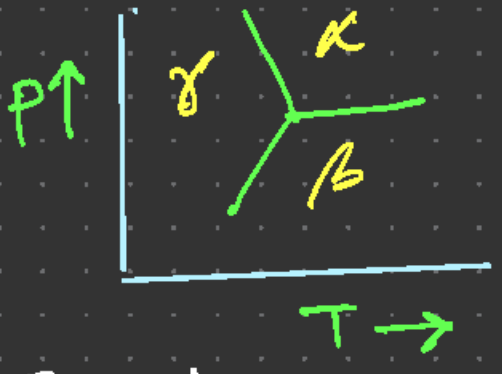
Phase change

- Phase diagrams in unary systems,
- Phase boundaries and Clausius Clapeyron equation
- Intro to partial molar properties in Solution

Unary System

↓

Phase Change



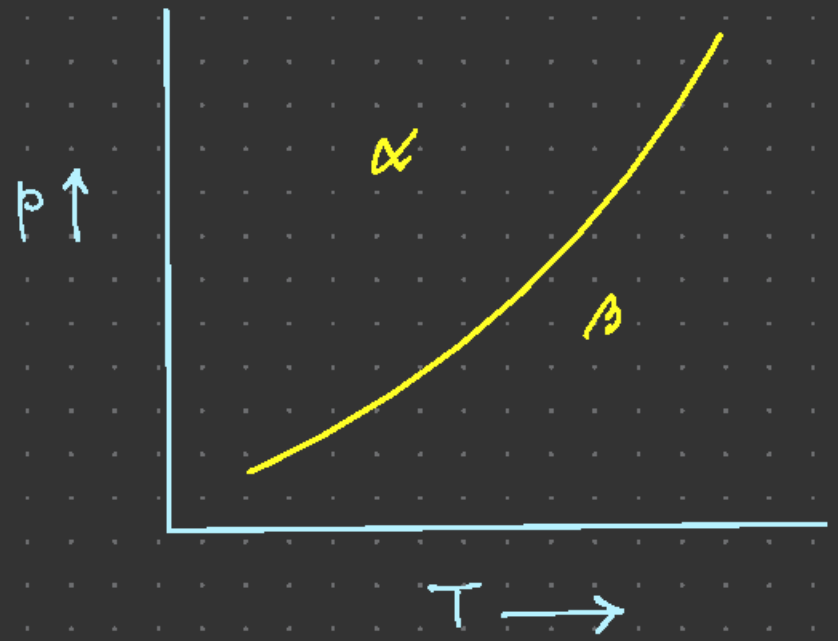
Clausius Clapeyron Equation

- phase change
- Slope of phase boundary

$\alpha \rightarrow \beta$ transformation

What is the slope of a phase boundary?

$G^\alpha = G^\beta$ $\quad \mu \to G_m$ $\quad \mu^\alpha(P,T) = \mu^\beta(P,T)$



$$d\mu^\alpha = -s^\alpha dT^\alpha + V_m^\alpha dp^\alpha$$

$$d\mu^\beta = -s^\beta dT^\beta + V_m^\beta dp^\beta$$

$$d\mu^\alpha = d\mu^\beta$$

$$-S^\alpha dT^\alpha + V_m^\alpha dp^\alpha = -S^\beta dT^\beta + V_m^\beta dp^\beta$$

$dG = V dP - S dT + \mu dN$

$p^\alpha = p^\beta = p$ (mechanical equilibrium)

$T^\alpha = T^\beta = T$ (thermal equilibrium)

$$\left(V_m^\beta - V_m^\alpha\right) dp = \left(S^\beta - S^\alpha\right) dT$$

$$\left(V_m^{\beta} - V_m^{\alpha}\right) dp = \left(S^{\beta} - S^{\alpha}\right) dT \qquad \alpha \rightleftharpoons \beta$$

$$\Delta V_m^{\alpha \to \beta} dp = \Delta S^{\alpha \to \beta} dT$$

$$\frac{dp}{dT} = \frac{\Delta S^{\alpha \to \beta}}{\Delta V_m^{\alpha \to \beta}} = \frac{\Delta S^{\beta \to \alpha}}{\Delta V_m^{\beta \to \alpha}}$$

Clausius Clapeyron Equation

$$\Delta V_m^{\alpha \to \beta} = -\Delta V_m^{\beta \to \alpha}$$

$$\left(V_m^{\beta} - V_m^{\alpha}\right) \qquad \left(V_m^{\alpha} - V_m^{\beta}\right)$$

Solid–Liquid boundary

$T_m \rightarrow$ Melting or freezing point

$$\alpha\,(\text{SOLID}) \underset{\text{freezing}}{\overset{\text{melting}}{\rightleftarrows}} \beta\,(\text{LIQUID})$$

$$\mu^{\alpha} = \mu^{\beta} \quad (G^{\alpha} = G^{\beta})$$

$$H^{\alpha} - TS^{\alpha} = H^{\beta} - TS^{\beta}$$

$$\text{or,} \quad H^{\beta} - H^{\alpha} = T(S^{\beta} - S^{\alpha})$$

$$\text{or,} \quad \Delta H^{\alpha \rightarrow \beta} = T \Delta S^{\alpha \rightarrow \beta}$$

$$T = T_{tr} = T_m$$

Clausius Clapeyron Equation

$$\frac{dp}{dT} = \frac{\Delta S^{\alpha \to \beta}}{\Delta V_m^{\alpha \to \beta}} = \frac{\Delta H^{\alpha \to \beta}}{T' \, \Delta V_m^{\alpha \to \beta}}$$

$T' \rightarrow$ transformation temperature at pressure p'

Let T_m^o be melting temperature at pressure p^o

T_m " " " " " p

If $\Delta H^{\alpha \to \beta}$ and $\Delta V_m^{\alpha \to \beta}$ do not vary with T,

$$\int_{p^o}^{p} dp = \frac{\Delta H^{\alpha \to \beta}}{\Delta V_m^{\alpha \to \beta}} \int_{T_m^o}^{T_m} \frac{dT}{T}$$

$$p = p^{\circ} + \frac{\Delta H^{\alpha \to \beta}}{\Delta V_m^{\alpha \to \beta}} \ln\left(\frac{T_m}{T_m^{\circ}}\right)$$

If $T_m - T_m^{\circ}$ is small,

$$\ln\left(T_m / T_m^{\circ}\right) = \ln\left(1 + \frac{T_m - T_m^{\circ}}{T_m^{\circ}}\right) \approx \frac{T_m - T_m^{\circ}}{T_m^{\circ}}$$

$$\approx \frac{\Delta T_m}{T_m^{\circ}}$$

$$p = p^{\circ} + \frac{\Delta H^{\alpha \to \beta}}{T_m^{\circ} \Delta V_m^{\alpha \to \beta}} \Delta T_m$$

$$\Delta p \simeq \frac{\Delta H^{\alpha \to \beta}}{T_m^{\circ} \Delta V_m^{\alpha \to \beta}} \Delta T_m$$

More generalized integration (ϵ (HCP) $\rightarrow$ β (BCC)) transformation in Ti

$$\frac{dP}{dT} = \frac{\Delta H_m^{\epsilon \rightarrow \beta}}{T \, \Delta V_m^{\epsilon \rightarrow \beta}}$$

$$\Delta H_m^{\epsilon \rightarrow \beta}(T, P) = H_m^{\beta} - H_m^{\epsilon}$$

$$d\left(\Delta H_m^{\epsilon \rightarrow \beta}\right) = d H_m^{\beta} - d H_m^{\epsilon}$$

$$dH = C_p \, dT + V \, (1 - T\alpha) \, dP$$

$$d \, \Delta H_m^{\epsilon \rightarrow \beta} = \Delta C_p \, dT + \Delta \left[V (1 - T\alpha) \right] dP$$

$$\Delta C_p = C_p^{\beta} - C_p^{\epsilon}$$

$$\Delta\left[V_m(1-T\alpha)\right] = \left[V_m^{\beta}(1-T\alpha^{\beta})\right] - \left[V_m^{\epsilon}(1-T\alpha^{\epsilon})\right]$$

If the phases are condensed, the term $\Delta\left[V_m(1-T\alpha)\right]$ is negligible till pressure changes up to 10^5 bar $= 10^{10}$ Pa $= 10$ GPa (Gigapascal)

$$\therefore \quad d\Delta H_m^{\epsilon\to\beta} = \Delta C_{p,m}^{\epsilon\to\beta}\, dT$$

$$C_p = a + bT + \frac{c}{T^2} + dT^2 \quad \text{(Experimental)}$$

$$\Delta C_p = \Delta a + \Delta b T + \frac{\Delta c}{T^2} + \Delta d T^2$$

$$\int_{T_0}^{T} d\Delta H = \int_{T_0}^{T} \Delta C_p(T)\, dT$$

$$= \int_{T_0}^{T} \left(\Delta a + \Delta b T + \frac{\Delta c}{T^2} + \Delta d T^2 \right) dT$$

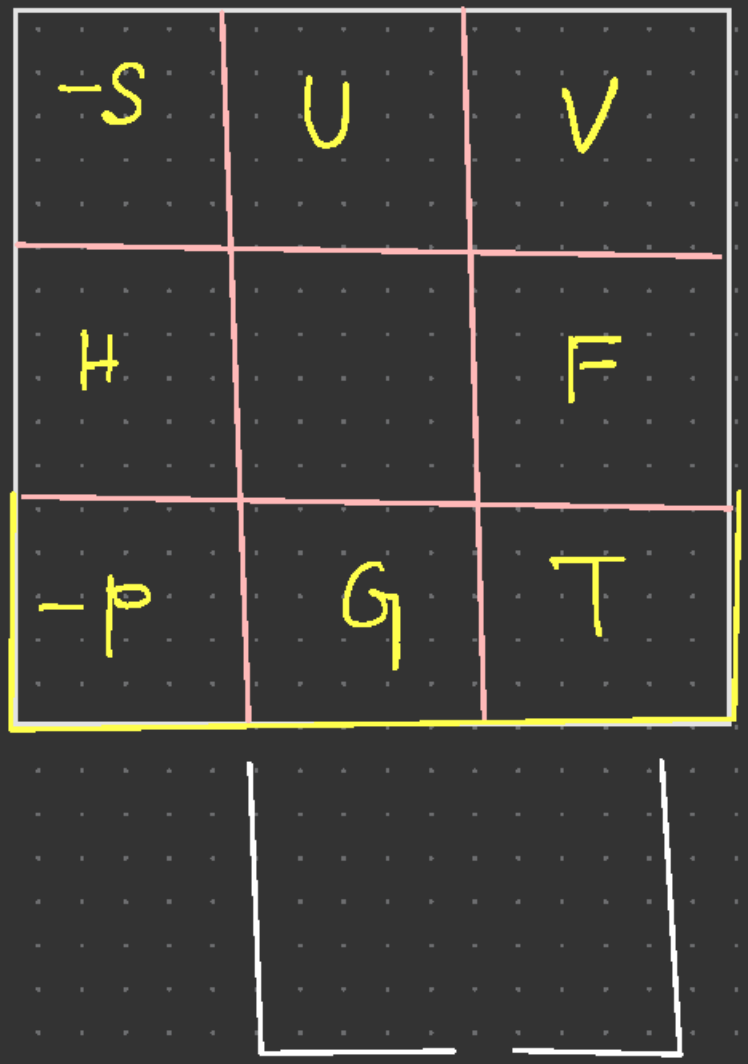
$$\Delta H(T) - \Delta H(T_0)$$

$$= \left[\Delta a T + \Delta b \frac{T^2}{2} - \frac{\Delta c}{T} + \frac{\Delta d}{3} T^3 \right]_{T_0}^{T}$$

$$\Delta V^{\alpha \to \beta} = V^{\beta} - V^{\alpha}(T, P)$$

$$P - P_0 = \frac{\left[\Delta a + \frac{\Delta b}{2} T - \frac{\Delta c}{T^2} + \frac{\Delta d}{3} T^2 \right]_{T_0}^{T}}{\Delta V^{\alpha \to \beta}}$$

Thermodynamic Square
Maxwell Relations



Good Physicists Have Studied Under Very Fine Teachers

$$dH = V\,dP + T\,dS$$

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

$S = S(T, P)$

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

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad dH = T\,dS = C_P\,dT$$

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

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

$$= C_P\,dT + V(1 - T\alpha)\,dP$$

Liquid - Vapor boundary

$$\alpha\,(\text{LIQUID}) \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \beta\,(\text{Vapor})$$

$V_m^{\beta}\,(\text{gas}) \gg V_m^{\alpha}\,(\text{liquid})$

$$\frac{dP}{dT} = \frac{\Delta H^{vap}}{T\,\Delta V_m^{vap}} = \frac{\Delta H^{vap}}{T\,V_m^{\beta}} \qquad \therefore \Delta V_m^{vap} = V_m^{\beta}$$

Let the vapor phase β be an ideal gas

$$V_m^{\beta} = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H^{vap}}{T\,(RT/P)} \Rightarrow \frac{dP}{dT} = \frac{P\,\Delta H^{vap}}{RT^2}$$

$$\frac{dp}{p} = \frac{\Delta H^{vap}}{RT^2} dT$$

$$d \ln p = \frac{\Delta H^{vap}}{R} \frac{dT}{T^2}$$

$T = T^\circ \qquad p = p^\circ$ (vapor pressure)

$T = T \qquad p = p$

$$\int_{p^\circ}^{p} d \ln p = \frac{\Delta H^{vap}}{R} \int_{T^\circ}^{T} \frac{dT}{T^2}$$

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

$$p = p_0 e^{-\chi} = p_0 \exp(-\chi)$$

$$\frac{p}{p_0} = \exp\left[-\frac{\Delta H^{vap}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

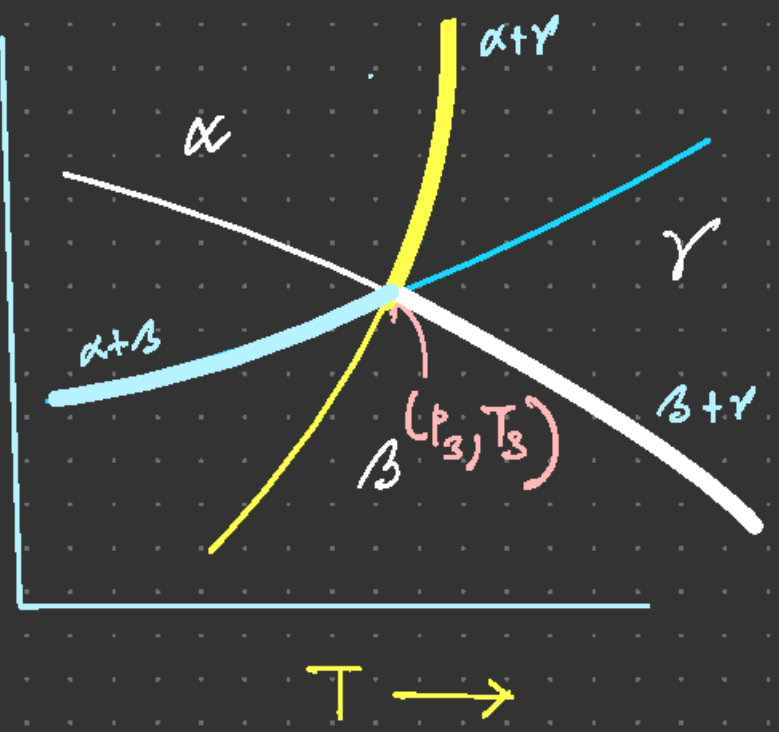
$$\therefore \quad \chi = \frac{\Delta H^{vap}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

Solid - Vapor boundary

$$\alpha(\text{solid}) \underset{\text{deposition}}{\overset{\text{sublimation}}{\rightleftharpoons}} \beta(\text{vapor})$$

$$\ln\left(\frac{P_s}{P_s^0}\right) = -\frac{\Delta H^{subl}}{R_v}\left(\frac{1}{T_s} - \frac{1}{T_s^0}\right)$$

Triple Point



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

α (Solid)
β (Liquid)
γ (gas)

$$\Delta V^{\alpha \to \gamma} = V_m^{\gamma} - V_m^{\alpha} = V^{\gamma} - V^{\beta} + V^{\beta} - V^{\alpha}$$

$$= V^{\gamma} - V^{\beta} + V^{\beta} - V^{\alpha}$$

$$= \Delta V^{\beta \to \gamma} + \Delta V^{\alpha \to \beta}$$

Solid — vapor equilibrium

$$p^s = A^s \exp\left(-\Delta H^{\alpha\to\gamma}/RT\right)$$

Liquid - vapor equilibrium

$$p^v = A^v \exp\left(-\Delta H^{\beta\to\gamma}/RT\right)$$

Triple point (p_3, T_3)

$$p_3 = A^s \exp\left(-\Delta H^{\alpha\to\gamma}/RT_3\right)$$

$$p_3 = A^v \exp\left(-\Delta H^{\beta\to\gamma}/RT_3\right)$$

A_s, A_v units of pressure

p_0^{Subl} or p_0^{Vapo}

$$\therefore \quad A^{s} \exp\left(-\Delta H^{\alpha \to \gamma} / RT_3\right)$$

$$= A^{v} \exp\left(-\Delta H^{\beta \to \gamma} / RT_3\right)$$

$$\ln A^{s} - \frac{\Delta H^{\alpha \to \gamma}}{RT_3} = \ln A^{v} - \frac{\Delta H^{\beta \to \gamma}}{RT_3}$$

$$RT_3 \ln\left(\frac{A^{s}}{A^{v}}\right) = \Delta H^{\alpha \to \gamma} - \Delta H^{\beta \to \gamma}$$

$$T_3 = \frac{\Delta H^{\alpha \to \gamma} - \Delta H^{\beta \to \gamma}}{R \ln\left(A^{s}/A^{v}\right)}$$

$$\Delta H^{d} = \Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}$$

$$\ln p_3 = \ln A^{s} - \frac{\Delta H^{\alpha\to\gamma}}{RT_3}$$

$$= \ln A^{s} - \frac{\Delta H^{\alpha\to\gamma} \ln\left(A_s/A_v\right)}{\Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}}$$

$$\Delta H_d \ln p_3 = \Delta H^{\alpha\to\gamma} \ln A^{s} - \Delta H^{\beta\to\gamma} \ln A^{s}$$

$$- \Delta H^{\alpha\to\gamma} \ln A^{s} + \Delta H^{\alpha\to\gamma} \ln A_v$$

$$\Delta H_d \ln p_3 = \Delta H^{\alpha\to\gamma} \ln A_v - \Delta H^{\beta\to\gamma} \ln A_v$$

$$- \Delta H^{\beta\to\gamma} \ln A_s + \Delta H^{\beta\to\gamma} \ln A_v$$

$$\Delta H_d \ln p_3 = -\Delta H^{\alpha\to\gamma} \ln A_s + \Delta H^{\alpha\to\gamma} \ln A_v$$

$$(-\Delta H^{\beta\to\gamma}) \qquad (\Delta H^{\alpha\to\gamma})$$

$$= \ln A_s + \ln A_v$$

$$\ln p_3^{\left(\Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}\right)} = \ln\left(A_S^{-\Delta H^{\beta\to\gamma}} A_V^{\Delta H^{\alpha\to\gamma}}\right)$$

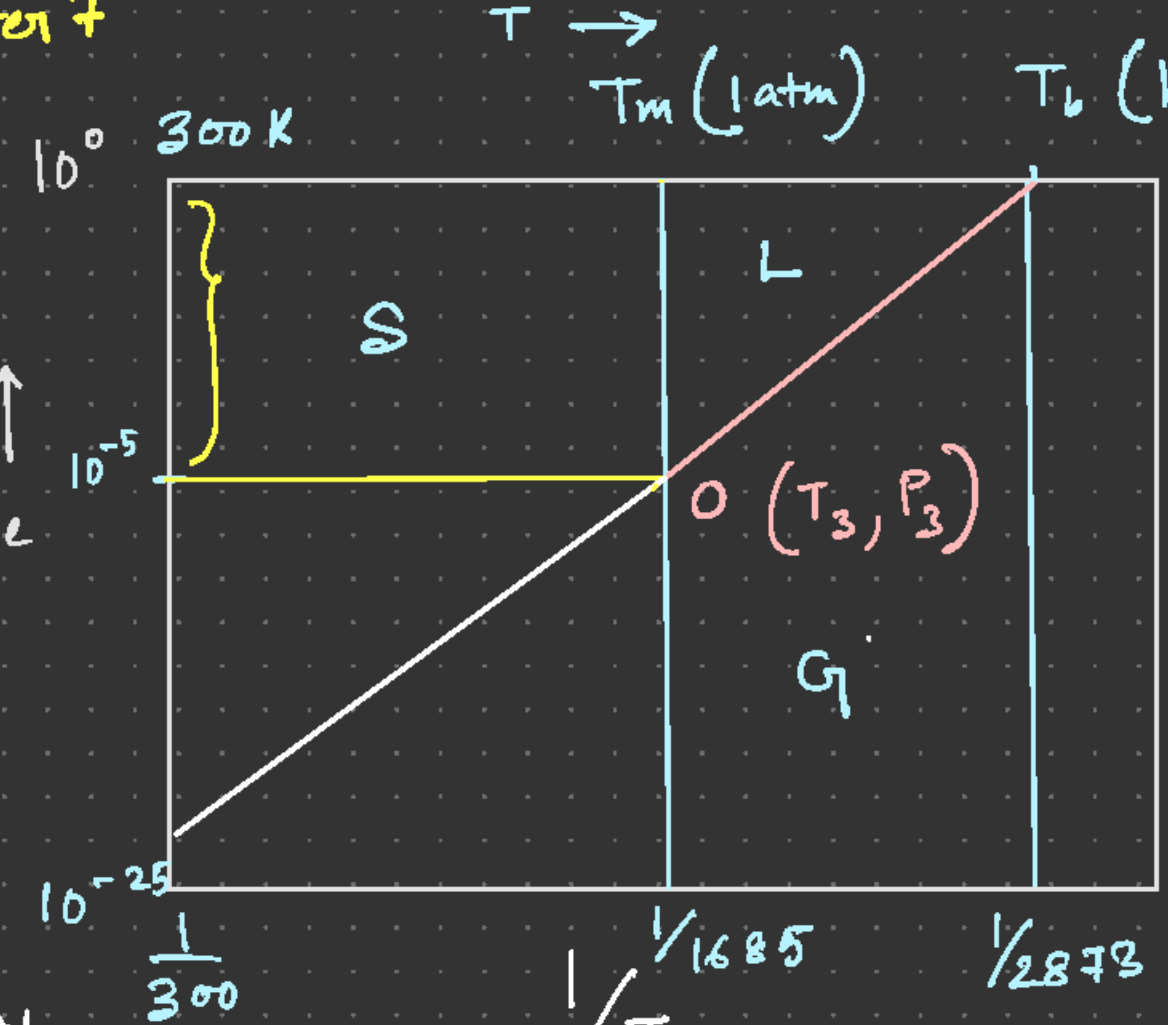
$$\left(p_3\right)^{\Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}} = \left(A_S\right)^{-\Delta H^{\beta\to\gamma}} \left(A_V\right)^{\Delta H^{\alpha\to\gamma}}$$

$$p_3 = \left(A_S\right)^{\left(\frac{\Delta H^{\beta\to\gamma}}{\Delta H^{\beta\to\gamma} - \Delta H^{\alpha\to\gamma}}\right)} \left(A_V\right)^{\left(\frac{\Delta H^{\alpha\to\gamma}}{\Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}}\right)}$$

Robert Dehoff's Chapter 7

Phase diagram of Si

$$\Delta H^{\alpha \to \gamma} = \Delta H^{\alpha \to \beta} + \Delta H^{\beta \to \gamma}$$



$$\Delta H_{Si}^{L \to V} = 386 \text{ kJ/mol}$$

$(P = 1 \text{ atm}, T_b = 2873 \text{ K})$

$$\therefore A^V = P^V e^{\Delta H_{Si}^{L \to V}/RT}$$

$$= 1.04 \times 10^7 \text{ atm}$$

$$\Delta H_{Si}^{S \to L} = 50.2 \text{ kJ/mol}$$

$T_m = 1685$ K (1 atm)

$T_3 = 1685$ K

$$P_V = 1.04 \times 10^7 \, e^{-\frac{386000}{8.314T}}$$

$$\therefore \quad P_3 = 1.04 \times 10^7 \, e^{-386000/8.314 \times 1685}$$

$$= 1.13 \times 10^{-5} \text{ atm.}$$

$$\Delta H_{Si}^{S \to V} = \Delta H_{Si}^{S \to L} + \Delta H_{Si}^{L \to V}$$

$$= 50.2 + 386$$

$$= 436.2 \text{ kJ/mol}$$

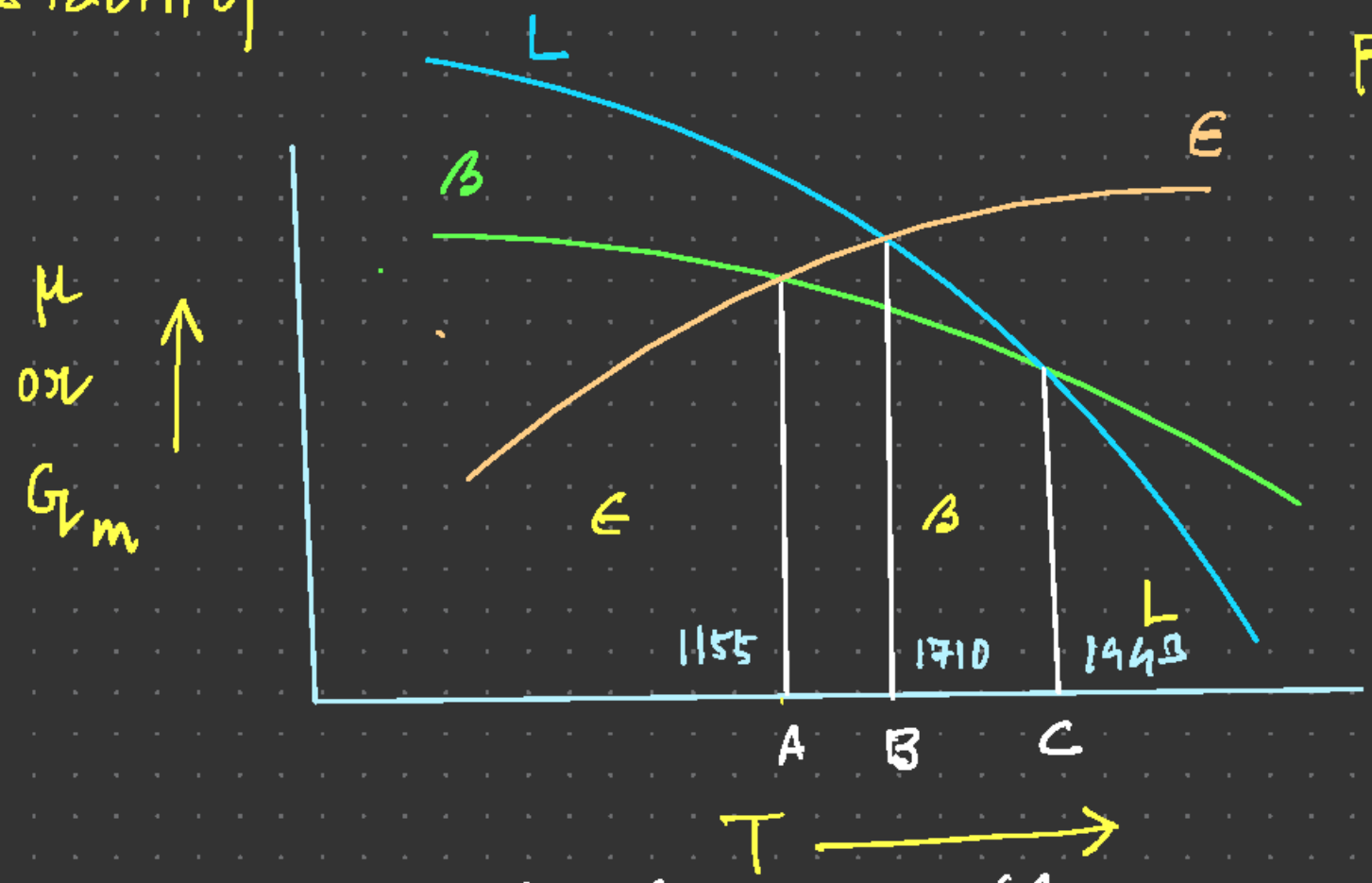
$$A_S = P_3 \exp\left(\frac{436200}{8.314 \times 1685}\right) \approx 3.8 \times 10^8 \text{ atm}$$

$$P^S = 3.8 \times 10^8 \, e^{-436200/RT}$$

Metastability

Ti

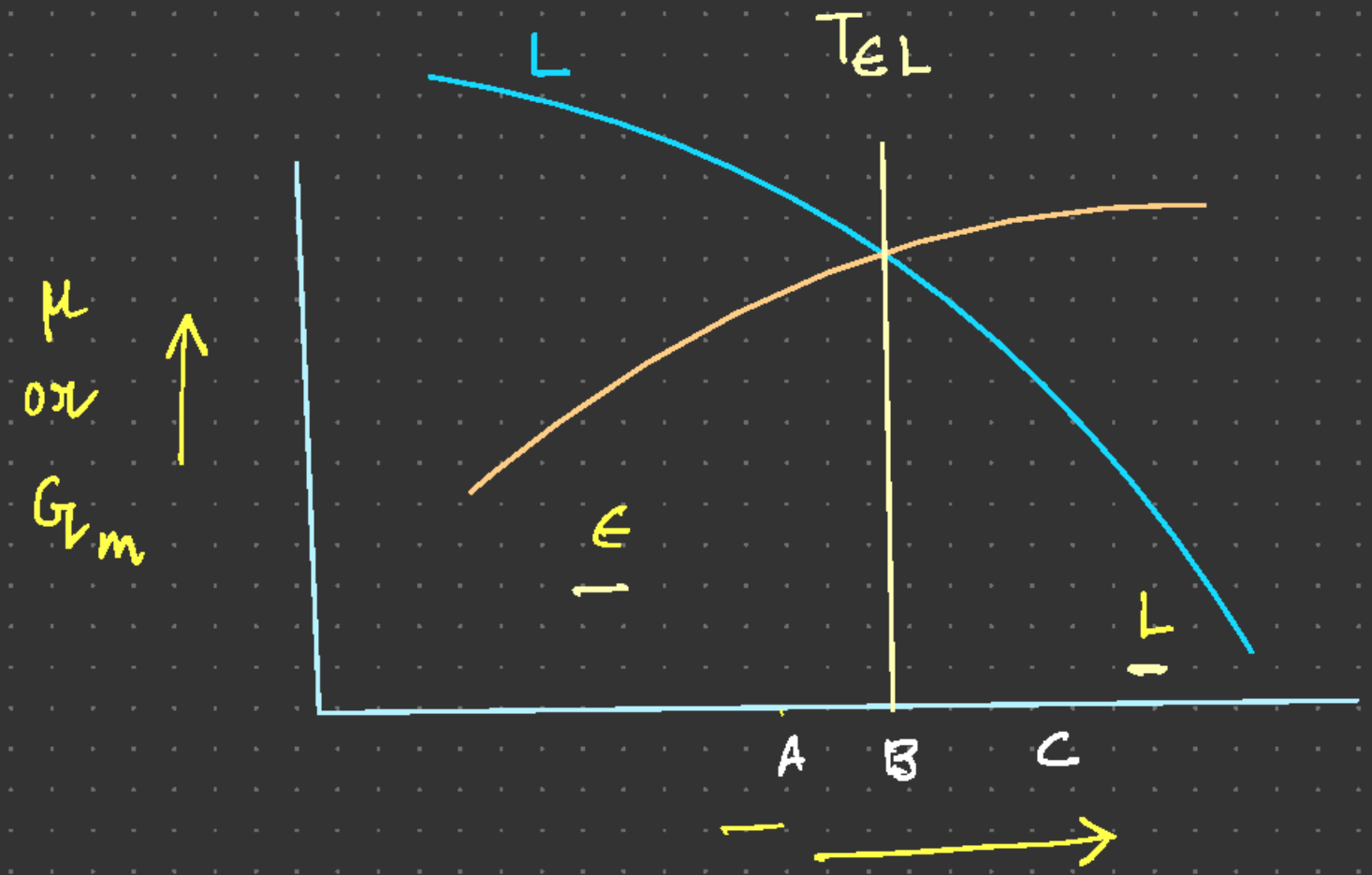
P = 1 bar



A : $T^{\varepsilon \to \beta}$ or $T^{\varepsilon\beta}$

B : $T^{\varepsilon \to L}$ or $T^{\varepsilon L}$

C : $T^{\beta \to L}$ or $T^{\beta L}$


L
$T_{\epsilon L}$
μ
or
G_{rm}
ϵ
L
A
B
C

Melting point of ϵ-Ti : $\mu^{\epsilon} = \mu^{L}$ $(T^{\epsilon L})$ or T_B

$\mu = -S\,dT + V\,dP$

$= -S\,dT$

$\mu^{\epsilon} - \mu^{\beta} = \mu^{L} - \mu^{\beta}$ $(T^{\epsilon L})$ $(T^{\epsilon L}$ or $T_B)$

— equi

At $T^{\epsilon L}$

$\Delta\mu^{\beta\to\epsilon} = \mu^{\epsilon} - \mu^{\beta}$

$= -(\mu^{\beta} - \mu^{\epsilon}) = -\Delta\mu^{\epsilon\to\beta}$ $(1155\,K)$

$T^{\epsilon\beta}$

$\Delta S_m^{\epsilon\to\beta}$ $(T^{\epsilon\beta})$

$\Delta S_m^{\epsilon\to\beta} = -\Delta S_m^{\beta\to\epsilon}$

$= +3.6\ J/mol\text{-}K$

$\mu^{\epsilon} > \mu^{\beta}$ at $T^{\epsilon L}$

$T^{\epsilon\to\beta} = T^{\epsilon\beta} = 1155\,K$

$$\int_{\beta}^{\epsilon} d\mu = -\Delta S_m^{\beta\to\epsilon} \int_{T^{\epsilon L}}^{T^{\epsilon\beta}} dT$$

$$\mu^{\epsilon} - \mu^{\alpha} = \Delta S_m^{\epsilon \to \alpha} \left(T^{\epsilon\alpha} - T^{\epsilon L} \right) \quad -(1)$$

$$\int_{\alpha}^{L} d\mu = -\Delta S_m^{\alpha \to L} \left(T^{\alpha L} - T^{\epsilon L} \right)$$

$$\mu^{L} - \mu^{\alpha} = -\Delta S_m^{\alpha \to L} \left(T^{\alpha L} - T^{\epsilon L} \right) \quad -(2)$$

From equi, (1) = (2)

$$\Delta S_m^{\epsilon \to \alpha} \left(T^{\epsilon\alpha} - T^{\epsilon L} \right) = -\Delta S_m^{\alpha \to L} \left(T^{\alpha L} - T^{\epsilon L} \right)$$

$$\therefore \quad \Delta S_m^{\epsilon \to \alpha} T^{\epsilon\alpha} + \Delta S_m^{\alpha \to L} T^{\alpha L} = \left(\Delta S_m^{\epsilon \to \alpha} + \Delta S_m^{\alpha \to L} \right) T^{\epsilon L} \quad -(3)$$

$$T^{\epsilon L} = ?$$

From (3)

$$T^{\epsilon L} = \frac{\Delta S_m^{\epsilon \to \beta} T^{\epsilon\beta} + \Delta S_m^{\beta \to L} T^{\epsilon L}}{\Delta S_m^{\epsilon \to \beta} + \Delta S_m^{\beta \to L}}$$

$T^{\epsilon\beta} = 1155\ K \quad \Delta S_m^{\epsilon \to \beta} = 3.6\ J/mol\text{-}K$

$T^{\beta L} = 1943\ K \quad \Delta S_m^{\beta \to L} = 8.6\ J/mol\text{-}K$

$\therefore \quad T^{\epsilon L} \approx 1710\ K$

THERMODYNAMICS

OF

SOLUTIONS / MIXTURES

Multicomponent System

Nonreacting

Partial molar / molal quantities

Partial Molar Quantities
Molal

$1\ l = 1\ dm^3 = 10^3\ cm^3$

Partial molar volume

1 liter of pure water is mixed with 1 mole of water at 25°C, 1 bar pressure

$$\rho_{H_2O} = 1\ gm/cm^3$$

1 mole of water = 18 gm of water

$$= \frac{18}{1}\ cm^3$$

$$= 18\ cm^3$$

$$= 18 \times 10^{-3}\ l = 18\ ml$$

New Volume = 1018 ml

ΔV = 18 ml

$\therefore$ Molar Volume $V_m^{H_2O(l)} = 18\ ml\ mol^{-1}$

$= 18\ cm^3\ mol^{-1}$

Add 1 mol water to 1 litre of pure ethanol, increase in volume (ΔV^{mix}) is $14\ cm^3$

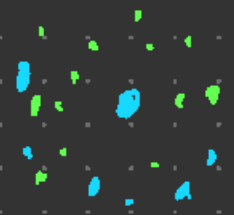
$= 14\ ml.$

Each water molecule surrounded by ethanol molecules

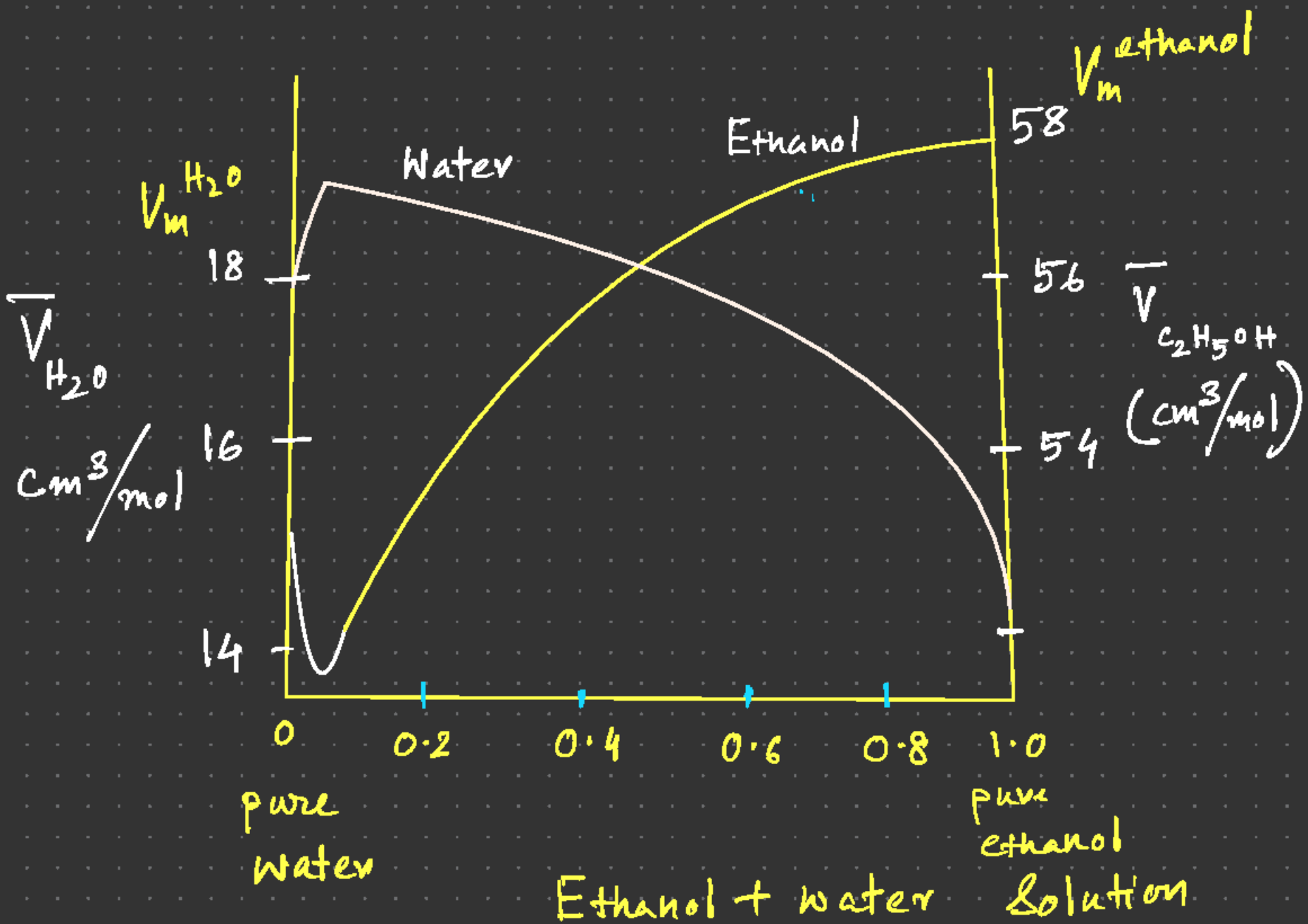
– packing in this fashion

result $\Delta V^{mix} = 14\ ml\ mol^{-1}$

$= 14\ cm^3\ mol^{-1}$



Partial molar volumes of the components of a mixture vary with composition as the environment of each type of component changes with change in composition from pure A to pure B.


$V_m^{ethanol}$
Water
Ethanol
$V_m^{H_2O}$
58
18
56
$\overline{V}_{H_2O}$
cm^3/mol
16
54
$\overline{V}_{C_2H_5OH}$
(cm^3/mol)
14
0
0·2
0·4
0·6
0·8
1·0
pure water
pure ethanol
Ethanol + water solution

Component i in a mixture with

n_1 moles of component 1
n_2 moles of component 2
$\vdots$
n_c moles of component c

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_{j \neq i}}$$

$\overline{V}_i$ is the partial molar volume of component i in the mixture

A mixture with 2 components

— binary mixture of A + B

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{P,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{P,T,n_A} dn_B$$

$$= \bar{V}_A \, dn_A + \bar{V}_B \, dn_B \quad -(1)$$

$$V = \bar{V}_A n_A + \bar{V}_B n_B \quad -(2)$$

Analogous to Euler equation

(Composition is preserved)

$$dV = \bar{V}_A\, dn_A + \bar{V}_B\, dn_B + n_A\, d\bar{V}_A$$

$$+ n_B\, d\bar{V}_B \quad \text{— (3)}$$

Compare (1) and (3)

$$n_A\, d\bar{V}_A + n_B\, d\bar{V}_B = 0$$

In general

Z — total property of a mixture

$\overline{Z}_i$ — partial molar property for component i in the mixture

n_1 moles of component 1

n_2 moles of component 2

$\vdots$

n_C moles of component C

} MIXTURE

Euler equation

$$G = H - TS + \mu_1 n_1 + \mu_2 n_2 + \cdots + \mu_j n_j$$

$$= U + PV - TS + \mu_1 n_1 + \mu_2 n_2 + \cdots + \mu_j n_j$$

$$dG = \cancel{dU + pdV - TdS} + Vdp - SdT$$

$$+ \mu_1 dn_1 + \mu_2 dn_2 + \cdots$$

$$+ n_1 d\mu_1 + n_2 d\mu_2 + \cdots$$

$$\therefore dU = TdS - pdV$$

$$dG = VdP - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_j dn_j$$

$$+ n_1 d\mu_1 + n_2 d\mu_2 + \cdots + n_j d\mu_j \quad \text{— (1)}$$

$G(T, P, n_i)$ Exact differential

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT \quad \text{— (2)}$$

$$+ \sum_{i=1}^{c} \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}} dn_i$$

Compare ① and ②

Gibbs Duhem relation

$$n_1 d\mu_1 + n_2 d\mu_2 + \cdots + n_i d\mu_i = 0$$

$$\sum_{i=1}^{c} n_i d\mu_i = 0$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}}$$ is the partial molar Gibbs free energy or chemical potential

$$Z = n_i \bar{Z}_i$$

$$\sum_{i=1}^{c} n_i \, d\bar{Z}_i = 0$$

$$dZ = \sum_{i=1}^{c} n_i \, d\bar{Z}_i$$

Concentration of Solutes in a Solution

[Mole %] = 100 x_i

Mole fraction

$$x_i = \frac{N_i}{\sum_{i=1}^{c} N_i}$$

i is a solute component

Solution = Solute + Solvent

$$\sum_{i=1}^{c} N_i = N$$

Weight fraction

$$w_i = \frac{W_i}{\sum_{i=1}^{c} W_i}$$

W_i – mass of i solute

$$\sum_{i=1}^{c} W_i = W$$

[wt %] = 100 w_i

Solution — Concentrated / Dilute

Solvent + '1' — $x_1 \gg x_2$

Solute '2'

N moles — N_1 moles of '1'
N_2 moles of '2'

$$x_1 = \frac{N_1}{N} \sim 1$$

$$x_2 = \frac{N_2}{N} \to 0$$

Molarity (dilute solutions)

Solute i

$$c_i = \frac{n_i}{V} \quad \text{moles / volume}$$

$$\text{mol}/\ell$$

Molality m_i (dilute solution)

Solute i

$$m_i = \frac{n_i}{W_{solvent}\,(kg)} \quad \text{moles / kg}$$

partial molar Gibbs free energy

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T, P, N_{j \neq i}}$$

$U(S, V, N)$			S, T
$H(S, P, N)$	–	mechanical reservoir	V, P
$G(T, P, N)$	–	thermal + mechanical reservoir	N, μ
$F(T, V, N)$	–	thermal reservoir	

Chemical potential

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}}$$

$$= \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}}$$

$$= \left(\frac{\partial F}{\partial n_i}\right)_{V,T,n_{j\neq i}}$$

$$= \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

Partial molar Gibbs free energy of i (when $T, P, n_{j\neq i}$ are constant)

T, S

P, V

μ, N

At constant T and P,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_j dn_j$$

$$G = \mu_1 n_1 + \mu_2 n_2 + \cdots + \mu_j n_j$$

Euler equation

$$\sum_{i=1}^{c} n_i d\mu_i = 0$$ — Gibbs Duhem equation

$$G = H - TS + \sum_{i=1}^{c} n_i \mu_i$$

Example – Mixing

1. Fix P, T
2. Mix solvent A with variable amount of solute B
3. n_A is fixed and n_B is varied

Step 1 – $V(n_B) = a_0 + a_1 n_B + a_2 n_B^2 + a_3 n_B^3$

[Total volume V fitted to a polynomial function]

Step 2 – Partial molar volume $\bar{V}_B$

$$\bar{V}_B = \left(\frac{\partial V}{\partial n_B}\right)_{n_A, P, T} = a_1 + 2a_2 n_B + 3a_3 n_B^2$$

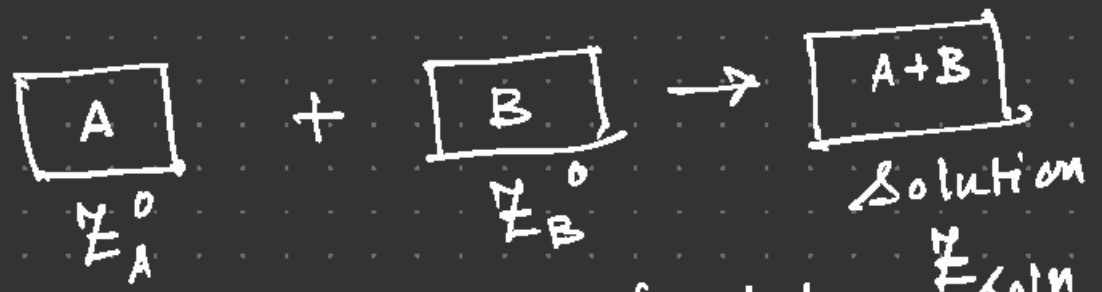
Step 3

$$V = n_A \bar{V}_A + n_B \bar{V}_B$$

$$\therefore \bar{V}_A = \left(V - n_B \bar{V}_B \right) / n_A$$

We have C components in a mixture

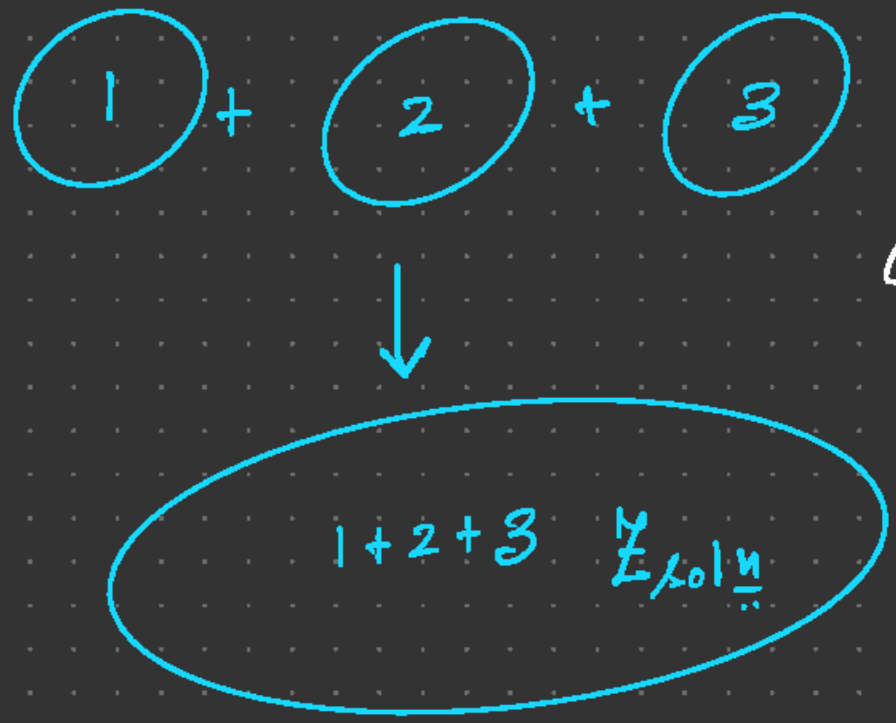
Property Z



Z_k^0 is the partial molar/molal value of property Z in a reference or standard state due to component k

$$Z^0 = \sum_{k=1}^{C} Z_k^0 n_k$$

$$\Delta Z_{mix} = Z_{soln} - Z^0$$



$G_1^\circ \quad G_2^\circ \quad G_3^\circ$

$G_{sol\,\underline{n}}$

$$\Delta G_{mix} = G_{sol\,\underline{n}} - n_1 G_1^\circ - n_2 G_2^\circ - n_3 G_3^\circ$$

$$Z_{sol\,\underline{n}} = \bar{Z}_1 n_1 + \bar{Z}_2 n_2 + \bar{Z}_3 n_3 + \cdots = \sum_{k=1}^{c} \bar{Z}_k n_k$$

$$G_{sol\,\underline{n}} = \sum_k \bar{G}_k n_k = \sum_k \mu_k n_k$$

$$\Delta Z_{mix} = \sum_{k=1}^{c} \bar{Z}_k n_k - \sum_{k=1}^{c} Z_k^0 n_k$$

$\bar{Z}_k$ – partial molar value of property Z associated with component k in solution

$$= \sum_{k=1}^{c} \left(\bar{Z}_k - Z_k^0 \right) n_k$$

$$= \sum_{k=1}^{c} \Delta \bar{Z}_k \, n_k$$

$$\Delta \bar{Z}_k = \bar{Z}_k - Z_k^0$$

$$d\Delta Z_{mix} = \sum_{k=1}^{c} \left[\bar{Z}_k \, dn_k + n_k d\bar{Z}_k - Z_k^0 \, dn_k - n_k dZ_k^0 \right]$$

Now, $\sum_{k=1}^{c} \left(n_k d\bar{Z}_k - n_k dZ_k^0 \right) = \sum_{k=1}^{c} n_k d\Delta\bar{Z}_k$

$= 0$

$$d\Delta Z_{mix} = \sum_{k=1}^{c} \Delta \bar{Z}_k \, dn_k$$

Example:

$$0 = \sum_k n_k \, d\Delta \bar{Z}_k$$

Gibbs-Duhem

$$G = \bar{G}_A n_A + \bar{G}_B n_B$$

$$= \mu_A n_A + \mu_B n_B \qquad n_A + n_B = n$$

$$\frac{G}{n} = G_m = \mu_A X_A + \mu_B X_B$$

G – total

G_m – molar

$\bar{G}_i$ or μ_i – partial molar

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$n_A + n_B = n$$

$$dG_m = d(G/n) = \mu_A dX_A + \mu_B dX_B$$

$$\Delta G_{m,mix} = \sum_{k=1}^{c} \Delta\mu_k X_k$$

$$\Delta\mu_k = \mu_k - \mu_k^0$$

$$X_k = \frac{n_k}{n}$$

$$\sum_{k=1}^{c} X_k \, d\mu_k = 0$$

$$dG_m = \mu_A dX_A + \mu_B dX_B$$

$$G_m = \mu_A X_A + \mu_B X_B$$

$$n_A + n_B = n$$

$$X_A + X_B = 1$$

$$dX_A = -dX_B$$

$$\therefore dX_A + dX_B = 0$$

$$X_A + X_B = 1$$

$$dX_A = -dX_B$$

$$\therefore dG_m = \mu_A \left(-dX_B\right) + \mu_B dX_B$$

$$= \left(\mu_B - \mu_A\right) dX_B$$

$$\frac{dG_m}{dX_B} = \mu_B - \mu_A$$

$n = n_A + n_B$

$$\mu_A = \mu_B - \frac{dG_m}{dX_B} \qquad \mu_B = \left(\frac{\partial G}{\partial n_B}\right)_{n_A, T, P}$$

$$G_m = \mu_A X_A + \mu_B X_B \qquad = \left(\frac{\partial n G_m}{\partial n_B}\right)_{n_A, T, P}$$

$$= \left(\mu_B - \frac{dG_m}{dX_B}\right) X_A + \mu_B X_B$$

$$= \left(X_A + X_B\right) \mu_B - X_A \frac{dG_m}{dX_B}$$

$$= \mu_B - \left(1 - X_B\right) \frac{dG_m}{dX_B}$$

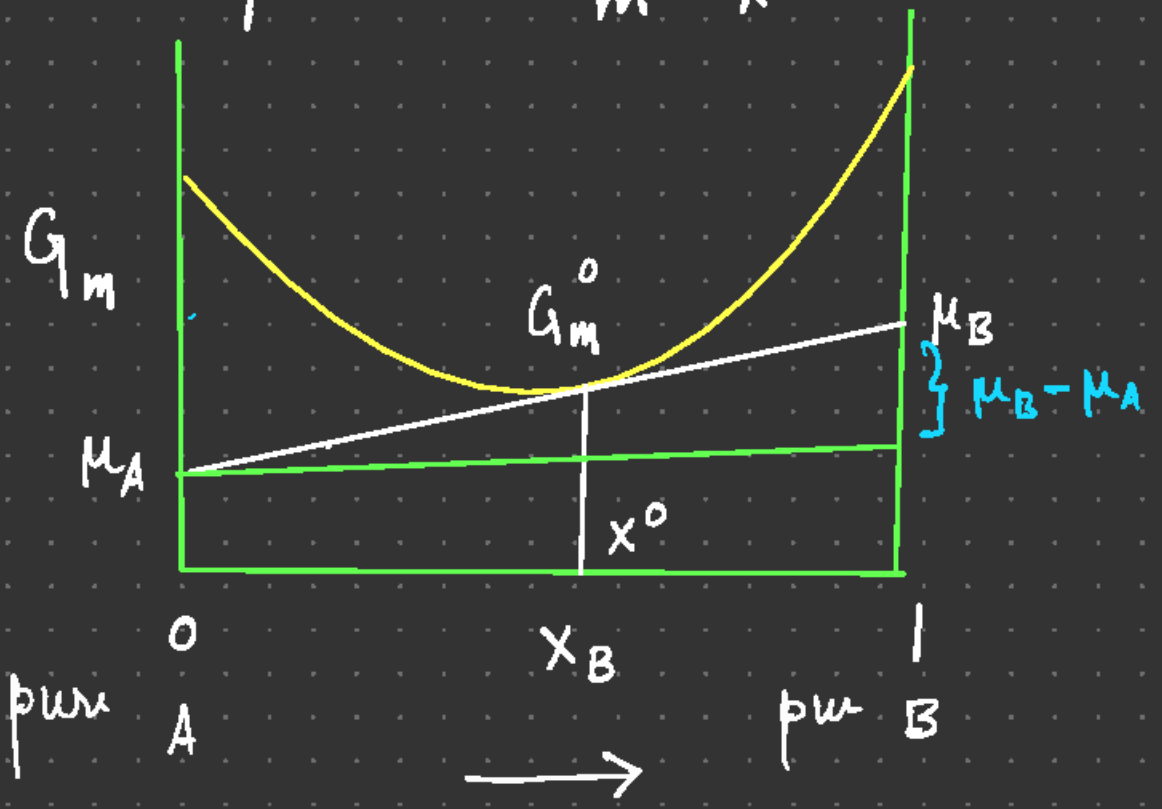
$$\therefore \quad \mu_B = G_m + \left(1 - X_B\right) \frac{dG_m}{dX_B}$$

$$\mu_B = G_m + (1 - x_B)\frac{dG_m}{dx_B} \quad \text{— (1)}$$

$$\mu_A = G_m - x_B \frac{dG_m}{dx_B} \quad \text{— (2)}$$

$$G_m = \frac{dG_m}{dx_B} x_B + \mu_A$$

$$y \quad = \quad m \quad x \quad + \quad c$$



$$\frac{dG_m}{dx_B} = \mu_B - \mu_A$$

$x \quad y$

$X_0, \; G_m$

$0, \; \mu_A$

$1, \; \mu_B$

$X_B, \; G_m$

$$\frac{G_m - \mu_A}{\mu_B - \mu_A} = \frac{X_B - 0}{1 - 0}$$

$$G_m = (\mu_B - \mu_A) X_B + \mu_A$$

$$\frac{dG_m}{dX_B} = \frac{\mu_B - \mu_A}{1 - 0} = \mu_B - \mu_A$$

$$G_m = \frac{dG_m}{dX_B} X_B + \mu_A$$

$y \quad m \quad x \quad + \quad c$

$$\frac{dG_m}{dX_B} = \frac{dG_m}{dX_A}\frac{dX_A}{dX_B} = -\frac{dG_m}{dX_A}$$

$$\frac{d\Delta G_{m,mix}}{dX_B} = -\frac{d\Delta G_{m,mix}}{dX_A}$$

$$\Delta G_{m,mix} = \frac{d\Delta G_{m,mix}}{dX_B} X_B + \mu_A$$

$$\frac{d\Delta B_{mix}}{dX_B} = -\frac{d\Delta B_{mix}}{dX_A}$$

Applications of Gibbs-Duhem Relation

$$\Delta H_{mix} = a X_1 X_2$$

molar enthalpy of mixing

$$= a X_2 - a X_2^2$$

$$\bar{H} - H^\circ$$

$$\sum \bar{H}_i n_i - \sum H_i^\circ n_i = \Delta H_{mix}$$

$X_1 + X_2 = 1$

$$\frac{d \Delta H_{mix}}{d X_2} = a(1 - 2X_2)$$

Wrong:

$$\left(\frac{\partial \Delta H_{mix}}{\partial X_2} \right)_{X_1} = a X_1 = a(1 - X_2)$$

— Cannot do this

= Wrong and has no thermodynamic meaning

$$\Delta H_{mix} = X_1 \bar{\Delta H_1} + X_2 \bar{\Delta H_2} \longrightarrow (1)$$

$$\frac{d\Delta H_{mix}}{dX_2} = \bar{\Delta H_2} - \bar{\Delta H_1} \longrightarrow (2)$$

$$X_1 \frac{d\Delta H_{mix}}{dX_2} = X_1 \bar{\Delta H_2} - X_1 \bar{\Delta H_1} \longrightarrow (3)$$

(1) + (3)

$$\bar{\Delta H_2} = \Delta H_{mix} + X_1 \frac{d\Delta H_{mix}}{dX_2}$$

$$= a X_1 X_2 + a X_1 (1 - 2X_2)$$

$$= a X_1 X_1 = a X_1^2$$

$$\Delta \bar{H}_2 = a x_1^2$$

$$\Delta H_{mix} = x_1 \Delta \bar{H}_1 + x_2 \Delta \bar{H}_2$$

$$= x_1 a x_2^2 + x_2 a x_1^2$$

$$= a x_1 x_2 (x_1 + x_2)$$

$$= a x_1 x_2$$

$$a x_1 x_2 = x_1 \Delta \bar{H}_1 + x_2 \Delta \bar{H}_2$$

$$+ a x_1^2 x_2$$

$$x_1 \Delta \bar{H}_1 = a x_1 x_2 - a x_1^2 x_2$$

$$\therefore \Delta \bar{H}_1 = a x_2^2 = a x_1 x_2 (1 - x_1) = a x_2^2 x_1$$

Gibbs-Duhem equation

$$X_1 \, d\Delta\bar{Z}_1 + X_2 \, d\Delta\bar{Z}_2 = 0$$

$$d\Delta\bar{Z}_1 = -\frac{X_2}{X_1} \, d\Delta\bar{Z}_2$$

$$\Delta\bar{Z}_1 = \int_{X_2=0}^{X_2} -\frac{X_2}{X_1} \, d\Delta\bar{Z}_2$$

$\Delta\bar{Z}_1 = \bar{Z}_1 - Z_1^0$

when $X_2 = 0$

$\bar{Z}_1 = Z_1^0$

or, $\Delta\bar{Z}_1 = 0$

$$d\Delta\bar{Z}_2 = \frac{d\Delta\bar{Z}_2}{dX_2} \, dX_2$$

Functional Relation between $\Delta\bar{Z}_2$ and Composition

$$\bar{\Delta H}_2 = a x_1^2$$

$$\frac{d\bar{\Delta H}_2}{dx_2} = a \frac{dx_1^2}{dx_1} \frac{dx_1}{dx_2}$$

$$= -2ax_1$$

$$\bar{\Delta H}_1 = -\int_0^{x_2} \frac{x_2}{x_1} \frac{d\bar{\Delta H}_2}{dx_2} dx_2$$

$$= -\int_0^{x_2} \frac{x_2}{x_1} (-2ax_1)\, dx_2$$

$$= 2a \left[x_2^2/2 \right]_0^{x_2} = a x_2^2$$

$$\mu_k = \bar{G}_k = \bar{H}_k - T\bar{S}_k \qquad G = H - TS$$

$$\mu_k = \bar{G}_k = \bar{H}_k - T\bar{S}_k$$

$$dG = V\,dP - S\,dT + \sum \mu_i\, dn_i$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,\, n_k}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,\, n_k}$$

$$\therefore \quad -\left(\frac{\partial S}{\partial n_k}\right)_{T,\,P,\,n_j} = \left[\frac{\partial}{\partial n_k}\left(\frac{\partial G}{\partial T}\right)_{P,\,n_k}\right]_{T,\,P,\,n_j}$$

$$-\bar{S}_k = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_k}\right)_{T,\,P,\,n_j}\right]_{P,\,n_k}$$

$$= \left(\frac{\partial \bar{G}_k}{\partial T}\right)_{P,\,n_k}$$

$$-\bar{S}_k = \left(\frac{\partial \bar{G}_k}{\partial T}\right)_{P, n_k}$$

$$\left(\frac{\partial V}{\partial n_k}\right)_{T, P, n_j} = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_k}\right)_{T, P, n_j}\right]_{T, n_k}$$

$$\bar{V}_k = \frac{\partial \bar{G}_k}{\partial P}$$

$$\bar{G}_k = \mu_k = \mu_k(T, P)$$

$$d\bar{G}_k = d\mu_k = \left(\frac{\partial \mu_k}{\partial T}\right)_{P, n_k} dT + \left(\frac{\partial \mu_k}{\partial P}\right)_{T, n_k} dP$$

$$= -\bar{S}_k \, dT + \bar{V}_k \, dP$$

Q. Partial molar volume of a solute in a binary solution depends on the molality of the solute given by

$$\overline{V_2} = a + b m_2$$

a, b are constants

Molecular weight of solvent = M_1 gm/mol

Volume of 1 mole of pure solvent is V_1^o. How does partial molar volume of solvent depend on solute molality?

$$n_1 d\bar{V}_1 + n_2 d\bar{V}_2 = 0 \quad \text{— (1)}$$

$$n_1 + n_2 = n$$

Dividing (1) by n we get

$$x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = 0$$

$\because$ $x_1 + x_2 = 1$ $\quad dx_1 = -dx_2$

$$\Rightarrow x_1 \frac{d\bar{V}_1}{dx_1} + x_2 \frac{d\bar{V}_2}{dx_1} = 0$$

$$\Rightarrow x_1 \frac{d\bar{V}_1}{dx_1} = -x_2 \frac{d\bar{V}_2}{dx_1} = x_2 \frac{d\bar{V}_2}{dx_2}$$

$$m_2 = \frac{n_2}{q_1} = \frac{n_2}{n_1 M_1/1000} \quad \frac{\text{moles}}{\text{kg}}$$

q_1 - weight of Solvent in kg

$$m_2 = \frac{1000}{M_1} \frac{n_2/n}{n_1/n} = \frac{1000}{M_1} \frac{x_2}{x_1}$$

$$= \frac{1000}{M_1} \frac{x_2}{1-x_2}$$

$$x_1 \frac{d\bar{V}_1}{dx_1} = x_2 \frac{d\bar{V}_2}{dx_2}$$

$$= x_2 \frac{d}{dx_2} \left\{ a + b \frac{1000}{M_1} \frac{x_2}{1-x_2} \right\}$$

$$= x_2 \frac{1000\,b}{M_1} \left\{ \frac{x_2}{(1-x_2)^2} + \frac{1}{1-x_2} \right\}$$

$$x_1 \frac{d\bar{v}_1}{dx_1} = x_2 \frac{1000\,b}{M_1} \frac{1}{(1-x_2)^2}$$

$$= (1-x_1) \frac{1000\,b}{M_1} \frac{1}{x_1^2}$$

$$\int_{v_1^0}^{\bar{v}_1} d\bar{v}_1 = \int_1^{x_1} \frac{1000\,b}{M_1} \frac{1-x_1}{x_1^3} dx_1$$

$$\bar{v}_1 = v_1^0 + \frac{1000\,b}{M_1} \left(-\frac{1}{2x_1^2} + \frac{1}{x_1} - \frac{1}{2} \right)$$

$$= v_1^0 - \frac{1000\,b}{2M_1} \frac{x_2^2}{x_1^2}$$