Chemistry 231 **<u>Physical Constants, Conversion Factors and Equations</u>** (final exam)

Physical Constants and Conversion Factors

$R = 8.3145$ J K^{-1} mol^{-1} = 0.083145 L bar K^{-1} mol^{-1} = 0.082058 L atm K^{-1} mol^{-1}

$N_A = 6.0221 \times 10^{23}$ mol^{-1} $\quad k_B = R/N_A \quad T/\text{K} = t/^{\circ}\text{C} + 273.15$

1 bar = 10^5 Pa $\quad$ 1 atm = 1.01325 bar $\quad$ 1 mm Hg = 133.32 Pa

1 L bar = 100 J $\quad$ 1 m^3 = 1000 L $\quad$ 1 L = 1000 cm^3

First Law

$dU = dq + dw \qquad \Delta U = q + w \qquad \Delta U = U_f - U_i$

$\Delta U = w_{\text{adiabatic}} \qquad (\Delta U = 0)_{\text{isolated system}} \qquad 0 = \oint dU$ (cyclic process)

$dw = -p_{\text{external}}dV$ (expansion/compression work) $\qquad w = -\int_{V_i}^{V_f} p_{\text{external}}dV$

$p = p_{\text{external}}$ (reversible) $\qquad p < p_{\text{external}}$ (irrev. compression) $\qquad p > p_{\text{external}}$ (irrev. expansion)

$w_{\text{rev}} = -\int_{V_i}^{V_f} p\,dV \qquad w_{\text{rev(const.}p)} = -p(V_f - V_i) \qquad w_{\text{irrev(const. external }p)} = -p_{\text{external}}(V_f - V_i)$

$H = U + pV \qquad \Delta H = H_f - H_i \qquad \Delta H = \Delta U + \Delta(pV) = U_f - U_i + p_fV_f - p_iV_i$

$C_V = \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_p = \frac{dq_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p \qquad C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p = \frac{\beta^2 VT}{\kappa}$

$q_V = \Delta U_V = \int_{T_i}^{T_f} C_V dT \qquad q_p = \Delta H_p = \int_{T_i}^{T_f} C_p dT$ (only $p-V$ work)

$\beta = V^{-1}(\partial V/\partial T)_p = -\rho^{-1}(\partial\rho/\partial T)_p \qquad \kappa = \kappa_T = -V^{-1}(\partial V/\partial p)_T = \rho^{-1}(\partial\rho/\partial p)_T$

$\beta_{\text{linear}} = \beta/3 = \ell^{-1}(\partial\ell/\partial T)_p \qquad (\partial p/\partial T)_V = \beta/\kappa \qquad \mu_{JT} = (\partial T/\partial p)_H = -V_m(1-\beta T)/C_{pm}$

$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V\,dT + \left(\frac{\beta T}{\kappa} - p\right)dV \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{\beta T}{\kappa} - p$

$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_p\,dT + V(1-\beta T)\,dp \qquad \left(\frac{\partial H}{\partial p}\right)_T = V(1-\beta T)$

$\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y = \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x \qquad \left(\frac{\partial f}{\partial y}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial f}\right)_x} \qquad \left(\frac{\partial f}{\partial y}\right)_x = -\left(\frac{\partial f}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_f$

$du = g(x,y)dx + h(x,y)dy \qquad du$ is exact and the function $u(x,y)$ exists if $\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$

Second Law

$$\Delta U_{\mathrm{cycle}} = q_{\mathrm{H}} + q_{\mathrm{C}} + w = 0 \qquad \varepsilon = \frac{-w}{q_{\mathrm{H}}} = 1 - \frac{T_{\mathrm{C}}}{T_{\mathrm{H}}} \qquad \frac{q_{\mathrm{H}}}{T_{\mathrm{H}}} + \frac{q_{\mathrm{C}}}{T_{\mathrm{C}}} = 0$$

$$\oint \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = 0 \qquad \mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T} \qquad \Delta S_{\mathrm{cycle}} = 0 \qquad (\Delta S \geq 0)_{\text{isolated system}} \qquad (\Delta S \geq 0)_{U,V}$$

$$\oint \frac{\mathrm{d}q}{T} \leq 0 \qquad S = k \ln W \qquad S_{\mathrm{m}}{}^{\mathrm{o}}(T, p^{\mathrm{o}}) = \int_{T=0}^{T} \frac{C_{p\mathrm{m}}{}^{\mathrm{o}}}{T}\mathrm{d}T + \sum_i \frac{\Delta H_{\mathrm{m}}{}^{\mathrm{o}}(\text{transition } i)}{T_i}$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad C_p = T\left(\frac{\partial S}{\partial T}\right)_p \qquad \mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \frac{\beta}{\kappa}\mathrm{d}V \qquad \mathrm{d}S = \frac{Cp}{T}\mathrm{d}T - \beta V \mathrm{d}p$$

Combined First and Second Laws

$$H = U + pV \qquad A = U - TS \qquad G = U + pV - TS$$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V \qquad \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p = \left(\frac{\partial H}{\partial S}\right)_p \mathrm{d}S + \left(\frac{\partial H}{\partial p}\right)_S \mathrm{d}p$$

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V = \left(\frac{\partial A}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial A}{\partial V}\right)_T \mathrm{d}V \qquad \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p = \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p \qquad \left(\frac{\partial H}{\partial S}\right)_p = T \qquad \left(\frac{\partial H}{\partial p}\right)_S = V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -p \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

$$-w_T \leq -\Delta A_T \qquad -w_T{}' \leq -\Delta G_T \qquad \mathrm{d}q \leq T\mathrm{d}S$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

$$\mathrm{d}U_{S,V} \leq 0 \qquad \mathrm{d}H_{S,p} \leq 0 \qquad \mathrm{d}A_{T,V} \leq 0 \qquad \mathrm{d}G_{T,p} \leq 0$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p \qquad \left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2} \qquad \mu_i = G_{\mathrm{m}i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{k\neq i}}$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu_1 \mathrm{d}n_1 + \mu_2 \mathrm{d}n_2 + \mu_3 \mathrm{d}n_3 + \cdots \quad \text{(systems of variable composition or variable mass)}$$

$$G = n_1\mu_1 + n_2\mu_2 + n_3\mu_3 + \cdots$$

Thermochemistry

$q_p = \Delta H^o = \Delta H_f^o(\text{products}) - \Delta H_f^o(\text{reactants})$ $\qquad w_p = -RT\Delta n_{gas}$ $\qquad \Delta U^o = \Delta H^o - RT\Delta n_{gas}$

$\Delta G_f^o(\text{products}) - \Delta G_f^o(\text{reactants})$ $\qquad T_{\text{ad,flame}} = T_i - \dfrac{\Delta H(T_i)}{C_p(\text{products})}$ $\quad$ [constant C_p(products)]

$\Delta H = \sum_i \nu_i H_m(i)$ $\qquad \Delta G = \sum_i \nu_i G_m(i)$ $\qquad \Delta C_p = \sum_i \nu_i C_{pm}(i)$ $\qquad \Delta V = \sum_i \nu_i V_m(i)$

$$\Delta H^o(T_2) = \Delta H^o(T_1) + \int_{T_1}^{T_2} \Delta C_p^o \mathrm{d}T \qquad \Delta H(T,p) = \Delta H^o(T,p^o) + \int_{p^o}^{p} \Delta V \mathrm{d}p$$

$\Delta G = \Delta G^o + RT\ln Q$ $\qquad K = Q_{\text{equil}}$ $\qquad K = \exp(-\Delta G^o/RT)$ $\qquad K_p = K_c(RT)^{\Delta n\text{gas}}$

$$\frac{\mathrm{d}(\Delta G^o/T)}{\mathrm{d}T} = -\frac{\Delta H^o}{T^2} \qquad \frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H^o}{RT^2} \qquad \frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = -\frac{\Delta H^o}{R}$$

$$\ln K(T_2) = \ln K(T_1) - \int_{1/T_1}^{1/T_2} \frac{\Delta H^o}{R} \mathrm{d}\frac{1}{T} \approx \ln K(T_1) - \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Ideal Gases

$p = nRT/V$ $\qquad p_i = n_i RT/V$ $\qquad p_i/p = n_i/(n_1 + n_2 + n_3 + \ldots) = x_i$

$p = Nk_BT/V$ $\qquad C_p - C_V = nR$ $\qquad C_{pm} - C_{Vm} = R$ $\qquad \beta = 1/T$ $\qquad \kappa = 1/p$

$(\partial U/\partial V)_T = 0$ $\qquad (\partial H/\partial p)_T = 0$ $\qquad (\partial C_V/\partial V)_T = 0$ $\qquad (\partial C_p/\partial p)_T = 0$ $\qquad \mu_{JT} = 0$

$$\mathrm{d}U = C_V \mathrm{d}T \qquad \Delta U = \int_{T_i}^{T_f} C_V \mathrm{d}T \qquad \Delta U(\text{const.}C_V) = C_V(T_f - T_i)$$

$$\mathrm{d}H = C_p \mathrm{d}T \qquad \Delta H = \int_{T_i}^{T_f} C_p \mathrm{d}T \qquad \Delta H(\text{const.}C_p) = C_p(T_f - T_i)$$

$w = -nRT\ln(V_f/V_i)$ (reversible isothermal expansion/compression, variable pressure)

$w = -p(V_f - V_i) = -nR(T_f - T_i)$ (isothermal expansion/compression at constant pressure)

isothermal: $p_iV_i = p_fV_f$ and $(\partial p/\partial V)_T = -p/V$

adiabatic: $\mathrm{d}U = C_V\mathrm{d}T = \mathrm{d}w$ and $\Delta U = w$ and $\int_{T_i}^{T_f} C_V \mathrm{d}T = -\int_{V_i}^{V_f} p_{\text{external}} \mathrm{d}V$

rev. adiabatic ($p = p_{\text{external}}$): $\int_{T_i}^{T_f} \frac{C_V}{T}\mathrm{d}T = -nR\int_{V_i}^{V_f} \frac{1}{V}\mathrm{d}V$ and $C_{Vm}\ln(T_f/T_i) = -R\ln(V_f/V_i)$ (const. C_{Vm})

rev. adiabatic ($p = p_{\text{external}}$), $\gamma = C_{pm}/C_{Vm}$ constant: $p_iV_i^{\gamma} = p_fV_f^{\gamma}$ and $(\partial p/\partial V)_{\text{ad.}} = -\gamma p/V$

$$\mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \frac{nR}{V}\mathrm{d}V \qquad \mathrm{d}S = \frac{C_p}{T}\mathrm{d}T - \frac{nR}{p}\mathrm{d}p \qquad G_m(T,p) = G_m^o(T,p^o) + RT\ln(p/p^o)$$

$\Delta G_{mix} = n_ART\ln x_A + n_BRT\ln x_B$ $\qquad \Delta S_{mix} = -n_AR\ln x_A - n_BR\ln x_B$

Real Gases

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}$$

$$\left(\frac{\partial p}{\partial V_m}\right)_{T=T_C} = 0$$

$$\left(\frac{\partial^2 p}{\partial V_m^2}\right)_{T=T_C} = 0$$

$$a = \frac{27R^2T_C^2}{64p_C}$$

$$b = \frac{RT_C}{8p_C}$$

$$Z_C = \frac{3}{8}$$

$$p_r = \frac{8}{3}\frac{T_r}{V_r - 1/3} - \frac{3}{V_r^2}$$

$p_r = p/p_c$ $\quad T_r = T/T_c$ $\quad V_r = V_m/V_{mc}$

$$Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{B(T)}{V_m^3} + \cdots$$

$$Z = pV/nRT = pV_m/RT = p/p_{ideal}$$

$$B(T) = b - \frac{a}{RT}$$

$$T_{Boyle} = a/Rb$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_{pm}}\left(\frac{2a}{RT} - b\right)$$

$$\mu^{real} - \mu^{ideal} = G_m^{real} - G_m^{ideal} = RT\ln(f/p) = RT\ln\gamma = \int_0^p \frac{Z-1}{p}\,dp$$

Phase Equilibrium

$F = 3 - P$ $\qquad F = C + 2 - P$

$$\left(\frac{\partial \mu}{\partial T}\right)_p = \left(\frac{\partial G_m}{\partial T}\right)_p = -S_m$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \left(\frac{\partial G_m}{\partial p}\right)_T = V_m$$

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\Delta V_m}$$

$$\frac{d\ln p}{d(1/T)} = -\frac{\Delta H_{vap,m}}{R}$$

$$\frac{d\ln p}{d(1/T)} = -\frac{\Delta H_{sub,m}}{R}$$

$$\frac{\text{vapor pressure at } p + \Delta p}{\text{vapor pressure at } p} = \exp\left(\frac{V_{ml}\Delta p}{RT}\right)$$

Surface Tension

$$dw_{surface} = \gamma d\sigma$$

$$\gamma = \left(\frac{\partial G}{\partial \sigma}\right)_{T,p}$$

$$\gamma \approx \gamma_o\left(1 - \frac{T}{T_C}\right)^n$$

$$V = (4/3)\pi r^3$$

$$\sigma = 4\pi r^2$$

$$p_{in} = p_{out} + \frac{2\gamma}{r}$$

$$h = \frac{2\gamma}{\rho g r}$$

$$h = \frac{2\gamma\cos\theta}{\rho g r}$$

$$p_{in} = p_{out} + \frac{4\gamma}{r}$$