Chemistry 231 **Physical Constants, Conversion Factors and Equations** (ver. 2)

Physical Constants and Conversion Factors

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

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

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

1 L bar = 100 J $1\ \text{m}^3 = 1000$ L $1\ \text{L} = 1000\ \text{cm}^3$

First Law

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Ideal Gases

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

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

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

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

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

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

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

Real Gases

$$p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} = \frac{RT}{V_\text{m} - b} - \frac{a}{V_\text{m}^2} \qquad \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_\text{m}^2}$$

$$Z = pV/nRT = pV_\text{m}/RT = p/p_{\text{ideal}} \qquad Z = 1 + \frac{B(T)}{V_\text{m}} + \frac{C(T)}{V_\text{m}^2} + \frac{B(T)}{V_\text{m}^3} + \cdots$$

$$B(T) = b - \frac{a}{RT} \qquad T_{\text{Boyle}} = a/Rb \qquad \mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_{pm}}\left(\frac{2a}{RT} - b\right)$$

Thermochemistry

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

$$\Delta H = \sum_i \nu_i H_\text{m}(i) \qquad \Delta C_p = \sum_i \nu_i C_{pm}(i) \qquad \Delta U = \sum_i \nu_i U_\text{m}(i) \qquad \Delta V = \sum_i \nu_i V_\text{m}(i)$$

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

$$T_{\text{ad.flame}} = T_i - \frac{\Delta H(T_i)}{C_p(\text{products})} \qquad (\text{const. } C_p(\text{products}))$$