PARTIAL DERIVATIVE RELATIONS FOR *f(x,y)*

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

If *f(x,y)* also depends on *z* then the following relations apply:

1. $\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$

2. $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$

3. $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$

2 and 3 combine to give Euler's Chain Relation: $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

When $df(x,y) = g(x,y)dx + h(x,y)dy$ then $\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$

all the equations in no particular order

Ch. 1 - $pV = nRT$; $Z = \frac{V_m}{V_m^\circ}$; $pV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2}\right)$; $p = \frac{nRT}{(V - nb)} - a\left(\frac{n}{V}\right)^2$

Ch. 2 - $\Delta U = q + w$; $dw = -Fdz$; $dw = -p_{ex}dV$; $w = -p_{ex}\Delta V$;

$w = -nRT\ln\left(\frac{V_f}{V_i}\right)$

$\Delta U = q_V$; $q = C\Delta T$; C=calorimeter constant; $C_V = \left(\frac{\partial U}{\partial T}\right)_V$; $dU = C_V dT$

$H = U + pV$; $\Delta H = q_p$; $\Delta H = \Delta U + \Delta n_g RT$; $C_p = \left(\frac{\partial H}{\partial T}\right)_p$; $C_p - C_V = nR$

$T_f = T_i\left(\frac{V_i}{V_f}\right)^{1/c}, c = \frac{C_{V,m}}{R}$; $\Delta_{rxn}H^\circ = \sum_{products} \nu\Delta_f H^\circ - \sum_{reactants} \nu\Delta_f H^\circ$

$\Delta_{rxn}H^\circ(T_2) = \Delta_{rxn}H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_{rxn}C_p^\circ dT$

$\mu = \left(\frac{\partial T}{\partial p}\right)_H$

Ch. 3 - $dS = \frac{dq_{rev}}{T}$; $\varepsilon = \frac{|w|}{q_h}$; $\varepsilon = 1 - \frac{T_c}{T_h}$; $dS \geq \frac{dq}{T}$; $\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$;

$\Delta S = nRln\frac{V_f}{V_i}$; $S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p}{T} dT$; $\Delta S_m = C_{p,m} \ln \frac{T_f}{T_i}$;

$\Delta S = \frac{q_{sur}}{T} = -\frac{q_{rev}}{T} = -nR \ln \frac{V_f}{V_i}$; $S(T) = S(0) + \sum_{phases} \int_0^T \frac{C_p}{T} dT + \sum_{transitions} \frac{\Delta_{trs}H}{T_{trs}}$;

$A=U-TS$; $dA=dU-TdS=-TdS-PdV$; $w_{max}=\Delta A$; $G=H-TS$; $dG=dH-TdS=-SdT+VdP$; $w_{add,\,max}=\Delta G$;

$dU=TdS-pdV$; $dH=TdS+VdP$;dA $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$; $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$;

$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$; $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$; $\left(\frac{\partial}{\partial T}\frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2}$; $(\frac{\partial \Delta G}{\partial p})_T = \Delta V$;

$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$; $G(p_f) = G(p_i) + V_m \Delta p$;

$G(p_f) = G(p_i) + nRT \ln \frac{p_f}{p_i}$;

Ch. 4 - $\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$; $\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$; $p = p^* e^{V_m \Delta p / RT}$;

$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} = \frac{\Delta_{trs}H}{T\Delta_{trs}V}$ *(any boundary);* ***s-l*** $p \approx p^* + \frac{\Delta_{fus}H}{T^*\Delta_{fus}V}(T - T^*)$; *l-g*

Clausius-Clapeyron equation: $\frac{d \ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$ ***OR*** $\ln \frac{p_f}{p_i} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$

OR $p = p^* e^{-\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)}$.

Ch. 5 - $V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$;

$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B$; $\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$;

$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \ldots$ but under constant pressure and temperature -

$dG = \mu_A dn_A + \mu_B dn_B + \ldots$; $\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'}$; $\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{p,S,n'}$;

$\mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{V,T,n'}$; $\sum_J n_J d\mu_J = 0$; $\mu = \mu^{\circ} + RT \ln \frac{p}{p^{\circ}}$; ; *for the mixing of ideal*

gases $\Delta_{mix}G = n_A RT \ln\frac{p_A}{p} + n_B RT \ln\frac{p_B}{p} = nRT\left(\chi_A \ln\chi_A + \chi_B \ln\chi_B\right)$;

$\Delta_{mix}S = -nR\left(\chi_A \ln\chi_A + \chi_B \ln\chi_B\right)$, *and* $\Delta_{mix}H = 0$ *Ideal-dilute solutions -*

$p_B = \chi_B K_B$ *(Henry's Law), Colligative Properties -* $\Delta T_b = K\chi_B$ *where* $K = \frac{RT_b^{*2}}{\Delta_{vap}H}$,

$\Delta T_f = K'\chi_B$ *where* $K' = \frac{RT_f^{*2}}{\Delta_{fus}H}$, $\prod = [B]RT$. *Solvent activity,* $a_A = \gamma_A\chi_A$ $\gamma_A \to 1$ *as*

$\chi_A \to 1$ *and* $\mu_A = \mu_A^* + RT\ln\chi_A + RT\ln\gamma_A$. *Solute activity, for ideal dilute solution -*

$\mu_B = \mu_B^* + RT\ln\frac{K_B}{p_B^*} + RT\ln\chi_B$ *or* $\mu_B = \mu_B^{\circ} + RT\ln\chi_B$ *where* $\mu_B^{\circ} = \mu_B^* + RT\ln\frac{K_B}{p_B^*}$.

For real solutions, $\mu_B = \mu_B^{\circ} + RT\ln a_B$ *where* $a_B = \gamma_B\chi_B$ *and* $\gamma_B \to 1$ *as* $\chi_B \to 0$. *Can also define activities in terms of molalities so that* $a_B = \gamma_B\frac{b_B}{b^{\circ}}$.

Ch. 6 *– The Phase Rule: F = C – P + 2.*

Ch. 7 - $\Delta G_{rxn} = \left(\frac{\partial G}{\partial\xi}\right)_{p,T} = \mu_B - \mu_A$, $\Delta G_{rxn}^{\circ} = \mu_B^{\circ} - \mu_A^{\circ} = \sum_J \nu_J \Delta G_f^{\circ}(J)$. *At any point in a reaction sequence:* $\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RT\ln Q$, *where* $Q = \prod_J a_J^{\nu_J}$. *BUT at equilibrium*

$\Delta G_{rxn} = 0 = \Delta G_{rxn}^{\circ} + RT\ln K$, *where* $K = \left(\prod_J a_J^{\nu_J}\right)_{equilibrium}$. *Responses to stresses:*

$\left(\frac{\partial K}{\partial p}\right)_T = 0$. *So that when* α *is the extent of dissociation partial pressures respond such that*

$\alpha = \left(\frac{1}{1+{}^{4p}\!/_{K}}\right)^{1/2}$. *The van't Hoff eqn.:* $\left(\frac{d\ln K}{dT}\right) = \frac{\Delta H_{rxn}^{\circ}}{RT^2}$ *or* $\left(\frac{d\ln K}{d\left(\frac{1}{T}\right)}\right) = -\frac{\Delta H_{rxn}^{\circ}}{R}$ *so*

that $\ln K_2 - \ln K_1 = -\frac{\Delta H_{rxn}^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$.

$\Delta_r G = -nFE$; $E = E^o - \frac{RT}{nF}\ln Q$; $\Delta_r G^0 = -nFE^0$; $E^0 = \frac{RT}{nF}\ln K$

Ch. 22 - *Rate* $= \frac{d\xi}{dt} = \frac{1}{v_J}\frac{dn_J}{dt} = \frac{1}{v_J}\frac{d[J]}{dt}$. *First order reactions:* $\frac{d[A]}{dt} = -k[A]$;

$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$ *or* $[A] = [A]_0 e^{-kt}$. $t_{1/2} = \frac{\ln 2}{k}$ *and* $\tau = \frac{1}{k}$. *Second order reactions*

(2A→P): $\frac{d[A]}{dt} = -k[A]^2$;

$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$ *or* $[A] = \frac{[A]_0}{1+kt[A]_0}$ *with* $t_{1/2} = \frac{1}{k[A]_0}$. *Arrhenius Equation -*

$\ln k = \ln A - \frac{E_a}{RT}$ *or* $k = Ae^{-\frac{E_a}{RT}}$ *For* $A \xrightarrow{k_a} I \xrightarrow{k_b} P$, *the steady state approximation assumes* $\frac{d[I]}{dt} = 0$