Chapter 7 Phase equilibrium in one component system

1. * Thermodynamic equil. $\begin{cases} \text{Thermal equilbrium} & T_\alpha = T_\beta \\ \text{Mechanical equilibrium} & P_\alpha = P_\beta \\ \text{Chemical equilibrium} & \mu_\alpha = \mu_\beta \end{cases}$

* At constant T, P. equil. ⇔ $G' = G_{min}$, $dG' = 0$

* G = H – TS

For constant P = 1 atm with H(T), S(T) known.

G(T) can be calculated for $\begin{cases} \text{one component} \\ \text{closed system} \\ \text{single phase} \end{cases}$

$G_\alpha(T)$ for different phases => stable (equilibrium) phase at specific T is the lowest G_α phase.

2. G(T), ΔG(T) at constant P = 1 atm

Consider: P = 1 atm, T = 273 K. $H_2O_{(s)} \rightarrow H_2O_{(l)}$

* Adding heat, if (ice + water) coexist, only ratio of ice/water changes, total Gibbs free energy G' remains constant.

$\Delta G = G_{H2O(l)} - G_{H2O(s)} = 0$

i.e. $G_{H2O(l)} = G_{H2O(s)}$

Assume: $\begin{cases} H_2O_{(s)} \text{ has } n_{H_2O_{(s)}} \text{ moles} \\ H_2O_{(l)} \text{ has } n_{H_2O_{(l)}} \text{ moles} \end{cases}$

$$\therefore G' = n_{H_2O_{(s)}} \cdot G_{H_2O_{(s)}} + n_{H_2O_{(l)}} \cdot G_{H_2O_{(l)}} \text{ ....} *1$$

$$= \left[n_{H_2O_{(s)}} + n_{H_2O_{(l)}}\right] \cdot G_{H_2O_{(s)}}$$

$$\therefore \left(n_{H_2O_{(s)}} + n_{H_2O_{(l)}}\right) \text{is fixed. (closed system)}$$

When $\dfrac{n_{H_2O_{(s)}}}{n_{H_2O_{(l)}}}$ is changed. G' does not change.

* $dG = -SdT + VdP + \sum \mu_i dn_i$ constant T, P.

$$\therefore G'_{T,P} = \int dG = \sum \int \mu_i dn_i$$

$$\therefore G' = \mu_{H_2O_{(s)}} \cdot n_{H_2O_{(s)}} + \mu_{H_2O_{(l)}} \cdot n_{H_2O_{(l)}} \text{ ....} *2$$

c.p. $\textcircled{*1}\textcircled{*2}$ $\therefore \mu_{H_2O} = G_{H_2O}$, $\mu_i = G_i$

Chemical potential ⇔ molar Gibbs free energy.

Definition: $\boxed{\mu_i \equiv \left(\frac{\partial G'}{\partial n_i}\right)_{n_j,T,P} = \overline{G_i}}$

For one component system (i), $n_j = 0$

Adding one mole of i, i.e. $\Delta n_i = 1$

$\therefore \quad \Delta G' = G_i = \mu_i$

* P = 1 atm, T < 0℃. $\qquad G_{H2O(s)} < G_{H2O(l)}$

$\therefore \Delta G = G_{H2O(l)} - G_{H2O(s)} > 0$ $\qquad$ ice is stable.

T > 0℃. $\qquad G_{H2O(s)} > G_{H2O(l)}$ $\qquad$ water is stable.

$G_{(s)}(T) = ?$ $\qquad G_{(l)} = ?$ $\quad$ ⇔ $C_{p(s)}, C_{p(l)}$

$$\text{* H}_2\text{O}\begin{cases} C_{p(s)} = 38 \quad J/k\cdot mole \\ C_{p(l)} = 75.44 \quad J/k\cdot mole \\ at\ \ 298\text{K} \qquad S_{(s)} = 44.77 \ J/k\cdot mole \qquad H_{(s)} = -6944 \ J/mole \\ \qquad\qquad\qquad S_{(l)} = 70.08 \ J/k\cdot mole \qquad H_{(l)} \equiv 0 \\ T_m = 0^oC = 273k, \qquad \Delta H_{s\to l} = \Delta H_m = 6008 \ J/mole \end{cases}$$

$$H(T) = \int_{298}^{T} C_p \cdot dT + H_{298}$$

$$S(T) = \int_{298}^{T} \frac{C_p}{T} \cdot dT + S_{298}$$

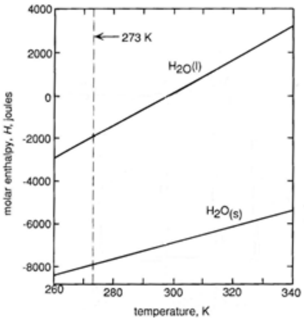
$$\therefore G(T) = H(T) - T \cdot S(T)$$

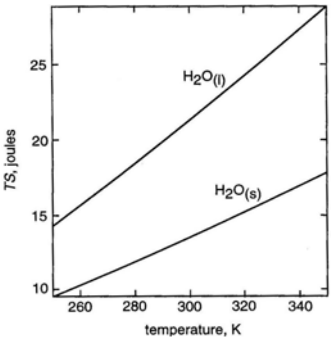
$$\therefore \begin{cases} G_{(s)} = H_{(s)} - T \cdot S_{(s)} \\ G_{(l)} = H_{(l)} - T \cdot S_{(l)} \end{cases}$$

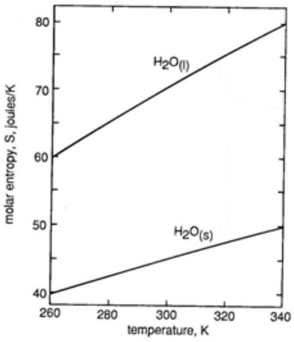
$$\Delta G_{s\to l} = G_l - G_s = \left[H_{(l)} - H_{(s)}\right] - T\left[S_{(l)} - S_{(s)}\right]$$

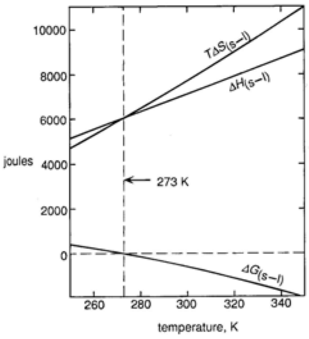
$$\Delta G_{s\to l} = \Delta H_{s\to l} - T \cdot \Delta S_{s\to l}$$

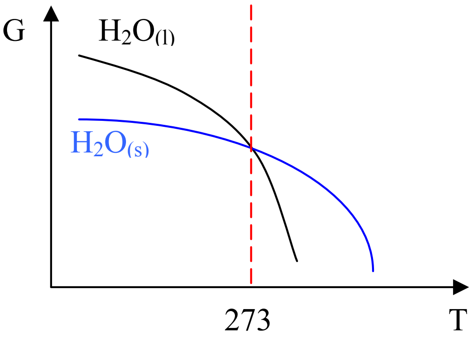
$$\text{when}\begin{cases} T = T_m & \Delta G_{s\to l} = 0 & \Delta H_m = T_m \Delta S_m \\ T < T_m & \Delta G_{s\to l} > 0 \\ T > T_m & \Delta G_{s\to l} < 0 \end{cases}$$











Note: $H_{(l)} > H_{(s)}$

$S_{(l)} > S_{(s)}$

$\Delta H = H_{(l)} - H_{(s)} > 0$

$\Delta S = S_{(l)} - S_{(s)} > 0$ but $\Delta H > \Delta S$

$$\Delta G = \Delta H - T\Delta S \begin{cases} \text{low T}: \Delta H \text{ dominates} \\ \text{high T}: -\Delta S \text{ dominates} \end{cases}$$

$\therefore$ low T : $\Delta G > 0$, higt T : $\Delta G < 0$

at $T = T_m$, $\Delta G = 0$

* Shape of G(T), ΔG(T) curves (P = 1 atm)

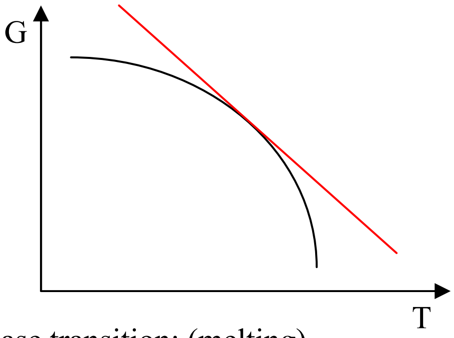
① single phase:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S < 0$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_P}{T} < 0$$

$\because$ T > 0, S > 0, $C_p > 0$

$\therefore$



② Phase transition: (melting)

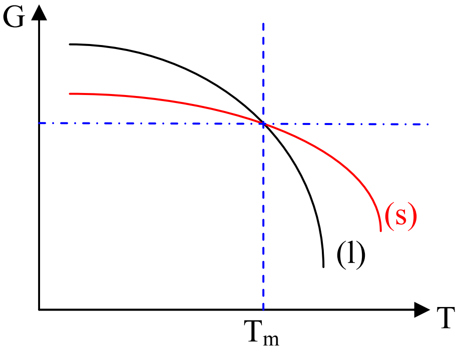
$\Delta G = G_{(l)} - G_{(s)}$

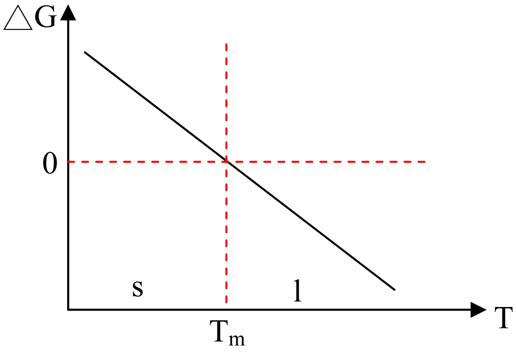
$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S = -\left(S_{(l)} - S_{(s)}\right) < 0$$

$$\left(\frac{\partial^2 \Delta G}{\partial T^2}\right)_p = -\left(\frac{\partial \Delta S}{\partial T}\right)_P \cong -\frac{\Delta C_p}{T} \approx \frac{-\left[C_{p(l)} - C_{p(s)}\right]}{T} \approx 0$$

* ΔC_p indep. of T

* Richards' $\Delta S_m \approx 8.4 \; {}^{J}\!/\!{}_{k \cdot mole}$

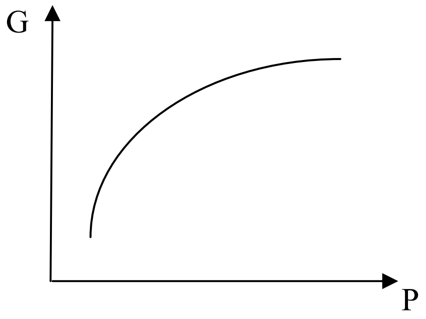




3. G(P), ΔG(P) at constant T.

* shape of curves

① Homogeneous single phase



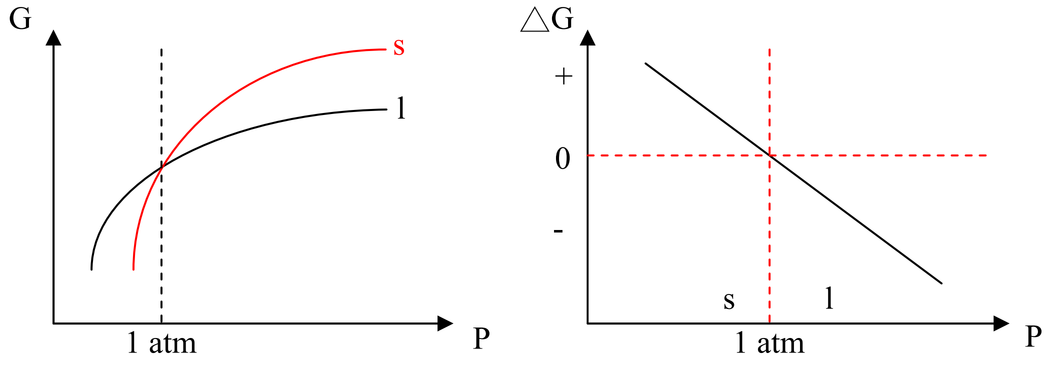
$$\left(\frac{\partial G}{\partial P}\right)_T = V > 0$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T = -\beta V < 0$$

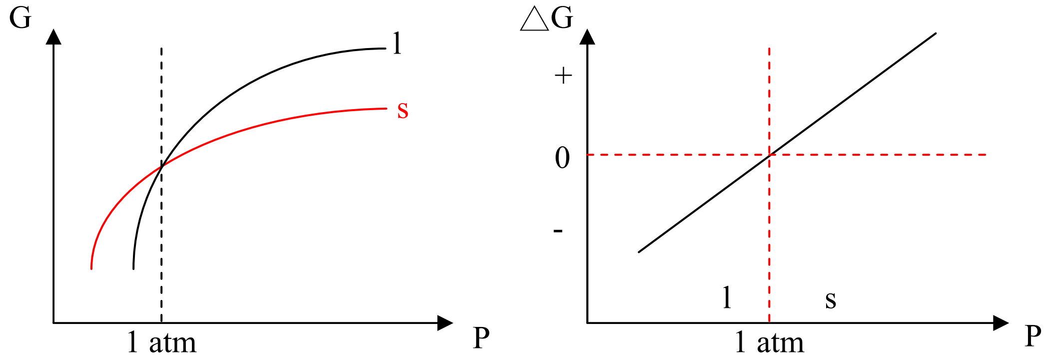
② Phase transition (melting)

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V = V_{(l)} - V_{(s)} \begin{cases} H_2O, \ \Delta V < 0 \\ \text{Usual}: \Delta V > 0 \end{cases}$$

$$\left(\frac{\partial^2 \Delta G}{\partial P^2}\right)_T = \left(\frac{\partial \Delta V}{\partial P}\right)_T \cong -\left[\beta_l V_l - \beta_s V_s\right] \begin{cases} > 0 \\ < 0 \end{cases}$$



For H_2O, $\because \triangle V>0$, P ↑ ⇔ $\triangle G \downarrow$ ⇔ liquid water is stable.



Usual

4. Phase equilibrium between solid and liquid. $T_{s\text{->}l}(P) = ?$ $T_m(P) = ?$

Equilibrium. $G_{(l)} = G_{(s)}$ $\therefore dG_{(l)} = dG_{(s)}$

$$\because \begin{cases} dG_{(l)} = -S_{(l)}dT + V_{(l)}dP \\ dG_{(s)} = -S_{(s)}dT + V_{(s)}dP \end{cases}$$

$$\therefore -S_{(l)}dT + V_{(l)}dP = -S_{(s)}dT + V_{(s)}dP$$

$$\left(\frac{dP}{dT}\right)_{eq.} = \frac{S_{(l)} - S_{(s)}}{V_{(l)} - V_{(s)}} = \frac{\Delta S_{(s\to l)}}{\Delta V_{(s\to l)}}$$

and $\because \Delta G = 0 \Rightarrow \Delta H = T \cdot \Delta S$

$$\therefore \boxed{\left(\frac{dP}{dT}\right)_{eq.} = \frac{\Delta H}{T \cdot \Delta V}} \quad \text{Clapeyron eq.}$$

Ex: H_2O: s-> l

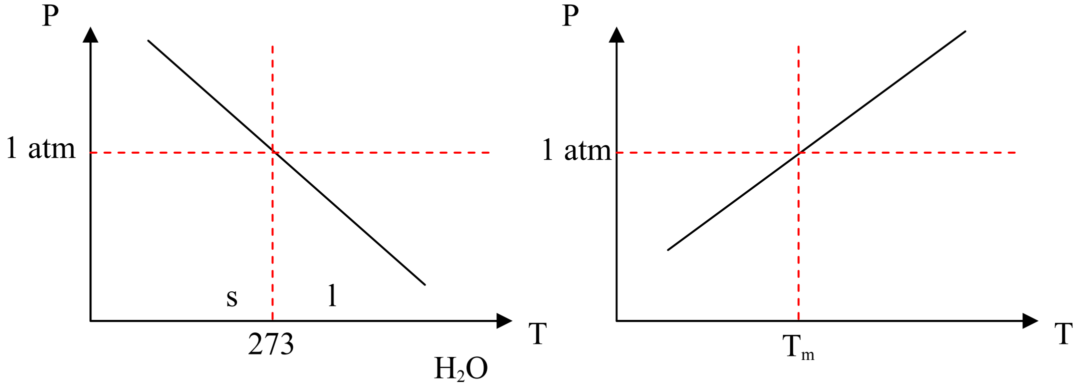
$$\left.\begin{matrix} \Delta H_{sl} > 0 \\ \Delta V_{sl} < 0 \end{matrix}\right\} \left(\frac{dP}{dT}\right) < 0$$

$$P \uparrow \Rightarrow T_{sl} \downarrow$$

If R.T. = -1$^\circ C$ under skate, (P ↑), $T_{sl} \approx -3^\circ C$, ice melts

⇒ water is lubricant.

Most materials, $\triangle V_{sl} > 0$. $\therefore$ P ↑ => T_m ↑



* Note: 3D diagram G-T-P (phase) Fig. 7-3(D) (or 7-8(G))

G(T,P) = H(T,P) – T × S(T,P)

Projection of $G_{(s)} = G_{(l)}$ curve on (T-P) plane.

5. Solid (liquid) ⬄ Vapor phase equilibrium

* Equilibrium vapor pressure over solid (liquid)?

Condensed phase → Vapor

$\Delta V = V_{vapor} - V_{cond.} \doteqdot V_{vapor}$

$$\therefore \left(\frac{dP}{dT}\right)_{eq.} = \frac{\Delta H}{T\cdot\Delta V} \approx \frac{\Delta H}{T\cdot V_{(v)}}$$

Assume ideal gas, PV = RT

$$\therefore \left(\frac{dP}{dT}\right)_{eq} = \frac{P\Delta H}{RT^2}$$

$$\because \frac{dP}{P} = \frac{\Delta H}{RT^2}dT$$

$$\boxed{d\ln P = \frac{\Delta H}{RT^2}dT}$$ Clausius-Clapeyron eq. (ideal gas)

①

If $\Delta H \neq f(T)$, *i.e.* $C_p(vapor) = C_p(cond.)$

$\therefore \Delta C_p = 0$

$$\therefore \ln P = -\frac{\Delta H}{RT} + const.$$

②

If $\Delta C_p = constant \neq f(T)$

$$\because \Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

$$\begin{aligned}\therefore \Delta H(T) &= \Delta H_{298} + \int_{298}^{T} \Delta C_p dT \\ &= \Delta H_{298} + \Delta C_p (T - 298) \\ &= (\Delta H_{298} - 298 \cdot \Delta C_p) + T \cdot \Delta C_p\end{aligned}$$

$$\therefore \int d\ln P = \int \frac{\Delta H_{298} - 298 \cdot \Delta C_p}{RT^2} \cdot dT + \int \frac{\Delta C_p}{RT} \cdot dT$$

Then $$\boxed{\ln P = \frac{A}{T} + B\ln T + C}$$

③

If T_b, $\triangle H_b$, $C_{p(l)}$, $C_{p(v)}$ are known, then saturated vapor pressure P(T) can be calculated.

Note: normal boiling temperature: Tb. At T = T_b, P = 1 atm.

e.g. $C_{p,H2O(l)}$ = 75.44 J/k

$C_{p,H2O(v)} = 30 + (10.7\times10^{-3})T + (0.33\times10^{-5})T^{-2}$ J/k

T_b = 100℃ = 373 k $\triangle H_b$ = 41090 J/mole

$$\because d\ln P = \frac{\Delta H_{evap}}{RT^2} dT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots * $$

$$\therefore \Delta H_{evap}(T) = \Delta H_{evap}(373) + \int_{373}^{T} \Delta C_p (l \to v) dT$$

$$\begin{cases}\Delta H_{evap}(373) = \Delta H_b \\ \Delta C_p (l \to v) = C_{p,H_2O(v)} - C_{p,H_2O(l)}\end{cases}$$

$$\begin{aligned}\Rightarrow \Delta H_{evap}(T) &= 41090 + \int_{373}^{T} \left[-45.44 + (10.7\times10^{-3})\times T + (0.33\times10^{-5})\times T^{-2}\right] dT \\ &= 41090 + (-45.44)(T - 373) + \frac{10.7\times10^{-3}}{2}(T^2 - 373^2) \\ &\quad - (0.33\times10^{-5})\left(\frac{1}{T} - \frac{1}{373}\right) \\ &= 58872 - 45.44T + (5.35\times10^{-3})\times T^{-2} - \frac{0.33\times10^{-5}}{T} \qquad \text{J}\end{aligned}$$

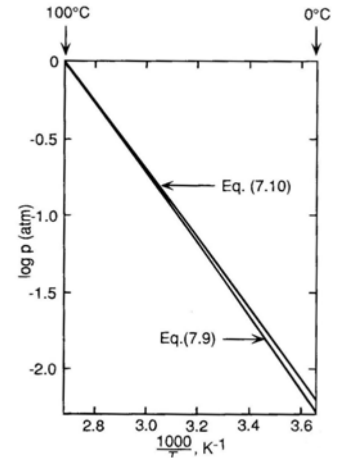
From the eq.*, we get

$$\Rightarrow \ln P = -\frac{58872}{RT} - \frac{45.44\ln T}{R} + \frac{(5.35\times10^{-3})\times T}{R} + \frac{0.33\times10^{-5}}{2RT^2} + \text{const.}$$

$$\because T = 373k,\quad P = 1\,atm,\quad \therefore const. = 51.1$$

$$\log P(atm) = -\frac{58872}{2.303RT} - \frac{45.44\log T}{R} + \frac{(5.35\times10^{-3})T}{2.303R} + \frac{0.33\times10^{-5}}{2.303\times 2RT^2} + \frac{51.1}{2.303}$$

Experimental data: $\log P(atm) = -\dfrac{2900}{T} - 4.65\log T + 19.732$



6. Phase diagram in one component system

On a P-T space, draw curves for:

s→l, l→v and s→v equilibrium

From $\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T \cdot \Delta V}$, obtain $P(T)$ curve.

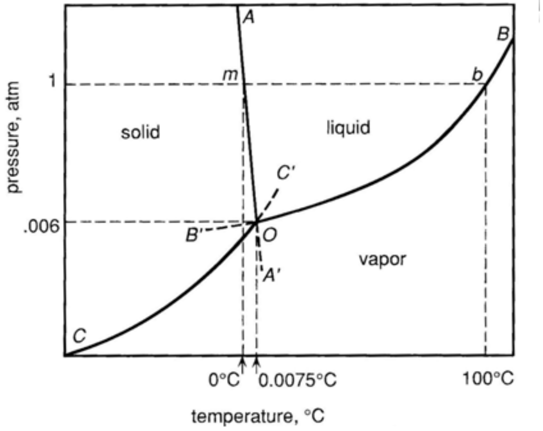
For s ↔ l: $\Delta H(T) = \Delta H_m + \int_{T_m}^{T} \left[C_{p(l)} - C_{p(s)}\right] \cdot dT$

$*$ if $\Delta H(T)$ is indep. of T, then $dP = \frac{\Delta H}{\Delta V}\frac{dT}{T}$

$\therefore P = \frac{\Delta H}{\Delta V} \cdot \ln T + const.$

Normal melting T_{mp}, $P = 1$ atm, $T = T_m \Rightarrow const.$

For $\left.\begin{matrix} l \leftrightarrow v \\ s \leftrightarrow v \end{matrix}\right\}$ $\log P = \frac{A}{T} + B \log T + C$



For H_2O

O: triple point

At triple point ⇔ P(s→v) = P(s→l) = P_{triple}

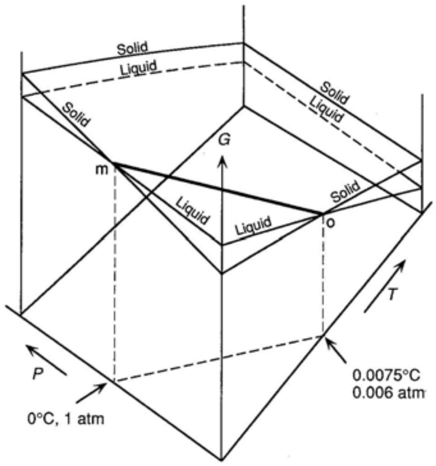
∴① if P(s→v)(T), and P(l→v)(T) are known,

T_t can be calculated.

$$\begin{cases} \log P_{sv} = \dfrac{A_s}{T} + B_s \cdot \log T + C_s \\ \log P_{lv} = \dfrac{A_l}{T} + B_l \cdot \log T + C_l \end{cases}$$

$$\therefore \frac{A_s}{T_t} + B_s \cdot \log T_t + C_s = \frac{A_l}{T_t} + B_l \cdot \log T_t + C_l$$

* 3D diagram G-T-P



* According $\boxed{\text{Gibbs Phase Rule: } F = C + 2 - P}$

$$\begin{cases} F: \text{ number of degree of freedom} \\ C: \text{ number of component} \\ P: \text{ number of phase} \\ 2: \text{ T, P variables} \end{cases}$$

$$\text{For} = 3 - \text{P:} \quad \begin{cases} \text{single phase region} \Rightarrow \text{F} = 2 \text{ (area)} \\ \text{two phase equil.} \Rightarrow \text{F} = 1 \text{ (line)} \\ \text{three phase equil.} \Rightarrow \text{F} = 0 \text{ (point)} \end{cases}$$

* G-T curves at different P (see Fig. 7.12)

* G-P curves at different T (see Fig. 7.13)

7. Solid-solid equilibria

* Allotropy: elements exist in more than one crystal form.

e.g. Fe: α, γ, δ

* Polymorphism: compounds exist in more than one crystal forms.

e.g. ZrO_2: monoclinic, tetragonal, cubic, (liquid)

* Solid(α) ⇔ Solid(β)

$$\left(\frac{dP}{dT}\right)_{eq}=\frac{\Delta H}{T\cdot\Delta V}=\frac{\Delta S}{\Delta V}$$

$$e.g.\ \ \alpha-Fe(BCC)\rightarrow\gamma-Fe(FCC)\rightarrow\delta-Fe(BCC)$$

$$\begin{cases}V(\alpha-Fe)>V(\gamma-Fe) & (\Delta V_{\alpha\gamma}<0)\ (\because\rho_{FCC}>\rho_{BCC})\\ V(\gamma-Fe)<V(\delta-Fe) & (\Delta V_{\gamma\delta}>0)\end{cases}$$

$$\therefore\Delta H>0$$

$$\therefore\left(\frac{dP}{dT}\right)_{\alpha\gamma}<0,\quad\left(\frac{dP}{dT}\right)_{\gamma\delta}>0$$

For phase transition between condensed phases,

$$\left(\frac{\Delta S}{\Delta V}\right)\approx const.\ \ (\text{insensitive to T, P})$$

$$\therefore P\cong\left(\frac{\Delta S}{\Delta V}\right)\cdot T+const.$$

Ex1. NaF

$$\begin{cases}s\leftrightarrow g:\ \ \ln P(atm)=-\left(\frac{34450}{T}\right)-2.01\times\ln T+33.74\text{................}(1)\\ l\leftrightarrow g:\ \ \ln P(atm)=-\left(\frac{31090}{T}\right)-2.52\times\ln T+34.66\text{...............}(2)\end{cases}$$

Q: (a) $T_b=?$ (b) $T_t=?$ $P_t=?$

(c) $\Delta H_b=?$ (d) When $T=T_t$ $\Delta H_{s,l}(T_t)$

(e) $\Delta C_p=C_{p(l)}-C_{p(s)}=?$

Solu:

(a) $T=T_b$, $P=1$ atm

$$\text{from (2)}\Leftrightarrow\ \ \ln 1=0=-\frac{31090}{T_b}-2.52\ln T_b+34.66$$

$$\therefore T_b=2006k$$

(b) At triple point: (1) = (2)

$$\therefore -\frac{34450}{T_t}-2.01\times\ln T_t+33.74=-\frac{31090}{T_t}-2.52\times\ln T+34.66$$

$$\therefore T_t=1239k$$

$$P_t=\exp\left(-\frac{34450}{1239}-2.01\cdot\ln 1239+33.74\right)=2.29\times10^{-4}\ \text{atm}$$

(c) $\because d\ln P=\frac{\Delta H}{RT^2}\cdot dT,\qquad\therefore\Delta H=RT^2\left(\frac{d\ln P}{dT}\right)$

$$l\rightarrow v:\ \ \ln P=-\frac{31090}{T}-2.52\cdot\ln T+34.66$$

$$\therefore \Delta H_g = RT^2\left[\frac{31090}{T^2} - 2.52\cdot\frac{1}{T}\right] = 258500 - 20.95T$$

$$T = T_b = 2006k,\ \Delta H_{l\to g} = \Delta H_b = 216500 \quad J$$

(d) $\Delta H_{sl} = H_l - H_s = H_l - H_g + H_g - H_s$

$$= -\left(\mathrm{H_g} - H_l\right) + \left(H_g - H_s\right) = \Delta H_{s\to g} - \Delta H_{l\to g}$$

$$\Delta H_{s\to g} = RT^2\cdot\left(\frac{d\ln P_{sg}}{dT}\right) = 286400 - 16.71\cdot T$$

$$\therefore \Delta \mathrm{H_{sl}} = \Delta H_{s\to g} - \Delta H_{l\to g} = 27900 + 4.24\times T$$

$$\mathrm{T = T_t = 1239k, \qquad \Delta H_{sl} = 33150\ \ J}$$

(e) $\Delta \mathrm{C_{p(s\to l)}} = \frac{\mathrm{d\cdot\Delta H_{s\to l}}}{\mathrm{dT}} = 4.24\ \ \mathrm{J/k\cdot mole}$

EX. 2: Carbon (Graphite) → Diamond $\qquad$ P = ?

T = 298 k, $\quad$ H(graphite) – H(diamond) = -1900 J

$S_{graphite}$ = 5.73 J/k-mole

$S_{diamond}$ = 2.43 J/k-mole

$\rho_{(graphite)}$ = 2.22 g/cm^3

$\rho_{(diamond)}$ = 3.515 g/cm^3

Solu: graphite → diamond at T = 298 k

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

$$= \left(H_d - H_g\right) - \mathrm{T}\cdot\left(\mathrm{S_d} - S_g\right)$$

$$= (+1900) - 298\times(2.43 - 5.73) = 2883\ \ \mathrm{J}$$

$$\left(\frac{\partial\Delta \mathrm{G}}{\partial \mathrm{P}}\right)_T = \Delta V, \qquad \text{const.} = \mathrm{T}$$

$$\int_{2883}^{\Delta G(P)} d(\Delta G) = \int_1^P \Delta V\cdot dP \qquad \Delta V = V_d - V_g$$

$$V_{diamond} = \frac{M}{\rho_d} = \frac{12}{3.515} = 3.415\ \ \mathrm{cm^3}/mole$$

$$V_{graphite} = \frac{M}{\rho_g} = \frac{12}{2.22} = 5.405\ \ \mathrm{cm^3}/mole$$

$$: \ \Delta V = -1.99\ \ \mathrm{cm^3}/mole$$

$$\therefore \Delta G(P) - 2883 \cong \left[\Delta V(P-1)\right]\times\left(0.1013\quad \frac{\mathrm{J}}{\mathrm{atm\cdot cm^3}}\right)$$

$$\therefore \Delta \mathrm{G(P)} = 2883 - 1.99\times 0.1013\times(\mathrm{P} - 1)$$

when $\Delta \mathrm{G(P)} \le 0$, phase transition occurs

$$\therefore\quad P \ge \frac{2883}{1.99\times 0.1013} + 1 \cong 14300\ \ \text{atm.}$$