Equations – P-Chem

Mixtures & Chemical Equilibria

Transitions

$\frac{dp}{dT} = \frac{\Delta_{trs}S_m}{\Delta_{trs}V_m}$ Clapeyron equation

$(\frac{\delta p}{\delta T})_{fusion} = \frac{\Delta S_{fusion}}{\Delta V_{fusion}}$ solid-liquid coexistence curve

$(\frac{\delta p}{\delta T})_{vap} = \frac{p\Delta H_{vap}}{RT^2}$ - [Integrated form] $\ln\frac{p_f}{p_i} = -\frac{\Delta H_{vap}}{R} \times (\frac{1}{T_f} - \frac{1}{T_i})$ Claisen-Clapeyron equation

$T_n = (\frac{1}{T_0} - \frac{R\ln(\frac{p_n}{p_0})}{\Delta H_{vap}})^{-1}$ *subscripts: n-new, o-original* Change of boiling point w/ change pressure

Fundamental Equation of Chemical Thermodynamics

$dG = (\frac{\delta G}{\delta T})_{P,n_1,n_2,\ldots}dT + (\frac{\delta G}{\delta p})_{T,n_1,n_2,\ldots}dp + (\frac{\delta G}{\delta n_1})_{T,n_2,n_3,\ldots}dn_1 + (\frac{\delta G}{\delta n_2})_{T,n_1,n_3,\ldots}dn_2 \ldots$

$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 + \ldots$

$dG = (\frac{\delta G}{\delta T})_{P,n_1,n_2,\ldots}dT + (\frac{\delta G}{\delta p})_{T,n_1,n_2,\ldots}dp + \Sigma\, n_i\mu_i$

$dG = \Sigma\, \mu_i dn_i$ *[At const T, p for a given mole ratio]*

Gibbs-Duhem Equation

$G = \Sigma\, n_i\mu_i$

$dG = \mu_A dn_A + \mu_B dn_B + \mu_A dn_B + \mu_B dn_A$ Const T, p :: $dG = \mu_A dn_A + \mu_B dn_B$

$n_A d\mu_A + n_B d\mu_B = 0$ **Gibbs-Duhem equation**

$X_A d\mu_A + X_B d\mu_B = 0$ in terms of mole fractions

$d\mu_B = -\frac{n_A}{n_B}d\mu_A$

Chemical potential

$d\mu = dG_m = -S_m dT + V_m dp = (\frac{d\mu}{dT})_p dT + (\frac{d\mu}{dp})_T dp$

$-S_m = (\frac{d\mu}{dT})_p$; $V_m = (\frac{d\mu}{dp})_T$

$\Delta G_m = \int_{p_i}^{p_f} V_m dP$

$\sim= V_m\Delta p$ solids/liquids

$= RT\ln(\frac{p_f}{p_i})$ perfect gases

$G_m(p) = G_m^o + RT\ln(\frac{p}{p_o})$

$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1)(\frac{1}{T_2} - \frac{1}{T_1})$ :: $\Delta G(T_2) = \Delta G(T_1)\frac{T_2}{T_1} + \Delta H(T_1)(1 - \frac{T_2}{T_1})$

Equilibrium

$AK_W + BL_X \text{ <–> } CM_Y + DN_W$

$\Delta_f G^o = \sum_i v_i G_f^0$; $\alpha = (n_r - n_p)/n_r$ (degree of dissociation)

$\Delta_r G = \Delta_r G^o + RT\ln(Q) = \mu_B - \mu_A$ $Q = \frac{p_M}{p_K} = \frac{p_M^C p_N^D}{p_K^A p_L^B}$

$\Delta_r G^o = -RT\ln(K)$ $K = Q_{equilibrium}$

$K_C = \prod_i (\frac{c_i}{c^o})^{v_i}$ $Q_p = \frac{p_M^C p_N^D}{p_K^A p_L^B} = \prod_i (\frac{c_i}{c^o})^{v_i}$ v is the coefficient or moles

$K_p = e^{\frac{-\Delta_r G^o}{RT}} = e^{(\frac{\Delta_r S^o}{R} - \frac{\Delta_r H^o}{RT})} = \prod_i \left(\frac{p_i}{p^o}\right)^{v_i} = \prod_i \left(\frac{x_i p}{p^o}\right)^{v_i} :: K_u = \prod_i (a_i)^{v_i} = \prod_i \left(\frac{u_i}{u^o}\right)^{v_i}$ *where u is p, c, or b*

$K_p = K_C\left(\frac{p}{p^o}\right)^{\Delta v} = K_C(\frac{T}{12.03})^{\Delta v}$ [$= K_x(\frac{p}{p^o})^{\Delta v}$ *where* $K_x = \prod_i x_i$]

$\ln K_p(T_2) = \ln K_p(T_1) - \frac{\Delta_r H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ :: $K_p(T_2) = K_p(T_1)e^{\frac{-\Delta_r H^o}{R}(\frac{1}{T_2} - \frac{1}{T_1})}$

Energy of Activation

$k = Ae^{-E_a/RT}$ (k is reaction rate) :: $k_2(T_2) = k_1(T_1)e^{\frac{-E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$

Mixing – Perfect gases and ideal solutions *unless otherwise noted A=solvent, B=Solute, * =pure substance*

Perfect/Ideal	Real
$p = \frac{p}{p^o}$ *if in bar*	
$x_i = \frac{p_i}{p_i^*}$	$a_i = \frac{p_i}{p_i^*} = \frac{p_i}{K_i} = \gamma_i x_i = \gamma_{b,i}\frac{b_i}{b^o} = \gamma_{c,i}\frac{c_i}{c^o}$ *(Effective mole fraction)*
$x_B = a_B$	$f = \gamma p = \gamma_{b,i}\frac{b_i}{b^o} = \gamma_{c,i}\frac{c_i}{c^o}$
$\mu_A = \mu_A^* + RT\ln(\frac{p_A}{p_A^*})$	$\mu_A(l) = \mu_A^*(l) + RTln(a_A)$
$\mu_B = \mu_B^o + RT\ln(x_B)$	$\mu_B = \mu_B^o + RT\ln(a_B)$
(where $\mu^* = \mu_B^o + RT\ln(\frac{p_B^*}{K_B})$ & $x_B = \frac{p_B}{K_B}$)	$\mu_A = \mu_B^* + RT\ln(x_B) + RT\ln(\gamma_B)$
$\mu_A = \mu_A^* + RT\ln(x_A)$	$\mu_A(l) = \mu_A^*(l) + RT\ln(x_A) + RT\ln(\gamma_A)$
	$\mu_A(l) = \mu_A^*(l) + RTln(a_A)$
$\mu(p) = \mu^o + RTln\left(\frac{p}{p^o}\right)$	$\mu(p) = \mu^o + RTln\left(\frac{f}{f^o}\right)$ :: $G_A = G_A^o + RT\ln(\frac{f}{f_A^o})$

$\mu = \mu^o + RT\ln\left(\frac{p}{p^o}\right) = \mu^o + RT\ln(\frac{f}{f^o})$

$\mu^*(l) = \mu^o(g) + RT\ln(p_{vap}^*)$

$\mu_A(l) = \mu_A^*(l) + RT\ln(x_A)$ :: $\mu_A^o(l) = \mu_A^*(l) + RT\ln(\frac{K_A}{p_A^*})$

$\mu_A^o(g) = \mu_A^*(l) + RT\ln(p_A^*)$

$\mu_A^*(g) = \mu_A^*(l) + RT\ln(x_A)$ boiling point elevation

$\Delta T_b = \frac{RT_{vap}^{2*}}{\Delta_{vap}H}x_B = K'x_B = \frac{RM_AT_{vap}^{2*}}{\Delta_{vap}H}b = K_b b$ *(at low molalities)*

$\mu_A^*(s) = \mu_A^*(l) + RT\ln(x_A)$ freezing point depression

$\Delta T_f = -\frac{RT_{fus}^{2*}}{\Delta_{fus}H}x_B = -K'x_B = -\frac{RM_AT_{fus}^{2*}}{\Delta_{fus}H}b = -K_b b$ *(at low molalities)*

$K' = \frac{RT_{trs}^{*2}}{\Delta_{trs}H}$ $K_b = \frac{RM_AT_{trs}^{*2}}{\Delta_{trs}H}$

$\Delta_{mix}G = nRT(\sum x_i ln x_i) = nRT\ln(\prod x_i^{x_i}) = RT(\sum n_i ln x_i)$ Ideal solution

$\Delta_{mix}\mu = RT(\sum x_i ln x_i) = RT\ln(\prod x_i^{x_i})$ Ideal solution

$\Delta_{mix}S = -nR(\sum x_i ln x_i) = -nR\ln(\prod x_i^{x_i}) = -R(\sum n_i ln x_i)$ Ideal solution

$\Delta_{mix}H = 0$ :: $\Delta_{mix}V = 0$

$p_i = x_i p_i^*$ **Raoul's Law**

$p_i = x_i K_i$ for solute **Henry's Law**

$\Pi = c_B RT = \frac{c_B RT}{(\rho - c_B M_B)} = \frac{n_B RT}{V} = \frac{RT}{V_{M,B}}$ **Van't Hoff Formula** (Osmotic pressure)

$\ln x_B = \frac{\Delta_{fus}H}{R}(\frac{1}{T_f} - \frac{1}{T})$ **Clausius-Clapeyron equation** (Solubility)

Electrochemical cells, potentials *n is number of electrons xferred in equation*

$\Delta G = -nFE$ $\Delta G^o = -nFE^o$

$\Delta_r G = \Delta_r G^o + RTln\frac{c_{M^{\#+}}}{c_{\mathbf{M}^{\#+}}}$

$E = E^o - \frac{RT}{nF}lnQ$ (Nernst Equation) $E^o = \frac{RT}{nF}lnK$

$E^o = E^o_{reduction} + E^o_{oxidation}$

@T = 298.15K $E = E^o - \frac{0.05916}{n}lnQ$

Partial – molar volume, potentials

$\mu_i = (\frac{\delta G}{\delta n_i})_{T,p,n'}$ Definition of chemical potential

$V_i = (\frac{\delta V}{\delta n_i})_{T,p,n'}$

$b_B = \frac{c_B}{(\rho - c_B M_B)} = \frac{n_B}{m_A}$ molality from molarity | b_B molality; c_B molarity

$c_B = \frac{b_B \rho}{(1 + b_B M_B)} = \frac{n_B}{V}$ molarity from molality

$p = p_B^* + (p_A^* - p_B^*) x_A$ Relationship total pressure to partial pressure

Molar fractions: y = vapor phase, x = solvent phase, z = for both phases

V subscript is vapor, L is liquid, l and l both refer to interval length in phase diagram

$$y_a = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} = \frac{n_{A,V}}{n_V} = \frac{n_{A,V}}{n_{A,V} + n_{B,V}}; \qquad y_B = 1 - y_A$$

$$x_A = \frac{y_A p_B^*}{p_A^* + (p_B^* - p_A^*) x_A} = \frac{n_{A,L}}{n_L} = \frac{n_{A,L}}{n_{A,L} + n_{B,L}}; \qquad x_B = 1 - a_A$$

$y_A = \frac{p_A^* p - p_A^* p_B^*}{p(p_A^* - p_B^*)}$ vapor mole fraction

$$z_A = \frac{y_A p_B^*}{p_A^* + (p_B^* - p_A^*) x_A} = \frac{n_A}{n} = \frac{n_{A,L} + n_{A,V}}{n_{A,V} + n_{B,V} + n_{A,L} + n_{B,L}}$$

$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A}$ total pressure

Lever Rule

$n_L(z_A - x_A) = n_V(y_A - z_A)$ or

$n_L l_L = n_V l_V$ :: $l_L = (z_A - x_A)$; $l_V = (y_A - z_A)$

Constants

R = Gas constant = $N_A k$ *(8.31446 J/Kmol or Pa m^3 /K mol)* = 0.0831445 *(dm^3 bar /K mol)*
= (0.0820574 dm^3 atm /K mol) = (62.364 dm^3 Torr/K mol) = (1.98721 cal/K mol)

C_s water = 4.184 $(\frac{J}{g\,K}) = 1\ \frac{cal}{g\,K}$; C_m water = 75.4 $(\frac{J}{mol\,K})$; k = Boltzmann's constant *(1.38065x10^{-23} J/K)*

atm = 1.01325 bar = 101325 Pa = 760 torr ; bar = 1.0x10^5 Pa torr = mmHg = 133.322 Pa

Legend

d = distance, Collision diam	A = area, Helmholtz free energy	p = pressure (N/m^2)
V = volume	V_m = molar volume (V/n)	V_m^0 = molar vol of ideal gas
H = Enthalpy (J)	G = Gibbs free energy	A = Helmholtz free energy
U = Internal energy	w = work (J)	q = heat energy (J)
M = molar mass (Kg/mol)	F = force (N; Kg m/s^2)	n = moles (mol)
$\mathcal{W}$ = number of microstates	N = total molecules	N_A = Avogadro's number
$\mathcal{N}$ = number density (N/V)	E = Energy; electric field (J; N/C or V/m)	J = Joules (Nm or kg m^2/s^2)
π_T = Internal pressure $(\frac{J}{m^3})$	α = expansion coefficient	$\mathcal{K}_T$ =compressibility coefficient
H° = Std Enthalpy (J)	G° = Std Gibbs free energy	A° = Std Helmholtz free energy
$C_{V,s} = C_s$ = Specific Heat Capacity $(\frac{J}{<unit>\,K})$	$C_{V,m} = C_m$ = Molar Heat Capacity, V	$C_{V,m}$ = Molar Heat Cap, const p
Q = Rxn quotient	R = Thermodynamic Equilibrium Const (= Q_{Equil})	
R = Gas constant = $N_A k$ *(8.31446* J/Kmol)	k = Boltzmann's constant *(1.38065x10^{-23} J/K)*	