \mathbf{p_C}$

(1) initial $\mathbf{n_A}$, $\therefore P_i = \mathbf{p_A} = \dfrac{\mathbf{n_A RT}}{\mathbf{V}'}$

(2) adding $\mathbf{n_B}$, $(\mathbf{n_A} + \mathbf{n_B})$ $\because$ $P = \mathbf{p_A} + \mathbf{p_B}$

$$\therefore\ P = \frac{(\mathbf{n_A} + \mathbf{n_B})\mathbf{RT}}{\mathbf{V'}} = (\mathbf{p_A} + \mathbf{p_B})$$

$$\therefore \frac{\mathbf{p_A}}{\mathbf{p_A} + \mathbf{p_B}} = \frac{\mathbf{n_A}}{\mathbf{n_A} + \mathbf{n_B}} = \mathbf{X_A}$$

$$\therefore \mathbf{p_A} = \mathbf{X_A}(\mathbf{p_A} + \mathbf{p_B}) = \mathbf{X_A} \cdot \mathbf{P}$$

∗ $\boxed{p_i = \mathbf{X_i P}}$, Dalton's law of partial pressure

∗Partial Molar Quantities :

$$(1)\quad \overline{\mathbf{Q_i}} \equiv \left(\frac{\partial \mathbf{Q'}}{\partial \mathbf{n_i}}\right)_{\mathbf{T,P,n_j\ldots}}$$

$$(2)\quad \overline{\mathbf{G_i}} = \left(\frac{\partial \mathbf{G'}}{\partial \mathbf{n_i}}\right)_{\mathbf{T,P,n_j\ldots}} = \boldsymbol{\mu}_\mathbf{i}$$, chemical potential

$$(3)\quad \left(\frac{\partial \overline{\mathbf{G_i}}}{\partial \mathbf{P}}\right)_{\mathbf{T,n_j\ldots}} = \overline{\mathbf{V_i}}$$

$$\because \left(\frac{\partial \mathbf{G'}}{\partial \mathbf{P}}\right)_{\mathbf{T,comp.}} = \mathbf{V'}$$

$$\therefore \left[\frac{\partial}{\partial \mathbf{n_i}}\left(\frac{\partial \mathbf{G'}}{\partial \mathbf{P}}\right)_{\mathbf{T,comp.}}\right]_{\mathbf{T,P,n_j\ldots}} = \left(\frac{\partial \mathbf{V'}}{\partial \mathbf{n_i}}\right)_{\mathbf{T,P,n_j\ldots}}$$

$$\Rightarrow \left[\frac{\partial}{\partial \mathbf{P}}\left(\frac{\partial \mathbf{G'}}{\partial \mathbf{n_i}}\right)_{\mathbf{T,P,n_j\ldots}}\right]_{\mathbf{T,comp.}} = \overline{\mathbf{V_i}}$$

(4) For fixed composition and T

$$d\overline{\mathbf{G_i}} = \overline{\mathbf{V_i}}\, dP$$

$$\because \overline{\mathbf{V_i}} = \left(\frac{\partial \mathbf{V'}}{\partial \mathbf{n_i}}\right)_{\mathbf{T,P,n_j\ldots}} = \left[\frac{\partial\left(\sum \mathbf{n_i}\right)\frac{\mathbf{RT}}{\mathbf{P}}}{\partial \mathbf{n_i}}\right]_{\mathbf{T,P,n_j\ldots}} = RT/P = \frac{\mathbf{X_i RT}}{p_i}$$

$$\therefore d\overline{\mathbf{G_i}} = \frac{\mathbf{X_i RT}}{p_\mathbf{i}}\, dP = \frac{\mathbf{X_i RT}}{p_\mathbf{i}}\, d\left(\frac{p_\mathbf{i}}{\mathbf{X_i}}\right) = \frac{\mathbf{RT}}{p_\mathbf{i}}\, d p_\mathbf{i}$$

$$\therefore \boxed{d\overline{\mathbf{G_i}} = RTd\ln \mathbf{p_i}}$$

$$\underline{\overline{\mathbf{G_i}} = \mathbf{G_i^\circ} + \mathbf{RT}\ \ln p_{\mathbf{i}}} \qquad \text{(constant T)},\ \ p_{\mathbf{i}}^\circ = 1\text{atm} = \text{P}$$

(5) Gibbs Free Energy of Mixing , $\Delta\mathbf{G'_{mix}}$

For each component *i*,

$$\begin{cases} \textbf{before mixing}, \mathbf{G_i} = \mathbf{G_i^\circ} + \mathbf{RT}\ \ln \text{P}_{\mathbf{i}} \\ \textbf{after mixing}, \overline{\mathbf{G_i}} = \mathbf{G_i^\circ} + \mathbf{RT}\ \ln p_{\mathbf{i}} \end{cases}$$

$$\therefore \Delta\mathbf{G_i} = \overline{\mathbf{G_i}} - \mathbf{G_i} = \mathbf{RT}\ \ln\left(\frac{p_i}{\text{P}_\text{i}}\right)$$

$$\Delta\mathbf{G'_{mix}} = \sum \mathbf{n_i}\Delta\mathbf{G_i} = \text{RT}\sum \mathbf{n_i} \ln\left(\frac{p_{\mathbf{i}}}{\mathbf{P_i}}\right)$$

If mixing is carried out at constant T ,

total volume ($\mathbf{V'}$) and $\mathbf{P_i} = \mathbf{P_j} = \mathbf{P_k} = ... = \mathbf{P_{mix}} = \text{P}$

$$\therefore \frac{p_i}{\mathbf{P_i}} = \frac{p_i}{\mathbf{P}} = \mathbf{X_i}$$

$$\therefore \underline{\Delta\mathbf{G'_{mix}} = \mathbf{RT}\sum \mathbf{n_i} \ln \mathbf{X_i}}$$

one mole mixture $\underline{\Delta\mathbf{G_{mix}} = \dfrac{\mathbf{RT}\sum \mathbf{n_i} \ln \mathbf{X_i}}{(\sum \mathbf{n_i})} = \mathbf{RT}\sum \mathbf{X_i} \ln \mathbf{X_i}}$

(6) Heat of mixing , $\Delta\mathbf{H'_{mix}} = 0$, $\Delta\mathbf{U'_{mix}} = 0$, $\Delta\mathbf{V'_{mix}} = 0$

Constant pressure and composition :

$$\left[\frac{\partial(\mathbf{G}/\mathbf{T})}{\partial\mathbf{T}}\right]_{\mathbf{P}} = -\frac{\mathbf{H}}{\mathbf{T}^2} \qquad \text{, before mixing}$$

$$\left[\frac{\partial(\overline{\mathbf{G_i}}/\mathbf{T})}{\partial\mathbf{T}}\right]_{\mathbf{P}} = -\frac{\overline{\mathbf{H_i}}}{\mathbf{T}^2} \qquad \text{, after mixing}$$

$$\overline{\mathbf{G_i}} = \mathbf{G_i^\circ} + \mathbf{RT}\ln p_{\mathbf{i}} = \mathbf{G_i^\circ} + \mathbf{RT}\ln X_{\mathbf{i}} + \mathbf{RT}\ln\mathbf{P}$$

$$\therefore \frac{\overline{G_i}}{T} = \frac{G_i^\circ}{T} + R \ln X_i + R \ln P$$

$$\therefore \frac{\partial(\overline{G_i}/T)}{\partial T} = \frac{\partial(G_i^\circ/T)}{\partial T} \qquad , \overline{H_i} = H_i^\circ$$

similarly, $H = H_i^\circ$

$$\therefore \Delta H'_{mix} = \sum n_i \Delta H_i = \sum n_i (\overline{H_i} - H_i) = 0$$

(note : no interaction between particles of ideal gas $\Rightarrow \Delta H'_{mix} = 0$

$\Rightarrow \overline{H_i}$ is a function of T only!! It is indep. of composition.)

(7) Entropy of mixing , $\Delta S'_{mix}$

$$\because \Delta G'_{mix} = \Delta H'_{mix} - T\Delta S'_{mix}$$

$$\therefore \Delta S'_{mix} = \frac{\Delta H'_{mix}}{T} - \frac{\Delta G'_{mix}}{T} = 0 - R\sum n_i \ln X_i$$

$$\therefore \Delta S'_{mix} = -R\sum n_i \ln X_i$$

one mole $\Delta S_{mix} = -R\sum X_i \ln X_i$

(8) $\Delta V'_{mix} = 0$

$$\because \Delta V'_{mix} = \sum n_i \Delta V_i = \sum n_i (\overline{V_i} - V_i)$$

$$\because \overline{V_i} = \left(\frac{\partial V'}{\partial n_i}\right)_{T,P,n_j\ldots} = \left[\frac{\partial\left(\sum n_i\right)RT/P}{\partial n_i}\right]_{T,P,n_j\ldots} = \frac{RT}{P}$$

$$V_i = \frac{RT}{P} \qquad \therefore \overline{V_i} = V_i \ , \ \Delta V'_{mix} = 0$$

(9) $\Delta U'_{mix} = 0$

$$\because \Delta H'_{mix} = \Delta U'_{mix} + P\Delta V'_{mix}$$

$$\therefore \Delta \mathbf{U}'_{\mathbf{mix}} = \Delta \mathbf{H}'_{\mathbf{mix}} + P\Delta \mathbf{V}'_{\mathbf{mix}} = 0$$

∗ Conclusions :

Mixing of Ideal Gas (total one mole)

$$\Delta \mathbf{G}_{\mathbf{mix}} = RT\sum \mathbf{X_i} \ln \mathbf{X_i}$$

$$\Delta \mathbf{S}_{\mathbf{mix}} = -R\sum \mathbf{X_i} \ln \mathbf{X_i}$$

$$\Delta \mathbf{H}_{\mathbf{mix}} = 0,\ \Delta \mathbf{U}_{\mathbf{mix}} = 0,\ \Delta \mathbf{V}_{\mathbf{mix}} = 0$$

§8-12. Thermodynamic Treatment of Nonideal Gas (Real Gas)

1. Consider nonideal gas itself, not mixture.

   Fugacity : $\boxed{dG \equiv RT\, d \ln f}$

   c.p. , ideal gas $dG = RT\, d \ln P$

Mixing of nonideal gas : $d\overline{\mathbf{G_i}} = RT\, d \ln \mathbf{f_i}$

$$\Delta \boldsymbol{\mu}_{\mathbf{i}} = RT \ln(\frac{\mathbf{f_i}}{\mathbf{P}}) \qquad (\Delta\overline{\boldsymbol{\mu}_{\mathbf{i}}} = \overline{\mathbf{G_i}} - \mathbf{G}_{\mathbf{i}}^{\circ})$$

※ (comparison with gas mixture):

$$\boldsymbol{\mu}_{\mathbf{i}} - \boldsymbol{\mu}_{\mathbf{i}}^{\circ} = \Delta\overline{\boldsymbol{\mu}_{\mathbf{i}}} \equiv RT \ln (\frac{\mathbf{f_i}}{\mathbf{P}})$$

$$\therefore \overline{\mathbf{G_i}} - \mathbf{G}_{\mathbf{i}}^{\circ} = RT \ln (\frac{\mathbf{f_i}}{\mathbf{P}})$$

$\mathbf{G}_{\mathbf{R}}^{\circ}$: pure gas at P = 1 atm , 1 mole $\mathbf{f}_{\mathbf{i}}^{\circ} = 1$

$$\therefore \boxed{\mathbf{d}\overline{\mathbf{G_i}} = \mathbf{RTd} \ln \mathbf{f_i}}$$

$$* \begin{cases} \textbf{Ideal gas}: \mathbf{f} = \mathbf{P} \\ \textbf{Ideal gas mixture}: \mathbf{f_i} = \mathbf{P_i} \\ \text{Re}\textbf{al gas}: \mathbf{P} \to 0, \mathbf{f} \to \mathbf{P} \ \ (\mathbf{f} = \mathbf{P}\mathbf{e}^{\frac{-\alpha P}{RT}}) \\ \text{Re}\textbf{al gas mixture}: \mathbf{P} \to 0, \mathbf{f_i} \to \mathbf{P_i} \ \ (\mathbf{f_i} = \mathbf{P_i}\mathbf{e}^{\frac{-1}{RT}\int_{P}^{P_i} \alpha_i dP}) \end{cases}$$

$$\text{as } P \to 0,\ (\frac{\mathbf{f}}{\mathbf{P}}) \to 1$$

deviation : $\alpha \equiv -\mathbf{V} + \dfrac{\mathbf{RT}}{\mathbf{P}} \quad (= \mathbf{V}^{\mathbf{id}} - \mathbf{V})$

const T $\quad dG = V\,dP = RT\,d\ln f$

$$(-\alpha + \frac{\mathbf{RT}}{\mathbf{P}})\,dP = RT\,d\ln f \qquad \therefore \int_{P=0}^{P} \mathbf{d}\ln(\frac{\mathbf{f}}{\mathbf{P}}) = \int_{P=0}^{P} \frac{-\alpha}{\mathbf{RT}}\mathbf{dP}$$

$$\because P \to 0,\ (\frac{\mathbf{f}}{\mathbf{P}}) \to 1,\ \ln(\frac{\mathbf{f}}{\mathbf{P}}) \to 0$$

$$\therefore \ln(\frac{\mathbf{f}}{\mathbf{P}}) = \frac{-\alpha\mathbf{P}}{\mathbf{RT}} \qquad (\text{If } \alpha = \text{const.})$$

$$\therefore \frac{\mathbf{f}}{\mathbf{P}} = \mathbf{e}^{\frac{-\alpha P}{RT}}, \text{ or } \quad f = P\,\mathbf{e}^{\frac{-\alpha P}{RT}} \quad \text{or } f = P\,\mathbf{e}^{\frac{-1}{RT}\int_{P=0}^{P} \alpha dP} \qquad (\text{ if } \alpha \neq \text{const.})$$

$*$ when α is very small $\quad \mathbf{e}^{\frac{-\alpha P}{RT}} \cong 1 - \dfrac{\alpha\mathbf{P}}{\mathbf{RT}}$

$$\frac{\mathbf{f}}{\mathbf{P}} \cong 1 - \frac{\alpha\mathbf{P}}{\mathbf{RT}} = 1 - \frac{\mathbf{P}}{\mathbf{RT}}(-\mathbf{V} + \frac{\mathbf{RT}}{\mathbf{P}}) = \frac{\mathbf{PV}}{\mathbf{RT}}$$

For one mole of ideal gas : $\mathbf{P_{id}} = \dfrac{\mathbf{RT}}{\mathbf{V}}$

$$\therefore \frac{\mathbf{f}}{\mathbf{P}} = \frac{\mathbf{P}}{\mathbf{P_{id}}} \qquad \text{i.e.} \quad \boxed{\mathbf{P} = (\mathbf{f}^{\circ}\mathbf{P_{id}})^{\frac{1}{2}}, \textbf{when } \alpha \to 0, \mathbf{P} \to 0}$$

$*$ Calculate *f* from equation of state of real gas $\begin{cases} \mathbf{Z} = \mathbf{Z(P)} \\ \mathbf{Z} = \mathbf{Z(V)} \end{cases}$

$$\because d\ln(\frac{\mathbf{f}}{\mathbf{P}}) = \frac{-\alpha}{\mathbf{RT}}\,dP = (\frac{\mathbf{V}}{\mathbf{RT}} - \frac{1}{\mathbf{P}})dP$$

$$Z = \frac{\mathbf{PV}}{\mathbf{RT}} \qquad \therefore \boxed{\mathbf{d}\ln(\frac{\mathbf{f}}{\mathbf{P}}) = \frac{\mathbf{Z}-1}{\mathbf{P}} \cdot \mathbf{dP}}$$

$$[\ln(\frac{\mathbf{f}}{\mathbf{P}})]_{\mathbf{P}} - [\ln(\frac{\mathbf{f}}{\mathbf{P}})]_{\mathbf{P}=0} = \int_0^{\mathbf{P}} \frac{\mathbf{Z-1}}{\mathbf{P}} \cdot \mathbf{dP}$$

$$\therefore \boxed{\ln(\frac{\mathbf{f}}{\mathbf{P}}) = \int_0^{\mathbf{P}} \frac{\mathbf{Z-1}}{\mathbf{P}} \mathbf{dP}}$$

<u>Ex.</u>

One mole $\mathbf{N}_2$ gas at T=273.16 K (0 °**C**)

$$PV = 22414.6 - 10.281P + 0.065189\mathbf{P}^2 + 5.2\times10^{-7}\mathbf{P}^4 - 1.32\times10^{-11}\mathbf{P}^6$$

$$+1.01\times10^{-16}\mathbf{P}^8 \quad (\text{atm}\cdot\mathbf{cm}^3)$$

when P=100atm , f=?

<u>Sol.</u>

$$Z = \frac{\mathbf{PV}}{\mathbf{RT}} = \frac{1}{\mathbf{RT}}(\mathbf{a} + \mathbf{bP} + \mathbf{cP}^2 + \mathbf{dP}^4 + \mathbf{mP}^6 + \mathbf{nP}^8)$$

$$\frac{\mathbf{Z-1}}{\mathbf{P}} = \frac{1}{\mathbf{RT}}(\mathbf{b} + \mathbf{cP} + \mathbf{dP}^3 + \mathbf{mP}^5 + \mathbf{nP}^7)$$

$$\ln(\frac{\mathbf{f}}{\mathbf{P}}) = \frac{1}{\mathbf{RT}}(\mathbf{bP} + \mathbf{cP}^2/2 + \mathbf{dP}^4/4 + \mathbf{mP}^6/6 + \mathbf{nP}^8/8)$$

$\therefore$ when P = 100 atm, f = 96.96 atm.