Chemistry 312 **Spring 2019** **Equation Guide**

Constants

$h = 6.626 \times 10^{-34}$ J s $\hbar = h/2\pi$ $N_A = 6.022 \times 10^{23}$ mol^{-1}

m(electron) = 9.1094×10^{-31} kg m(proton) = 1.6726×10^{-27} kg

m(neutron) = 1.6749×10^{-27} kg c (vacuum) = 2.9979×10^{8} ms^{-1}

Charge of an electron, $e = 1.602 \times 10^{-19}$ C

$k = 1.381 \times 10^{-23}$ J K^{-1} R = 8.314 J K^{-1} mol^{-1} = 0.08206 L atm K^{-1} mol^{-1}

Pressure conversions: 1 atm = 1.01325 bar = 1.01325×10^{5} Pa = 760 mm Hg = 760 torr

Particle in a box $$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$ $n_x, n_y, n_z = 1,2,3,...$

Rigid Rotor $$E_J = \frac{\hbar^2}{2I}J(J+1) \qquad I = \mu r_e^2$$ $$g_J = 2J+1 \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$ $J = 0,1,2,...$

Harmonic Oscillator $E_v = h\nu_{vib}(v+1/2)$ $v = 0,1,2,...$

$\nu_{vib} = 1/2\pi\,(k/\mu)^{1/2}$

Quantum Theory (Electronic levels and light) $E_{photon} = h\nu = hc/\lambda$

Gas Equations $PV = nRT$ (ideal)

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$ (van der Waals)

Connections with B

$$Z = \frac{P\overline{V}}{RT}$$

$Z = 1 + B'P + C'P^2 + ...$ (virial) $B = B'RT$

$$Z = 1 + \frac{B}{\overline{V}} + \frac{C}{\overline{V}^2} + ...$$ (virial) $B = b - a/RT$

(with van der Waals)

Kinetic molecular theory of Gases

$$PV = \frac{1}{3}Nmv_{rms}^2 \qquad P = \frac{1}{3}\rho v_{rms}^2 \qquad v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{MM}}$$

Dalton's Law of Partial Pressures $P_{tot} = P_A + P_B + P_c + ...$

Mole fraction $\chi_A = \dfrac{n_A}{n_{tot}}$ $\qquad P_A = \chi_A P_{tot}$

Distributions

Number of arrangements, $W = \left(g_1^{N_1} g_2^{N_2} g_3^{N_3} ...\right)\dfrac{N!}{N_1!N_2!N_3!...}$ $\qquad probability = W\left(\dfrac{1}{\sum g_i}\right)^N$

Boltzmann distribution

$$\frac{N_i}{N_j} = \frac{g_i}{g_j}\exp\left(\frac{-(E_i - E_j)}{kT}\right)$$

$$\frac{N_i}{N} = \frac{g_i}{q}\exp\left(\frac{-(E_i - E_0)}{kT}\right) \qquad N = \sum_i N_i$$

Partition functions

$$q = \sum_i g_i \exp\left(\frac{-(E_i - E_0)}{kT}\right)$$

$$q_{trans(1d)} = \frac{\sqrt{\pi}}{2}\left[\frac{kT}{h^2/8ma^2}\right]^{1/2} \qquad q_{trans(3d)} = \left[\frac{2\pi mkT}{h^2}\right]^{3/2} V$$

$$q_{rot} = \frac{2IkT}{\sigma\hbar^2}$$

$$q_{vib} = \frac{1}{1-\exp(-x)} \quad ; \quad x = \frac{h\nu_{vib}}{kT}$$

Maxwell-Boltzmann Distribution: $\dfrac{1}{N}\dfrac{dN}{dE} = 2\pi\left(\dfrac{1}{\pi kT}\right)^{3/2} E^{1/2}\exp\left(\dfrac{-E}{kT}\right)$

Thermal Energy

$$(U - U_o) = \frac{RT^2}{q}\frac{dq}{dT} = RT^2\frac{d(\ln q)}{dT}$$

For ideal gases: $(U - U_o)_{\text{trans}}$ and $(U - U_o)_{\text{rot}}$ have 0.5 RT per degree of freedom

$$(U - U_o)_{vib} = RT\left(\frac{x}{\exp(x) - 1}\right) \quad ; \quad x = \frac{h\nu_{vib}}{kT} \text{ per mode}$$

Heat Capacity $C_v = \dfrac{d(U - U_o)}{dT}$

For ideal gases: $C_v = 0.5\,R$ per degree of freedom for translation, rotation

$C_v = R\dfrac{x^2\exp(x)}{\left(\exp(x) - 1\right)^2}$; $x = \dfrac{h\nu_{vib}}{kT}$ per vibrational mode

$C_v = 3R$ for crystals of monoatomic ions or atoms
(law of Dulong and Petit)

First Law of Thermodynamics

$\Delta U_{univ} = \Delta U + \Delta U_{therm} + \Delta U_{mech} = 0$

$\Delta U = q + w$ where $q = -\Delta U_{therm}$ and $w = -\Delta U_{mech}$

$dU_{mech} = PdV$ $\Delta U_{mech} = \int PdV$

$\Delta U = -\,\Delta U_{therm}$ for constant volume processes

$C_v = \left(\dfrac{\partial U}{\partial T}\right)_v$ for 1 mol $dU = nC_v dT$

Enthalpy $H = U + PV$

$\Delta H = H_{pdt} - H_{rct}$ $\Delta H^o = \Delta H_f^o(pdt) - \Delta H_f^o(rct)$

$\Delta H = -\,\Delta U_{therm}$ for constant pressure processes

$C_p = \left(\dfrac{\partial H}{\partial T}\right)_p$ for 1 mol $dH = nC_p dT$

$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_p dT$ $\Delta H_T = \Delta H_{298} + \Delta(H_T - H_{298})$

Relationship between C_p and C_v $C_p - C_v = R$

Adiabatic Processes $\Delta U = -\,\Delta U_{mech}$

Reversible adiabatic process: $V_1 T_1^{C_v/R} = V_2 T_2^{C_v/R}$ $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$ $\gamma = \dfrac{C_p}{C_v}$

Bond Energies (gas phase reactions only) $\Delta H = BE_{rct} - BE_{pdt}$

Entropy

$\Delta S_{therm} = \Delta U_{therm}/T$ or $dS_{therm} = dU_{therm}/T$ $$S_T - S_0 = -\int_0^T \frac{dU_{therm}}{T}$$

For a reversible process, $\Delta S = -\Delta S_{therm} = q/\mathrm{T}$

$\Delta S_{mech} = 0$ for all processes

$\Delta S_{univ} = 0$ for reversible processes $\Delta S_{univ} = \Delta S + \Delta S_{therm} + \Delta S_{mech}$

Heat Engine Efficiency(%) = $\dfrac{dU_{mech}(output)}{-dU_{therm}(input)} \times 100 = \dfrac{T_h - T_l}{T_h} \times 100$

Connection to the microworld: $S = k\ ln\ W$

$$S = \frac{U - U_0}{T} + R\ln\frac{q}{N_A} + R$$

$$S_{trans} = \frac{(U - U_o)_{trans}}{T} + R\ln\frac{q_{trans}}{N_A} + R = \frac{5}{2}R + R\ln\frac{q_{trans}}{N_A}$$

$$S_{rot} = \frac{(U - U_o)_{rot}}{T} + R\ln q_{rot}$$

$$S_{vib} = \frac{(U - U_o)_{vib}}{T} + R\ln q_{vib}$$

$\Delta S_{vap} = \Delta H_{vap}/T$ (Trouton's rule)

Free Energy and Equilibria

$G = H - TS$ $\Delta G = \Delta H - T\Delta S$ (constant T)

$\Delta G = -T\Delta S_{univ}$

$dG = dU + P\,dV + V\,dP - T\,dS - S\,dT$

$G = G^0 + RT\ ln\ P$ *(P in bar)* [Pressure dependence]

$$\Delta G = \Delta G^0 + RT\ln\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$ for the reaction aA + bB → cC + dD

$$\Delta G^0 = -RT\ln K_{P,eq} \quad ; \quad K_{p,eq} = \left[\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}\right]_{eq}$$

$$K = \frac{N_B}{N_A} = \frac{q_B}{q_A}\exp\left(\frac{-\Delta U_o}{RT}\right)$$ for the reaction A ↔ B at equilibrium

$$\frac{d(\ln K_P)}{dT} = \frac{\Delta H^o}{RT^2} \qquad \frac{d(\ln K_P)}{d(1/T)} = \frac{-\Delta H^o}{R}$$ [Temperature dependence]

Free energy functions:

$$\frac{G^o - H^o_{298}}{T} = \frac{H^o - H^o_{298}}{T} - S^o$$

$$\frac{G^o - U^o_0}{T} = -R\ln\frac{q^o}{N_A}$$

Fugacity, f Activity coefficient, $\gamma = f/\mathrm{P}$

$$G_2 - G_1 = RT\ln\frac{f_2}{f_1}$$

Inter-relation of thermodynamic properties

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad ; \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad ; \quad \left(\frac{\partial\left(\Delta G/T\right)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Relation between C_P and C_v

$$C_p - C_v = \frac{-T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T}$$

for van der Waals gas (ignoring high order terms) $C_p - C_v = R\left(1 + \frac{2a}{R^2T^2}P\right)$

for liquids and solids $C_p - C_v = \frac{\alpha^2\overline{V}T}{\beta}$; $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

where α is the thermal expansivity and β is the isothermal compressibility

Raoult's Law: $x_i = \frac{P_A}{P_A^o}$; $\overline{G_A^{liq}} = G_A^o + RT\ln x_A$ for solvent A.

$\Delta G_{mix} = x_A RT\ln x_A + x_B RT\ln x_B$ for a binary solution A-B.

Henry's Law: $P_B = kx_B = k'm$; $\overline{G_B} = G_B^o + RT\ln m$ for solvent B, standard state $m = 1$

$\overline{G_B} = G_B^o + RT\ln\gamma m$ where γ is the activity coefficient

Chemical Potential: $\mu_i = \overline{G_i}$, partial molal Gibbs free energy

$\mu_i = \mu_i{}^{\circ} + RT \ln x_i$

In a fixed composition two-component system: $dG = -S\,dT + V\,dP + \mu_1\,dn_1 + \mu_2\,dn_2$

Gibbs-Duhem: $x_1\,\mathrm{d}\mu_1 + x_2\,\mathrm{d}\mu_2 = 0$ in a two-component system

Kinetics

For the general reaction $\mathrm{aA + bB \rightarrow cC + dD}$

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} = k[A]^m[B]^n$$

Integrated Rate Laws:		Half-lives:
Zeroth order:	$[A] = [A]_0 - kt$	$[A]_0/2k$
First order:	$\ln[A] = \ln[A]_0 - kt$	$0.693/k$
Second order:	$1/[A] = 1/[A]_0 + kt$	$1/(k[A]_0)$

Equilibria & Rates: For the elementary equilibrium $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$, $\dfrac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$

Temperature dependence $k = A\exp\left(\dfrac{-E_a}{RT}\right)$

Steady state approximation: If [M] is constant, d[M]/dt = 0

Rate equation for Michaelis-Menten enzyme catalyzed reactions

$$\text{Rate} = \frac{k_2[E_{tot}][S]}{K_M + [S]} \quad ; \quad K_M = \frac{k_{-1} + k_2}{k_1} = \frac{[E][S]}{[E \bullet S]}$$

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E \bullet S$$
$$E \bullet S \xrightarrow{k_2} E + products$$

Rate equation for Lindemann mechanism for unimolecular gas phase reactions

$$\text{Rate} = \frac{k_1 k_2 [A]^2}{k_{-2}[A] + k_1}$$

$$A + A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A + A^*$$
$$A^* \xrightarrow{k_1} products$$

Collision Theory: $Z_{AB} = N_A^* N_B^* \left(\frac{1}{\pi\mu}\right)^{1/2} \left(\frac{2}{kT}\right)^{3/2} \int_0^{\infty} \sigma_{AB}\,\varepsilon \exp(-\varepsilon/kT)\, d\varepsilon$

Transition State Theory: $K^{\neq} = \dfrac{q_{AB\neq}}{q_A q_B} \exp\left(-\dfrac{U_0(AB^{\neq})}{RT}\right)$