

Physical Constants and Conversion Factors

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

$$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$$

$$k_B = R/N_A$$

$$T/\text{K} = t/^{\circ}\text{C} + 273.15$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$1 \text{ atm} = 1.01325 \text{ bar}$$

$$1 \text{ mm Hg} = 133.32 \text{ Pa}$$

$$1 \text{ L bar} = 100 \text{ J}$$

$$1 \text{ m}^3 = 1000 \text{ L}$$

$$1 \text{ L} = 1000 \text{ cm}^3$$

First Law

$$dU = dq + dw$$

$$\Delta U = q + w$$

$$\Delta U = U_f - U_i$$

$$\Delta U = w_{\text{adiabatic}}$$

$$(\Delta U = 0) \text{ isolated system}$$

$$0 = \oint dU \quad (\text{cyclic process})$$

$$dw = -p_{\text{external}}dV \quad (\text{expansion/compression work})$$

$$w = - \int_{V_i}^{V_f} p_{\text{external}} dV$$

$$p = p_{\text{external}} \quad (\text{reversible})$$

$$p < p_{\text{external}} \quad (\text{irrev. compression})$$

$$p > p_{\text{external}} \quad (\text{irrev. expansion})$$

$$w_{\text{rev}} = - \int_{V_i}^{V_f} p dV$$

$$w_{\text{rev(const.}p)} = -p(V_f - V_i)$$

$$w_{\text{irrev(const. external }p)} = -p_{\text{external}}(V_f - V_i)$$

$$H = U + pV$$

$$\Delta H = H_f - H_i$$

$$\Delta H = \Delta U + \Delta(pV) = U_f - U_i + p_f V_f - p_i V_i$$

$$C_v = \frac{dq_v}{dT} = \left(\frac{\partial U}{\partial T} \right)_v$$

$$C_p = \frac{dq_p}{dT} = \left(\frac{\partial H}{\partial T} \right)_p$$

$$C_p - C_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial V}{\partial T} \right)_p = \frac{\beta^2 VT}{\kappa}$$

$$q_v = \Delta U_v = \int_{T_i}^{T_f} C_v dT$$

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

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

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

$$\beta_{\text{linear}} = \beta/3 = \ell^{-1}(\partial \ell/\partial T)_p$$

$$(\partial p/\partial T)_v = \beta/\kappa$$

$$\mu_{\text{T}} = (\partial T/\partial p)_H = -V_m(1 - \beta T)/C_{pm}$$

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

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p = \frac{\beta T}{\kappa} - p$$

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

$$\left(\frac{\partial H}{\partial p} \right)_T = V(1 - \beta T)$$

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

$$\left(\frac{\partial f}{\partial y} \right)_x = \frac{1}{\left(\frac{\partial y}{\partial f} \right)_x}$$

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

$$du = g(x, y)dx + h(x, y)dy$$

du is exact and the function $u(x, y)$ exists if

$$\left(\frac{\partial g}{\partial y} \right)_x = \left(\frac{\partial h}{\partial x} \right)_y$$

Second Law

$$\Delta U_{\text{cycle}} = q_H + q_C + w = 0 \quad \varepsilon = \frac{-w}{q_H} = 1 - \frac{T_C}{T_H} \quad \frac{q_H}{T_H} + \frac{q_C}{T_C} = 0$$

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \quad dS = \frac{dq_{\text{rev}}}{T} \quad \Delta S_{\text{cycle}} = 0 \quad (\Delta S \geq 0)_{\text{isolated system}} \quad (\Delta S \geq 0)_{U,V}$$

$$\oint \frac{dq}{T} \leq 0 \quad S = k \ln W \quad S_m^\circ(T, p^\circ) = \int_{T=0}^T \frac{C_{pm}^\circ}{T} dT + \sum_i \frac{\Delta H_m^\circ(\text{transition } i)}{T_i}$$

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad C_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV \quad dS = \frac{C_p}{T} dT - \beta V dp$$

Combined First and Second Laws

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

$$dU = TdS - pdV = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \quad dH = TdS + Vdp = \left(\frac{\partial H}{\partial S} \right)_p dS + \left(\frac{\partial H}{\partial p} \right)_S dp$$

$$dA = -SdT - pdV = \left(\frac{\partial A}{\partial T} \right)_V dT + \left(\frac{\partial A}{\partial V} \right)_T dV \quad dG = -SdT + Vdp = \left(\frac{\partial G}{\partial T} \right)_p dT + \left(\frac{\partial G}{\partial p} \right)_T dp$$

$\left(\frac{\partial U}{\partial S} \right)_V = T$	$\left(\frac{\partial U}{\partial V} \right)_S = -p$	$\left(\frac{\partial H}{\partial S} \right)_p = T$	$\left(\frac{\partial H}{\partial p} \right)_S = V$	$-w_T \leq -\Delta A_T$
$\left(\frac{\partial A}{\partial T} \right)_V = -S$	$\left(\frac{\partial A}{\partial V} \right)_T = -p$	$\left(\frac{\partial G}{\partial T} \right)_p = -S$	$\left(\frac{\partial G}{\partial p} \right)_T = V$	$-w_T' \leq -\Delta G_T$
				$dq \leq TdS$

$\left(\frac{\partial T}{\partial V} \right)_S = -\left(\frac{\partial p}{\partial S} \right)_V$	$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$	$dU_{S,V} \leq 0$	$dH_{S,p} \leq 0$
$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$	$-\left(\frac{\partial S}{\partial p} \right)_T = \left(\frac{\partial V}{\partial T} \right)_p$	$dA_{T,V} \leq 0$	$dG_{T,p} \leq 0$

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

$$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots \quad (\text{systems of variable composition or variable mass})$$

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

Thermochemistry

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

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

$$\Delta H = \sum_i v_i H_m(i) \quad \Delta G = \sum_i v_i G_m(i) \quad \Delta C_p = \sum_i v_i C_{p,m}(i) \quad \Delta V = \sum_i v_i V_m(i)$$

$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_p^\circ dT \quad \Delta H(T, p) = \Delta H^\circ(T, p^\circ) + \int_{p^\circ}^p \Delta V dp$$

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

$$\frac{d(\Delta G^\circ/T)}{dT} = -\frac{\Delta H^\circ}{T^2} \quad \frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad \frac{d \ln K}{d(1/T)} = -\frac{\Delta H^\circ}{R}$$

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

Ideal Gases

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

$$p = Nk_B T/V \quad C_p - C_V = nR \quad C_{p,m} - C_{v,m} = R \quad \beta = 1/T \quad \kappa = 1/p$$

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

$$dU = C_V dT \quad \Delta U = \int_{T_i}^{T_f} C_V dT \quad \Delta U(\text{const. } C_V) = C_V(T_f - T_i)$$

$$dH = C_p dT \quad \Delta H = \int_{T_i}^{T_f} C_p dT \quad \Delta H(\text{const. } C_p) = C_p(T_f - T_i)$$

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

$$w = -p(V_f - V_i) = -nR(T_f - T_i) \quad (\text{isothermal expansion/compression at constant pressure})$$

$$\text{isothermal: } p_i V_i = p_f V_f \quad \text{and } (\partial p/\partial V)_T = -p/V$$

$$\text{adiabatic: } dU = C_V dT = dw \quad \text{and } \Delta U = w \quad \text{and } \int_{T_i}^{T_f} C_V dT = - \int_{V_i}^{V_f} p_{\text{external}} dV$$

$$\text{rev. adiabatic } (p = p_{\text{external}}): \int_{T_i}^{T_f} \frac{C_V}{T} dT = -nR \int_{V_i}^{V_f} \frac{1}{V} dV \quad \text{and} \quad C_{v,m} \ln(T_f/T_i) = -R \ln(V_f/V_i) \quad (\text{const. } C_{v,m})$$

$$\text{rev. adiabatic } (p = p_{\text{external}}), \gamma = C_{p,m}/C_{v,m} \text{ constant: } p_i V_i^\gamma = p_f V_f^\gamma \quad \text{and} \quad (\partial p/\partial V)_{\text{ad.}} = -\gamma p/V$$

$$dS = \frac{C_V}{T} dT + \frac{nR}{V} dV \quad dS = \frac{C_p}{T} dT - \frac{nR}{p} dp \quad G_m(T, p) = G_m^\circ(T, p^\circ) + RT \ln(p/p^\circ)$$

$$\Delta G_{\text{mix}} = n_A RT \ln x_A + n_B RT \ln x_B \quad \Delta S_{\text{mix}} = -n_A R \ln x_A - n_B R \ln x_B$$

Real Gases

$$p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} = \frac{RT}{V_m-b} - \frac{a}{V_m^2} \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2} \quad \left(\frac{\partial p}{\partial V_m}\right)_{T=T_c} = 0 \quad \left(\frac{\partial^2 p}{\partial V_m^2}\right)_{T=T_c} = 0$$

$$a = \frac{27R^2T_c^2}{64p_c} \quad b = \frac{RT_c}{8p_c} \quad Z_c = \frac{3}{8} \quad p_r = \frac{8}{3} \frac{T_r}{V_r - 1/3} - \frac{3}{V_r^2}$$

$$p_r = p/p_c \quad T_r = T/T_c \quad V_r = V_m/V_{mc} \quad Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \dots$$

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

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

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