Lecture 12

Tuesday, October 24, 2023 11:29

Topic 4A continued

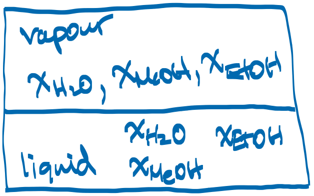
The Phase Rule for $C > 1$

Number of intensive variables

p, T, $(C-1)$ mole fractions

↑ multiply by P

$$x_1 + x_2 + \cdots + x_C = 1$$ constraint


vapour
$x_{H_2O}, x_{MeOH}, x_{EtOH}$
liquid
x_{H_2O} x_{EtOH}
x_{MeOH}

H_2O

MeOH

EtOH

$$x_{H_2O} + x_{MeOH} + x_{EtOH} = 1$$ in any phase

$P(C-1)+2$ total number of intensive variables

At equilibrium,

$\mu_J(\alpha; p, T) = \mu_J(\beta; p, T) = \cdots$

for P phases

$A = B = C \cdots = P$

letter

$A = B$, $B = C$, $C = D \ldots$, $O = P$

reduce degrees of freedom by P−1

for every component

$\boxed{C(P-1) \text{ reductions to the total number of intensive variables}}$

$$P(C-1) + 2 - C(P-1)$$

$$= \cancel{PC} - P + 2 - \cancel{CP} + C$$

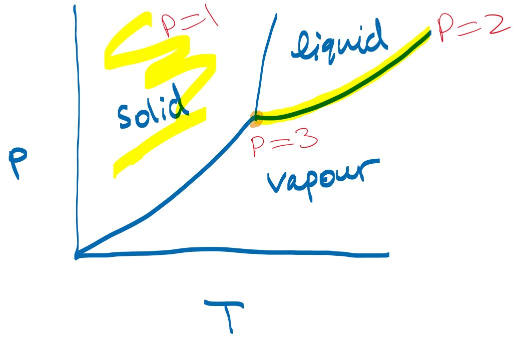
$$\boxed{F = C - P + 2}$$

general phase rule

when $C = 1$

$$\boxed{F = 1 - P + 2 = 3 - P}$$

consistent


P=1
P=2
P=3
solid
liquid
vapour
p
T

Topic 4B: Thermodynamic aspects of phase transitions

$$dG = Vdp - SdT$$

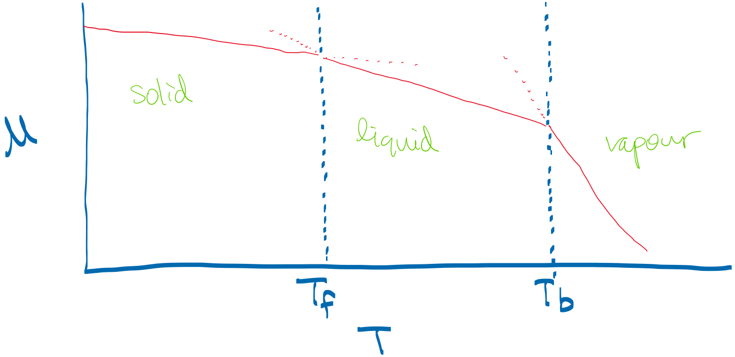
divide by n for a single component

$$d\mu = V_m dp - S_m dT$$

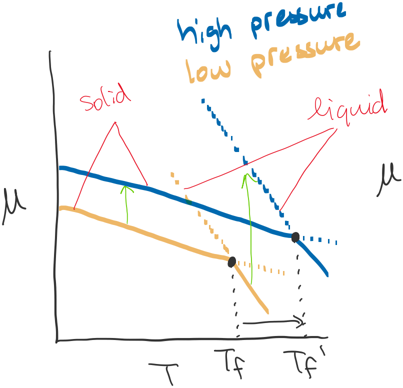
$$\mu = \frac{G}{n} = G_m$$

$$\boxed{\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m}$$

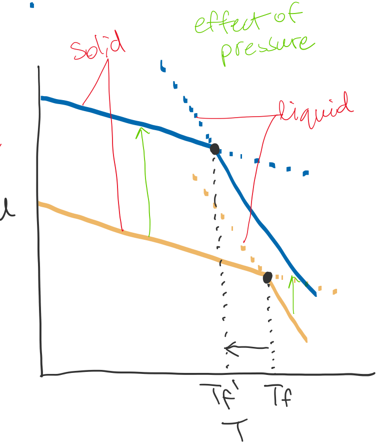
$$\boxed{\left(\frac{\partial \mu}{\partial p}\right)_T = V_m}$$


μ
solid
liquid
vapour
Tf
Tb
T

Effect of pressure :

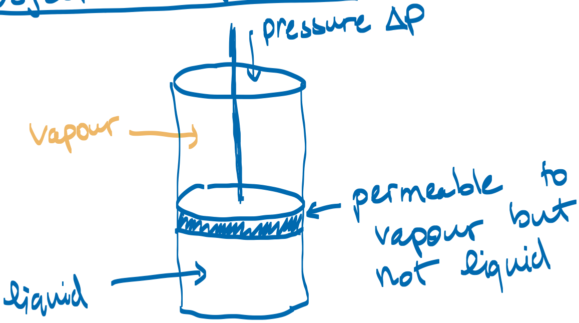

high pressure
low pressure
solid
liquid
μ
T
Tf
Tf'

$V_m(s) < V_m(l)$


solid
effect of pressure
liquid
μ
Tf'
Tf
T

$V_m(s) > V_m(l)$

The vapour pressure of a liquid subjected to pressure


pressure ΔP
vapour
permeable to vapour but not liquid
liquid

at equilibrium :

$$\mu(l) = \mu(g)$$

$$\boxed{d\mu(l) = d\mu(g)}$$

Apply external pressure dP :

$$d\mu(l) = V_m(l)\, dP$$

$$d\mu(g) = V_m(g)\, \underbrace{dp}_{} \quad \text{change in vapour pressure}$$

assume perfect gas

$$d\mu(g) = \frac{RT}{p}\, dp$$

$$\boxed{V_m(l)\, dP = \frac{RT}{p}\, dp}$$

Limits of integration :

normal vapour pressure

no additional pressure : $P = p^*$

$p = p^*$

apply external pressure ΔP : $P = p + \Delta P$

$p = p$

assume the effect of ΔP on p^* is small, so replace $p + \Delta P$ with $p^* + \Delta P$

$$RT \int_{p^*}^{p} \frac{1}{p'}\, dp' = \int_{p^*}^{p^* + \Delta P} V_m(l)\, dP$$

stays constant in this pressure

$$\int_{p^*}^{p} \frac{1}{p'}\,dp' = \frac{V_m(l)}{RT} \int_{p^*}^{\overset{\text{range}}{p^*+\Delta P}} dP$$

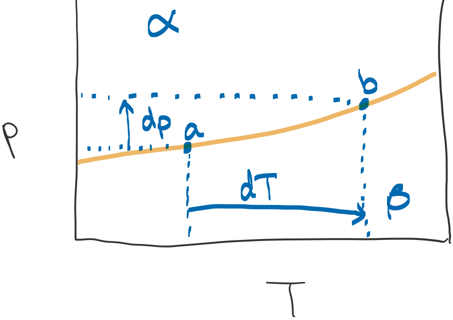
$$\ln \frac{p}{p^*} = \frac{V_m(l)}{RT} \Delta P$$

$$\frac{p}{p^*} = e^{V_m(l)/RT \cdot \Delta P}$$

$$\boxed{p = p^* e^{V_m(l)\Delta P/RT}}$$

effect of applied pressure ΔP on partial vapour pressure p

The Location of Phase Boundaries


α
b
dp
a
p
dT
β
T

$$\mu(\alpha; p, T) = \mu(\beta; p, T)$$

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

$$d\mu = V_m\,dp - S_m\,dT$$

$$\boxed{V_m(\alpha)\,dp} - S_m(\alpha)\,dT$$

$$= V_m(\beta)\,dp - \boxed{S_m(\beta)\,dT}$$

$$\underline{[S_m(\beta) - S_m(\alpha)]}\,dT = \underline{[V_m(\beta) - V_m(\alpha)]}\,dp$$

$$S_m(\beta) - S_m(\alpha) = \Delta_{trs} S$$

$$V_m(\beta) - V_m(\alpha) = \Delta_{trs} V$$

$$\Delta_{trs} S \, dT = \Delta_{trs} V \, dp$$

$$\boxed{\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}}$$

Clapeyron equation

Solid-liquid boundary

$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$

$$\boxed{\frac{dp}{dT} = \frac{\Delta_{fus} H}{T \Delta_{fus} V}}$$

slope of solid-liquid boundary

$\Delta_{fus} H$: generally positive

$\Delta_{fus} V$: generally small and positive

$\frac{dp}{dT}$: steep, generally positive

$$\int_{p^*}^{p} dp' = \frac{\Delta_{fus} H}{\Delta_{fus} V} \int_{T^*}^{T} \frac{1}{T'} \, dT'$$

$$p - p^* = \frac{\Delta_{fus} H}{\Delta_{fus} V} \ln \frac{T}{T^*}$$

$$\boxed{p = p^* + \frac{\Delta_{fus} H}{\Delta_{fus} V} \ln \frac{T}{T^*}}$$

If T is close to T^*, can use

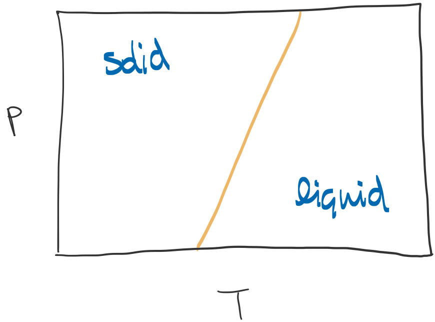
$$\ln \boxed{(1+x)} = x - \frac{1}{2} x^2 + \ldots$$

$$\frac{T}{T^*} + 1 - 1 = \frac{T}{T^*} + 1 - \frac{T^*}{T^*}$$

$$= \boxed{1 + \frac{T - T^*}{T^*}}$$

$$\ln\left(1+\frac{T-T^*}{T^*}\right) \approx \frac{T-T^*}{T^*}$$

$$\boxed{p \approx p^* + \frac{\Delta_{fus}H}{T^*\Delta_{fus}V}(T-T^*)}$$


solid
p
liquid
T

The Liquid-Vapour Boundary

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\boxed{\Delta_{vap}V}}$$

slope of liquid-vapour boundary

$$\Delta_{vap}V = V_m(g) - V_m(\ell)$$

$V_m(g) \gg V_m(\ell)$

$$\Delta_{vap}V \approx V_m(g)$$

assume perfect gas:

$$V_m(g) = \boxed{\frac{RT}{p}}$$

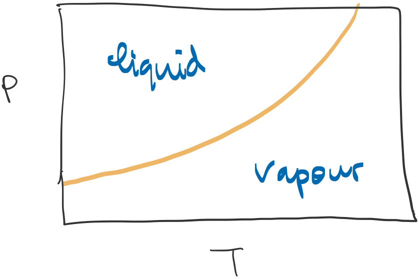
$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)} = \frac{p\,\Delta_{vap}H}{RT^2}$$

$$\frac{1}{p}\,dp = \frac{\Delta_{vap}H}{R}\,\frac{1}{T^2}\,dT$$

$$\int_{p^*}^{p}\frac{1}{p'}\,dp' = \frac{\Delta_{vap}H}{R}\int_{T^*}^{T}\frac{1}{T'^2}\,dT'$$

$$\ln\frac{p}{p^*} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$\boxed{p = p^* e^{-\chi}, \quad \chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)}$$


p
T
liquid
vapour

$$\boxed{\frac{d \ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}}$$

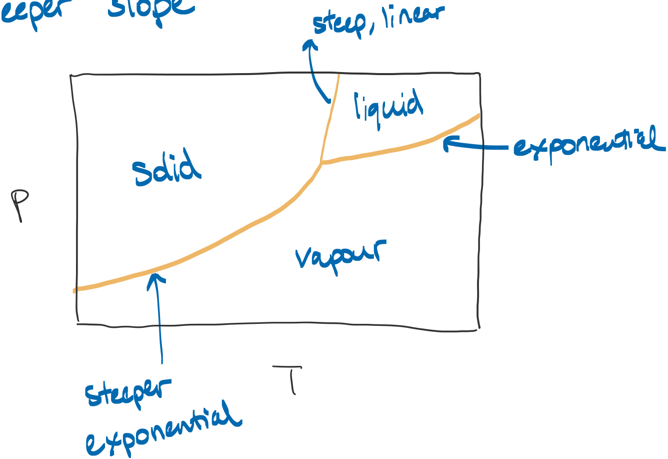
Clausius-Clapeyron equation (approximation)

Solid-Vapour Boundary

$$\frac{dp}{dT} = \frac{\Delta_{sub}H}{T\Delta_{sub}V}$$

$\Delta_{sub} H = \Delta_{fus} H + \Delta_{vap} H$

steeper slope


steep, linear
liquid
solid
exponential
P
vapour
T
steeper exponential