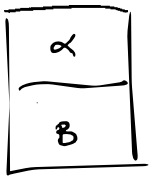
Equilibrium



$T^\alpha = T^\beta$

$P^\alpha = P^\beta$

$\mu_i^\alpha = \mu_i^\beta \quad i = 1, 2, \ldots C$

Phase rule $F = C - \Pi + 2$

Clapeyron Equation $d\mu^\alpha = d\mu^\beta \Rightarrow$

$$\left.\frac{dP}{dT}\right)_{\alpha\text{-}\beta\ coex} = \frac{\Delta S}{\Delta V} = \frac{\Delta h}{T\Delta v}$$ } no assumptions

If β = gas $V^\beta \gg V^\alpha$ $\quad \frac{d\ln P}{d(1/T)} = -\frac{\Delta h^{vap}}{R}$ (approximate)

Stability conditions

Starting point E is min @ const $S, V, \{N\}$; $y^{(0)} = E$

Necessary conditions: $y^{(0)}_{ii} > 0$ for any ordering

Nec. + sufficient : $y^{(0)}_{11} > 0$ $y^{(1)}_{22} > 0 \ldots$ $y^{(n)}_{u+1,u+1} > 0$

key stability condition (get violated first when starting in stable region $\boxed{y^{(n)}_{u+1,u+1} > 0}$ n-component system.

E.g. $n=1$ $y^{(0)} = E(S,V,N)$ $y^{(0)}_{11} = \left(\frac{\partial^2 E}{\partial S^2}\right)_{V,N} = \frac{T}{C_V} > 0$

$y^{(1)} = A(T,V,N)$ $y^{(1)}_{22} = \left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial P}{\partial V}\right)_{T,N} > 0$

Criticality conditions (stable stability limit)

$y^{(n)}_{u+1,u+1} = 0$ and $y^{(n)}_{n+1,u+1,u+1} = 0$

e.g. for $n=1$ $\left(\frac{\partial P}{\partial V}\right)_T = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$

Ideal solutions

$\Delta S_{mix} = -N k_B \sum_{i=1}^{n} x_i \ln x_i$ n components

$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \mu_i(T,P,\text{pure } i) + k_B T \ln x_i$

Activities: $k_B T \ln \gamma_i x_i = \mu_i(T,P,\{N_i\}) - \mu_i(T,P,\text{pure } i)$

Ideal VLE $\mu_i^G = \mu_i^L \Rightarrow y_i P = x_i P_i^{vap}$

For solutions, even non-ideal, $\gamma_i \to 1$ as $x_i \to 1$ (Raoult's law)

Osmotic pressure / Boiling point elevation / eutectics obtained from $\left(\frac{\partial \mu}{\partial P}\right)_T = v$ $\left(\frac{\partial(\mu/T)}{\partial T}\right)_P = -\frac{h}{T^2}$ along with ideal-solution assumption

Non-ideal Solutions

$\Delta E_{mix} = N x_1 x_2 k_B T \chi$ $\Delta A_{mix} = N k_B T \left[x_1 \ln x_1 + x_2 \ln x_2 + x_1 x_2 \chi \right]$

$\chi = \frac{z}{k_B T} \left[w_{12} - \frac{w_{11} + w_{22}}{2} \right]$

Gibbs-Duhem connects μ_i's @ const. T, P:

$\sum_{i=1}^{n} N_i d\mu_i = 0$ [Euler-integrated Fundam. Equ.]

Partial molar quantities $\bar{B}_i = \left(\frac{\partial B}{\partial N_i}\right)_{T,P,N_{\neq i}}$

Same relationships as for "normal" properties,

$A = E - TS \Rightarrow \bar{A}_i = \bar{E}_i - T\bar{S}_i$

Useful for differential expressions on phase boundaries

Flory-Huggins $\Delta A_{mix} = \chi \phi_p \phi_s + \frac{\phi_p}{M} \ln \phi_p + \phi_s \ln \phi_s$

Solids (Einstein model only) $E = \left(n_t + \frac{3N}{2}\right) h\nu$

$\Omega(E, V, N) = \frac{(n_t + 3N - 1)!}{(3N-1)!\, n_t!} \rightarrow E, C_V$

Canonical (NVT) ensemble

$\mathcal{P}_m \propto \exp(-\beta E_m)$ $Q(N,V,T) = \sum_{\text{all } m} e^{-\beta E_m}$

$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$ $A = -k_B T \ln Q$

Canonical Ensemble (cont.)

For independent degrees of freedom,

$Q = \prod_i q_i$ where $q_i = \sum_{x_i} e^{-\beta \mathcal{E}_i(x_i)}$ molec. partition function

For identical, indistinguishable molecules,

$Q = q^N / N!$

Fluctuations $\sigma_\mathcal{E}^2 = \langle \mathcal{E}^2 \rangle - \langle \mathcal{E} \rangle^2 = \frac{\partial^2 \ln Q}{\partial \beta^2} = k_B T^2 C_V$

Relative fluctuations go down as $1/\sqrt{N}$

Stability conditions are directly connected to fluctuations, which diverge at limit of stability.

Generalized Ensembles

$\mathcal{P}_m \propto \exp(-x_1 \mathcal{Y}_1 - x_2 \mathcal{Y}_2 \cdots)$

$\Xi = \sum_{\text{all microstates}} \exp(-x_1 \mathcal{Y}_1 - x_2 \mathcal{Y}_2 \cdots)$

Gibbs S

$S = -k_B \sum_m P \ln P$ for any ensemble

E.g., μVT ensemble $\mathcal{P}_m = \exp(-\beta E_m + \beta \mu N_m)$

Fluctuations are the second derivative of the corresponding partition function, e.g.,

$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{\partial^2 \ln \Xi}{\partial (\beta\mu)^2} = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{T,V}$

Classical Systems

Maxwell-Boltzmann distribution of molecular speeds v $\mathcal{P}(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(-\frac{m v^2}{2 k_B T} \right)$

valid for solids, liquids, gases

Virial expression for Pressure: $P = \frac{NkT}{V} + \frac{1}{3V}\left\langle \sum_i \vec{r}_i \cdot \vec{f}_i \right\rangle$

At low densities $\frac{P}{k_B T} \simeq \rho - \rho^2 \left[2\pi \int_0^\infty \left[e^{-B u(r)} - 1 \right] r^2 dr \right]$

Second virial coeff., B

Distribution functions

$g(r)$ = (mean # of particles bet. r, r+dr) / N_{random}

$E_{pot}/N = \frac{1}{2} \rho_0 \int_0^\infty u(r)\, 4\pi r^2 g(r)\, dr$

At low densities, $g(r) \simeq \exp[-B u(r)]$

Reactions

$\nu_1 M_1 + \nu_2 M_2 + \cdots \nu_n M_n = 0$

for any ensemble $\sum_i \nu_i \mu_i = 0$

where ν_i are the stoichiometric coefficients

$K(T) = \prod_i f_i^{\nu_i} = \exp\left(-\frac{\Delta g^\circ(T)}{k_B T} \right)$

$\frac{d \ln K(T)}{d(1/T)} = -\frac{\Delta e^\circ}{k_B}$

At microscopic level, for $A \rightleftharpoons B$

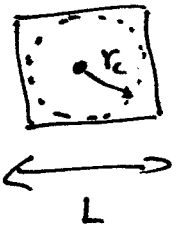
$K(T) = \frac{\langle N_B \rangle}{\langle N_A \rangle} = \frac{q_B}{q_A}$

Simulations

Periodic Boundary Conditions

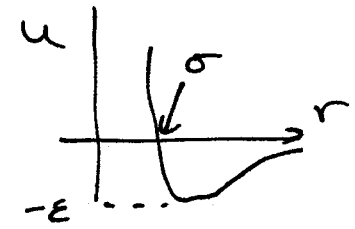
Cutoff r_c for potentials

$r_c \leq L/2$



Typical intermolecular potential (Lennard-Jones)

$$U_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$



$$E_{pot} = \sum_{i}\sum_{j>i} U_{ij}$$

Molecular Dynamics: NVE ensemble, solve Newton's equ. of motion using $\delta t \simeq 1$ fs

Monte Carlo: in any ensemble,

$$\frac{\text{Accept}\ (o \to n)}{\text{Accept}\ (n \to o)} = \frac{N(n)}{N(o)} = \exp(-\beta \Delta U) \quad \left(\text{in } NVT\right)$$

moves must be ergodic, efficient, microscopically reversible