# Final Exam

March 17, 2008

Law I $\Delta U = q + w$

$U = U(T,V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

LawII: $dS = \frac{q_{rev}}{T}$

$S = S(T,V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Comb I,II: $dU = TdS - PdV$

$H = U + PV; \ A = U - TS$

$G = H - TS; \ dG = -SdT + VdP$

Thermodynamic Equation of State

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}; \ \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P;$$

$$\mu_A = \mu_A^o + RT\ln\frac{P_A}{P_o}$$

Dalton's Law

$P_A = \chi_A P_{Tot}; \quad P_T = \sum_A P_A; \ G = \sum n_i \mu_i$

$$\Delta G_{mix} = RT\sum n_i \ln\left(\frac{P_i}{P_o}\right)$$

$P_A = x_A P_A^* = y_A P_{Tot}$ Raoult/Dalton Law

$n_\ell(Z - \chi) = n_v(y - Z)$ Lever Rule

Calculus Identities:

$$\Delta Z = \int_{x_i}^{x_f}\left(\frac{\partial Z}{\partial x}\right)_y dx$$

Cyclic rule: $\left(\frac{dx}{dy}\right)_z\left(\frac{dz}{dx}\right)_y\left(\frac{dy}{dz}\right)_x = -1$

$$\frac{d(yz)}{dx} = z\frac{d(y)}{dx} + y\frac{d(z)}{dx}$$

$$\frac{dx}{dz} = \frac{dy}{dz}\frac{dx}{dy}; \ \left(\frac{\partial x}{\partial z}\right)_a = \left(\frac{\partial y}{\partial z}\right)_a\left(\frac{\partial x}{\partial y}\right)_a$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \kappa = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

vdW Gas EoS: $P = \frac{RT}{V_m - b} - \frac{a}{V_m^{\ 2}}$

$$\Delta H_{rxn}^o = \sum_i \nu_i \Delta H_f^o(i)$$

$$\Delta S_{rxn}^o = \sum_i \nu_i S_f^o(i)$$

$$dn_i = n_i - n_i^{Init} = \nu_i dX$$

$$\Delta C_{P,rxn} = \sum_i \nu_i C_{P,m}(i)$$

$$\Delta H^o = \Delta H_{rxn}^o dX$$

$$\Delta G_{rxn} = \Delta G_{rxn}^o + RT\ln Q_P = RT\ln\frac{Q_P}{K_P}$$

$\Delta E = \Delta E^o - \frac{RT}{\nu_e F}\ln Q_P$ Nernst Eqn.

$Q_P = \prod_{i=1}^{N}\left(\frac{P_i}{P_o}\right)^{\nu_i}$ @Eq $Q_P = K_P$

$$K_P = \left(\frac{P}{P_o}\right)^{\Delta\nu} K_x = \left(\frac{c_o RT}{P_o}\right)^{\Delta\nu} K_c$$

$\ln\left(\frac{K_P(T_2)}{K_P(T_1)}\right) = -\frac{\Delta H_{rxn}^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ Van't Hoff Eqn :

$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H^{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ Clausius-Clapeyron

$\left(\frac{\partial P}{\partial T}\right)_{\Delta\mu} = \frac{\Delta S}{\Delta V}$ Clapeyron

Constants:

$R = 8.3 J / mol - K$

$R = 0.082 L - atm / mol - K$

$R \cdot 300 = 2.5\ kJ / mol$

$\frac{R \cdot 300}{F} = 25 mV$

$1 bar = 10^5 Pa$

$T(K) = T(C) + 273.15$

F=96,500Coulombs/mole-e

**Show your work throughout; clearly show what equations you are using, and always show units for computed quantities**.

More equations of state and Maxwell relations:

$dU = TdS - PdV \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$

$\frac{\Delta S_{\alpha,\beta}}{\Delta V_{\alpha,\beta}} = \frac{dP}{dT}$

Useful equations for non-ideal gases:

$z = \frac{PV}{RT} \qquad \ln\gamma = \int_0^P \frac{\{z-1\}}{P'}dP'$

Useful equations for ionic solutions and electrochemistry:

$\Delta G_{rxn} = -\nu_e F \mathrm{E}(V)$

$dq = Idt$

$dG = \Delta G_{rxn} dX$

$I = \frac{1}{2}\left(\nu_+ z_+^2 + \nu_- z_-^2\right)m$

$\ln\gamma_\pm = -1.173|z_+ z_-|\sqrt{I}$

$\ln\gamma_\pm = 2.3 \cdot \log_{10}\gamma_\pm$

Appx Values $\quad \log_{10} 5 = .7 \qquad \ln 2 = .7 \qquad \log_{10} 2 = .3$

$E = E^o - \frac{RT}{\nu_e F}\ln Q = -\frac{RT}{\nu_e F}\ln\frac{Q}{K} \qquad Q = \prod_{i=1}^{N}(a_i)^{\nu_i} = \prod_{i=1}^{N}\left(\gamma_i \frac{c_i}{c_o}\right)^{\nu_i}$

$\mu_A = \mu_A^o + RT\ln a_A$

$a_A = \gamma_A x_A$

Cu half cell reduction potential: $Cu^{2+} + 2e^- \rightarrow Cu \qquad E^o = 0.34V$