

Selected Equations for Chemistry BC3254y

Partial molar quantities: $Y_k = (\partial Y / \partial n_k)_{p,T,n'}$ Gibbs-Duhem equation: $\sum_k n_k Y_k = 0$

At fixed (p, T) $\rightarrow \sum_k n_k d\mu_k = 0 \rightarrow \sum_k n_k d \ln a_k = 0$

Non-ideal gases:

Fugacity: $f = \gamma p$ $\alpha = RT/p - V_m$ $\ln \gamma = -(1/RT) \int \alpha dp$ integral from 0 to p
for intermediate pressures, $\ln \gamma = Bp/RT$

where B = second virial coefficient: $pV_m = RT + Bp$

Non-ideal Solutions: A = solvent, B = solute, $a_k = \gamma_k [k]$

Convention I Activities $a_A = p_A / p_A^*$ $a_B = p_B / p_B^*$

Convention II Activities $a_A = p_A / p_A^*$ $a_B = p_B / K_{B(A)}$

Osmotic coefficient $\phi = -(n_A/n_B) \ln a_A$

$\ln \gamma_A = (\phi - 1) + \int [(\phi - 1)/m] dm$ integral from 0 to m.

Colligative properties: approximate better

BP elevation $\Delta T = i K_b m$ $\ln a_A = (\Delta_{\text{vap}} H^\circ / R)(1/T - 1/T^*)$ $\phi = \Delta T / i K_b m$

Osmosis $\Pi = i c RT$ $\ln a_A = -\Pi V_A / RT$ $\phi = \Pi / i c RT$

Ionic solutions: $I = \frac{1}{2} \sum_{\text{all ions}} c_j z_j^2$ $a_{\pm}^v = (a_+)^{v+} (a_-)^{v-}$ $\gamma_{\pm}^v = (\gamma_+)^{v+} (\gamma_-)^{v-}$

Debye-Hückel Limiting law: $\ln \gamma_j = -A z_j^2 I^{1/2}$ A = 0.5911 (molality), 0.5115 (molarity)

Statistical Thermodynamics

$W = N! / \prod_k n_k!$

$p_j = n_j / N = q_j / q \exp\{-(\epsilon_j - \epsilon_0) / kT\}$ $q = \sum_j g_j \exp\{-(\epsilon_j - \epsilon_0) / kT\}$

$q = q^E q^T q^V q^R q^N$ $q^T = V / \Lambda^3$ where $\Lambda = h / (2\pi m kT)^{1/2}$

$q^V = \prod_j [1 / (1 - \exp(-h\nu_j / kT))]$ when $h\nu_j \gg kT$

q^R (linear) = $(1/\sigma) \sum_J (2J+1) \exp(-BJ(J+1)/kT)$ $B = \hbar^2 / 2I \rightarrow kT / \sigma B$ when $B \ll kT$

q^R (non-linear) = $(\pi^{1/2} / \sigma) (kT/A)^{1/2} (kT/B)^{1/2} (kT/C)^{1/2}$ where $A = \hbar^2 / 2I_A$ etc.

In most cases, $q^E = g_0$ (degeneracy of ground electronic state)

$Q = q^N$ when distinguishable, $Q = q^N / N!$ when not distinguishable

$U = U_0 = nRT^2 (\partial \ln q / \partial T)_{V,n}$ $G = U_0 - nRT \ln (q / N_A)$

Sackur-Tetrode (monatomic gas): $S_m / R = (5/2) + \ln(V / N \Lambda^3)$

$K_{\text{eq}} = \exp(-\Delta_r U^\circ) \prod (q_j / N_A)^{v_j}$

Maxwell-Boltzmann Distribution and Collisions

1D: $D(u) du = (m/2\pi kT) \exp(-mu^2/2kT) du$

3D: $D(u) du = 4\pi(m/2\pi kT)^{3/2} u^2 \exp(-mu^2/2kT) du$

$D(\epsilon) d\epsilon = 2\pi / (\pi kT)^{3/2} \epsilon^{1/2} \exp(-\epsilon/kT) d\epsilon$

$\langle u \rangle = (8RT/\pi M)^{1/2} = (8kT/\pi m)^{1/2}$ $\langle u_{\text{rel}} \rangle = (8kT/\pi \mu)^{1/2}$ $u_{\text{RMS}} = (3kT/m)^{1/2}$

$Z_W = n^* \langle u \rangle / 4$ $Z_A = n^* \sigma_{AA} \langle u \rangle \sqrt{2}$ Mean free path $\lambda = \langle u \rangle / Z_A$

$Z_{AA} = (n_A^*)^2 \sigma_{AA} \langle u \rangle / \sqrt{2}$ $Z_{AB} = n_A^* n_B^* \sigma_{AB} \langle u_{\text{rel}} \rangle$

Transport Properties: $v_{ss} = -F/f$

Partial specific volume: $\bar{v}_s = (\partial V / \partial w)_{p,T,n'}$

Buoyancy $b = (1 - \rho_0 / \rho) = (1 - \rho_0 \bar{v}_s)$ $v_{ss} = mbg/f$

Thermal Conductivity $J_x = -\kappa dT/dx$ Kinetic theory: $\kappa = (25\pi/64) \lambda \langle u \rangle n^* c_v$

Diffusion

Fick's 1st Law (1D): $J_x = -D dc/dx$ 2nd Law(1D): $(\partial c / \partial t)_x = D (\partial^2 c / \partial x^2)$

$D = kT/f$ Einstein-Smoluchowski: $\langle \Delta x^2 \rangle = 2Dt$

Stokes' Law (sphere): $f = 6\pi\eta r$ Stokes-Einstein: $D = kT/6\pi\eta r$

Kinetic theory: $D = (3\pi/16) \lambda \langle u \rangle$

Viscosity

Newton's Law of viscous flow: $F = \eta A (dv/dx)$

Poiseuille's law (liquids): $V = (\pi r^4 \Delta p / 8\eta l) t$

Kinetic theory: $\eta = (5\pi/32) \lambda \langle u \rangle \rho$

Macromolecules: $\eta_{sp} \equiv (\eta - \eta_0) / \eta_0 = v \Phi$ $\Phi = V_{solute} / V_{solution} = \bar{v}_s c$ where $c = w_s / V$
 $v = 2.5$ for spheres, > 2.5 otherwise.

Reynolds Number: $R = 2\rho r v / \eta$

Sedimentation:

$s = v_{ss} / \omega^2 r = mb/f$ $M = RTs / Db$

Electrochemistry

Nernst equation: $\Delta \mathcal{E} = \Delta \mathcal{E}^\circ - (RT/n\mathcal{F}) \ln Q = \Delta \mathcal{E}^\circ - (k_N/n) \log Q$

Ions in Motion

Ohm's Law: $I = \mathcal{E} / R$

$R = \rho (\ell / A)$ $G = 1/R$ $\kappa = 1/\rho$

$\Lambda = \kappa / c^*$, $\Lambda_m = \kappa / c$ Kohlrausch's Law: $\Lambda = \Lambda^\circ - K\sqrt{c}$

$\Lambda^\circ = \sum_k \lambda_k^\circ$ Mobility: $u = v/E = ze / f$ $u_k = \lambda_k / |z_k| \mathcal{F}$

Radiochemistry

$A = \lambda N$ $N = N_0 \exp(-\lambda t)$ $t_{1/2} = \ln 2 / \lambda$