

Chemistry 311

Equation Guide

Constants and Conversions

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

$$m(\text{electron}) = 9.1094 \times 10^{-31} \text{ kg} \quad e = 1.602 \times 10^{-19} \text{ C}$$

$$m(\text{proton}) = 1.6726 \times 10^{-27} \text{ kg} \quad c(\text{vacuum}) = 2.9979 \times 10^8 \text{ m/s}$$

$$\epsilon_0 = 8.855 \times 10^{-12} \text{ C}^2 \text{N}^{-1} \text{m}^{-2} \quad k_B \text{ (or } k) = 1.381 \times 10^{-23} \text{ J K}^{-1} \quad R_H = 1.0974 \times 10^7 \text{ m}^{-1}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} \quad 1 \text{ Debye} = 3.3356 \times 10^{-30} \text{ C m} \quad a_0 = 5.29 \times 10^{-11} \text{ m}$$

<u>Reduced Mass</u>	$\mu = \frac{m_1 m_2}{m_1 + m_2}$	<u>Moment of Inertia</u>	$I = \mu r^2$
<u>Coulomb's Law</u>	$F = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2}$	$V = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$	
<u>Rydberg Equation</u>	$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right); n_1, n_2 = 1, 2, 3, \dots; n_2 > n_1$		
<u>Planck relation</u>	$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$	<u>deBroglie relation</u>	$\lambda = \frac{h}{p}$
<u>Bohr model</u>	$r = \left(\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2} \right) n^2 = a_0 n^2; n = 1, 2, 3, \dots$		$V = -\frac{e^2}{4\pi\epsilon_0 r}$

Classical Wave Equation

$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x,t)}{\partial t^2}$	$u(x,t) = \sum_{n=1}^{\infty} \left(\sin \frac{n\pi x}{l} \right) \left(A_n \cos(\omega_n t + \phi) \right) ; n = 1, 2, 3, \dots$	<u>Time-Independent Schrodinger Equation</u> $\hat{H}\Psi = E\Psi$	
$\frac{d^2 y(x)}{dx^2} - \beta^2 y(x) = 0$	$y(x) = c_1 e^{\beta x} + c_2 e^{-\beta x}$		
$\frac{d^2 y(x)}{dx^2} + \beta^2 y(x) = 0$	$y(x) = A \cos(\beta x) + B \sin(\beta x); v = \frac{\beta}{2\pi}$		
<u>Expectation/Average Values</u>	$\langle M \rangle = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau}$		
<u>Root-mean-square Value</u>	$= \sqrt{\langle M^2 \rangle}$	<u>Uncertainty</u>	$\sigma_M = \sqrt{\langle M^2 \rangle - (\langle M \rangle)^2}$
<u>Normalization Condition</u>	$\int \Psi^* \Psi d\tau = 1$		
<u>Orthogonalization Condition</u>	$\int \Psi^* \Phi d\tau = 0$		

Limits and volume elements: integrating over all space

$$\text{Cartesian: } \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz \quad \text{Spherical: } \int_0^{\infty} r^2 dr \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi \quad \text{or} \quad \int_0^{\infty} 4\pi r^2 dr \text{ if no angular parts}$$

Operators

$$\hat{A} \text{ is hermitian if } \int \Psi^* \hat{A} \phi d\tau = \int \phi \hat{A}^* \Psi^* d\tau \quad \text{Commutator} = [\hat{A}, \hat{B}] = \hat{A} \hat{B} - \hat{B} \hat{A}$$

$$\hat{x} = x \quad \hat{r} = r \quad \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad \hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 + V$$

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right) \quad \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \text{ or } \hat{L}_z = -i\hbar \left(\frac{\partial}{\partial \phi} \right)$$

$$\text{Particle-in-a-box} \quad \psi = C \sin \left(\frac{n\pi x}{a} \right) \quad E_n = \frac{n^2 \hbar^2}{8ma^2} ; n = 1, 2, 3, \dots$$

$$E = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

$$\text{Harmonic Oscillator} \quad V = \frac{1}{2} kx^2 \quad \alpha = \frac{\sqrt{k\mu}}{\hbar}$$

$$\psi_{v=0}(x) = \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} \quad \psi_{v=1}(x) = \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\alpha x^2/2} \quad \psi_{v=2}(x) = \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad E_v = \left(v + \frac{1}{2} \right) \hbar\nu ; v = 0, 1, 2, \dots$$

$$\text{Rigid Rotor} \quad E_J = \frac{\hbar^2}{2I} J(J+1) ; J = 0, 1, 2, \dots \quad g_J = 2J + 1$$

$$L^2 = \hbar^2 J(J+1) \quad L_z = m\hbar ; m = 0, 1, \dots, \pm J$$

(In the hydrogen atom l is the equivalent of J .)

$$\text{Euler's Relation} \quad \exp(i\theta) = \cos \theta \pm i \sin \theta$$

$$\text{Trig. Identities} \quad \sin^2 A + \cos^2 B = 1 \quad \sin 2A = 2 \sin A \cos A$$

$$\sin^2 A - \cos^2 B = \cos 2A = 2 \cos^2 A - 1$$

$$\sin(A \pm B) = \sin A \cos B \pm \cos A \sin B \quad \cos(A \pm B) = \cos A \cos B \mp \sin A \sin B$$

Hydrogen-like Atoms/Ions

$$V = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi) = R_{nl}(r)Y_l^m(\theta, \phi) ; n = 1, 2, 3, \dots \quad l = 0, 1, 2, \dots, n-1 \quad m = 0, \pm 1, \dots, \pm l$$

$$E = E_n = -\frac{\mu Z^2 e^4}{2(4\pi\epsilon_0 \hbar n)^2} = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{(13.6)Z^2}{n^2} \text{eV} ; n = 1, 2, 3, \dots$$

$$\begin{aligned}\psi_{1s} &= \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-\sigma} & \sigma &= \frac{Zr}{a_0} \\ \psi_{2s} &= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} (2-\sigma) e^{-\sigma/2} & \psi_{2p_z} &= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \sigma e^{-\sigma/2} \cos\theta \\ \psi_{2p_x} &= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \cos\phi & \psi_{2p_y} &= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \sin\phi\end{aligned}$$

Operating on Spin Functions

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$

$$\hat{S}_{zi}\alpha(i) = \frac{\hbar}{2}\alpha(i) \quad \hat{S}_{zi}\beta(i) = -\frac{\hbar}{2}\beta(i) \quad \hat{S}_z = \sum_i \hat{S}_{zi}$$

Term Symbols Atomic: $^{2S+1}L_J$ $J = L + S, L + S - 1, \dots, |L - S|$

$$M_L = \sum_i m_l(i) \quad M_S = \sum_i m_s(i) \quad M_J = M_L + M_S$$

$$L = -M_L, -M_L + 1, \dots, M_L - 1, M_L \quad S = -M_S, -M_S + 1, \dots, M_S - 1, M_S$$

$$\text{Quadratic Equation} \quad \text{For } ax^2 + bx + c = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

General Integrals

$$\int_0^\infty x^n e^{-ax} dx = \frac{1}{a^{n+1}} n! \quad \int_0^\pi \cos^n \theta \sin \theta d\theta = \int_{-1}^1 x^n dx = 0 \quad \begin{aligned} &\text{if } n \text{ is odd} \\ &= \frac{2}{n+1} \quad \text{if } n \text{ is even} \end{aligned}$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a} \right)^{1/2}$$

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$$

$$\int \sin^2(ax) dx = \frac{x}{2} - \frac{1}{4a} \sin(2ax)$$

$$\int \cos^2(ax) dx = \frac{x}{2} + \frac{\sin(2ax)}{4a}$$

$$\int x \sin^2(ax) dx = \frac{x^2}{4} - \frac{x \sin(2ax)}{4a} - \frac{\cos(2ax)}{8a^2}$$

$$\int x \cos^2(ax) dx = \frac{x^2}{4} + \frac{x \sin(2ax)}{4a} + \frac{\cos(2ax)}{8a^2}$$

*In Spectroscopy, ν and ω are often, but not always, used interchangeably for the frequency. This is potentially confusing because in the wave equation, they are different by a factor of 2π (as in the difference between \hbar and h) In the equations below, I have used ν , to remind you that it's related to the frequency. The tilde (\sim) above a symbol usually means that you should convert to wavenumbers (cm^{-1}), the frequency or energy units used in spectroscopy.

Rotational and Vibrational Spectroscopy

No corrections: $\tilde{E}_{v,J} = \tilde{\nu} \left(v + \frac{1}{2} \right) + \tilde{B}J(J+1)$; $v = 0, 1, 2, \dots$; $J = 0, 1, 2, \dots$

$$\text{where } \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} ; \quad \tilde{B} = \frac{h}{8\pi^2 c I}$$

With corrections: $\tilde{E}_{v,J} = \tilde{\nu}_e \left(v + \frac{1}{2} \right) - \tilde{\chi}_e \tilde{\nu}_e \left(v + \frac{1}{2} \right)^2 + \tilde{B}_v J(J+1) - \tilde{D} J^2 (J+1)^2$

$$\text{where } \tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e \left(v + \frac{1}{2} \right)$$

For vibrational excitations from $v = 0$ to a higher level v ,

$$\tilde{\nu}_{obs} = \tilde{E}_v - \tilde{E}_{v=0} = \tilde{\nu}_e v - \tilde{\chi}_e \tilde{\nu}_e v(v+1)$$

First few lines

$$v = 0 \rightarrow 1 \quad \tilde{\nu}_{obs} = \tilde{\nu}_e - 2\tilde{\chi}_e \tilde{\nu}_e$$

$$v = 0 \rightarrow 2 \quad \tilde{\nu}_{obs} = 2\tilde{\nu}_e - 6\tilde{\chi}_e \tilde{\nu}_e$$

For rovibrational excitations from $v = 0 \rightarrow 1, \Delta J = +1$

$$\tilde{\nu}_{obs} = \tilde{E}_{v=1,J+1} - \tilde{E}_{v=0,J} = \tilde{\nu}_0 + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J - (\tilde{B}_1 - \tilde{B}_0)J^2; J = 0, 1, 2, \dots$$

and from $v = 0 \rightarrow 1, \Delta J = -1$

$$\tilde{\nu}_{obs} = \tilde{E}_{v=1,J-1} - \tilde{E}_{v=0,J} = \tilde{\nu}_0 - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2; J = 1, 2, 3, \dots$$

First few lines of R and P branches

$$v = 0 \rightarrow 1, J = 0 \rightarrow 1 \quad \tilde{\nu}_{obs} = \tilde{\nu}_0 + 2\tilde{B}_1$$

$$v = 0 \rightarrow 1, J = 1 \rightarrow 2 \quad \tilde{\nu}_{obs} = \tilde{\nu}_0 + 6\tilde{B}_1 - 2\tilde{B}_0$$

$$v = 0 \rightarrow 1, J = 1 \rightarrow 0 \quad \tilde{\nu}_{obs} = \tilde{\nu}_0 - 2\tilde{B}_0$$

$$v = 0 \rightarrow 1, J = 2 \rightarrow 1 \quad \tilde{\nu}_{obs} = \tilde{\nu}_0 + 2\tilde{B}_1 - 6\tilde{B}_0$$

Electronic Spectroscopy

$$\tilde{E}_{elec} = \tilde{\nu}_{elec} + \tilde{\nu}_e \left(v + \frac{1}{2} \right) - \tilde{\chi}_e \tilde{\nu}_e \left(v + \frac{1}{2} \right)^2; v = 0, 1, 2, \dots$$

For electronic excitations from $v'' = 0$ to $v' = 0, 1, 2, \dots$

$$\tilde{\nu}_{obs} = \tilde{T}_e + \frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e \tilde{\nu}'_e - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e \tilde{\nu}''_e \right) + \tilde{\nu}'_e v' - \tilde{\chi}'_e \tilde{\nu}'_e v'(v'+1)$$

Beer's Law: $A = \log_{10} \left(\frac{I_0}{I} \right) = \epsilon CL$