

CHEM*2820 Fall 2024 Final Exam Equation Sheet

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Constants and Conversions

$$R = 8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}, \quad T(\text{K}) = \theta(\text{°C}) + 273.15$$

$$1 \text{ m} = 10 \text{ dm} = 100 \text{ cm}, \quad 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

Mathematical Relations

$$e^x e^y e^z \dots = e^{x+y+z+\dots}$$

$$\ln x + \ln y + \dots = \ln xy \dots, \quad \ln x - \ln y = \ln \frac{x}{y}$$

$$d(fg) = f dg + g df, \quad d\left(\frac{f}{g}\right) = \frac{1}{g} df - \frac{f}{g^2} dg$$

$$\int \frac{1}{x} dx = \ln x + C$$

$$\int \frac{1}{ax+b} dx = \frac{1}{a} \ln(ax+b) + C$$

The Properties of Gases

The Perfect Gas

$$pV = nRT \quad \text{or} \quad pV_m = RT$$

$$p_J = x_J p, \quad x_J = \frac{n_J}{n}, \quad n = \sum_J n_J$$

The Kinetic Model

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}, \quad v_{\text{rms}} = \left(\frac{3RT}{M} \right)^{1/2}$$

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M} \right)^{1/2}, \quad v_{\text{mp}} = \left(\frac{2RT}{M} \right)^{1/2}$$

Real Gases

$$Z = \frac{V_m}{V_m^\ominus}, \quad pV_m = RTZ$$

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

The First Law

Internal Energy

$$dU = dq + dw \quad \text{or} \quad \Delta U = q + w$$

$$dw = -|\mathbf{F}|dz, \quad w_{\text{rev}} = -nRT \ln \frac{V_f}{V_i}$$

$$dw = -p_{\text{ex}} dV \quad \text{or} \quad w = -p_{\text{ex}} \Delta V$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V, \quad \Delta U = C_V \Delta T, \quad \Delta U = q_V$$

Enthalpy

$$H = U + pV$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p, \quad \Delta H = C_p \Delta T, \quad \Delta H = q_p$$

$$C_p - C_V = nR \quad \text{or} \quad C_{p,m} - C_{V,m} = R$$

Thermochimistry

$$\Delta_r H^\ominus = \sum_{\text{products}} \nu \Delta_f H^\ominus - \sum_{\text{reactants}} \nu \Delta_f H^\ominus$$

$$\Delta_r C_p^\ominus = \sum_{\text{products}} \nu C_{p,m}^\ominus - \sum_{\text{reactants}} \nu C_{p,m}^\ominus$$

$$\Delta_r H^\ominus (T_2) = \Delta_r H^\ominus (T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

Measurement of Entropy

$$\Delta_r S^\ominus = \sum_{\text{products}} \nu S_m^\ominus - \sum_{\text{reactants}} \nu S_m^\ominus$$

$$\Delta_r S^\ominus (T_2) = \Delta_r S^\ominus (T_1) + \int_{T_1}^{T_2} \frac{\Delta_r C_p^\ominus}{T} dT$$

Concentrating on the System

$$A = U - TS, \quad G = H - TS$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$$

$$\Delta_r G^\ominus = \sum_{\text{products}} \nu \Delta_f G^\ominus - \sum_{\text{reactants}} \nu \Delta_f G^\ominus$$

State Functions and Exact Differentials

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

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T, \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

$$\left(\frac{\partial U}{\partial T} \right)_p = \alpha \pi_T V + C_V$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T, \quad C_p - C_V = \frac{\alpha^2 TV}{\kappa_T}$$

Adiabatic Changes

$$V_i T_i^c = V_f T_f^c, \quad c = \frac{C_{V,m}}{R}$$

$$p_i V_i^\gamma = p_f V_f^\gamma, \quad \gamma = \frac{C_{p,m}}{C_{V,m}}$$

The Second and Third Laws

Entropy

$$dS = \frac{dq_{\text{rev}}}{T}, \quad S = k_B \ln \Omega$$

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}}$$

$$\eta = 1 - \frac{|q_c|}{|q_h|}, \quad \eta = 1 - \frac{T_c}{T_h}$$

Entropy Changes for Specific Processes

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$\Delta_{\text{trs}} S = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}$$

Combining the First and Second Laws

$$dU = TdS - pdV, \quad \left(\frac{\partial T}{\partial V} \right)_S = -\left(\frac{\partial p}{\partial S} \right)_V$$

$$dH = TdS + Vdp, \quad \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

$$dA = -pdV - SdT, \quad \left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

$$dG = Vdp - SdT, \quad \left(\frac{\partial V}{\partial T} \right)_p = -\left(\frac{\partial S}{\partial p} \right)_T$$

$$\left(\frac{\partial G}{\partial p} \right)_T = V, \quad \left(\frac{\partial G}{\partial T} \right)_p = -S$$

$$\left(\frac{\partial (G/T)}{\partial T} \right)_p = -\frac{H}{T^2}$$

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Simple Mixtures

The Thermodynamic Description of Mixtures

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

$$\mu_J = \left(\frac{\partial G}{\partial n_J} \right)_{p,T,n'}$$

$$G = n_A \mu_A + n_B \mu_B$$

$$dG = V dp - S dT + \mu_A dn_A + \mu_B dn_B + \dots$$

$$\sum_J n_J d\mu_J = 0$$

$$d\mu = V_m dp - S_m dT$$

$$\mu = \mu^\ominus + RT \ln \frac{p}{p^\ominus}$$

$$\Delta_{\text{mix}} G = nRT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{\text{mix}} S = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{\text{mix}} H = 0$$

$$p_A = x_A p_A^*$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln x_A$$

$$p_B = x_B K_B$$

Binary Phase Diagrams of Liquids

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A}$$

$$y_B = 1 - y_A$$

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A}$$

$$n_L l_L = n_V l_V$$

Chemical Equilibrium

The Equilibrium Constant

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

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q, \quad Q = \prod_J a_J^{\nu_J}$$

$$\Delta_r G^\ominus = \sum_J \nu_J \Delta_f G^\ominus (J)$$

$$K = \left(\prod_J a_J^{\nu_J} \right)_{\text{equilibrium}}$$

$$\Delta_r G^\ominus = -RT \ln K$$

$$K = e^{-\Delta_r G^\ominus / RT}$$

Response of Equilibria to the Conditions

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\ominus}{RT^2}, \quad \frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^\ominus}{R}$$

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Chemical Kinetics

The Rates of Chemical Reactions

$$v = \frac{1}{V} \frac{d\xi}{dt}$$

$$v = \frac{1}{\nu_J} \frac{d[J]}{dt}$$

$$v = k[A]^a [B]^b \dots$$

$$\log v_0 = \log k_{\text{eff}} + a \log [A]_0$$

Integrated Rate Laws

$$[A] = [A]_0 - kt$$

$$\ln \frac{[A]}{[A]_0} = -kt, \quad [A] = [A]_0 e^{-kt}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt, \quad [A] = \frac{[A]_0}{1 + kt[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$$

$$\frac{\ln ([B]/[B]_0)}{\ln ([A]/[A]_0)} = (([B]_0 - [A]_0)/kt)$$

Reactions Approaching Equilibrium

$$K = \frac{k_{1f}}{k_{1r}} \times \frac{k_{2f}}{k_{2r}} \times \dots$$

Note: use c^\ominus to balance out units

The Arrhenius Equation

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$E_a = RT^2 \frac{d \ln k}{dT}$$

$$k = Ae^{-E_a/RT}$$

Reaction Mechanisms

$$\frac{d[A]}{dt} = -k[A]$$

$$\frac{d[A]}{dt} = -k[A][B]$$

$$[A] = [A]_0 e^{-k_1 t}$$

$$[I] = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) [A]_0$$

$$[P] = \frac{1 + (k_1 e^{-k_2 t} - k_2 e^{-k_1 t})}{k_2 - k_1} [A]_0$$

$$\frac{d[I]}{dt} \approx 0$$