

①

Simple Mixtures, TD description of ↑

→ ((Atkins chapter 7))

Partial molar quantities (PWA pp. 161 - 166)

Regard the binary mixture water (W, H_2O) with ethanol (E, CH_3CH_2OH), e.g. n_E moles ethanol and n_W moles water

The "mole fractions" are defined as

$$x_E \equiv \frac{n_E}{n_E + n_W} \quad (1)$$

$$x_W \equiv \frac{n_W}{n_E + n_W}$$

→ Generalization for C components

$$x_k = \frac{n_k}{n} \quad n = \sum_{k=1}^C n_k$$

$$\sum_{k=1}^C x_k = 1$$

We have $x_E + x_W = 1$

The volume of the mixture is an extensive quantity of the mole numbers n_1, n_2 (at $p, T = \text{const}$)

$$\underline{V}(n_1, n_2)$$

(IUPAC recommends to underline extensive quantities)

and for extensive quantities the Euler theorem for homogeneous functions is valid

$$\underline{V}(\alpha n_1, \alpha n_2) = \alpha \underline{V}(n_1, n_2) \quad (\text{cf. 3rd lecture!})$$

differentiate with respect to scaling factor α

$$n_1 \left(\frac{\partial \underline{V}(\alpha n_1, \alpha n_2)}{\partial n_1} \right)_{n_2} + n_2 \left(\frac{\partial \underline{V}(\alpha n_1, \alpha n_2)}{\partial n_2} \right)_{n_1} = \underline{V}(n_1, n_2)$$

and set $\alpha = 1$. We obtain

$$n_1 \bar{V}_1 + n_2 \bar{V}_2 = \underline{V} \quad (2)$$

with $\bar{V}_1 \equiv \left(\frac{\partial \underline{V}(n_1, n_2)}{\partial n_1} \right)_{n_2}$

$$\bar{V}_2 \equiv \left(\frac{\partial \underline{V}(n_1, n_2)}{\partial n_2} \right)_{n_1} \quad (3)$$

② The quantities \bar{V}_1, \bar{V}_2 are the partial molar volumes of species 1 and 2 in the mixture, and they depend only on the mole fractions x_1, x_2 , i.e. \bar{V}_1 and \bar{V}_2 are intensive quantities (argue why?)

(IUPAC recommends to denote partial molar quantities by a superscribed bar \bar{V})

Example

→ Mixture of water and ethanol

Molar mass of pure substances $M_W = M(\text{H}_2\text{O}) \approx (2 \cdot 1008 + 1 \cdot 16) \frac{\text{g}}{\text{mol}} = 18 \frac{\text{g}}{\text{mol}}$ molar mass W

$M_E = M(\text{CH}_3\text{CH}_2\text{OH}) \approx (2 \cdot 12011 + 6 \cdot 1007 + 1 \cdot 16) \frac{\text{g}}{\text{mol}} = 46 \frac{\text{g}}{\text{mol}}$ molar mass E

((18.0153))
((46.07))

→ Molar volume of pure substances

$V^\circ = \frac{M}{\rho_0}$ ρ° density of pure species at given T and p

25°C 1 atm
298.15 K 10⁵ Pa

$\rho_W = 0.99707 \frac{\text{g}}{\text{cm}^3} \approx 1 \frac{\text{g}}{\text{cm}^3}$

$\rho_E = 0.791 \frac{\text{g}}{\text{cm}^3} \approx 0.8 \frac{\text{g}}{\text{cm}^3}$

$V_W^\circ = \frac{M_W}{\rho_W} \approx \frac{18 \text{ g/mol}}{1 \text{ g/cm}^3} = 18 \frac{\text{cm}^3}{\text{mol}}$ ((18.07))

$V_E^\circ = \frac{M_E}{\rho_E} \approx \frac{46 \text{ g/mol}}{0.8 \text{ g/cm}^3} = 58 \frac{\text{cm}^3}{\text{mol}}$ ((58.24))

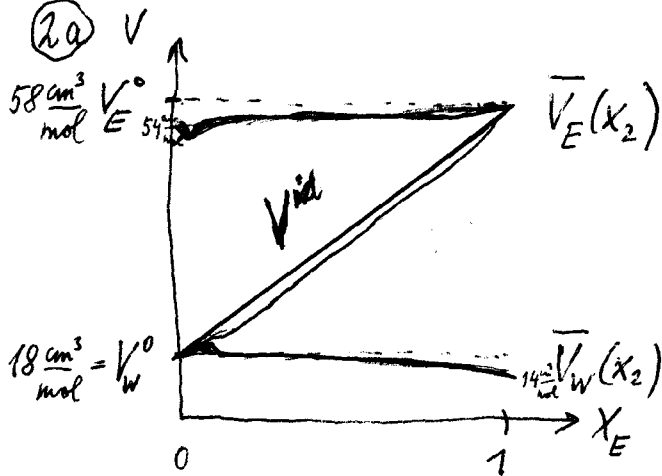
→ Molar mass of mixture W, E

$M(x_1, x_2) = x_W M_W + x_E M_E$

molar fractions $x_W = \frac{n_W}{n}$
 $n \equiv n_W + n_E$ $x_E = \frac{n_E}{n}$

→ Molar volume of mixture in case of "ideal mixing"

$V(x_1, x_2) = x_W V_W^\circ + x_E V_E^\circ = V_W^\circ + (V_E^\circ - V_W^\circ) x_E$



cf. Fig. 7.1 in PWA p.167

→ Real molar volume of mixture W/E

$$V = X_W \bar{V}_W + X_E \bar{V}_E \equiv \bar{V}_W(x_2) + [\bar{V}_E(x_2) - \bar{V}_W(x_2)] X_2$$

$$X_W = 1 - X_E \quad X_E \equiv X_2$$

→ Experimental determination of $V(x_2)$ by measuring the density $\rho(x_2)$ of the mixture and calculating

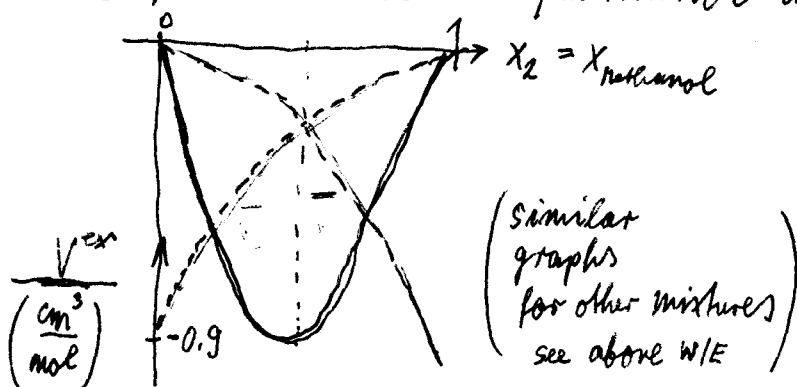
$$V(x_2) = \frac{M_1 + X_2(M_2 - M_1)}{\rho(x_2)} \quad (\text{see green graph in the Fig. above})$$

→ Excess volume $V^{\text{ex}}(x_2)$ of the mixture defined by

$$V^{\text{ex}}(x_2) \equiv V(x_2) - V^{\text{id}}(x_2) \Rightarrow (\text{for water/ethanol})$$

$$V^{\text{ex}}(x_2) = [\bar{V}_W(x_2) - V_W^0](1 - X_2) + [\bar{V}_E(x_2) - V_E^0] X_2$$

Example: mixture water/methanol at 25°C, p_0



$$\underline{V^{\text{ex}}(x_2=0) = V^{\text{ex}}(x_2=1) = 0}$$

③ → The properties of many solutions are given as function of the mass % of the components (usually "2" component,

$$A\% \equiv m_{2pc} \equiv \frac{m_2 \cdot 100\%}{m_1 + m_2} = \frac{n_2 M_2 \cdot 100\%}{n_1 M_1 + n_2 M_2} = \frac{M_2 x_2}{M_1 x_1 + M_2 x_2} \cdot 100\% \quad (4)$$

$m_{1,2}$ = mass of (1, 2) in the mixture

$M_{1,2}$ = molar masses of (1, 2)

→ The CRC Handbook of Chemistry and Physics gives the density ρ of many aqueous solutions as a function of the mass % of solute ($\equiv m_{2pc}$). How to find from $\rho(m_{pc})$ the partial molar volumes of (1) = solvent = water and (2) = solute?

The (molar) volume \underline{V} of the mixture is given by

$$\underline{V} = \frac{n_1 M_1 + n_2 M_2}{\rho(m_{2pc})}$$

We get

$$\underline{V}_1 \equiv \left(\frac{\partial \underline{V}}{\partial n_1} \right)_{n_2} = \frac{M_1}{\rho(m_{2pc})} - \frac{n_1 M_1 + n_2 M_2}{\rho^2(m_{2pc})} \left(\frac{\partial \rho(m_{2pc})}{\partial n_1} \right)_{n_2}$$

$$\begin{aligned} \left[\frac{\partial \rho(m_{2pc})}{\partial n_1} \right]_{n_2} &= \left(\frac{d\rho}{dm_{2pc}} \right) \left(\frac{\partial m_{2pc}}{\partial n_1} \right)_{n_2} = \left(\frac{d\rho}{dm_{2pc}} \right) \left[- \frac{M_1 M_2 n_2 \cdot 100\%}{(n_1 M_1 + n_2 M_2)^2} \right] = \\ &= - \left(\frac{d\rho}{dm_{2pc}} \right) \left(\frac{m_{2pc} M_1}{n_1 M_1 + n_2 M_2} \right), \quad \text{therefore} \end{aligned}$$

$$\underline{V}_1 = \frac{M_1}{\rho(m_{2pc})} \left[1 - \frac{m_{2pc}}{\rho(m_{2pc})} \left(\frac{d\rho(m_{2pc})}{dm_{2pc}} \right) \right]$$

analogous

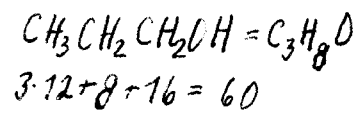
\underline{V}_2

Prove that $n_1 \underline{V}_1 + n_2 \underline{V}_2 = \underline{V}$

(4)

Example:

The density (in $g\ mol^{-1}$) of a 1-propanol/water solution at $20^\circ C$ as a function of $x_2 =$ the mole fraction of 1-propanol, can be expressed as



$$\rho(x_2) = \sum_{j=0}^4 a_j x_2^j$$

where $a_0 = 0.99823$ $a_1 = -0.48503$ $a_2 = 0.47518$
 $a_3 = -0.17163$ $a_4 = -5.11387$ (see Fig.)

Use this expression to find \bar{V}_{H_2O} and \bar{V}_{1-prop} as a function of x_2 . Method of tangent intercepts = graphical finding of \bar{V}_1, \bar{V}_2 from

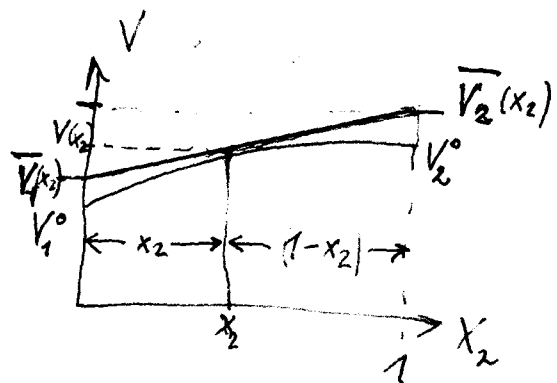
$$\bar{V} = \frac{x_1 M_1 + x_2 M_2}{\rho(x_2)} = \frac{M_1 + x_2 (M_2 - M_1)}{\rho(x_2)} = x_1 \bar{V}_1 + x_2 \bar{V}_2$$
$$= \bar{V}_1 + x_2 (\bar{V}_2 - \bar{V}_1)$$

$$\frac{d\bar{V}}{dx_2} = \bar{V}_2 - \bar{V}_1$$

$$\bar{V}_1 = \bar{V} - x_2 \left(\frac{d\bar{V}}{dx_2} \right)$$

$$\bar{V}_2 = \bar{V} + (1-x_2) \frac{d\bar{V}}{dx_2}$$

$$\frac{d\bar{V}}{dx_2} = \frac{M_2 - M_1}{\rho(x_2)} - \frac{V}{\rho} \left(\frac{d\rho}{dx_2} \right)$$



method of tangent intercepts

$M_1 = 18\ g/mol$

$M_2 = 60\ g/mol$

⑤ → Gibbs-Duhem - Equation applied to binary mixture

$$V(x_2) = \bar{V}_1(x_2) + [\bar{V}_2(x_2) - \bar{V}_1(x_2)]x_2$$

Molar volume of the binary mixture as function of mole fraction $x_2 = \frac{n_2}{n_1+n_2}$

We wrote (in deriving the method of tangent intercepts)

$$\frac{dV(x_2)}{dx_2} = \bar{V}_2(x_2) - \bar{V}_1(x_2)$$

but what about the other terms obtained by differentiating $V(x_2)$

$$\frac{d\bar{V}_2(x_2)}{dx_2} + x_2 \left[\frac{d\bar{V}_2(x_2)}{dx_2} - \frac{d\bar{V}_1(x_2)}{dx_2} \right] \implies 0 \quad (\text{Gibbs-Duhem})$$

Proof:

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

molar volume of the binary mixture

$$dV = \bar{V}_1 dx_1 + \bar{V}_2 dx_2$$

(at const. p and T)

$$x_1 d\bar{V}_1 + x_2 d\bar{V}_2 \equiv 0 \stackrel{\text{Gibbs-Duhem}}{=} \cdot n = n_1 + n_2$$

$$n_1 d\bar{V}_1 + n_2 d\bar{V}_2 = \left[n_1 \left(\frac{\partial \bar{V}_1}{\partial n_1} \right)_{n_2} + n_2 \left(\frac{\partial \bar{V}_2}{\partial n_1} \right)_{n_2} \right] dn_1 + \left[n_1 \left(\frac{\partial \bar{V}_1}{\partial n_2} \right)_{n_1} + n_2 \left(\frac{\partial \bar{V}_2}{\partial n_2} \right)_{n_1} \right] dn_2$$

$$n_1 \left(\frac{\partial \bar{V}_1}{\partial n_1} \right)_{n_2} + n_2 \left(\frac{\partial \bar{V}_2}{\partial n_2} \right)_{n_1} \equiv 0$$

$$n_2 \left(\frac{\partial \bar{V}_1}{\partial n_2} \right)_{n_1}$$

|||
0

$$= n_1 \left(\frac{d\bar{V}_1}{dx_2} \right) \left(\frac{\partial x_2}{\partial n_1} \right)_{n_2} + n_2 \left(\frac{d\bar{V}_2}{dx_2} \right) \left(\frac{\partial x_2}{\partial n_2} \right)_{n_1} = \left(\frac{d\bar{V}_2}{dx_2} \right) \left\{ n_1 \left(-\frac{n_2}{n^2} \right) + n_2 \left[\frac{1}{n} - \frac{n_2}{n^2} \right] \right\}$$

$$\frac{-n_1 n_2 + (n_1 + n_2) n_2 - n_2^2}{n^2} \equiv 0$$

q.e.d.

i.e. partial molar volumes are not independent of one another

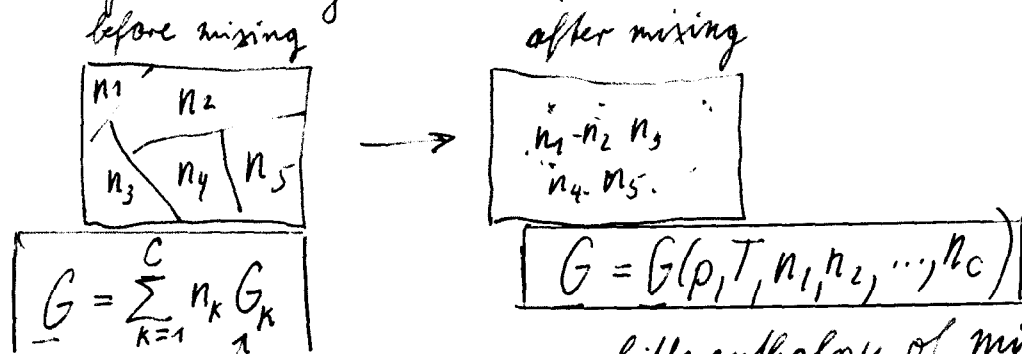
$$d\bar{V}_1 = -\frac{n_2}{n_1} d\bar{V}_2$$

cf. Fig. 7.1 P.W.A.

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Partial molar Gibbs energies $\hat{=}$ chemical potentials

→ Regard mixing of C components at const. p, T



molar Gibbs enthalpy of component (pure) k

Gibbs enthalpy of mixture is extensive in n_k , and can be written in the form (Euler-theorem)

$$\underline{G} = \sum_k n_k \bar{G}_k(p, T, x_k) \equiv \sum_k n_k \mu_k$$

$$\bar{G}_k = \left(\frac{\partial \underline{G}}{\partial n_k} \right)_{p, T, n_{i \neq k}} \equiv \mu_k$$

partial molar Gibbs energy \equiv chemical potential of species k in the mixture

$$d\underline{G} = \left(\frac{\partial \underline{G}}{\partial p} \right)_{T, n_k} dp + \left(\frac{\partial \underline{G}}{\partial T} \right)_{p, n_k} dT + \sum_{k=1}^C \left(\frac{\partial \underline{G}}{\partial n_k} \right)_{p, T, n_{i \neq k}} dn_k$$

$$d\underline{G} = \underline{V} dp - \underline{S} dT + \sum_k \mu_k dn_k$$

fundamental equation of chemical TD

→ Gibbs-Duhem equation

$$\sum_{k=1}^C n_k d\mu_k = \underline{V} dp - \underline{S} dT (= 0 \text{ for } p, T = \text{const})$$

- For a binary mixture (at const p, T)

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

$$d\mu_2 = - \frac{x_1}{1-x_1} d\mu_1$$

$$\mu_2(x_1) = \mu_2(0) - \int_0^{x_1} \frac{x_1}{1-x_1} d\mu_1$$

((proofs of TD consistency))

Assume, $\mu_1(x_1)$ is known, then $\mu_2(x_1)$ can be obtained by integration

((cf. Example 7.1 PWA))

⑦ Gibbs energy of mixing (perfect gases)

→ pure component k EOS $pV = RT$

$$\boxed{G = U + pV - TS \Rightarrow C_p T - T(-R \ln p) \Rightarrow \mu^\ominus(T) + RT \ln p}$$

$$S \Rightarrow C_v \ln T + R \ln V \Rightarrow C_v \ln T + R \ln \frac{RT}{p} \Rightarrow C_p \ln T - R \ln p$$

$$\left(dU = TdS - pdV \quad dS = C_v \frac{dT}{T} + \frac{p}{T} dV \right)$$

$$\boxed{\mu_k(p, T) = \mu_k^\ominus(T) + RT \ln p_k} \quad (p \text{ in units } p_0)$$

n_1	n_2
-------	-------

p, T

— Before mixing:

$$\boxed{G_i = \sum_k n_k (\mu_k^\ominus + RT \ln p)}$$

→ After mixing the pressure of component k becomes

$$\boxed{p_k = \frac{n_k}{n} p = x_k p}$$

(partial pressure of component k)

$$\boxed{G_f = \sum_k n_k [\mu_k^\ominus + RT \ln(x_k p)]}$$

The mixing Gibbs energy is defined as

$$\boxed{\Delta G^{mix} = G_f - G_i \Rightarrow RT \sum_k n_k \ln x_k = nRT \sum_k x_k \ln x_k}$$

$$\Delta G^{mix} = -T \Delta S^{mix}$$

$$\boxed{\Delta S^{mix} = -R \sum_k x_k \ln x_k}$$

molar entropy of mixing

$$\boxed{\left(\frac{\partial \Delta G^{mix}}{\partial T} \right)_{p, n_k} = -\Delta S^{mix}}$$

→ The "enthalpy of mixing" $\Delta H^{mix} = H_f - H_i$ of two perfect gases (const. p, T) is zero.

proof:

$$\left[\frac{\partial \left(\frac{\Delta G^{mix}}{T} \right)}{\partial T} \right]_{p, n} = -\frac{\Delta H^{mix}}{T^2} = 0$$

(Gibbs-Helmholtz equation)

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Chemical potential of liquids (mixtures)

pure substance ^(*) liquid in equilibrium with its vapor

$$\boxed{\mu_{lA}^* = \mu_{gA}^* = \mu_A^\ominus + RT \ln p_A^*} \quad (1) \quad (*) \text{ notation for pure subst}$$

↑
standard (molar) Gibbs energy of the gas

If the liquid itself is a mixture with another liquid, then the chemical potential of A is changed $\mu_{lA}^* \rightarrow \mu_{lA}$

$$\boxed{\mu_{lA} = \mu_A^\ominus + RT \ln p_A} \quad (2)$$

Combining (1) and (2) (eliminate μ_A^\ominus)

$$\boxed{\mu_{lA} = \mu_{lA}^* + RT \left(\frac{p_A}{p_A^*} \right)} \quad (3)$$

→ If the liquid forms an ideal solution, then

$$\boxed{\mu_{lA} = \mu_{lA}^* + RT \ln X_A} \quad (4)$$

Regard (4) as definition of an ideal solution

Comparison (3) with (4) gives

$$\boxed{p_A = X_A p_A^*}$$

Raoult's law

- ⑨ Colligative properties (arising from the presence of a solute)
- boiling-point elevation
 - freezing-point depression
 - vapor pressure lowering
 - osmotic pressure
- } in dilute solutions depend only on the mole fraction (x_2) of the solute, not on its identity.

→ Simplifying assumptions (in the following description)

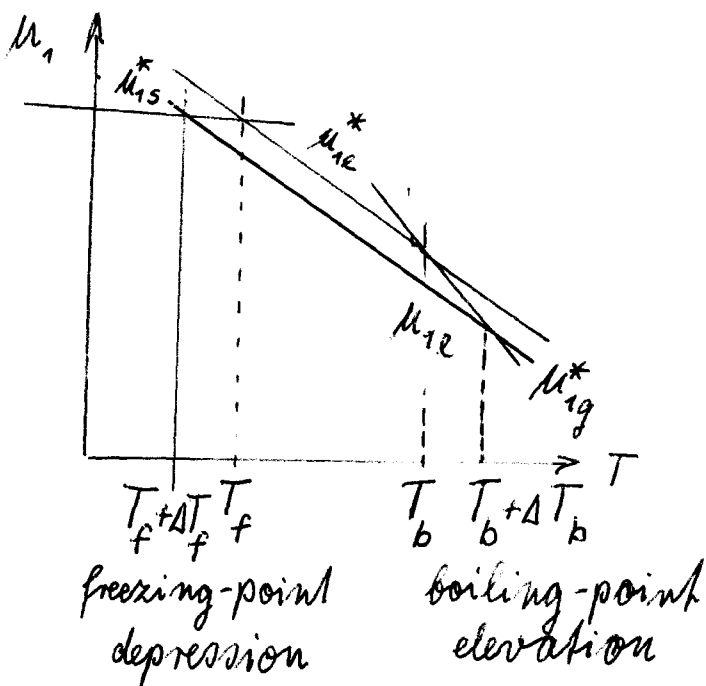
- solute^(a) is not volatile, i.e. solute remains in the liquid solvent^(l) both at evaporation or freezing of the solvent

- diluted solutions $x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \ll 1$

so that $\ln x_1 = \ln(1 - x_2) \approx -x_2$

→ The common feature of the colligative properties is the lowering of the chemical potential of the ^{liq.} solvent^(l) upon adding the solute⁽²⁾

$\mu_{e1}(p, T, x_1) = \mu_{e1}^*(p, T) + RT \ln x_1 \approx \mu_{e1}^*(p, T) - RT x_2$



- molecular interpretation

The entropy of the solvent in the solution is higher than that of the pure liquid solvent (by $\Delta S^{mix} = -R x_1 \ln x_1 > 0$)

→ there is a tendency for solv. mol. to remain in the solution.
lower vapor pressure

⑩ → Vapor pressure lowering by nonvolatile solutes

Nonvolatile solute (2) in liquid solvent (1) $x_2 = \frac{n_2}{n_1 + n_2}$

$$\mu_{e1}(p_1', T, x_1) = \mu_{g1}^*(p_1', T) \quad \text{equilibrium pure vapor with solution at } T \text{ and } p_1'$$

$$\mu_{e1}^*(p_1', T) + RT \ln x_1 = \mu_{g1}^*(p_1', T) \quad (1)$$

For pure solvent we had $\mu_{e1}^*(p_0, T) = \mu_{g1}^*(p_0, T)$
equilibrium pressure at T was p_0 .

(1) can be fulfilled at $\boxed{p_1' = p_0 + \Delta p}$

$$\mu_{e1}^*(p_0, T) + v_{e1} \Delta p - RT x_2 = \mu_{g1}^*(p_0, T) + v_{g1} \Delta p$$

$$\boxed{\Delta p = - \frac{RT}{v_{g1} - v_{e1}} \cdot x_2 < 0}$$

→ Vapor pressure lowering leads to boiling-point elevation:

For pure solvent at p_0 boiling point at T_b

$$\mu_{e1}^*(p_0, T_b) = \mu_{g1}^*(p_0, T_b)$$

For solution we have equilibrium at $\boxed{T_b' = T_b + \Delta T_b}$

$$\mu_{e1}(p_0, T_b', x_1) = \mu_{g1}^*(p_0, T_b')$$

$$\mu_{e1}^*(p_0, T_b) - S_{e1} \Delta T_b - RT_b x_2 = \mu_{g1}^*(p_0, T_b) - S_g \Delta T_b$$

$$\text{i.e. } \boxed{\Delta T_b \approx \frac{RT_b}{S_{g1} - S_{e1}} x_2 = \frac{RT_b^2}{\Delta H_{ge}} x_2 > 0}$$

① → Freezing point depression

$$\mu_{cl}^*(p_0, T_f) = \mu_{sl}^*(p_0, T_f) \quad \text{freezing of pure solvent at } p_0, T_f$$

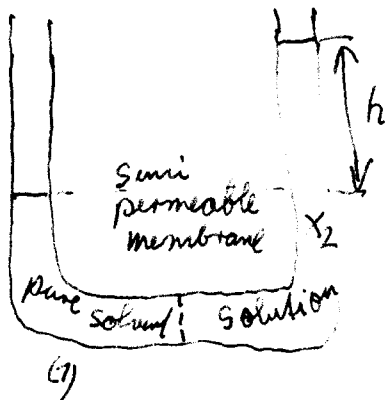
For solution freezing at $T'_f = T_f + \Delta T_f$

$$\mu_{cl}(p_0, T_f + \Delta T_f, x_1) = \mu_{sl}^*(p_0, T_f + \Delta T_f)$$

$$\mu_{cl}^*(p_0, T_f) - S_{f1} \Delta T_f - RT_f x_2 \approx \mu_{sl}^*(p_0, T_f) - S_{s1} \Delta T_f$$

$$\Delta T_f \approx - \frac{RT_f x_2}{S_{f1} - S_{s1}} = - \frac{RT_f^2}{\Delta H_{fs}} x_2 \sim C$$

→ Osmotic pressure



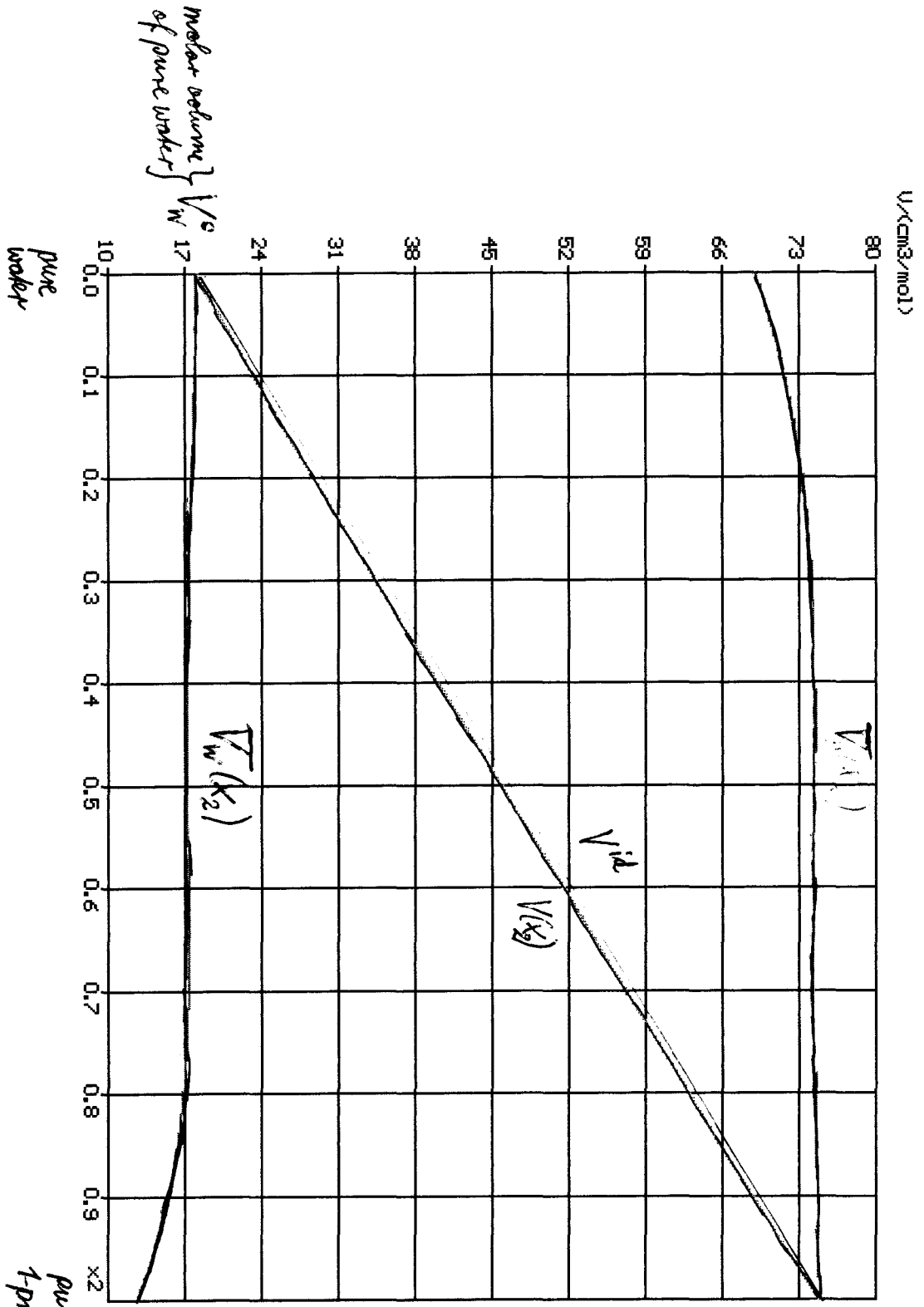
$$\Delta P_{osm} = \rho_s g h$$

$$\mu_{cl}^*(p_0, T) = \mu_{cl}(p_0 + \Delta P_{osm}, T, x_2)$$

$$\mu_{cl}^*(p_0, T) \approx \mu_{cl}^*(p_0, T) + V_{cl} \Delta P_{osm} - RT x_2$$

$$\Delta P_{osm} \approx \frac{RT}{V_{cl}} \cdot x_2$$

cf. ideal gas EOS



$V_m(x_2) = V_m^0 + (V_p^0 - V_m^0) X_2$

→ Molar volume $V(x_2)$

of aqueous 1-propanol solution

→ Partial molar volumes of water, V_m , and of 1-propanol, V_p

→ $V_{id} = V_m^0 + (V_p^0 - V_m^0) X_2$

→ Regular solution model

$$V^{ex} = V_{00} X_2 (1 - X_2)$$

$$\begin{aligned} \bar{V}_m(x_2) &= V_{00} X_2^2 \\ \bar{V}_p(x_2) &= V_{00} (1 - X_2)^2 \end{aligned}$$