CHEM*2820 Fall 2022 Midterm Exam Equation Sheet

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The Properties of Gases

The Perfect Gas

$$T(\mathrm{K}) = \theta(^\circ\mathrm{C}) + 273.15$$
$$pV = nRT$$
$$p_\mathrm{J} = x_\mathrm{J} p, \quad x_\mathrm{J} = \frac{n_\mathrm{J}}{n}, \quad n = \sum_\mathrm{J} n_\mathrm{J}$$

The Kinetic Model

$$pV = \frac{1}{3} nMv_\mathrm{rms}^2$$
$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$
$$v_\mathrm{rms} = \left(\frac{3RT}{M}\right)^{1/2}$$
$$v_\mathrm{mean} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$
$$v_\mathrm{mp} = \left(\frac{2RT}{M}\right)^{1/2}$$
$$v_\mathrm{rel} = \left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{1/2}, \quad \mu = \frac{m_\mathrm{A}m_\mathrm{B}}{m_\mathrm{A} + m_\mathrm{B}}$$
$$z = \frac{\sigma v_\mathrm{rel} p}{k_\mathrm{B}T}, \quad \sigma = \pi d^2, \quad \lambda = \frac{v_\mathrm{rel}}{z}$$

Real Gases

$$Z = \frac{V_\mathrm{m}}{V_\mathrm{m}^\circ}$$
$$pV_\mathrm{m} = RT\left(1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \cdots\right)$$
$$p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$
$$X_\mathrm{r} = \frac{X}{X_\mathrm{c}}, \quad X = p, T, V_\mathrm{m}$$

The First Law

Internal Energy

$$\Delta U = q + w$$
$$\mathrm{d}w = -p_\mathrm{ex}\mathrm{d}V, \quad w = -p_\mathrm{ex}\Delta V$$
$$w = -nRT\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$
$$\Delta U = q_V$$
$$q = It\Delta\phi$$
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Enthalpy

$$H = U + pV$$
$$\mathrm{d}H = \mathrm{d}q_p, \quad \Delta H = q_p$$
$$\Delta H = \Delta U + \Delta n_\mathrm{g} RT$$
$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$
$$C_p - C_V = nR$$

Thermochemistry

$$\Delta_\mathrm{r}H^\circ = \sum_\mathrm{products} \nu\Delta_\mathrm{f}H^\circ - \sum_\mathrm{reactants} \nu\Delta_\mathrm{f}H^\circ$$
$$\Delta_\mathrm{r}H^\circ = \sum_\mathrm{J} \nu_\mathrm{J}\Delta_\mathrm{f}H^\circ(\mathrm{J})$$
$$\Delta_\mathrm{r}H^\circ(T_2) = \Delta_\mathrm{r}H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_\mathrm{r}C_p^\circ \mathrm{d}T$$
$$\Delta_\mathrm{r}C_p^\circ = \sum_\mathrm{J} \nu_\mathrm{J} C_{p,\mathrm{m}}^\circ(\mathrm{J})$$
$$\Delta_\mathrm{r}H^\circ(T_2) = \Delta_\mathrm{r}H^\circ(T_1) + (T_2 - T_1)\Delta_\mathrm{r}C_p^\circ$$

State Functions and Exact Differentials

$$\mathrm{d}U = \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T$$
$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T, \quad \mathrm{d}U = \pi_T\mathrm{d}V + C_V\mathrm{d}T$$
$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$
$$C_p - C_V = \frac{\alpha^2 TV}{\kappa_T}$$
$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$
$$\mathrm{d}H = -\mu C_p\mathrm{d}p + C_p\mathrm{d}T$$

Adiabatic Changes

$$w_\mathrm{ad} = C_V\Delta T$$
$$T_\mathrm{f} = T_\mathrm{i}\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{1/c}, \quad c = \frac{C_{V,\mathrm{m}}}{R}$$
$$V_\mathrm{i}T_\mathrm{i}^c = V_\mathrm{f}T_\mathrm{f}^c$$
$$p_\mathrm{i}V_\mathrm{i}^\gamma = p_\mathrm{f}V_\mathrm{f}^\gamma, \quad \gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}}$$

The Second and Third Laws

Entropy

$$\mathrm{d}S = \frac{\mathrm{d}q_\mathrm{rev}}{T}, \quad \mathrm{d}S \geq \frac{\mathrm{d}q}{T}$$
$$\Delta S_\mathrm{sur} = \frac{q_\mathrm{sur}}{T_\mathrm{sur}}$$
$$S = k_\mathrm{B}\ln\Omega$$
$$\eta = 1 - \frac{T_\mathrm{c}}{T_\mathrm{h}}, \quad T = (1 - \eta)T_\mathrm{h}$$

Entropy Changes for Specific Processes

$$\Delta S = nR\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$
$$\Delta_\mathrm{trs}S = \frac{\Delta_\mathrm{trs}H}{T_\mathrm{trs}}$$
$$S(T_\mathrm{f}) = S(T_\mathrm{i}) + C\ln\frac{T_\mathrm{f}}{T_\mathrm{i}}, \quad \text{for } C = C_p, C_V$$

Measurement of Entropy

$$S_\mathrm{m}(T_\mathrm{a}) = S_\mathrm{m}(0) + \int_0^{T_\mathrm{fus}} \frac{C_{p,\mathrm{m,\ solid}}(T)}{T}\mathrm{d}T + \frac{\Delta_\mathrm{fus}H}{T_\mathrm{fus}} + \int_{T_\mathrm{fus}}^{T_\mathrm{vap}} \frac{C_{p,\mathrm{m,\ liquid}}(T)}{T}\mathrm{d}T + \frac{\Delta_\mathrm{vap}H}{T_\mathrm{vap}} + \int_{T_\mathrm{vap}}^{T_\mathrm{a}} \frac{C_{p,\mathrm{m,\ gas}}(T)}{T}\mathrm{d}T$$
$$\Delta_\mathrm{r}S^\circ = \sum_\mathrm{products} \nu S_\mathrm{m}^\circ - \sum_\mathrm{reactants} \nu S_\mathrm{m}^\circ$$
$$\Delta_\mathrm{r}S^\circ = \sum_\mathrm{J} \nu_\mathrm{J} S_\mathrm{m}^\circ(\mathrm{J})$$
$$\Delta_\mathrm{r}S^\circ(T_2) = \Delta_\mathrm{r}S^\circ(T_1) + \int_{T_1}^{T_2} \frac{\Delta_\mathrm{r}C_p^\circ}{T}\mathrm{d}T$$
$$\Delta_\mathrm{r}S^\circ(T_2) = \Delta_\mathrm{r}S^\circ(T_1) + \Delta_\mathrm{r}C_p^\circ \ln\frac{T_2}{T_1}$$

Concentrating on the System

$$\mathrm{d}S_{U,V} \geq 0, \quad \mathrm{d}S_{H,p} \geq 0$$
$$A = U - TS, \quad G = H - TS$$
$$\mathrm{d}A_{T,V} \leq 0, \quad \mathrm{d}G_{T,p} \leq 0$$
$$\mathrm{d}w_{\max} = \mathrm{d}A, \quad w_{\max} = \Delta A$$
$$\mathrm{d}w_{\text{add, max}} = \mathrm{d}G, \quad w_{\text{add, max}} = \Delta G$$
$$\Delta_\mathrm{r} G^\ominus = \Delta_\mathrm{r} H^\ominus - T\Delta_\mathrm{r} S^\ominus$$
$$\Delta_\mathrm{r} G^\ominus = \sum_\mathrm{J} \nu_\mathrm{J} \Delta_\mathrm{f} G^\ominus\,(\mathrm{J})$$
$$\Delta_\mathrm{f} G^\ominus\left(\mathrm{H}^+, \mathrm{aq}\right) = 0$$
$$\Delta_\text{solv} G^\ominus = -\frac{z_\mathrm{i}^2 e^2 N_\mathrm{A}}{8\pi\epsilon_0 r_\mathrm{i}}\left(1 - \frac{1}{\epsilon_\mathrm{r}}\right)$$

Combining the First and Second Laws

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$
$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$$
$$\mathrm{d}A = -p\mathrm{d}V - S\mathrm{d}T$$
$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$$
$$\left(\frac{\partial G}{\partial p}\right)_T = V, \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$$
$$\left(\frac{\partial\,(G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$$
$$G_\mathrm{m}\,(p_\mathrm{f}) = G_\mathrm{m}\,(p_\mathrm{i}) + V_\mathrm{m}\,(p_\mathrm{f} - p_\mathrm{i})$$
$$G_\mathrm{m}\,(p_\mathrm{f}) = G_\mathrm{m}\,(p_\mathrm{i}) + RT\ln\frac{p_\mathrm{f}}{p_\mathrm{i}}$$
$$G_\mathrm{m}\,(p) = G_\mathrm{m}^\ominus + RT\ln\frac{p}{p^\ominus}$$

Mathematical Relations

Logarithms and Exponentials

$$\ln x + \ln y + \cdots = \ln xy \cdots, \quad \ln x - \ln y = \ln\frac{x}{y}$$
$$a\ln x = \ln x^a$$
$$e^x e^y e^z \cdots = e^{x+y+z+\cdots}$$
$$\frac{e^x}{e^y} = e^{x-y}, \quad (e^x)^a = e^{ax}$$

Derivatives

$$\mathrm{d}\,(f+g) = \mathrm{d}f + \mathrm{d}g$$
$$\mathrm{d}\,(fg) = f\mathrm{d}g + g\mathrm{d}f, \quad \mathrm{d}\left(\frac{f}{g}\right) = \frac{1}{g}\mathrm{d}f - \frac{f}{g^2}\mathrm{d}g$$
$$\frac{\mathrm{d}f}{\mathrm{d}t} = \left(\frac{\mathrm{d}f}{\mathrm{d}g}\right)\left(\frac{\mathrm{d}g}{\mathrm{d}t}\right) \quad \text{for} \quad f = f\,(g\,(t))$$
$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{1}{(\partial x/\partial y)}\right)_z$$
$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1$$
$$\frac{\mathrm{d}x^n}{\mathrm{d}x} = nx^{n-1}, \quad \frac{\mathrm{d}e^{ax}}{\mathrm{d}x} = ae^{ax}, \quad \frac{\mathrm{d}\ln(ax)}{\mathrm{d}x} = \frac{1}{x}$$
$$\mathrm{d}f = g\,(x,y)\,\mathrm{d}x + h\,(x,y)\,\mathrm{d}y \text{ is exact if } \left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

Integrals

$$\int x^n \mathrm{d}x = \frac{1}{n+1}x^{n+1} + C, \quad n \neq -1$$
$$\int \frac{1}{x}\mathrm{d}x = \ln x + C$$
$$\int \frac{1}{ax+b}\mathrm{d}x = \frac{1}{a}\ln\,(ax+b) + C$$
$$\int \frac{1}{(A-x)\,(B-x)}\mathrm{d}x = \frac{1}{B-A}\ln\left(\frac{B-x}{A-x}\right) + C, \quad A \neq B$$
$$\int e^{-kx}\mathrm{d}x = -\frac{1}{k}e^{-kx} + C$$
$$\int xe^{-kx}\mathrm{d}x = -\frac{1}{k^2}e^{-kx} - \frac{x}{k}e^{-kx} + C$$
$$\int xe^{-kx^2}\mathrm{d}x = -\frac{1}{2k}e^{-kx^2} + C$$
$$\int x^3 e^{-kx^2}\mathrm{d}x = -\frac{1}{2k^2}e^{-kx^2} - \frac{x^2}{2k}e^{-kx^2} + C$$
$$\int \sin\,(kx)\,\mathrm{d}x = -\frac{1}{k}\cos\,(kx) + C$$
$$\int \sin^2(kx)\,\mathrm{d}x = \frac{1}{2}x - \frac{1}{4k}\sin\,(2kx) + C$$
$$\int \sin\,(kx)\cos\,(kx)\,\mathrm{d}x = \frac{1}{2k}\sin^2(kx) + C$$