Condensed-Phase TD (Pure Liquids & Solids)

EoS of solids and liquids have limited response of volume to pressure and ***T***

Isoth. compressibility

$$\kappa_T := -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

Vol. expansion coefficient

$$\alpha := \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{dV = \alpha \cdot V \cdot dT - \kappa_T \cdot V \cdot dp}$$

EoS

α, κ_T weak T-dependence

$$\boxed{V(p,T) \approx V(p_0,T_0)\left[1+\alpha(T-T_0)-\kappa_T(p-p_0)\right]}$$

Molar entropy $S(T,p) \rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$

$$T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial Q}{\partial T}\right)_p = C_p \quad per\ mol; \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\alpha \cdot V \quad for\ n\ moles \in V$$

$$dS = n \cdot \frac{c_{m,p}}{T} dT - \alpha \cdot V\, dp \Rightarrow \boxed{S(p,T) = S(0,0) + n \cdot \int_0^T \frac{c_{m,p}(T')}{T'} dT' - n \cdot \alpha \cdot \int_0^p V_m(p')\, dp'}$$

Condensed-Phase TD Free Energy

$$\textit{Chemical potential}\;\; \mu := \partial G/\partial n : \textit{Gibbs} - \textit{Duhem}$$

$$\boxed{d\mu = -S_m \cdot dT + V_m \cdot dp} \;\; (\textit{molar quantities})$$

$$S_m(p,T) = S_m(0,0) + \int_0^T \frac{c_{m,p}(T')}{T'}dT' - \alpha \cdot \int_0^p V_m(p')dp' \approx S_m(0,0) + \int_0^T \frac{c_{m,p}(T')}{T'}dT'$$

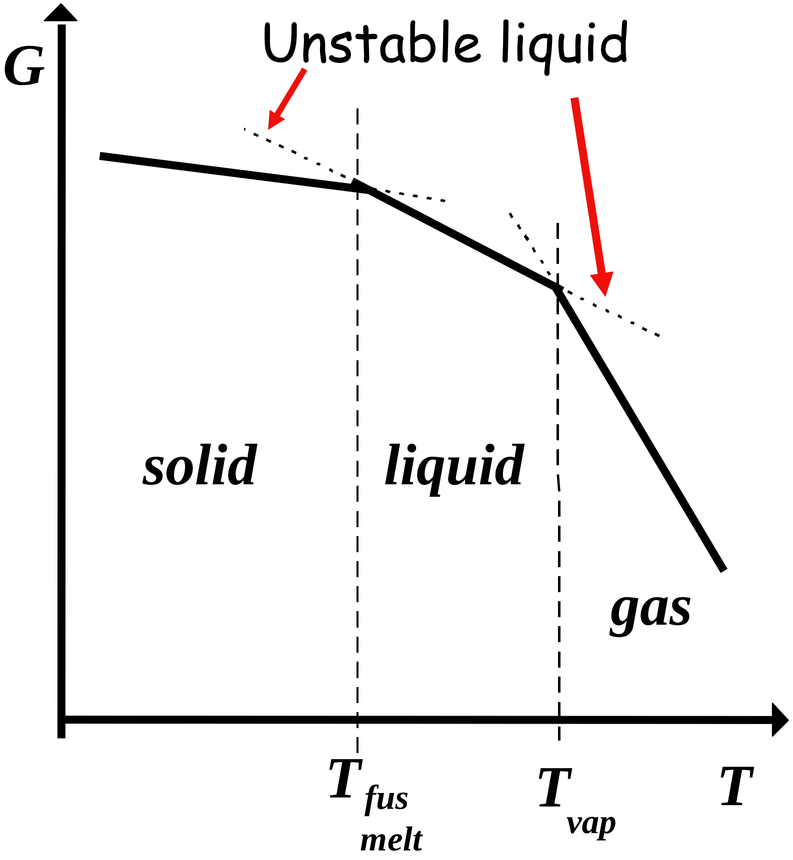
$$\mu(p,T) = \mu(0,0) - \int_0^T S_m(T')dT' + \int_0^p V_m(p')dp' \approx \mu(T) + V_m \cdot p$$

$$\boxed{\mu(p,T) \approx \mu^0(T) + V_m \cdot p} \;\Rightarrow\; \boxed{\mu(p,T) =: \mu^0(T) + R \cdot T \cdot Ln\, a}$$

Activities for liquids & solids $a = \textit{effective pressure}/p_0 = 1$

Phase Domains of Pure Substances

Gibbs Free Energy for a Pure Substance $H_2O(s) \leftrightarrow H_2O(l)$ $\Delta G = G(l) - G(s)$



$G(p,T) = H - TS$ approx. *linear in T*

$dG(p,T) = -\boldsymbol{S \cdot dT} + V \cdot dp$

slope of line ***G*** vs, ***T***: *negative* of

$|S\ (gas)| > |S\ (liquid)| > |S\ (solid)|$

Most stable: Phase with minimal ***G***

Phase equilibrium with $\Delta G = 0$

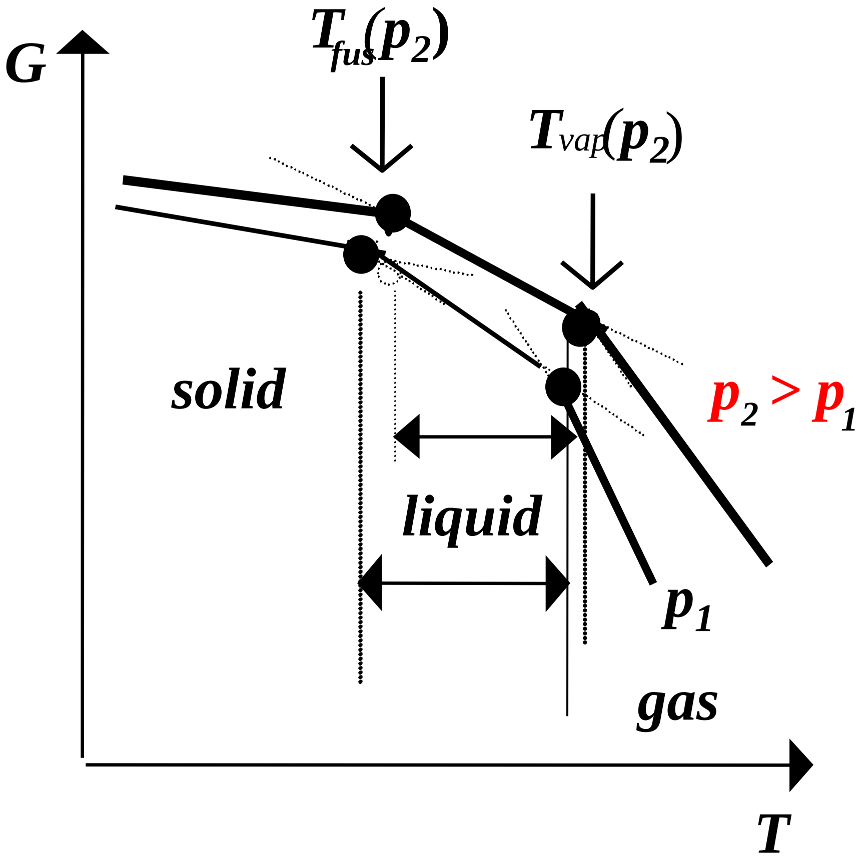
At melting and boiling points:

$\Delta S_{melt} = (\Delta H/T)_{fus} > 0 \quad \Delta G < 0$

$\Delta S_{vap} = (\Delta H/T)_{vap} > 0 \quad \Delta G < 0$

p-Dependence of Phase Domains

p-T Dependence of Gibbs Free Energy



p-dependence of ΔG → $V \cdot dp$ determines sign (increase or decrease)

$$V = (\Delta G/\Delta p)_{T=const}$$

p-dependence strongest for gas phase (largest ***V***).

Increased pressure → boiling point *T* increases, freezing point *T* increases.

Width of liquid domain shrinks with increasing pressure, vanishes at critical point
→only super critical vapor phase for $T > T_c$.

Pure Substance Phase Equilibrium

Equilibrium mixture of gas (*vapor*) and liquid

$\Delta G = G_g(p,T) - G_\ell(p,T) \approx 0$ *Phase equilibrium*

Equilibrium: Component *driving forces* ΔG_i . cancel each other. Per mol: $\Delta G_i \rightarrow N_i \cdot \Delta\mu_i$

$$\boxed{\begin{aligned} dG_g(p,T) &= V_g(p,T)\,dp - S_g(p,T)\,dT = \\ &= V_\ell(p,T)\,dp - S_\ell(p,T)\,dT = dG_\ell(p,T) \end{aligned}}$$

$$\begin{aligned} &\left(V_g(p,T) - V_\ell(p,T)\right)dp = \\ &= \left(S_g(p,T) - S_\ell(p,T)\right)dT \end{aligned} \quad \Rightarrow \quad \frac{dp}{dT} = \frac{S_g(p,T) - S_\ell(p,T)}{V_g(p,T) - V_\ell(p,T)}$$

Since for phase equilibrium

$\Delta G_{PE} = 0 \rightarrow \Delta H_{PE} = T_{PE} \cdot \Delta S_{PE}$

Clapeyron

Equation

$$\boxed{\frac{dp(T)}{dT} = \left(\frac{\Delta H}{T \cdot \Delta V}\right)_{PE}}$$

Clapeyron Equation defines ***p,T*** dependence of phase equilibrium. For Water:

Pure Substance Liquid-Gas Equilibrium

Equilibrium mixture of gas (*vapor*) and liquid

$\Delta G = G(g) - G(\ell) \approx 0$ *Phase equilibrium*

Equilibrium: Component *driving forces* ΔG_i . cancel each other.

$\boxed{dG_g(p,T) = dG_\ell(p,T)}$ N_g/N_ℓ adjusts

Large volume change in *liquid-gas phase transition:*

Water : $V_\ell(p,100^0C) \approx 18\,mL/mol \ll V_g(p,100^0C) = 30.2\,L/mol$

$$\Delta V_{\ell\to g} = [V_g(p,T) - V_\ell(p,T)] \approx V_g(p,T)$$

$$\frac{dp(T)}{dT} = \frac{\Delta H_{vap}}{T \cdot V_g} = \frac{\Delta H_{vap}}{T \cdot (RT/p)} \Rightarrow \boxed{\frac{d}{dT}(Ln\,p) = \frac{\Delta H_{vap}}{R \cdot T^2}}$$

Clausius-Clapeyron Equation

Example boiling point increase for water: dT(p)/dp=0.28 K/kPa >0

T_{boil}=373.1K & ΔH_{vap}= 40.6 kJ/mol

Pure Substance Liquid-Gas Equilibrium

Equilibrium mixture of gas (*vapor*) and liquid in ***V***

$\Delta G = G(g) - G(\ell) \approx 0$ =*Min*@ *Phase Equilibrium*

Equilibrium: Component *driving forces* ΔG . cancel each other.

$$\boxed{dG_g(p,T) = dG_\ell(p,T)} \qquad N_g / N_\ell \text{ adjusts}$$

Large volume change in *liquid-gas and solid-gas phase transitions*

$$\Delta V_{PT} = [V_g(p,T) - V_{\ell,s}(p,T)] \approx V_g(p,T)$$

$$\frac{d}{dT}(Ln\,p) = \frac{\Delta H_{vap}}{R \cdot T^2} \Rightarrow \boxed{Ln\,p_2 - Ln\,p_1 = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Example boiling point increase for water: $dT(p)/dp = 0.28$ K/kPa >0

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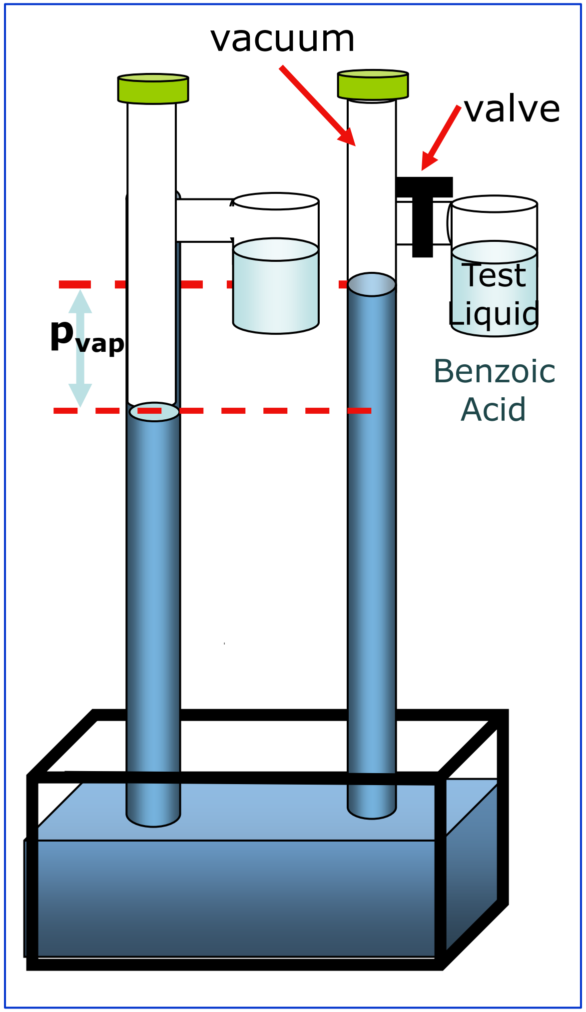
Measuring and Predicting Vapor Pressures



$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T\cdot\Delta V} \quad \text{with} \quad \Delta V \approx V(\overset{\overset{\text{vapor}}{\Downarrow}}{g}) = \frac{nRT}{p}$$

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T\cdot\frac{nRT}{p}} = p\,\frac{\Delta H_{vap}}{nRT^2} \rightarrow \frac{dp}{p\,dT} = \frac{\Delta H_{vap}}{nRT^2}$$

Clausius – Clapeyron Equation

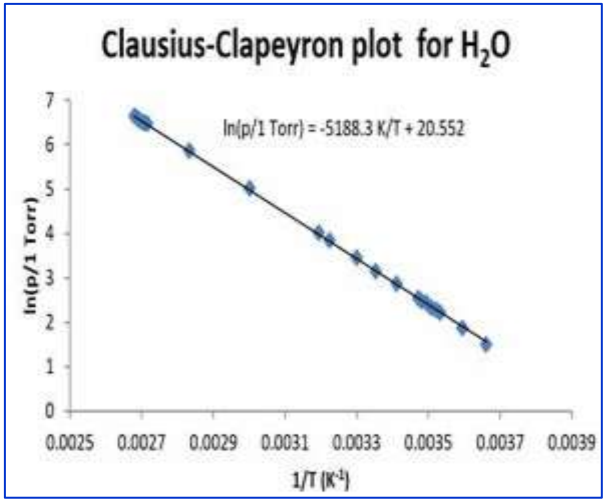
$$\boxed{\frac{d\,Ln(p)}{d(1/T)} = -\frac{\Delta H_{vap}}{n\cdot R}}$$

$$\boxed{Ln\left(p(T)\right) = A - \frac{\Delta H_{vap}}{nR}\cdot\frac{1}{T}}$$

A=const. (Antoine)

$$Ln\left(\frac{p(T_2)}{p(T_1)}\right) = -\frac{\Delta H_{vap}}{nR}\cdot\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Arrhenius, van’t Hoff *p-1/T* Plots

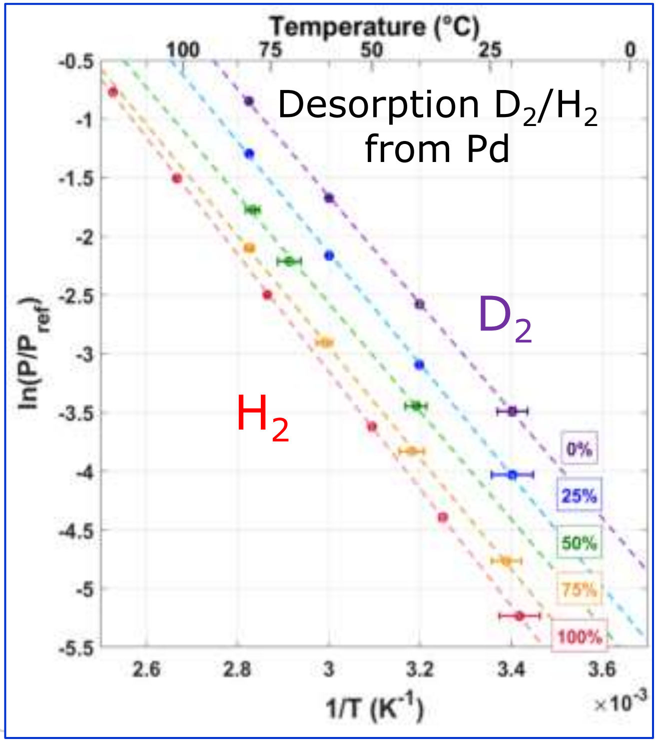


$$Ln\, p_2 - Ln\, p_1 = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Example: Vapor pressure vs. 1/T for water:

ΔH_{vap}= 40.6 kJ/mol → $T_{boil}=T_{vap}$=373.1K @ p=101kPa

dp/d(1/T)<0 → dT(p)/dp=0.28 K/kPa >0



Example: Hydrogen (H, D isotopic mix) in solid (in metallic palladium PdH_x) & gas.

Arrhenius plots for matter transitions involving a transition state = a barrier in G(ξ)

Example: Vaporizing Benzene

Normal boiling point of a liquid (T_b): vapor p = 1 atm (760 Torr).

Measured vapor pressure of benzene: p = 75 Torr at $T=20^{o}C$.

Q: What is boiling point of benzene @ *p=1atm*?

Hint: Use Clausius-Clapeyron. Tables: ΔH_{vap} = 30.8 kJ/mol

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A: Calculate T_b for benzene, when $p_1 = 75\ Torr$ at $T_1 = 293K$ is known.

$$\frac{1}{T_2} = \frac{1}{T_1} - Ln\left(\frac{p(T_2)}{p(T_1)}\right)\cdot\frac{nR}{\Delta H_{vap}}$$

$$\frac{1}{T_2} = \frac{1}{293K} - Ln\left(\frac{760\,Torr}{75\,Torr}\right)\frac{8.3145J/Kmol}{30.8kJ/mol} = \frac{1}{359K}$$

$$T_{boil}\left(C_6H_6\right) = T_2 = 359K\ \left(86^oC\right)$$

Ideal Solutions

Ideal solutions = mixtures of pure quasi-ideal substances (assume similar interactions between different types of atoms/molecules), each with different phases,

i = *1,2,…., A* counts substances and phases, ***n_i* moles**

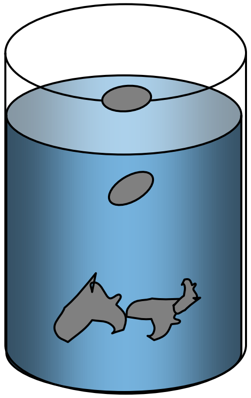
e.g., ***i* = *1*** (*liquid* water), ***i* = *2*** (water *vapor=gas*),

i* = *3 (*solid* NaCl), ***i* = *4*** (Na^+ *aqu*),

i* = *5 (Cl^- *aqu*)

Chemical potential (for substances, each in a given phase ***i***)

***p,T* =const.** → $\boxed{\mu_i = G_i/n_i}$



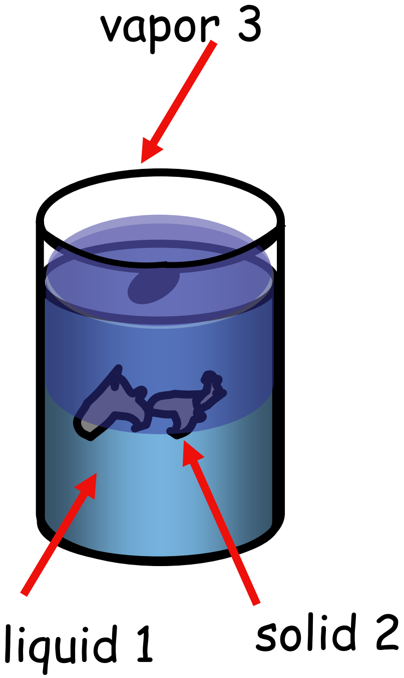
$$\textit{Total free energy}\left(\textit{extensive}\right)$$

$$G = n_1 \cdot \mu_1 + \ldots + n_A \cdot \mu_A = \sum_{i=1}^{A} n_i \cdot \mu_i$$

$$\textit{Equilibrium}: \; G = \textit{minimum}, \quad \Delta G = 0$$

$$\Delta G = \sum_{i=1}^{A} \mu_i \Delta n_i = \mu_1 \Delta n_1 + \ldots + \mu_A \Delta n_A = 0$$

Multi-Component Solutions



$$\text{Free energy of individual vapor component } i$$

$$\mu_i(g) = \mu_i^0(g) + RT\ln(p_i) \qquad i = 1, 2, \ldots, A$$

$$\text{in equilibrium with its own pure liquid } i:$$

$$\underline{\mu_i^{pure}(l) = \mu_i(g)} = \mu_i^0(g) + RT\ln(p_i^{vap})$$

$$\text{If component } i \text{ is part of (mix) equil. solution}$$

$$\mu_i(sol) = \mu_i^0(g) + RT\ln(p_i) =$$

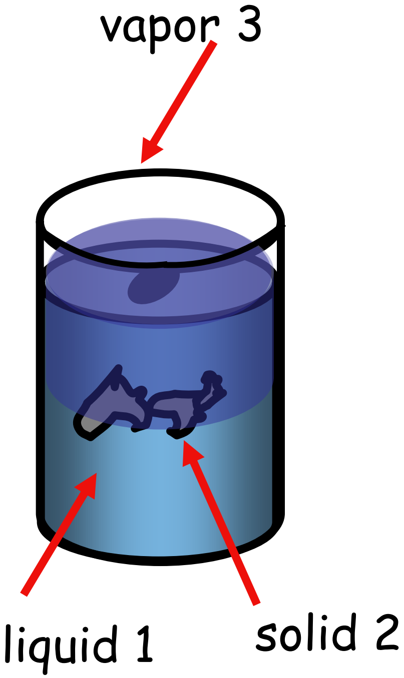
$$= \left[\mu_i^{pure}(l) - RT\ln(p_i^{vap})\right] + RT\ln(p_i)$$

$$= \mu_i^{pure}(l) + RT\ln\left(p_i / p_i^{vap}\right)$$

Multi-Component Solutions

If substance *i* (*i* =*1,…,A)* is part of a solution, then its vapor pressure and chemical potential are different, influenced by other components (they all interact).

$$\mu_i(sol) = \mu_i^{pure}(l) + RT\ln\left(p_i / p_i^{vap}\right)$$



Raoult's Law: vapor pressure of component in solution is reduced by mole fraction:

$p_i = x_i \cdot p_i^{vap}$ (plausible)

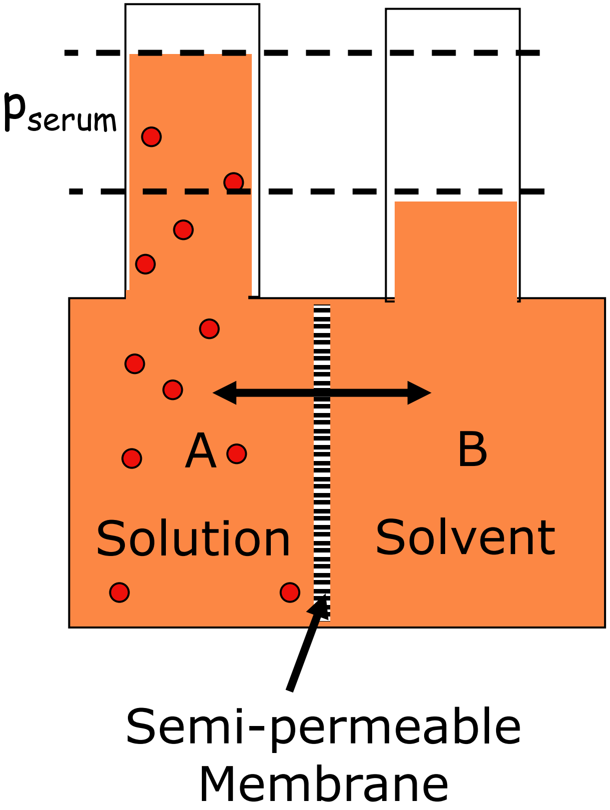
$$\mu_i(sol) = \mu_i^{pure}(l) + RT\ln\left(x_i\right)$$

Adding an impurity to a liquid *i*, lowers x_i and its potential

$$\mu_i(sol) = \mu_i^{pure}(l) + RT\ln\left(x_i\right) < \mu_i^{pure}(l)$$

Example: Osmotic Pressure

Volume B containing a pure solvent (e.g. blood serum) is in contact with volume A (cell) containing solvent and solute. Semi-permeable membrane lets solvent pass but not solute.



$$\mu_{serum}(sol) = \mu_{serum}^{pure}(l) + RT\ln\left(x_{serum}\right)$$

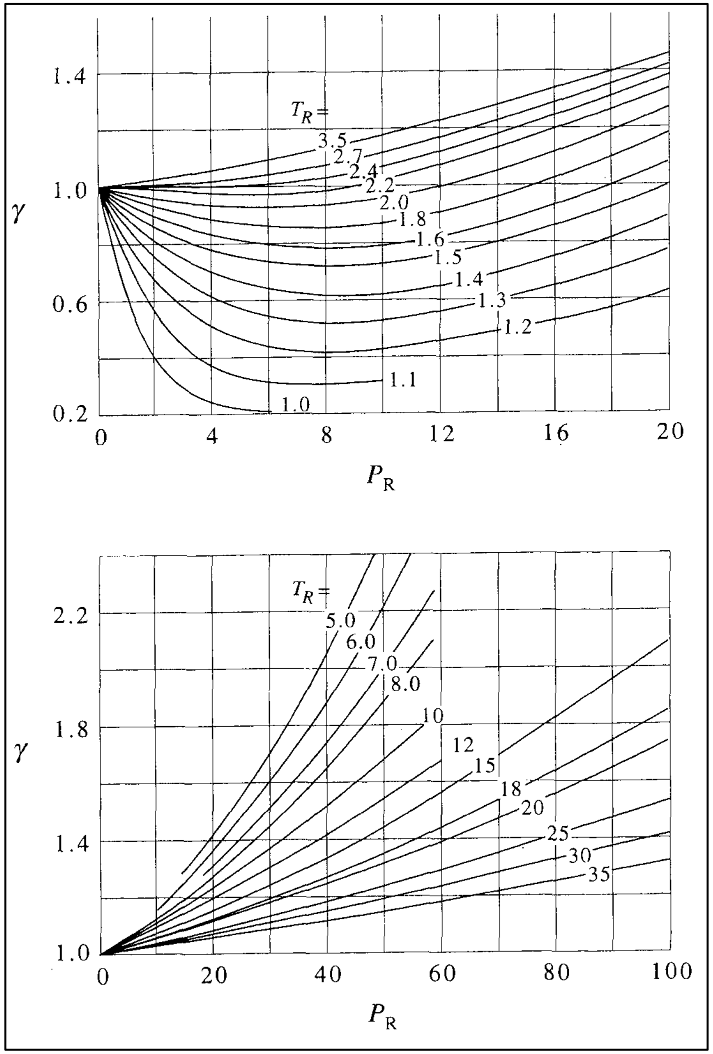
$$\mu_{serum}(sol) < \mu_{serum}^{pure}(l)$$

Solution (A) has lower potential → solvent flows spontaneously through the membrane

→ increases mole fraction and pressure inside A. Increased pressure/activity prevents such flow:

$$\ln\left(p_{serum}\right) = -\left(\frac{\mu_{serum}(sol) - \mu_{serum}^{pure}(l)}{RT}\right)$$

Fugacity of Gases vs Reduced Pressure



Reduced variables : $\boxed{p_R = p/p_{critical}\ ;\ T_R = T/T_{critical}}$

Activity a : $G(a) = G^o + nRT\cdot Ln(a)$

ideal gas activity $a = p/1atm$

real gas $a = \gamma\cdot p$ $\gamma = activity\ coefficient$

pure solids or liquids $a = 1$

solutions $a = \gamma\cdot c$ $c = concentration\,(mol/L)$

standard state : $\gamma = 1$ like dilute solutions

solvent : $a = \gamma\cdot x$ $x = mole\ fraction$

Activity~fugacity, different reference pressures

Real gases & liquids $\boxed{a = f/p}$ → "Fugacity" f:

$$\left(\frac{\partial}{\partial p}Ln f\right)_T = \frac{V_m}{R\cdot T}$$ molar volume V_m

$$Ln\left(\frac{f}{p}\right) = \int_0^p \frac{(Z-1)}{p}dp; \rightarrow \boxed{f = p\cdot\exp\left\{\int_0^p \frac{(Z-1)}{p}dp\right\}}$$

$$\underbrace{\int_0^p \frac{(Z-1)}{p}dp}_{\sim\frac{(\Delta V)_{vdW-IG}}{RT}dp}$$