CHEM E 457 Principles of Molecular Engineering

Counting and Probability

| Counting

Description	Equations
Total possible events if each event E_i can occur in n_i ways	$\prod n_i$
Permutation of n elements taken r at a time	$P(n, r) = \dfrac{n!}{(n-r)!}$
Distinguishable permutations of n objects, with n_i are alike of one kind	$\dfrac{n!}{n_1! n_2! \cdots n_k!}$
Combination of n elements taken r at a time	$C(n, r) = \dbinom{n}{r} = \dfrac{n!}{r!(n-r)!}$
Stirling's approximation	$x! \approx \left(\dfrac{x}{e}\right)^x$
Stirling's approximation	$\ln(x!) = x\ln(x) - x$

| Probability

Description	Equations
Probability	$\mathbf{P}(A) = \dfrac{n_A}{N}$
Addition rule of mutually exclusive outcomes	$\mathbf{P}\left(\bigcup A_i\right) = \sum \mathbf{P}(A_i)$
Multiplication rule of independent outcomes	$\mathbf{P}\left(\bigcap A_i\right) = \prod \mathbf{P}(A_i)$
General addition rule	$\mathbf{P}(A \cup B) = \mathbf{P}(A) + \mathbf{P}(B) - \mathbf{P}(A \cap B)$
Conditional probability	$\mathbf{P}(A|B) \equiv \dfrac{\mathbf{P}(A \cap B)}{\mathbf{P}(B)}$
Bayes' rule	$\mathbf{P}(A|B) = \dfrac{\mathbf{P}(A)\mathbf{P}(B|A)}{\mathbf{P}(B)}$
Total probability theorem	$\mathbf{P}(B) = \mathbf{P}(A)\mathbf{P}(B|A) + \mathbf{P}(A^c)\mathbf{P}(B|A^c)$
Degree of correlation	$g = \dfrac{\mathbf{P}(B|A)}{\mathbf{P}(B)} = \dfrac{\mathbf{P}(A \cap B)}{\mathbf{P}(A)\mathbf{P}(B)}$

| Continuous probability distribution

Description	Equations
Normalization condition of probability distribution function	$\displaystyle\int_a^b P(x)\,dx = 1$
Binomial distribution	$P(n, N) = \dfrac{N!}{n!(N-n)!} p^n (1-p)^{N-n}$
Multinomial distribution	$P(n_1, n_2, \ldots, n_t, N) = \dfrac{N!}{\prod n_i!} \prod p_i^{n_i}$
Average	$\langle x \rangle = \displaystyle\int_a^b x P(x)\,dx$
Average of a function	$\langle f(x) \rangle = \displaystyle\int_a^b f(x) P(x)\,dx$

Description	Equations
nth moment	$\langle x^n \rangle = \int_a^b x^n P(x) dx$
Variance	$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$

Extremum Principles Predicts Equilibria

Physical Description	Math Description	Equations
Equilibrium	Critical point	$f'(x) = 0$
Stable equilibrium	Minimum	$f'(x) = 0, f''(x) > 0$
Unstable equilibrium	Maximum	$f'(x) = 0, f''(x) < 0$
Metastable equilibrium	Local minimum	$f'(x) = 0, f''(x) > 0$ in some dx
Neutral equilibrium	Constant	$f'(x) = 0$ for all x

- Extremum principles
  - Minimization of energy
  - Maximization of entropy (multiplicity)

Description	Equations
Method of Lagrange multiplier Finding extremum of objective function $f(\mathbf{x})$ subjected to constraint $g(\mathbf{x})$	$\nabla f(\mathbf{x}) = \lambda \nabla g(\mathbf{x})$

Entropy and Boltzmann Law

- Ground state - state of lowest energy
- Excited state - states of higher energy
- Microstate - microscopic configuration
- Macrostate - collection of microstate

| General applications

Description	Equations
Entropy in terms of multiplicity	$S = k \ln(W)$
Entropy in terms of probability	$S = -k \sum p_i \ln(p_i)$
Probability of a microstate ★ No constraint on observation ★ Maximized entropy	$p_i = \dfrac{1}{t}$
Boltzmann distribution law Probability of a microstate ★ With constraint on observation ★ Maximized entropy	$p_i = \dfrac{e^{-\beta \varepsilon_i}}{\sum e^{-\beta \varepsilon_i}} = \dfrac{e^{-\beta \varepsilon_i}}{q}$
Partition function	$q = \sum e^{-\beta \varepsilon_i}$
Average observation	$\langle \varepsilon \rangle = \sum \varepsilon_i p_i$

| Molecular distributions

Description	Boltzmann Distribution Law	Partition Function
System with energy levels	$p_i = \dfrac{\exp(-E_i/kT)}{Q}$	$Q = \sum \exp\left(-E_i/kT\right)$
System with energy differences	$p_i = \dfrac{\exp(-(E_i - E_j)/kT)}{Q}$	$Q = \sum \exp\left(-(E_i - E_j)/kT\right)$
System with degenerate energy levels	$p_i = \dfrac{W(E_l)\exp(-E_l/kT)}{Q}$	$Q = \sum W(E_l)\exp(-E_l/kT)$

Description	Equations
Thermodynamic beta	$\beta = \dfrac{1}{kT}$
Relative populations of particles in energy level i and j at equilibrium	$\dfrac{p_i}{p_j} = \exp\left(-\dfrac{E_i - E_j}{kT}\right)$
Partition function of subsystem of independent distinguishable particles (solid)	$Q = \prod_i^N q_i = q^N$
Partition function of subsystem of independent indistinguishable particles (gas)	$Q = \dfrac{q^N}{N!}$
Internal energy	$U = kT^2 \left(\dfrac{\partial \ln Q}{\partial T}\right)_{V,N}$
Average particle energy	$\langle \varepsilon \rangle = \dfrac{U}{N} = \dfrac{kT^2}{N}\left(\dfrac{\partial \ln Q}{\partial T}\right)_{V,N}$
Entropy	$S = k \ln Q + \dfrac{U}{T}$
Helmholtz free energy	$F = U - TS = -kT \ln Q$
Chemical potential	$\mu = \left(\dfrac{\partial F}{\partial N}\right)_{T,V} = -kT\left(\dfrac{\partial \ln Q}{\partial N}\right)_{T,V}$
Pressure	$p = -\left(\dfrac{\partial F}{\partial V}\right)_{T,N} = kT\left(\dfrac{\partial \ln Q}{\partial N}\right)_{T,N}$

| Ensembles

- controlled set of variables
- collection of all the possible microstates

Description	Equations
Canonical ensemble	(T, V, N)
Microcanonical ensemble	(U, V, N)
Isobaric-isothermal ensemble	(T, P, N)
Grand canonical ensemble	(T, V, μ)

Ch 13 Chemical Equilibrium

| Multicomponent reactions

Description	Equations
Multicomponent gas phase reaction ★ No intermolecular interactions	$a\,A + b\,B \longrightarrow c\,C + d\,D$

Description	Equations
Difference in ground state energy	$\Delta\varepsilon_0 = d\varepsilon_{0D} + c\varepsilon_{0C} - b\varepsilon_{0B} - a\varepsilon_{0A}$
Difference in Dissociation energy	$\Delta D = dD_D + cD_C - bD_B - aD_A$
Dissociation energy	$D = -\varepsilon_0$ $\Delta D = -\Delta\varepsilon_0$
Equilibrium constant	$K = \dfrac{N_C^c N_D^d}{N_A^a N_B^b} = \dfrac{q_C^c q_D^d}{q_A^a q_B^b} \exp\left(\dfrac{\Delta D}{kT}\right)$
Pressure-based equilibrium constant	$K_p = \dfrac{p_C^c p_D^d}{p_A^a p_B^b} = \left(\dfrac{kT}{V}\right)^{(c+d)-(a+b)} \dfrac{q_C^c q_D^d}{q_A^a q_B^b} \exp\left(\dfrac{\Delta D}{kT}\right)$
Chemical potential	$\mu = kT\ln\left(\dfrac{p}{p_{int}^\circ}\right) = \mu^\circ + kT\ln p$
Internal pressure	$p_{int}^\circ = q_0' kT$

| T, P dependence of equilibrium

Description	Equations
	$\ln K_p = -\dfrac{\Delta\mu^\circ}{kT}$
vant's Hoff equation ★ $\Delta h^\circ \neq \Delta h^\circ(T)$	$\dfrac{\partial(\ln K_p)}{\partial T} = \dfrac{\Delta h^\circ}{kT^2}$
vant's Hoff plot ★ $\Delta h^\circ \neq \Delta h^\circ(T)$	$\dfrac{\partial(\ln K_p)}{\partial(1/T)} = -\dfrac{\Delta h^\circ}{k}$
vant's Hoff equation extrapolation ★ $\Delta h^\circ \neq \Delta h^\circ(T)$	$\ln\left(\dfrac{K_{p2}}{K_{p1}}\right) = -\dfrac{\Delta h^\circ}{k}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$
Gibbs-Helmholtz equation	$\dfrac{\partial}{\partial T}\left(\dfrac{G}{T}\right) = -\dfrac{H}{T^2}$
Gibbs-Helmholtz equation	$\dfrac{\partial}{\partial T}\left(\dfrac{F}{T}\right) = -\dfrac{U}{T^2}$
Pressure dependence of equilibrium constant	$\dfrac{\partial(\ln K)}{\partial p} = -\dfrac{\Delta v^\circ}{kT}$

Ch 14 Physical Equilibrium

Description	Equations
Equilibrium condition	$\mu_{\text{vapor}} = \mu_{\text{condensed}}$
Chemical potential of vapor	$\mu_{\text{vapor}} = kT\ln\left(\dfrac{p}{p_{int}^\circ}\right)$
Entropy of condensed phase	$\Delta S_{\text{condensed}} = 0$
Internal energy of condensed phase	$\Delta U_{\text{condensed}} = \frac{1}{2} N z w_{AA}$
Free energy of condensed phase	$\Delta F_{\text{condensed}} = \frac{1}{2} N z w_{AA}$
Chemical potential of condensed phase	$\mu_{\text{condensed}} = \left(\dfrac{\partial F}{\partial N}\right)_{T,V} = \dfrac{1}{2} z w_{AA}$

Description	Equations
Equilibrium vapor pressure	$p = p_{int}^\circ \exp\left(\dfrac{z w_{AA}}{2kT}\right)$

Description	Equations
Clausius Clapyeron equation	$\ln\left(\dfrac{p_2}{p_1^{\text{sat}}}\right) = \dfrac{\Delta h}{R}\left(\dfrac{1}{T_2}\quad\dfrac{1}{T_1}\right)$
Enthalpy of vaporization	$\Delta h_{\text{vap}} = -\frac{1}{2}zw_{AA}$
Internal energy to close a cavity	$\Delta U = \frac{1}{2}zw_{AA}$
Internal energy to open a cavity	$\Delta U = -\frac{1}{2}zw_{AA}$
Surface tension	$\sigma = -\dfrac{w_{AA}}{2a}$
Free energy of adsorption	$F_{\text{ads}} = \sigma a = -\dfrac{w_{AA}}{2a}$

Ch 15 Mixtures

| Ideal solutions

Description	Equations
Entropy of solution for binary systems	$\Delta S_{\text{soln}} = -Nk(x_A \ln x_A + x_B \ln x_B)$
Entropy of solution for multicomponent systems	$\Delta S_{\text{soln}} = -Nk\sum x_i \ln x_i$
Internal energy of solution	$\Delta U_{\text{soln}} = 0$
Free energy of solution	$\Delta F_{\text{soln}} = -T\Delta S_{\text{soln}}$

| Regular solutions

Description	Equations
Exchange parameter (dimensionless free energy)	$\chi_{AB} = \dfrac{z}{kT}\left(w_{AB} - \frac{1}{2}\left(w_{AA} + w_{BB}\right)\right)$
Exchange parameter	$\chi_{AB} = -\ln K_{\text{exch}}$
Exchange parameter interpretation	$\chi_{AB} > 0$, mixing unfavorable $\chi_{AB} < 0$, mixing favorable
Exchange energy	$RT\chi_{AB}$
Constant	$c_1 = \chi_{AB}T$ $= \dfrac{z}{k}\left(w_{AB} - \dfrac{1}{2}\left(w_{AA} + w_{BB}\right)\right)$
Entropy of solution for binary systems	$\Delta S_{\text{soln}} = -Nk(x_A \ln x_A + x_B \ln x_B)$
Entropy of solution for multicomponent systems	$\Delta S_{\text{soln}} = -Nk\sum x_i \ln x_i$
Internal energy of solution of binary systems	$\Delta U_{\text{soln}} = NkT\chi_{AB}x_A x_B$
Internal energy of solution of multicomponent systems	$\Delta U_{\text{soln}} = NkT\sum \chi_{ij}x_i x_j$
Free energy of solution	$\Delta F_{\text{soln}} = \Delta U_{\text{soln}} - T\Delta S_{\text{soln}}$
Free energy of solution of binary systems	$\Delta F_{\text{soln}} = NkT(x_A \ln x_A + x_B \ln x_B + \chi_{AB}x_A x_B)$
Free energy of solution of multicomponent systems	$\Delta F_{\text{soln}} = NkT(\sum x_i \ln x_i + \sum \chi_{ij}x_i x_j)$
Chemical potentials of binary systems	$\mu_A = \ln x_A + \dfrac{zw_{AA}}{2kT} + \chi_{AB}x_B^2$ $\mu_B = \ln x_B + \dfrac{zw_{BB}}{2kT} + \chi_{AB}x_A^2$

Description	Equations
Chemical potentials of multicomponent systems	$\mu_i = \ln x_i + \dfrac{zw_{ii}}{kT} + \chi_{ij}(1 - x_i)^2$ $= \mu^\circ + kT\ln(\gamma x)$

| Surface tension

Description	Equations
Interfacial tension	$\sigma_{AB} = \dfrac{1}{a}(w_{AB} - \dfrac{1}{2}(w_{AA} + w_{BB}))$ $= \dfrac{kT}{za}\chi_{AB}$
Free energy of adsorption	$F_{\text{ads}} = \sigma a = \dfrac{kT}{z}\chi_{AB}$

Ch 16 Solvation and Phase Transfer

| Lewis/Randall rule

Description	Equations
Notation ★ Solvent, pure limit $x_B \to 1$	A - non-volatile solute (e.g. NaCl) B - volatile solvent (e.g. $\mathrm{H_2O}$)
Lewis/Randall rule reference state	$p_B = p^\circ_{B,int}x_B \exp\left(\chi_{AB}x_A^2 + \dfrac{zw_{BB}}{2kT}\right)$ $= p^\circ_B x_B \exp\left(\chi_{AB}x_A^2\right)$
Raoult's law ★ Ideal solution $\chi_{AB} = 0$	$p_B = p^\circ_B x_B$
Vapor pressure of B	$p^\circ_B = p^\circ_{B,int}\exp\left(\dfrac{zw_{BB}}{2kT}\right)$

| Henry's law

Description	Equations
Notation ★ Solute, dilute limit $x_B \to 0$	A - non-volatile solvent (e.g. $\mathrm{H_2O}$) B - volatile solute (e.g. $\mathrm{CO_2}$)
Henry's law reference state	$p_B = p^\circ_{B,int}x_B \exp\left(\chi_{AB} + \dfrac{aw_{BB}}{2kT}\right)$ $= p^\circ_{B,int}x_B \exp\left(w_{AB} - \dfrac{w_{AA}}{2}\right)$ $= \mathcal{H}_B x_B$
Henry's constant	$\mathcal{H}_B = p^\circ_{B,int}\exp\left(\dfrac{z}{kT}w_{AB} - \dfrac{w_{AA}}{2}\right)$ $= p^\circ_{B,int}\exp\left(\dfrac{\Delta h^\circ_{\text{soln}}}{kT}\right)$
Enthalpy of solution	$\Delta h^\circ_{\text{soln}} = z\left(w_{AB} - \dfrac{w_{AA}}{2}\right)$

| Activity coefficient

Description	Equations
Standard state chemical potential	$\Delta\mu_B^\circ = \mu_B^\circ(\text{liquid}) - \mu_B^\circ(\text{gas})$
Activity coefficient	$\gamma_B = \dfrac{p_B}{x_B}\exp\left(-\dfrac{\Delta\mu_B^\circ}{kT}\right)$
Activity coefficient in Lewis/Randall solvent convection	$\gamma_B = \exp[\chi_{AB}(1 - x_B)^2]$
Activity coefficient in Henry's solute convection	$\gamma_B = \exp[\chi_{AB}x_B(x_B - 2)]$

| Colligative properties

Description	Equations
Boiling point elevation	$\Delta T_b = \dfrac{RT_b^2 x_A}{\Delta h_{\text{vap}}^\circ}$
Freezing point depression	$\Delta T_f = \dfrac{RT_f^2 x_A}{\Delta h_{\text{fus}}^\circ}$
Osmotic pressure	$\pi = \dfrac{RT x_A}{v_B} = RT c_A$

| Solute partition

Description	Equations
Notation	A - immiscible solvent B - immiscible solvent s - solute
Partition coefficient from solvent A to B	$K_A^B = \dfrac{x_{sB}}{x_{sA}}$
Free energy of transfer	$\Delta\mu^\circ = \mu_s^\circ(B) - \mu_s^\circ(A)$
Statistical mechanical interpretation	$\ln K_A^B = \chi_{sA}(1 - x_{sA})^2 - \chi_{sB}(1 - x_{sB})^2$
Thermodynamical interpretation	$\ln K_A^B = -\dfrac{\mu_s^\circ(B) - \mu_s^\circ(A)}{kT} - \ln\left(\dfrac{\gamma_{sB}}{\gamma_{sA}}\right)$
Partition coefficient at infinite dilution ★ Infinite dilution of solute in both phases $x_{sa} \ll 1, x_{sB} \ll 1$, $\gamma_{sa} \to 1, \gamma_{sB} \to 1$	$\ln K_A^B = -\dfrac{\mu_s^\circ(B) - \mu_s^\circ(A)}{kT}$ $= \chi_{sA} - \chi_{sB}$

Ch 25 Phase Transitions

Description	Equations
Fractions	$f^\alpha = \dfrac{n^\alpha}{n}$
Lever rule	$f' = \dfrac{x'' - x_0}{x'' - x'}$ $f'' = \dfrac{x_0 - x'}{x'' - x'}$
Lever rule	$v_A = f^\alpha v_A^\alpha + f^\beta v_A^\beta$
Binodal curve	$\dfrac{\partial(\Delta F_{\text{mix}})}{\partial x} = 0 = NkT\left[\ln\left(\dfrac{x}{1 - x}\right) + \chi_{AB}(1 - 2x)\right]$
Binodal curve ★ Dilute solute $x' \ll 1$, large χ_{AB}	$\chi_{AB} = -\ln x'$

Description	Equations
Spinodal curve	$\dfrac{\partial^2 F}{\partial x^2} = 0 = NkT \left[\frac{1}{x} + \frac{1}{1-x} - 2\chi_{AB} \right]$
Spinodal curve ★ Dilute solute $x' \ll 1$, large χ_{AB}	$x' = \dfrac{1}{2\chi_{AB} - 1}$
Critical point	$\dfrac{\partial^3 F}{\partial x^2} = 0$
Critical composition	$x_c = \dfrac{1}{2}$
Critical exchange parameter	$\chi_c = 2$
Critical exchange temperature	$T_c = \dfrac{c_1}{2}$
van der Waals EOS	$\left(p + \dfrac{a}{v^2} \right)(v - b) = RT$
Reduced form of van der Waals EOS	$\left(p_r + \dfrac{3}{v_r^2} \right)\left(v_r - \dfrac{1}{3} \right) = \dfrac{8}{3} T_r$