Chapter 1

The Dawn of the Quantum Theory

$$d\rho(\nu,T) = \rho_\nu(T)d\nu = \frac{8\pi k_\mathrm{B}T}{c^3}\nu^2 d\nu \tag{1.1}$$

$$d\rho(\nu,T) = \rho_\nu(T)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3 d\nu}{e^{h\nu/k_\mathrm{B}T}-1} \tag{1.2}$$

$$d\rho(\lambda,T) = \rho_\lambda(T)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{hc/\lambda k_\mathrm{B}T}-1} \tag{1.3}$$

$$\lambda_\mathrm{max}T = 2.90\times 10^{-3}\ \mathrm{m{\cdot}K} \tag{1.4}$$

$$\lambda_\mathrm{max}T = \frac{hc}{4.965k_\mathrm{B}} \tag{1.5}$$

$$\mathrm{KE} = \frac{1}{2}mv^2 = h\nu - \phi \tag{1.6}$$

$$h\nu_0 = \phi \tag{1.7}$$

$$\mathrm{KE} = h\nu - h\nu_0 \qquad\qquad \nu \geq \nu_0 \tag{1.8}$$

$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} = 109,680\left(\frac{1}{2^2}-\frac{1}{n^2}\right)\mathrm{cm}^{-1} \qquad n = 3,\ 4,\ \ldots \tag{1.9}$$

$$\tilde{\nu} = \frac{1}{\lambda} = 109,680 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \mathrm{cm}^{-1} \qquad (n_2 > n_1) \tag{1.10}$$

$$\tilde{\nu} = R_{\mathrm{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.11}$$

$$\lambda = \frac{h}{p} \tag{1.12}$$

$$f = \frac{m_{\mathrm{e}} v^2}{r} \tag{1.13}$$

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m_{\mathrm{e}} v^2}{r} \tag{1.14}$$

$$2\pi r = n\lambda \qquad n = 1,\ 2,\ 3,\ \ldots \tag{1.15}$$

$$m_{\mathrm{e}} v r = n\hbar \qquad n = 1,\ 2,\ 3,\ \ldots \tag{1.16}$$

$$r = \frac{\varepsilon_0 h^2 n^2}{\pi m_{\mathrm{e}} e^2} = \frac{4\pi\varepsilon_0 \hbar^2 n^2}{m_{\mathrm{e}} e^2} \tag{1.17}$$

$$\begin{aligned} r &= \frac{4\pi(8.85419 \times 10^{-12}\ \mathrm{C}^2 \cdot \mathrm{N}^{-1} \cdot \mathrm{m}^{-2})(1.055 \times 10^{-34}\ \mathrm{J} \cdot \mathrm{s})^2}{(9.109 \times 10^{-31}\ \mathrm{kg})(1.6023 \times 10^{-19}\ \mathrm{C})^2} \\ &= 5.292 \times 10^{-11}\ \mathrm{m} = 52.92\ \mathrm{pm} \end{aligned} \tag{1.18}$$

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{1.19}$$

$$E = \mathrm{KE} + V(r) = \frac{1}{2} m_{\mathrm{e}} v^2 - \frac{e^2}{4\pi\varepsilon_0 r} \tag{1.20}$$

$$E = \frac{1}{2} \left(\frac{e^2}{4\pi\varepsilon_0 r} \right) - \frac{e^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{8\pi\varepsilon_0 r} \tag{1.21}$$

$$E_n = -\frac{m_{\mathrm{e}} e^4}{8\varepsilon_0^2 h^2} \frac{1}{n^2} \qquad n = 1,\ 2,\ \ldots \tag{1.22}$$

$$\Delta E = \frac{m_\mathrm{e} e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu \tag{1.23}$$

$$\tilde{\nu} = \frac{m_\mathrm{e} e^4}{8\varepsilon_0^2 c h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1.24}$$

$$R_\infty = \frac{m_\mathrm{e} e^4}{8\varepsilon_0^2 c h^3} \tag{1.25}$$

$$\Delta x \Delta p \geq h \tag{1.26}$$

$$|\Delta \mathbf{r}| \approx \Delta s = r\Delta\theta \tag{1.27}$$

$$v = \lim_{\Delta t \to 0} \frac{\Delta s}{\Delta t} = r \lim_{\Delta t \to 0} \frac{\Delta\theta}{\Delta t} = r\omega \tag{1.28}$$

$$\Delta v = |\Delta \mathbf{v}| = v\Delta\theta \tag{1.29}$$

$$a = \lim_{\Delta t \to 0} \frac{\Delta v}{\Delta t} = v \lim_{\Delta t \to 0} \frac{\Delta\theta}{\Delta t} = v\omega \tag{1.30}$$

Chapter 2

The Classical Wave Equation

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2} \tag{2.1}$$

$$u(0,t) = 0 \quad \text{and} \quad u(l,t) = 0 \qquad \text{(for all } t\text{)} \tag{2.2}$$

$$u(x,t) = X(x)T(t) \tag{2.3}$$

$$T(t)\frac{d^2X(x)}{dx^2} = \frac{1}{v^2}X(x)\frac{d^2T(t)}{dt^2} \tag{2.4}$$

$$\frac{1}{X(x)}\frac{d^2X(x)}{dx^2} = \frac{1}{v^2T(t)}\frac{d^2T(t)}{dt^2} \tag{2.5}$$

$$\frac{1}{X(x)}\frac{d^2X(x)}{dx^2} = K \tag{2.6}$$

$$\frac{1}{v^2T(t)}\frac{d^2T(t)}{dt^2} = K \tag{2.7}$$

$$\frac{d^2X(x)}{dx^2} - KX(x) = 0 \tag{2.8}$$

$$\frac{d^2T(t)}{dt^2} - Kv^2T(t) = 0 \tag{2.9}$$

$$X(x) = a_1 x + b_1 \tag{2.10}$$

$$T(t) = a_2 t + b_2 \tag{2.11}$$

$$u(0,t) = X(0)T(t) = 0 \tag{2.12}$$

$$u(l,t) = X(l)T(t) = 0 \tag{2.13}$$

$$X(0) = 0 \qquad \text{and} \qquad X(l) = 0 \tag{2.14}$$

$$\frac{d^2y}{dx^2} - k^2 y(x) = 0 \tag{2.15}$$

$$\frac{d^2y}{dx^2} + y(x) = 0 \tag{2.16}$$

$$y(x) = c_1 e^{ix} + c_2 e^{-ix} \tag{2.17}$$

$$X(l) = B \sin \beta l = 0 \tag{2.18}$$

$$\beta l = n\pi \qquad n = 1,\ 2,\ 3,\ \ldots \tag{2.19}$$

$$X(x) = B \sin \frac{n\pi x}{l} \tag{2.20}$$

$$\frac{d^2T(t)}{dt^2} + \beta^2 v^2 T(t) = 0 \tag{2.21}$$

$$T(t) = D \cos \omega_n t + E \sin \omega_n t \tag{2.22}$$

$$u_n(x,t) = (F_n \cos \omega_n t + G_n \sin \omega_n t) \sin \frac{n\pi x}{l} \qquad n = 1,\ 2,\ \ldots \tag{2.23}$$

$$u(x,t) = \sum_{n=1}^{\infty} (F_n \cos \omega_n t + G_n \sin \omega_n t) \sin \frac{n\pi x}{l} \qquad n = 1,\ 2,\ \ldots \tag{2.24}$$

$$u(x,t) = \sum_{n=1}^{\infty} A_n \cos(\omega_n t + \phi_n) \sin \frac{n\pi x}{l} = \sum_{n=1}^{\infty} u_n(x,t) \tag{2.25}$$

$$\nu_n = \frac{\omega_n}{2\pi} = \frac{vn}{2l} \tag{2.26}$$

$$u(x,t) = \cos \omega_1 t \sin \frac{\pi x}{l} + \frac{1}{2} \cos\left(\omega_2 t + \frac{\pi}{2}\right) \sin \frac{2\pi x}{l} \tag{2.27}$$

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} \tag{2.28}$$

$$\begin{aligned} &u(0,y) = u(a,y) = 0 \\ &u(x,0) = u(x,b) = 0 \end{aligned} \qquad \text{(for all } t\text{)} \tag{2.29}$$

$$u(x,y,t) = F(x,y)T(t) \tag{2.30}$$

$$\frac{1}{v^2 T(t)} \frac{d^2 T}{dt^2} = \frac{1}{F(x,y)} \left(\frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial y^2} \right) \tag{2.31}$$

$$\frac{d^2 T}{dt^2} + v^2 \beta^2 T(t) = 0 \tag{2.32}$$

$$\frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial y^2} + \beta^2 F(x,y) = 0 \tag{2.33}$$

$$\frac{1}{X(x)} \frac{d^2 X}{dx^2} + \frac{1}{Y(y)} \frac{d^2 Y}{dy^2} + \beta^2 = 0 \tag{2.34}$$

$$\frac{1}{X(x)} \frac{d^2 X}{dx^2} = -p^2 \tag{2.35}$$

$$\frac{1}{Y(y)} \frac{d^2 Y}{dy^2} = -q^2 \tag{2.36}$$

$$p^2 + q^2 = \beta^2 \tag{2.37}$$

$$\frac{d^2 X}{dx^2} + p^2 X(x) = 0 \tag{2.38}$$

$$\frac{d^2Y}{dy^2} + q^2Y(y) = 0 \tag{2.39}$$

$$X(x) = A\cos px + B\sin px \tag{2.40}$$

$$Y(y) = C\cos qy + D\sin qy \tag{2.41}$$

$$\begin{aligned} X(0) = X(a) = 0 \\ Y(0) = Y(b) = 0 \end{aligned} \tag{2.42}$$

$$X(x) = B\sin\frac{n\pi x}{a} \qquad n = 1,\ 2,\ \ldots \tag{2.43}$$

$$Y(y) = D\sin\frac{m\pi y}{b} \qquad m = 1,\ 2,\ \ldots \tag{2.44}$$

$$\beta_{nm} = \pi\left(\frac{n^2}{a^2} + \frac{m^2}{b^2}\right)^{1/2} \qquad \begin{aligned} n = 1,\ 2,\ \ldots \\ m = 1,\ 2,\ \ldots \end{aligned} \tag{2.45}$$

$$T_{nm}(t) = E_{nm}\cos\omega_{nm}t + F_{nm}\sin\omega_{nm}t \tag{2.46}$$

$$\begin{aligned} \omega_{nm} &= v\beta_{nm} \\ &= v\pi\left(\frac{n^2}{a^2} + \frac{m^2}{b^2}\right)^{1/2} \end{aligned} \tag{2.47}$$

$$T_{nm}(t) = G_{nm}\cos(\omega_{nm}t + \phi_{nm}) \tag{2.48}$$

$$\begin{aligned} u(x, y, t) &= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} u_{nm}(x, y, t) \\ &= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} A_{nm}\cos(\omega_{nm}t + \phi_{nm})\sin\frac{n\pi x}{a}\sin\frac{m\pi y}{b} \end{aligned} \tag{2.49}$$

$$\omega_{nm} = \frac{v\pi}{a}\left(n^2 + m^2\right)^{1/2} \tag{2.50}$$

Chapter 3

The Schrödinger Equation and a Particle in a Box

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2} \tag{3.1}$$

$$u(x,t) = \psi(x)\cos\omega t \tag{3.2}$$

$$\frac{d^2\psi}{dx^2} + \frac{\omega^2}{v^2}\psi(x) = 0 \tag{3.3}$$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0 \tag{3.4}$$

$$E = \frac{p^2}{2m} + V(x) \tag{3.5}$$

$$p = \{2m[E - V(x)]\}^{1/2} \tag{3.6}$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0 \tag{3.7}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{3.8}$$

$$\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] = c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x) \tag{3.9}$$

$$\hat{A}\phi(x) = a\phi(x) \tag{3.10}$$

$$\hat{P}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.11}$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x) \tag{3.12}$$

$$\hat{H}\psi(x) = E\psi(x) \tag{3.13}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{3.14}$$

$$\hat{K}_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{3.15}$$

$$\hat{P}_x^2 = -\hbar^2\frac{d^2}{dx^2} \tag{3.16}$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0 \qquad 0 \le x \le a \tag{3.17}$$

$$k = \frac{(2mE)^{1/2}}{\hbar} \tag{3.18}$$

$$\psi(a) = B\sin ka = 0 \tag{3.19}$$

$$ka = n\pi \qquad n = 1,\ 2,\ \ldots \tag{3.20}$$

$$E_n = \frac{h^2 n^2}{8ma^2} \qquad n = 1,\ 2,\ \ldots \tag{3.21}$$

$$\begin{aligned} \psi(x) &= B\sin kx \\ &= B\sin\frac{n\pi x}{a} \qquad n = 1,\ 2,\ \ldots \end{aligned} \tag{3.22}$$

$$\psi_n^*(x)\psi_n(x)dx = B^*B\sin^2\frac{n\pi x}{a}dx \tag{3.23}$$

$$\int_0^a \psi_n^*(x)\psi_n(x)dx = 1 \tag{3.24}$$

$$|B|^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = 1 \tag{3.25}$$

$$\int_0^a \sin^2 \frac{n\pi x}{a} dx = \frac{a}{n\pi} \int_0^{n\pi} \sin^2 z dz = \frac{a}{n\pi} \left(\frac{n\pi}{2}\right) = \frac{a}{2} \tag{3.26}$$

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a} \qquad 0 \le x \le a \qquad n = 1,\ 2,\ \ldots \tag{3.27}$$

$$\text{Prob}[x_1 \le x \le x_2] = \int_{x_1}^{x_2} \psi^*(x)\psi(x)dx \tag{3.28}$$

$$\begin{aligned} f(x)dx &= \frac{2}{a} \sin^2 \frac{n\pi x}{a} dx && 0 \le x \le a \\ &= 0 && \text{otherwise} \end{aligned} \tag{3.29}$$

$$\langle x \rangle = \frac{2}{a} \int_0^a x \sin^2 \frac{n\pi x}{a} dx \tag{3.30}$$

$$\langle x \rangle = \frac{2}{a} \cdot \frac{a^2}{4} = \frac{a}{2} \qquad \text{(for all } n) \tag{3.31}$$

$$\begin{aligned} \langle x^2 \rangle &= \frac{2}{a} \int_0^a x^2 \sin^2 \frac{n\pi x}{a} dx \\ &= \left(\frac{a}{2\pi n}\right)^2 \left(\frac{4\pi^2 n^2}{3} - 2\right) = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} \end{aligned} \tag{3.32}$$

$$\sigma_x = \frac{a}{2\pi n} \left(\frac{\pi^2 n^2}{3} - 2\right)^{1/2} \tag{3.33}$$

$$\hat{H}\psi_n(x) = E_n \psi_n(x) \tag{3.34}$$

$$\int \psi_n^*(x)\hat{H}\psi_n(x)dx = \int \psi_n^*(x)E_n\psi_n(x)dx = E_n \int \psi_n^*(x)\psi_n(x)dx = E_n \tag{3.35}$$

$$\langle s \rangle = \int \psi_n^*(x) \hat{S} \psi_n(x) dx \tag{3.36}$$

$$\langle p \rangle = \int_0^a \left[\left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \right] \left(-i\hbar \frac{d}{dx} \right) \left[\left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \right] dx \tag{3.37}$$

$$\langle p \rangle = 0 \tag{3.38}$$

$$\langle p^2 \rangle = \int \psi_n^*(x) \hat{P}_x^2 \psi_n(x) dx \tag{3.39}$$

$$\begin{aligned} \langle p^2 \rangle &= \int_0^a \left[\left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \right] \left(-\hbar^2 \frac{d^2}{dx^2} \right) \left[\left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \right] dx \\ &= \frac{2n^2\pi^2\hbar^2}{a^3} \int_0^a \sin \frac{n\pi x}{a} \sin \frac{n\pi x}{a} dx \\ &= \frac{2n^2\pi^2\hbar^2}{a^3} \cdot \frac{a}{2} = \frac{n^2\pi^2\hbar^2}{a^2} \end{aligned} \tag{3.40}$$

$$\sigma_p = \frac{n\pi\hbar}{a} \tag{3.41}$$

$$\sigma_x \sigma_p = \frac{\hbar}{2} \left(\frac{\pi^2 n^2}{3} - 2 \right)^{1/2} \tag{3.42}$$

$$\sigma_x \sigma_p > \frac{\hbar}{2} \tag{3.43}$$

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E\psi(x, y, z) \qquad \begin{array}{l} 0 \le x \le a \\ 0 \le y \le b \\ 0 \le z \le c \end{array} \tag{3.44}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{3.45}$$

$$\begin{array}{ll} \psi(0, y, z) = \psi(a, y, z) = 0 & \text{for all } y \text{ and } z \\ \psi(x, 0, z) = \psi(x, b, z) = 0 & \text{for all } x \text{ and } z \\ \psi(x, y, 0) = \psi(x, y, c) = 0 & \text{for all } x \text{ and } y \end{array} \tag{3.46}$$

$$\psi(x,y,z) = X(x)Y(y)Z(z) \tag{3.47}$$

$$-\frac{\hbar^2}{2m}\frac{1}{X(x)}\frac{d^2X}{dx^2} - \frac{\hbar^2}{2m}\frac{1}{Y(y)}\frac{d^2Y}{dy^2} - \frac{\hbar^2}{2m}\frac{1}{Z(z)}\frac{d^2Z}{dz^2} = E \tag{3.48}$$

$$E_x + E_y + E_z = E \tag{3.49}$$

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{1}{X(x)}\frac{d^2X}{dx^2} &= E_x \\ -\frac{\hbar^2}{2m}\frac{1}{Y(y)}\frac{d^2Y}{dy^2} &= E_y \\ -\frac{\hbar^2}{2m}\frac{1}{Z(z)}\frac{d^2Z}{dz^2} &= E_z \end{aligned} \tag{3.50}$$

$$\begin{aligned} X(0) = X(a) = 0 \\ Y(0) = Y(b) = 0 \\ Z(0) = Z(c) = 0 \end{aligned} \tag{3.51}$$

$$\begin{aligned} X(x) &= A_x \sin\frac{n_x\pi x}{a} \qquad && n_x = 1,\ 2,\ 3,\ \ldots \\ Y(y) &= A_y \sin\frac{n_y\pi y}{b} \qquad && n_y = 1,\ 2,\ 3,\ \ldots \\ Z(z) &= A_z \sin\frac{n_z\pi z}{c} \qquad && n_z = 1,\ 2,\ 3,\ \ldots \end{aligned} \tag{3.52}$$

$$\psi(x,y,z) = A_xA_yA_z \sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\sin\frac{n_z\pi z}{c} \tag{3.53}$$

$$\int_0^a dx \int_0^b dy \int_0^c dz \psi^*(x,y,z)\psi(x,y,z) = 1 \tag{3.54}$$

$$A_xA_yA_z = \left(\frac{8}{abc}\right)^{1/2} \tag{3.55}$$

$$\psi_{n_xn_yn_z} = \left(\frac{8}{abc}\right)^{1/2} \sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\sin\frac{n_z\pi z}{c} \qquad \begin{aligned} n_x &= 1,\ 2,\ 3,\ \ldots \\ n_y &= 1,\ 2,\ 3,\ \ldots \\ n_z &= 1,\ 2,\ 3,\ \ldots \end{aligned} \tag{3.56}$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad \begin{array}{l} n_x = 1,\ 2,\ 3,\ \ldots \\ n_y = 1,\ 2,\ 3,\ \ldots \\ n_z = 1,\ 2,\ 3,\ \ldots \end{array} \tag{3.57}$$

$$\hat{\mathbf{P}} = -i\hbar\left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}\right) \tag{3.58}$$

$$\langle \mathbf{p} \rangle = \int_0^a dx \int_0^b dy \int_0^c dz \psi^*(x,y,z)\hat{\mathbf{P}}\psi(x,y,z) \tag{3.59}$$

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \tag{3.60}$$

$$\hat{H} = \hat{H}_1(s) + \hat{H}_2(w) \tag{3.61}$$

$$\psi_{nm}(s,w) = \phi_n(s)\varphi_m(w) \tag{3.62}$$

$$\begin{aligned} \hat{H}_1(s)\phi_n(s) &= E_n\phi_n(s) \\ \hat{H}_2(w)\varphi_m(w) &= E_m\varphi_m(w) \end{aligned} \tag{3.63}$$

$$E_{nm} = E_n + E_m \tag{3.64}$$

Chapter 4

Some Postulates and General Principles of Quantum Mechanics

$$m\frac{d^2x}{dt^2} = F_x(x,y,z), \quad m\frac{d^2y}{dt^2} = F_y(x,y,z), \quad m\frac{d^2z}{dt^2} = F_z(x,y,z) \tag{4.1}$$

$$\int_{\text{all space}} \psi^*(x)\psi(x)dx = 1 \tag{4.2}$$

$$K = \frac{1}{2}mv^2 = \frac{1}{2}mr^2\omega^2 = \frac{1}{2}I\omega^2 \tag{4.3}$$

$$L = I\omega = (mr^2)\left(\frac{v}{r}\right) = mvr \tag{4.4}$$

$$K = \frac{mv^2}{2} = \frac{(mv)^2}{2m} = \frac{p^2}{2m} \tag{4.5}$$

$$K = \frac{I\omega^2}{2} = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \tag{4.6}$$

$$\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - yp_x \end{aligned} \tag{4.7}$$

$$\hat{A}\psi_n = a_n\psi_n \tag{4.8}$$

$$\hat{H}\psi_n = E_n\psi_n \tag{4.9}$$

$$\begin{aligned}
\langle x \rangle &= \int_0^a \psi_n^*(x) x \psi_n(x) dx \\
&= \frac{2}{a}\int_0^a x \sin^2 \frac{n_x \pi x}{a} dx = \frac{a}{2} \quad \text{(for all } n\text{)}
\end{aligned} \tag{4.10}$$

$$\langle a \rangle = \int\limits_{\text{all space}} \psi^* \hat{A} \psi dx \tag{4.11}$$

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\hat{A}\psi_n(x)dx = \int_{-\infty}^{\infty} \psi_n^*(x) a_n \psi_n(x) dx = a_n \int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)dx = a_n \tag{4.12}$$

$$\langle a^2 \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\hat{A}^2\psi_n(x)dx = a_n^2 \tag{4.13}$$

$$\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2 = a_n^2 - a_n^2 = 0 \tag{4.14}$$

$$\hat{H}\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} \tag{4.15}$$

$$\frac{1}{\psi(x)}\hat{H}\psi(x) = \frac{i\hbar}{f(t)}\frac{df(t)}{dt} \tag{4.16}$$

$$\hat{H}\psi(x) = E\psi(x) \tag{4.17}$$

$$\frac{df(t)}{dt} = -\frac{i}{\hbar}Ef(t) \tag{4.18}$$

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{4.19}$$

$$\Psi(x,t) = \psi(x)e^{-i\omega t} \tag{4.20}$$

$$\Psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar} \tag{4.21}$$

$$\Psi_n^*(x,t)\Psi_n(x,t)dx = e^{iE_n t/\hbar}\psi_n^*(x) e^{-iE_n t/\hbar}\psi_n(x)dx = \psi_n^*(x)\psi_n(x)dx \tag{4.22}$$

$$\hat{A}\psi_n = a_n \psi_n \tag{4.23}$$

$$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)dx = 0 \qquad m \neq n \tag{4.24}$$

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a} \qquad n = 1,\ 2,\ \ldots \tag{4.25}$$

$$\frac{2}{a}\int_0^a \sin\frac{n\pi x}{a}\sin\frac{m\pi x}{a}dx = \frac{1}{a}\int_0^a \cos\frac{(n-m)\pi x}{a}dx - \frac{1}{a}\int_0^a \cos\frac{(n+m)\pi x}{a}dx \tag{4.26}$$

$$\frac{2}{a}\int_0^a \sin\frac{n\pi x}{a}\sin\frac{m\pi x}{a}dx = 0 \qquad m \neq n \tag{4.27}$$

$$\frac{2}{a}\int_0^a \sin^2\frac{n\pi x}{a}dx = 1 \tag{4.28}$$

$$\int_{-\infty}^{\infty} \psi_i^*\psi_j dx = \delta_{ij} \tag{4.29}$$

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \tag{4.30}$$

$$\int\limits_{\text{all space}} f^*(x)\hat{A}g(x)dx = \int\limits_{\text{all space}} g(x)\hat{A}^* f^*(x)dx \tag{4.31}$$

$$\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x) \qquad \text{(commutative)} \tag{4.32}$$

$$\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x) \qquad \text{(noncommutative)} \tag{4.33}$$

$$\hat{K}_x\hat{P}_x\psi(x) = \hat{P}_x\hat{K}_x\psi(x) \tag{4.34}$$

$$(\hat{K}_x\hat{P}_x - \hat{P}_x\hat{K}_x)\psi(x) = \hat{O}\psi(x) \tag{4.35}$$

$$\hat{K}_x\hat{P}_x - \hat{P}_x\hat{K}_x = \hat{O} \tag{4.36}$$

$$[\hat{K}_x, \hat{P}_x] = \hat{K}_x\hat{P}_x - \hat{P}_x\hat{K}_x \tag{4.37}$$

$$[\hat{K}_x, \hat{P}_x] = \hat{O} \tag{4.38}$$

$$\hat{P}_x\hat{X}\psi(x) \neq \hat{X}\hat{P}_x\psi(x) \tag{4.39}$$

$$(\hat{P}_x\hat{X} - \hat{X}\hat{P}_x)\psi(x) = -i\hbar\hat{I}\psi(x) \tag{4.40}$$

$$\hat{P}_x\hat{X} - \hat{X}\hat{P}_x = -i\hbar\hat{I} \tag{4.41}$$

$$[\hat{P}_x, \hat{X}] = -i\hbar\hat{I} \tag{4.42}$$

$$\langle A^2\rangle - \langle A\rangle^2 = \sigma_a^2 = \int \psi(x)\hat{A}^2\psi(x)dx - \left[\int \psi(x)\hat{A}\psi(x)dx\right]^2 \tag{4.43}$$

$$\sigma_a\sigma_b \geq \frac{1}{2}\left|\int \psi^*(x)[\hat{A},\hat{B}]\psi(x)\right| dx \tag{4.44}$$

$$\begin{aligned} \sigma_p\sigma_x &\geq \frac{1}{2}\left|\int \psi^*(x)(-i\hbar\hat{I})\psi(x)dx\right| \\ &\geq \frac{1}{2}|-i\hbar| \geq \frac{\hbar}{2} \end{aligned} \tag{4.45}$$

Chapter 5

The Harmonic Oscillator and the Rigid Rotator: Two Spectroscopic Models

$$f = -k(l - l_0) = -kx \tag{5.1}$$

$$m\frac{d^2l}{dt^2} = -k(l - l_0) \tag{5.2}$$

$$m\frac{d^2x}{dt^2} + kx = 0 \tag{5.3}$$

$$x(t) = c_1 \sin \omega t + c_2 \cos \omega t \tag{5.4}$$

$$\omega = \left(\frac{k}{m}\right)^{1/2} \tag{5.5}$$

$$x(t) = A \sin(\omega t + \phi) \tag{5.6}$$

$$x(t) = A \cos \omega t \tag{5.7}$$

$$f(x) = -\frac{dV}{dx} \tag{5.8}$$

$$V(x) = -\int f(x)dx + \text{constant} \tag{5.9}$$

$$V(x) = \frac{k}{2}x^2 + \text{constant} \tag{5.10}$$

$$V(x) = \frac{k}{2}x^2 \tag{5.11}$$

$$K = \frac{1}{2}m\left(\frac{dl}{dt}\right)^2 = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 \tag{5.12}$$

$$K = \frac{1}{2}m\omega^2 A^2 \sin^2 \omega t \tag{5.13}$$

$$V = \frac{1}{2}kA^2 \cos^2 \omega t \tag{5.14}$$

$$\begin{aligned} E &= \frac{kA^2}{2}(\sin^2 \omega t + \cos^2 \omega t) \\ &= \frac{kA^2}{2} \end{aligned} \tag{5.15}$$

$$m_1 \frac{d^2 x_1}{dt^2} = k(x_2 - x_1 - l_0) \tag{5.16}$$

$$m_2 \frac{d^2 x_2}{dt^2} = -k(x_2 - x_1 - l_0) \tag{5.17}$$

$$\frac{d^2}{dt^2}(m_1 x_1 + m_2 x_2) = 0 \tag{5.18}$$

$$X = \frac{m_1 x_1 + m_2 x_2}{M} \tag{5.19}$$

$$M \frac{d^2 X}{dt^2} = 0 \tag{5.20}$$

$$x = x_2 - x_1 \tag{5.21}$$

$$\mu\frac{d^2x}{dt^2} + kx = 0 \tag{5.22}$$

$$\begin{aligned} V(l) &= V(l_0) + \left(\frac{dV}{dl}\right)_{l=l_0}(l-l_0) + \frac{1}{2!}\left(\frac{d^2V}{dl^2}\right)_{l=l_0}(l-l_0)^2 \\ &\quad + \frac{1}{3!}\left(\frac{d^3V}{dl^3}\right)_{l=l_0}(l-l_0)^3 + \cdots \end{aligned} \tag{5.23}$$

$$\begin{aligned} V(x) &= \frac{1}{2}k(l-l_0)^2 + \frac{1}{6}\gamma(l-l_0)^3 + \cdots \\ &= \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \cdots \end{aligned} \tag{5.24}$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{5.25}$$

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi(x) = 0 \tag{5.26}$$

$$\begin{aligned} E_v &= \hbar\left(\frac{k}{\mu}\right)^{1/2}\left(v + \frac{1}{2}\right) \\ &= \hbar\omega\left(v + \frac{1}{2}\right) = h\nu\left(v + \frac{1}{2}\right) \qquad v = 0,\ 1,\ 2,\ \ldots \end{aligned} \tag{5.27}$$

$$\omega = \left(\frac{k}{\mu}\right)^{1/2} \tag{5.28}$$

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \tag{5.29}$$

$$E_v = \hbar\left(\frac{k}{\mu}\right)^{1/2}\left(v + \frac{1}{2}\right) \qquad v = 0,\ 1,\ 2,\ \ldots \tag{5.30}$$

$$\Delta E = h\nu_{\text{obs}} \tag{5.31}$$

$$\Delta E = E_{v+1} - E_v = \hbar \left(\frac{k}{\mu} \right)^{1/2} \tag{5.32}$$

$$\nu_{\text{obs}} = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \tag{5.33}$$

$$\tilde{\nu}_{\text{obs}} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \tag{5.34}$$

$$\psi_v(x) = N_v H_v(\alpha^{1/2} x) e^{-\alpha x^2/2} \tag{5.35}$$

$$\alpha = \left(\frac{k\mu}{\hbar^2} \right)^{1/2} \tag{5.36}$$

$$N_v = \frac{1}{(2^v v!)^{1/2}} \left(\frac{\alpha}{\pi} \right)^{1/4} \tag{5.37}$$

$$f(x) = f(-x) \qquad \text{(even)} \tag{5.38}$$

$$f(x) = -f(-x) \qquad \text{(odd)} \tag{5.39}$$

$$\int_{-A}^{A} f(x) dx = 0 \qquad f(x) \text{ odd} \tag{5.40}$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_v(x) x \psi_v(x) dx = 0 \tag{5.41}$$

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_v(x) \left(-i\hbar \frac{d}{dx} \right) \psi_v(x) dx \tag{5.42}$$

$$\begin{aligned} K &= \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \omega^2 \\ &= \frac{1}{2} I \omega^2 \end{aligned} \tag{5.43}$$

$$I = m_1 r_1^2 + m_2 r_2^2 \tag{5.44}$$

$$I = \mu r^2 \tag{5.45}$$

$$L = I\omega \tag{5.46}$$

$$K = \frac{L^2}{2I} \tag{5.47}$$

$$\hat{H} = \hat{K} = -\frac{\hbar^2}{2\mu}\nabla^2 \qquad (r \text{ constant}) \tag{5.48}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta} \tag{5.49}$$

$$\nabla^2 = \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \qquad (r \text{ constant}) \tag{5.50}$$

$$\hat{H} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right] \tag{5.51}$$

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right] \tag{5.52}$$

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]Y(\theta,\phi) = EY(\theta,\phi) \tag{5.53}$$

$$\beta = \frac{2IE}{\hbar^2} \tag{5.54}$$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} + (\beta\sin^2\theta)Y = 0 \tag{5.55}$$

$$\beta = J(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots \tag{5.56}$$

$$E_J = \frac{\hbar^2}{2I}J(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots \tag{5.57}$$

$$\Delta J = \pm 1 \tag{5.58}$$

$$\begin{aligned}\Delta E &= E_{J+1} - E_J = \frac{\hbar^2}{2I}\left[(J+1)(J+2) - J(J+1)\right] \\ &= \frac{\hbar^2}{I}(J+1) = \frac{h^2}{4\pi^2 I}(J+1)\end{aligned} \tag{5.59}$$

$$\nu = \frac{h}{4\pi^2 I}(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots \tag{5.60}$$

$$\nu = 2B(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots \tag{5.61}$$

$$B = \frac{h}{8\pi^2 I} \tag{5.62}$$

$$\tilde{\nu} = 2\tilde{B}(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots \tag{5.63}$$

$$\tilde{B} = \frac{h}{8\pi^2 c I} \qquad (\mathrm{cm}^{-1}) \tag{5.64}$$

Chapter 6

The Hydrogen Atom

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{6.1}$$

$$\hat{H} = -\frac{\hbar^2}{2m_\text{e}}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \tag{6.2}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{6.3}$$

$$-\frac{\hbar^2}{2m_\text{e}}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$
$$+\frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \tag{6.4}$$

$$-\hbar^2\left(\frac{\partial}{\partial r}r^2\frac{\partial\psi}{\partial r}\right) - \hbar^2\left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi}\right]$$
$$+2m_\text{e}r^2\left[\frac{e^2}{4\pi\varepsilon_0 r} - E\right]\psi(r,\theta,\phi) = 0 \tag{6.5}$$

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{6.6}$$

$$-\frac{\hbar^2}{R(r)}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+2m_{\mathrm{e}}r^2\left(\frac{e^2}{4\pi\varepsilon_0 r}-E\right)-\frac{\hbar^2}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=0 \tag{6.7}$$

$$-\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m_{\mathrm{e}}r^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r}-E\right)=-\beta \tag{6.8}$$

$$-\frac{1}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=\beta \tag{6.9}$$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}+(\beta\sin^2\theta)Y=0 \tag{6.10}$$

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi) \tag{6.11}$$

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\beta\sin^2\theta+\frac{1}{\Phi(\phi)}\frac{d^2\Phi}{d\phi^2}=0 \tag{6.12}$$

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\beta\sin^2\theta=m^2 \tag{6.13}$$

$$\frac{1}{\Phi(\phi)}\frac{d^2\Phi}{d\phi^2}=-m^2 \tag{6.14}$$

$$\Phi(\phi)=A_m e^{im\phi} \quad \text{and} \quad \Phi(\phi)=A_{-m}e^{-im\phi} \tag{6.15}$$

$$\Phi(\phi+2\pi)=\Phi(\phi) \tag{6.16}$$

$$A_m e^{im(\phi+2\pi)}=A_m e^{im\phi} \tag{6.17}$$

$$A_{-m}e^{-im(\phi+2\pi)}=A_{-m}e^{-im\phi} \tag{6.18}$$

$$e^{\pm i2\pi m}=1 \tag{6.19}$$

$$\Phi_m(\phi)=A_m e^{im\phi} \qquad m=0,\ \pm1,\ \pm2,\ \ldots \tag{6.20}$$

$$\Phi_m(\phi) = \frac{1}{(2\pi)^{1/2}} e^{im\phi} \qquad m = 0,\ \pm1,\ \pm2,\ \ldots \tag{6.21}$$

$$(1 - x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left[\beta - \frac{m^2}{1 - x^2}\right] P(x) = 0 \tag{6.22}$$

$$(1 - x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left[l(l+1) - \frac{m^2}{1 - x^2}\right] P(x) = 0 \tag{6.23}$$

$$\int_{-1}^{1} P_l(x) P_n(x) dx = 0 \qquad l \neq n \tag{6.24}$$

$$\int_{-1}^{1} [P_l(x)]^2 dx = \frac{2}{2l+1} \tag{6.25}$$

$$P_l^{|m|}(x) = (1 - x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x) \tag{6.26}$$

$$\int_{-1}^{1} P_l(x) P_n(x) dx = \int_0^{\pi} P_l(\cos\theta) P_n(\cos\theta) \sin\theta d\theta = \frac{2\delta_{ln}}{2l+1} \tag{6.27}$$

$$\begin{aligned} \int_{-1}^{1} P_l^{|m|}(x) P_n^{|m|}(x) dx &= \int_0^{\pi} P_l^{|m|}(\cos\theta) P_n^{|m|}(\cos\theta) \sin\theta d\theta \\ &= \frac{2}{(2l+1)} \frac{(l+|m|)!}{(l-|m|)!} \delta_{ln} \end{aligned} \tag{6.28}$$

$$N_{lm} = \left[\frac{(2l+1)}{2} \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \tag{6.29}$$

$$Y_l^m(\theta, \phi) = \left[\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta) e^{im\phi} \tag{6.30}$$

$$\int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi\, Y_l^m(\theta, \phi)^* Y_n^k(\theta, \phi) = \delta_{nl}\delta_{mk} \tag{6.31}$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2}\right] \tag{6.32}$$

$$\hat{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi) \tag{6.33}$$

$$L^2 = \hbar^2 l(l+1) \qquad l = 0,\ 1,\ 2,\ \ldots \tag{6.34}$$

$$\hat{H} Y_l^m(\theta,\phi) = \frac{\hbar^2 l(l+1)}{2I} Y_l^m(\theta,\phi) \tag{6.35}$$

$$\begin{aligned}
\hat{L}_x &= y\hat{P}_z - z\hat{P}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\
\hat{L}_y &= z\hat{P}_x - x\hat{P}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\
\hat{L}_z &= x\hat{P}_y - y\hat{P}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)
\end{aligned} \tag{6.36}$$

$$\begin{aligned}
\hat{L}_x &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\
\hat{L}_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\
\hat{L}_z &= -i\hbar\frac{\partial}{\partial\phi}
\end{aligned} \tag{6.37}$$

$$\begin{aligned}
\hat{L}_z Y_l^m(\theta,\phi) &= N_{lm}\hat{L}_z P_l^{|m|}(\cos\theta)e^{im\phi} \\
&= N_{lm} P_l^{|m|}(\cos\theta)\hat{L}_z e^{im\phi} \\
&= \hbar m Y_l^m(\theta,\phi)
\end{aligned} \tag{6.38}$$

$$\hat{L}_z^2 Y_l^m(\theta,\phi) = L_z^2 Y_l^m(\theta,\phi) = m^2\hbar^2 Y_l^m(\theta,\phi) \tag{6.39}$$

$$(\hat{L}^2 - \hat{L}_z^2)Y_l^m(\theta,\phi) = (\hat{L}_x^2 + \hat{L}_y^2)Y_l^m(\theta,\phi) = [l(l+1) - m^2]\hbar^2 Y_l^m(\theta,\phi) \tag{6.40}$$

$$l(l+1) \geq m^2 \tag{6.41}$$

$$m = 0,\ \pm 1,\ \pm 2,\ \ldots,\ \pm l \tag{6.42}$$

$$-\frac{\hbar^2}{2m_\mathrm{e}r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{\hbar^2 l(l+1)}{2m_\mathrm{e}r^2}+\frac{e^2}{4\pi\varepsilon_0 r}-E\right]R(r)=0 \tag{6.43}$$

$$E_n=-\frac{m_\mathrm{e}e^4}{8\varepsilon_0^2h^2n^2}=-\frac{m_\mathrm{e}e^4}{32\pi^2\varepsilon_0^2\hbar^2n^2} \qquad n=1,\ 2,\ \ldots \tag{6.44}$$

$$E_n=-\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \qquad n=1,\ 2,\ \ldots \tag{6.45}$$

$$0\le l\le n-1 \qquad n=1,\ 2,\ \ldots \tag{6.46}$$

$$R_{nl}(r)=-\left\{\frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2}\left(\frac{2}{na_0}\right)^{l+3/2}r^l e^{-r/na_0}L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right) \tag{6.47}$$

$$\int_0^\infty R_{nl}^*(r)R_{nl}(r)r^2dr=1 \tag{6.48}$$

$$\int_0^\infty drr^2\int_0^\pi d\theta\sin\theta\int_0^{2\pi}d\phi\,\psi_{nlm}^*(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi)=1 \tag{6.49}$$

$$\int_0^\infty drr^2\int_0^\pi d\theta\sin\theta\int_0^{2\pi}d\phi\,\psi_{n'l'm'}^*(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi)=\delta_{nn'}\cdot\delta_{ll'}\cdot\delta_{mm'} \tag{6.50}$$

$$\int_0^\infty[R_{1s}(r)]^2r^2dr=\frac{4}{a_0^3}\int_0^\infty r^2e^{-2r/a_0}dr=1 \tag{6.51}$$

$$\mathrm{Prob}=\frac{4}{a_0^3}r^2e^{-2r/a_0}dr \tag{6.52}$$

$$\psi_{1s}(r,\theta,\phi)=R_{10}(r)Y_0^0(\theta,\phi)=(\pi a_0^3)^{-1/2}e^{-r/a_0} \tag{6.53}$$

$$\begin{aligned}\mathrm{Prob}(1s) &= r^2dr\int_0^\pi d\theta\sin\theta\int_0^{2\pi}d\phi\,\psi_{1s}^*(r,\theta,\phi)\psi_{1s}(r,\theta,\phi)\\ &= \frac{4}{a_0^3}r^2e^{-2r/a_0}dr\end{aligned} \tag{6.54}$$

$$\langle r\rangle_{1s} = \frac{4}{a_0^3}\int_0^\infty r^3 e^{-2r/a_0} dr = \frac{3}{2}a_0 \tag{6.55}$$

$$\psi_{2s}(r,\theta,\phi) = R_{20}(r)Y_0^0(\theta,\phi) \tag{6.56}$$

$$\psi_{2s}(r,\theta,\phi) = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0} \tag{6.57}$$

$$\langle r\rangle_{2s} = \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, \psi_{2s}^*(r,\theta,\phi)\psi_{2s}(r,\theta,\phi) = 6a_0 \tag{6.58}$$

$$Y_1^0(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta \tag{6.59}$$

$$\begin{aligned} Y_1^{+1}(\theta,\phi) &= \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{+i\phi} \\ Y_1^{-1}(\theta,\phi) &= \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{-i\phi} \end{aligned} \tag{6.60}$$

$$|Y_1^{+1}(\theta,\phi)|^2 = \frac{3}{8\pi}\sin^2\theta \tag{6.61}$$

$$\begin{aligned} p_x &= \frac{1}{\sqrt{2}}(Y_1^{+1}+Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi \\ p_y &= \frac{1}{\sqrt{2}i}(Y_1^{+1}-Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi \end{aligned} \tag{6.62}$$

$$\begin{aligned} d_{z^2} &= Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1) \\ d_{xz} &= \frac{1}{\sqrt{2}}(Y_2^{+1}+Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\cos\phi \\ d_{yz} &= \frac{1}{\sqrt{2}i}(Y_2^{+1}-Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\sin\phi \\ d_{x^2-y^2} &= \frac{1}{\sqrt{2}}(Y_2^{+2}+Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi \\ d_{xy} &= \frac{1}{\sqrt{2}i}(Y_2^{+2}-Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi \end{aligned} \tag{6.63}$$

$$
\left(-\frac{\hbar^2}{2M}\nabla^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2\right)\psi(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2) +
$$

$$
\left(-\frac{2e^2}{4\pi\varepsilon_0|\mathbf{R}-\mathbf{r}_1|} - \frac{2e^2}{4\pi\varepsilon_0|\mathbf{R}-\mathbf{r}_2|} + \frac{e^2}{4\pi\varepsilon_0|\mathbf{r_1}-\mathbf{r}_2|}\right)\psi(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)
$$

$$
= E\psi(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2) \tag{6.64}
$$

$$
-\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_1^2)\psi(\mathbf{r}_1,\mathbf{r}_2) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi(\mathbf{r}_1,\mathbf{r}_2)
$$

$$
+\frac{e^2}{4\pi\varepsilon|\mathbf{r}_1-\mathbf{r}_2|}\psi(\mathbf{r}_1,\mathbf{r}_2) = E\psi(\mathbf{r}_1,\mathbf{r}_2) \tag{6.65}
$$

Chapter 7

Approximation Methods

$$\hat{H}\psi_0 = E_0\psi_0 \tag{7.1}$$

$$E_0 = \frac{\int \psi_0^* \hat{H} \psi_0 d\tau}{\int \psi_0^* \psi_0 d\tau} \tag{7.2}$$

$$E_\phi = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \tag{7.3}$$

$$E_\phi \geq E_0 \tag{7.4}$$

$$E_\phi(\alpha, \beta, \gamma, \ldots) \geq E_0 \tag{7.5}$$

$$\hat{H} = -\frac{\hbar^2}{2m_\mathrm{e} r^2}\frac{d}{dr}\left(r^2 \frac{d}{dr}\right) - \frac{e^2}{4\pi\epsilon_0 r} \tag{7.6}$$

$$E(\alpha) = \frac{3\hbar^2\alpha}{2m_\mathrm{e}} - \frac{e^2\alpha^{1/2}}{2^{1/2}\epsilon_0\pi^{3/2}} \tag{7.7}$$

$$\alpha = \frac{m_\mathrm{e}^2 e^4}{18\pi^3\epsilon_0^2\hbar^4} \tag{7.8}$$

$$E_\mathrm{min} = -\frac{4}{3\pi}\left(\frac{m_\mathrm{e} e^4}{16\pi^2\epsilon_0^2\hbar^2}\right) = -0.424\left(\frac{m_\mathrm{e} e^4}{16\pi^2\epsilon_0^2\hbar^2}\right) \tag{7.9}$$

$$E_0 = -\frac{1}{2}\left(\frac{m_\mathrm{e} e^4}{16\pi^2\epsilon_0^2\hbar^2}\right) = -0.500\left(\frac{m_\mathrm{e} e^4}{16\pi^2\epsilon_0^2\hbar^2}\right) \tag{7.10}$$

$$\hat{H} = -\frac{\hbar^2}{2m_\mathrm{e}}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} \tag{7.11}$$

$$\hat{H} = \hat{H}_\mathrm{H}(1) + \hat{H}_\mathrm{H}(2) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} \tag{7.12}$$

$$\hat{H}_\mathrm{H}(j) = -\frac{\hbar^2}{2m_\mathrm{e}}\nabla_j^2 - \frac{2e^2}{4\pi\epsilon_0}\frac{1}{r_j} \qquad j = 1 \text{ and } 2 \tag{7.13}$$

$$\hat{H}_\mathrm{H}(j)\psi_\mathrm{H}(r_j, \theta_j, \phi_j) = E_j\psi_\mathrm{H}(r_j, \theta_j, \phi_j) \qquad j = 1 \text{ or } 2 \tag{7.14}$$

$$E_j = -\frac{Z^2 m_\mathrm{e} e^4}{32\pi^2\epsilon_0^2\hbar^2 n_j^2} \qquad j = 1 \text{ or } 2 \tag{7.15}$$

$$\phi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \tag{7.16}$$

$$\psi_{1s}(\mathbf{r}_j) = \left(\frac{Z^3}{\pi a_0}\right)^{1/2} e^{-Zr_j/a_0} \qquad j = 1 \text{ or } 2 \tag{7.17}$$

$$E(Z) = \int \phi_0(\mathbf{r}_1, \mathbf{r}_2)\hat{H}\phi_0(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{7.18}$$

$$E(Z) = \frac{m_\mathrm{e} e^4}{16\pi^2\epsilon_0^2\hbar^2}(Z^2 - \frac{27}{8}Z) \tag{7.19}$$

$$E(Z) = Z^2 - \frac{27}{8}Z \tag{7.20}$$

$$E_\mathrm{min} = -\left(\frac{27}{16}\right)^2 = -2.8477 \tag{7.21}$$

$$\phi = c_1 x(a - x) + c_2 x^2(a - x)^2 \tag{7.22}$$

$$E_\mathrm{min} = 0.125002\frac{h^2}{ma^2} \tag{7.23}$$

$$E_\mathrm{exact} = \frac{h^2}{8ma^2} = 0.125000\frac{h^2}{ma^2} \tag{7.24}$$

$$\phi = \sum_{n=1}^{N} c_n f_n \tag{7.25}$$

$$\begin{aligned}
\int \phi \hat{H} \phi d\tau &= \int (c_1 f_1 + c_2 f_2) \hat{H} (c_1 f_1 + c_2 f_2) d\tau \\
&= c_1^2 \int f_1 \hat{H} f_1 d\tau + c_1 c_2 \int f_1 \hat{H} f_2 d\tau \\
&\quad + c_1 c_2 \int f_2 \hat{H} f_1 d\tau + c_2^2 \int f_2 \hat{H} f_2 d\tau \\
&= c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22}
\end{aligned} \tag{7.26}$$

$$H_{ij} = \int f_i \hat{H} f_j d\tau \tag{7.27}$$

$$\int f_i \hat{H} f_j d\tau = \int f_j \hat{H} f_i d\tau \tag{7.28}$$

$$\int \phi \hat{H} \phi d\tau = c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22} \tag{7.29}$$

$$\int \phi^2 d\tau = c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22} \tag{7.30}$$

$$S_{ij} = S_{ji} = \int \phi_i \phi_j d\tau \tag{7.31}$$

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}} \tag{7.32}$$

$$E(c_1, c_2)(c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}) = c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22} \tag{7.33}$$

$$(2c_1 S_{11} + 2c_2 S_{12})E + \frac{\partial E}{\partial c_1}(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = 2c_1 H_{11} + 2c_2 H_{12} \tag{7.34}$$

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{7.35}$$

$$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0 \tag{7.36}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{7.37}$$

$$f_1 = x(1-x) \quad \text{and} \quad f_2 = x^2(1-x)^2 \tag{7.38}$$

$$\begin{aligned}
c_1(H_{11} - ES_{11}) + c_2(H_{21} - ES_{21}) + \cdots + c_N(H_{1N} - ES_{1N}) &= 0 \\
c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) + \cdots + c_N(H_{2N} - ES_{2N}) &= 0 \\
\vdots \qquad\qquad \vdots \qquad\qquad \vdots \qquad & \\
c_1(H_{1N} - ES_{1N}) + c_2(H_{2N} - ES_{2N}) + \cdots + c_N(H_{NN} - ES_{NN}) &= 0
\end{aligned} \tag{7.39}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{1N} - ES_{1N} & H_{2N} - ES_{2N} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0 \tag{7.40}$$

$$\hat{H}\psi = E\psi \tag{7.41}$$

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \tag{7.42}$$

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \tag{7.43}$$

$$\begin{aligned}
\hat{H}^{(0)} &= -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \\
\psi_v^{(0)}(x) &= \left[\left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{2^v v!}\right]^{1/2} H_v(\alpha^{1/2}x)e^{-\alpha x^2/2} \\
E_v^{(0)} &= \left(v + \frac{1}{2}\right)h\nu \qquad v = 0,\ 1,\ 2,\ \ldots \\
H^{(1)} &= \frac{1}{6}\gamma x^3 + \frac{b}{24}x^4
\end{aligned} \tag{7.44}$$

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \cdots \tag{7.45}$$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots \tag{7.46}$$

$$E^{(1)} = \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} d\tau \tag{7.47}$$

$$E = E^{(0)} + E^{(1)} \tag{7.48}$$

$$\begin{aligned} \hat{H}^{(0)} &= \hat{H}_{\mathrm{H}}(1) + \hat{H}_{\mathrm{H}}(2) \\ \psi^{(0)} &= \psi_{1s}(r_1, \theta_1, \phi_1)\psi_{1s}(r_2, \theta_2, \phi_2) \\ E^{(0)} &= -\frac{Z^2 m_{\mathrm{e}} e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n_1^2} - \frac{Z^2 m_{\mathrm{e}} e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n_2^2} \end{aligned} \tag{7.49}$$

$$E^{(1)} = \int\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \tag{7.50}$$

$$E^{(1)} = \frac{5Z}{8}\left(\frac{m_{\mathrm{e}} e^4}{16\pi^2 \epsilon_0^2 \hbar^2}\right) \tag{7.51}$$

$$\begin{aligned} E &= E^{(0)} + E^{(1)} = -\frac{1}{2}Z^2 - \frac{1}{2}Z^2 + \frac{5}{8}Z \\ &= -Z^2 + \frac{5}{8}Z \end{aligned} \tag{7.52}$$

Chapter 8

Multielectron Atoms

$$\left\{\hat{H}_{\mathrm{H}}(1) + \hat{H}_{\mathrm{H}}(2) + \frac{e^2}{4\pi\epsilon_0 r_{12}}\right\}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.1}$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_{\mathrm{e}}e^4} \tag{8.2}$$

$$E = \frac{m_{\mathrm{e}}e^4}{16\pi^2\epsilon_0^2\hbar^2} \tag{8.3}$$

$$\hat{H} = -\frac{\hbar^2}{2m_{\mathrm{e}}}\nabla_1^2 - \frac{\hbar^2}{2m_{\mathrm{e}}}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{8.4}$$

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \tag{8.5}$$

$$E = -Z^2 + \frac{5}{8}Z = -\frac{11}{4}E_{\mathrm{h}} = -2.750\ E_{\mathrm{h}} \tag{8.6}$$

$$E = -Z^2 + \frac{5}{8}Z - 0.15766 + \frac{0.00870}{Z} + \frac{0.000889}{Z^2} + \cdots \tag{8.7}$$

$$\phi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \tag{8.8}$$

$$\psi_{1s}(\mathbf{r}_j) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr_j} \tag{8.9}$$

$$E = -\left(\frac{27}{16}\right)^2 = -2.8477\ E_{\mathrm{h}} \tag{8.10}$$

$$\text{IE} = E_{\text{He}^+} - E_{\text{He}} \tag{8.11}$$

$$S_{nlm}(r,\theta,\phi) = N_{nl} r^{n-1} e^{-\zeta r} Y_l^m(\theta,\phi) \tag{8.12}$$

$$\begin{aligned} \psi &= S_{100}(r_1,\theta_1,\phi_1) S_{100}(r_2,\theta_2,\phi_2) \\ &= \frac{\zeta^3}{\pi} e^{-2\zeta(r_1+r_2)} \end{aligned} \tag{8.13}$$

$$\begin{aligned} \psi &= S_{n00}(r_1,\theta_1,\phi_1) S_{n00}(r_2,\theta_2,\phi_2) \\ &= \frac{(2\zeta)^{2n+1}}{4\pi(2n)!} r_1^{n-1} r_2^{n-1} e^{-\zeta(r_1+r_2)} \end{aligned} \tag{8.14}$$

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) \tag{8.15}$$

$$\psi(r_1,r_2,r_{12}) = e^{-Zr_1} e^{-Zr_2} [1 + cr_{12}] \tag{8.16}$$

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) \tag{8.17}$$

$$V_1^{\text{eff}}(\mathbf{r}_1) = \int \phi^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi(\mathbf{r}_2) d\mathbf{r}_2 \tag{8.18}$$

$$\hat{H}_1^{\text{eff}}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{\text{eff}}(\mathbf{r}_1) \tag{8.19}$$

$$\hat{H}_1^{\text{eff}}(\mathbf{r}_1)\phi(\mathbf{r}_1) = \epsilon_1 \phi(\mathbf{r}_1) \tag{8.20}$$

$$\text{correlation energy} = \text{CE} = E_{\text{exact}} - E_{\text{HF}} \tag{8.21}$$

$$\begin{aligned} \hat{L}^2 Y_l^m(\theta,\phi) &= \hbar^2 l(l+1) Y_l^m(\theta,\phi) \\ \hat{L}_z Y_l^m(\theta,\phi) &= m\hbar Y_l^m(\theta,\phi) \end{aligned} \tag{8.22}$$

$$\hat{S}^2\alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\alpha \qquad \hat{S}^2\beta = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\beta \tag{8.23}$$

$$\hat{S}_z\alpha = \frac{1}{2}\hbar\alpha \qquad \hat{S}_z\beta = -\frac{1}{2}\hbar\beta \tag{8.24}$$

$$L^2 = \hbar^2 l(l+1) \tag{8.25}$$

$$S^2 = \hbar^2 s(s+1) \tag{8.26}$$

$$\begin{aligned} \int \alpha^*(\sigma)\alpha(\sigma)d\sigma &= \int \beta^*(\sigma)\beta(\sigma)d\sigma = 1 \\ \int \alpha^*(\sigma)\beta(\sigma)d\sigma &= \int \alpha(\sigma)\beta^*(\sigma)d\sigma = 0 \end{aligned} \tag{8.27}$$

$$\Psi(x,y,z,\sigma) = \psi(x,y,z)\alpha(\sigma) \quad \text{or} \quad \psi(x,y,z)\beta(\sigma) \tag{8.28}$$

$$\begin{aligned} \Psi_{100\frac{1}{2}} &= \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}\alpha \\ \Psi_{100-\frac{1}{2}} &= \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}\beta \end{aligned} \tag{8.29}$$

$$\int \Psi^*_{100\frac{1}{2}}(\mathbf{r},\sigma)\Psi_{100\frac{1}{2}}(\mathbf{r},\sigma)4\pi r^2 dr d\sigma = \int_0^\infty \frac{Z^3}{\pi}e^{-2Zr}4\pi r^2 dr \int \alpha^*\alpha d\sigma = 1 \tag{8.30}$$

$$\int \Psi^*_{100\frac{1}{2}}(\mathbf{r},\sigma)\Psi_{100-\frac{1}{2}}(\mathbf{r},\sigma)4\pi r^2 dr d\sigma = \int_0^\infty \frac{Z^3}{\pi}e^{-2Zr}4\pi r^2 dr \int \alpha^*\beta d\sigma = 0 \tag{8.31}$$

$$\psi(1,2) = 1s\alpha(1)1s\beta(2) \tag{8.32}$$

$$\psi(2,1) = 1s\alpha(2)1s\beta(1) \tag{8.33}$$

$$\Psi_1 = \psi(1,2) + \psi(2,1) = 1s\alpha(1)1s\beta(2) + 1s\alpha(2)1s\beta(1) \tag{8.34}$$

$$\Psi_2 = \psi(1,2) - \psi(2,1) = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1) \tag{8.35}$$

$$\Psi_2(2,1) = \psi(2,1) - \psi(1,2) = -\Psi_2(1,2) \tag{8.36}$$

$$\begin{aligned}\Psi_2(1,2) &= 1s(1)1s(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\ &= 1s(\mathbf{r}_1)1s(\mathbf{r}_2)[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)]\end{aligned} \tag{8.37}$$

$$E = \frac{\int \Psi_2^*(1,2)\hat{H}\Psi_2(1,2)d\mathbf{r}_1 d\mathbf{r_2} d\sigma_1 d\sigma_2}{\int \Psi_2^*(1,2)\Psi_2(1,2)d\mathbf{r}_1 d\mathbf{r_2} d\sigma_1 d\sigma_2} \tag{8.38}$$

$$\begin{aligned}\int 1s^*(\mathbf{r}_1)1s^*(\mathbf{r}_2)[\alpha^*(\sigma_1)\beta^*(\sigma_2) - \alpha^*(\sigma_2)\beta^*(\sigma_1)] \\ \times\ \hat{H}1s(\mathbf{r}_1)1s(\mathbf{r}_2)[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)]d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2\end{aligned} \tag{8.39}$$

$$\begin{aligned}\int 1s^*(\mathbf{r}_1)1s^*(\mathbf{r}_2)\hat{H}1s(\mathbf{r}_1)1s(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \\ \times\int[\alpha^*(\sigma_1)\beta^*(\sigma_2) - \alpha^*(\sigma_2)\beta^*(\sigma_1)][\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)]d\sigma_1 d\sigma_2\end{aligned} \tag{8.40}$$

$$E = \frac{\int \psi^*(\mathbf{r}_1,\mathbf{r}_2)\hat{H}\psi(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2}{\int \psi^*(\mathbf{r}_1,\mathbf{r}_2)\psi(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2} \tag{8.41}$$

$$\Psi(1,2) = \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} \tag{8.42}$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} \tag{8.43}$$

$$\Psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} u_1(1) & u_2(1) & \cdots & u_N(1) \\ u_1(2) & u_2(2) & \cdots & u_N(2) \\ \vdots & \vdots & \vdots & \vdots \\ u_1(N) & u_2(N) & \cdots & u_N(N) \end{vmatrix} \tag{8.44}$$

$$\Psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix} \tag{8.45}$$

$$\hat{F}_i \phi_i = \epsilon_i \phi_i \tag{8.46}$$

$$\mathbf{L} = \sum_i \mathbf{l}_i \tag{8.47}$$

$$\mathbf{S} = \sum_i \mathbf{s}_i \tag{8.48}$$

$$L_z = \sum_i l_{zi} = \sum_i m_{il} = M_L \tag{8.49}$$

$$S_z = \sum_i s_{zi} = \sum_i m_{is} = M_S \tag{8.50}$$

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{8.51}$$

$$J_z = L_z + S_z = (M_L + M_S) = M_J = 0 \tag{8.52}$$

$$\frac{G!}{N!(G-N)!} \quad \text{(equivalent orbitals)} \tag{8.53}$$

$$J = L+S,\ L+S-1,\ L+S-2,\ \ldots,\ |L-S| \tag{8.54}$$

$$\hat{H} = -\frac{1}{2}\sum_j \nabla_j^2 - \sum_j \frac{Z}{r_j} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_j \xi(r_j)\mathbf{l}_j \cdot \mathbf{s}_j \tag{8.55}$$

$$\tilde{\nu} = 109,677.58\left(1 - \frac{1}{n^2}\right)\text{cm}^{-1} \qquad n = 2,\ 3,\ \ldots \tag{8.56}$$

$$\begin{aligned} \Delta L &= \pm 1 \\ \Delta S &= 0 \\ \Delta J &= 0, \pm 1 \end{aligned} \tag{8.57}$$

$$\tilde{\nu} = (82,258.917 - 0.00)\text{cm}^{-1} = 82,258.917\ \text{cm}^{-1}$$

and

$$\tilde{\nu} = (82,259.272 - 0.00)\text{cm}^{-1} = 82,259.272\ \text{cm}^{-1} \tag{8.58}$$

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 \hbar^2 n^2} \qquad n = 1, 2, 3, \ldots \tag{8.59}$$

Chapter 9

The Chemical Bond: Diatomic Molecules

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2M}(\nabla_{\rm A}^2+\nabla_{\rm B}^2)-\frac{\hbar^2}{2m_{\rm e}}(\nabla_1^2+\nabla_2^2)-\frac{e^2}{4\pi\epsilon_0 r_{1\rm A}}-\frac{e^2}{4\pi\epsilon_0 r_{1\rm B}}\\ &\quad -\frac{e^2}{4\pi\epsilon_0 r_{2\rm A}}-\frac{e^2}{4\pi\epsilon_0 r_{2\rm B}}+\frac{e^2}{4\pi\epsilon_0 r_{12}}+\frac{e^2}{4\pi\epsilon_0 R} \end{aligned} \tag{9.1}$$

$$\begin{aligned}\hat{H} &= -\frac{\hbar}{2m_{\rm e}}(\nabla_1^2+\nabla_2^2)-\frac{e^2}{4\pi\epsilon_0 r_{1\rm A}}-\frac{e^2}{4\pi\epsilon_0 r_{1\rm B}}-\frac{e^2}{4\pi\epsilon_0 r_{2\rm A}}-\frac{e^2}{4\pi\epsilon_0 r_{2\rm B}}\\ &\quad +\frac{e^2}{4\pi\epsilon_0 r_{12}}+\frac{e^2}{4\pi\epsilon_0 R} \end{aligned} \tag{9.2}$$

$$\hat{H} = -\frac{1}{2}(\nabla_1^2+\nabla_2^2)-\frac{1}{r_{1\rm A}}-\frac{1}{r_{1\rm B}}-\frac{1}{r_{2\rm A}}-\frac{1}{r_{2\rm B}}+\frac{1}{r_{12}}+\frac{1}{R} \tag{9.3}$$

$$\hat{H} = -\frac{1}{2}\nabla^2-\frac{1}{r_{\rm A}}-\frac{1}{r_{\rm B}}+\frac{1}{R} \tag{9.4}$$

$$\hat{H}\psi_j(r_{\rm A},r_{\rm B};R) = E_j\psi_j(r_{\rm A},r_{\rm B};R) \tag{9.5}$$

$$\psi_\pm = c_1 1s_{\rm A} \pm c_2 1s_{\rm B} \tag{9.6}$$

$$E_+ = \frac{\int d\mathbf{r}\psi_+^*\hat{H}\psi_+}{\int d\mathbf{r}\psi_+^*\psi_+} \tag{9.7}$$

$$\begin{aligned}\int d\mathbf{r}\psi_+^*\psi_+ &= \int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)(1s_\mathrm{A} + 1s_\mathrm{B}) \\ &= \int d\mathbf{r}1s_\mathrm{A}^*1s_\mathrm{A} + \int d\mathbf{r}1s_\mathrm{A}^*1s_\mathrm{B} + \int d\mathbf{r}1s_\mathrm{B}^*1s_\mathrm{A} + \int d\mathbf{r}1s_\mathrm{B}^*1s_\mathrm{B}\end{aligned} \tag{9.8}$$

$$\int d\mathbf{r}1s_\mathrm{A}^*1s_\mathrm{A} = \int d\mathbf{r}1s_\mathrm{B}^*1s_\mathrm{B} = 1 \tag{9.9}$$

$$S = \int d\mathbf{r}1s_\mathrm{A}^*1s_\mathrm{B} = \int d\mathbf{r}1s_\mathrm{B}^*1s_\mathrm{A} = \int d\mathbf{r}1s_\mathrm{A}1s_\mathrm{B} \tag{9.10}$$

$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right) \tag{9.11}$$

$$\int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)(1s_\mathrm{A} + 1s_\mathrm{B}) = 2 + 2S(R) \tag{9.12}$$

$$\begin{aligned}\int d\mathbf{r}\psi_+^*\hat{H}\psi_+ &= \int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\hat{H}(1s_\mathrm{A} + 1s_\mathrm{B}) \\ &= \int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)(1s_\mathrm{A} + 1s_\mathrm{B})\end{aligned} \tag{9.13}$$

$$\begin{aligned}\int d\mathbf{r}\psi_+^*\hat{H}\psi_+ &= \int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} \\ &\quad + \int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{B}\end{aligned} \tag{9.14}$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}}\right)1s_\mathrm{A} = E_{1s}1s_\mathrm{A} \tag{9.15}$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{B}}\right)1s_\mathrm{B} = E_{1s}1s_\mathrm{B} \tag{9.16}$$

$$\int d\mathbf{r}\psi_+^*\hat{H}\psi_+ = \int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\left(E_{1s} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} + \int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\left(E_{1s} - \frac{1}{r_\mathrm{A}} + \frac{1}{R}\right)1s_\mathrm{B} \quad (9.17)$$

$$\int d\mathbf{r}\psi_+^*\hat{H}\psi_+ = 2E_{1s}(1+S) + \int d\mathbf{r}1s_\mathrm{A}^*\left(-\frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} + \int d\mathbf{r}1s_\mathrm{B}^*\left(-\frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} + \int d\mathbf{r}1s_\mathrm{A}^*\left(-\frac{1}{r_\mathrm{A}} + \frac{1}{R}\right)1s_\mathrm{B} + \int d\mathbf{r}1s_\mathrm{B}^*\left(-\frac{1}{r_\mathrm{A}} + \frac{1}{R}\right)1s_\mathrm{B} \quad (9.18)$$

$$J = \int d\mathbf{r}1s_\mathrm{A}^*\left(-\frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} = -\int \frac{d\mathbf{r}1s_\mathrm{A}^*1s_\mathrm{A}}{r_\mathrm{B}} + \frac{1}{R} \quad (9.19)$$

$$K = \int d\mathbf{r}1s_\mathrm{B}^*\left(-\frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} = -\int \frac{d\mathbf{r}1s_\mathrm{B}^*1s_\mathrm{A}}{r_\mathrm{B}} + \frac{S}{R} \quad (9.20)$$

$$\int d\mathbf{r}\psi_+^*\hat{H}\psi_+ = 2E_{1s}(1+S) + 2J + 2K \quad (9.21)$$

$$\Delta E_+ = E_+ - E_{1s} = \frac{J+K}{1+S} \quad (9.22)$$

$$J = e^{-2R}\left(1 + \frac{1}{R}\right) \quad (9.23)$$

$$K = \frac{S}{R} - e^{-R}(1+R) \quad (9.24)$$

$$\psi_- = c_1 1s_\mathrm{A} - c_2 1s_\mathrm{B} \quad (9.25)$$

$$\Delta E_- = E_- - E_{1s} = \frac{J-K}{1-S} \tag{9.26}$$

$$\psi_\mathrm{b} = \psi_+ = \frac{1}{\sqrt{2(1+S)}}(1s_\mathrm{A} + 1s_\mathrm{B}) \tag{9.27}$$

$$\psi_\mathrm{a} = \psi_- = \frac{1}{\sqrt{2(1-S)}}(1s_\mathrm{A} - 1s_\mathrm{B}) \tag{9.28}$$

$$\begin{aligned} \psi &= \frac{1}{\sqrt{2!}}\begin{vmatrix} \psi_\mathrm{b}\alpha(1) & \psi_\mathrm{b}\beta(1) \\ \psi_\mathrm{b}\alpha(2) & \psi_\mathrm{b}\beta(2) \end{vmatrix} \\ &= \psi_\mathrm{b}(1)\psi_\mathrm{b}(2)\left\{\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]\right\} \end{aligned} \tag{9.29}$$

$$\psi_\mathrm{MO} = \frac{1}{2(1+S)}[1s_\mathrm{A}(1) + 1s_\mathrm{B}(1)][1s_\mathrm{A}(2) + 1s_\mathrm{B}(2)] \tag{9.30}$$

$$E_\mathrm{MO} = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi^*_\mathrm{MO}(1,2)\hat{H}\psi_\mathrm{MO}(1,2) \tag{9.31}$$

$$\psi_\pm = 1s_\mathrm{A} \pm 1s_\mathrm{B} \tag{9.32}$$

$$\begin{matrix}\text{bond} \\ \text{order}\end{matrix} = \frac{1}{2}\left[\begin{pmatrix}\text{number of electrons} \\ \text{in bonding orbitals}\end{pmatrix} - \begin{pmatrix}\text{number of electrons} \\ \text{in antibonding orbitals}\end{pmatrix}\right] \tag{9.33}$$

$$\psi = c_1 1s_\mathrm{H} \pm c_2 2p_{z,\mathrm{F}} \tag{9.34}$$

$$\psi = c_1(1s_\mathrm{A} + 1s_\mathrm{B}) + c_2(2s_\mathrm{A} + 2s_\mathrm{B}) + c_3(2p_{z\mathrm{A}} + 2p_{z\mathrm{B}}) + \cdots \tag{9.35}$$

$$M_L = m_{l1} + m_{l2} + \cdots \tag{9.36}$$

$$M_s = m_{s1} + m_{s2} + \cdots \tag{9.37}$$

Chapter 10

Bonding in Polyatomic Molecules

$$\psi_{\text{Be-H}} = c_1\psi_{\text{Be}(2s)} + c_2\psi_{\text{Be}(2p)} + c_3\psi_{\text{H}(1s)} \tag{10.1}$$

$$\psi_{sp} = \frac{1}{\sqrt{2}}(2s \pm 2p_z) \tag{10.2}$$

$$\psi_1 = \frac{1}{\sqrt{3}}2s + \sqrt{\frac{2}{3}}2p_z \tag{10.3}$$

$$\psi_2 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z + \frac{1}{\sqrt{2}}2p_x \tag{10.4}$$

$$\psi_3 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z - \frac{1}{\sqrt{2}}2p_x \tag{10.5}$$

$$\psi_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z) \tag{10.6}$$

$$\psi_2 = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z) \tag{10.7}$$

$$\psi_3 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z) \tag{10.8}$$

$$\psi_4 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z) \tag{10.9}$$

$$\begin{aligned} \phi_1 &= c_1 1s_{\mathrm{H_A}} + c_2 2p_{y,\mathrm{O}} \\ \phi_2 &= c_3 1s_{\mathrm{H_B}} + c_4 2p_{z,\mathrm{O}} \end{aligned} \tag{10.10}$$

$$\psi = c_1 2s + c_2 2p_z + c_3 2p_y \tag{10.11}$$

$$\psi_1 = 0.45(2s) + 0.71(2p_y) + 0.55(2p_z) \tag{10.12}$$

$$\psi_2 = 0.45(2s) - 0.71(2p_y) + 0.55(2p_z) \tag{10.13}$$

$$\psi = c_1 1s_{\mathrm{H_a}} + c_2 1s_{\mathrm{H_b}} + c_3 2s_{\mathrm{A}} + c_4 2p_{x,\mathrm{A}} + c_5 2p_{y,\mathrm{A}} + c_6 2p_{z,\mathrm{A}} \tag{10.14}$$

$$\psi_\pi = c_1 2p_{z,\mathrm{A}} + c_2 2p_{z,\mathrm{B}} \tag{10.15}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{10.16}$$

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \tag{10.17}$$

$$\psi_i = \sum_{j=1}^{4} c_{ij} 2p_{zj} \tag{10.18}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & H_{23} - ES_{23} & H_{24} - ES_{24} \\ H_{13} - ES_{13} & H_{23} - ES_{23} & H_{33} - ES_{33} & H_{34} - ES_{34} \\ H_{14} - ES_{14} & H_{24} - ES_{24} & H_{34} - ES_{34} & H_{44} - ES_{44} \end{vmatrix} = 0 \tag{10.19}$$

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{10.20}$$

$$\beta^4 \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.21}$$

$$x^4 - 3x^2 + 1 = 0 \tag{10.22}$$

$$x^2 = \frac{3 \pm \sqrt{5}}{2} \tag{10.23}$$

$$\begin{aligned} E_\pi &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned} \tag{10.24}$$

$$E_{\text{deloc}} = E_\pi(\text{butadiene}) - 2E_\pi(\text{ethene}) = 0.472\beta < 0 \tag{10.25}$$

$$\begin{aligned} \psi_1 &= 0.3717 \cdot 2p_{z1} + 0.6015 \cdot 2p_{z2} + 0.6015 \cdot 2p_{z3} + 0.3717 \cdot 2p_{z4} \\ & \qquad E_1 = \alpha + 1.618\beta \\ \psi_2 &= 0.6015 \cdot 2p_{z1} + 0.3717 \cdot 2p_{z2} 0.3717 \cdot 2p_{z3} - 0.6015 \cdot 2p_{z4} \\ & \qquad E_2 = \alpha + 0.618\beta \\ \psi_3 &= 0.6015 \cdot 2p_{z1} - 0.3717 \cdot 2p_{z2} - 0.3717 \cdot 2p_{z3} + 0.6015 \cdot 2p_{z4} \\ & \qquad E_3 = \alpha - 0.618\beta \\ \psi_4 &= 0.3717 \cdot 2p_{z1} - 0.6015 \cdot 2p_{z2} + 0.6015 \cdot 2p_{z3} - 0.3717 \cdot 2p_{z4} \\ & \qquad E_4 = \alpha - 1.618\beta \end{aligned} \tag{10.26}$$

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{10.27}$$

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \tag{10.28}$$

$$\begin{aligned} E_1 &= \alpha + 2\beta \\ E_2 = E_3 &= \alpha + \beta \\ E_4 = E_5 &= \alpha - \beta \\ E_6 &= \alpha - 2\beta \end{aligned} \tag{10.29}$$

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta \tag{10.30}$$

$$\begin{aligned}
\psi_1 &= \tfrac{1}{\sqrt{6}}(2p_{z1} + 2p_{z2} + 2p_{z3} + 2p_{z4} + 2p_{z5} + 2p_{z6}) & E_1 &= \alpha + 2\beta \\
\psi_2 &= \tfrac{1}{\sqrt{4}}(2p_{z2} + 2p_{z3} - 2p_{z5} - 2p_{z6}) & E_2 &= \alpha + \beta \\
\psi_3 &= \tfrac{1}{\sqrt{3}}(2p_{z1} + 2p_{z2} - \tfrac{1}{2}2p_{z3} - 2p_{z4} - \tfrac{1}{2}2p_{z5} + \tfrac{1}{2}2p_{z6}) & E_3 &= \alpha + \beta \\
\psi_4 &= \tfrac{1}{\sqrt{4}}(2p_{z2} - 2p_{z3} + 2p_{z5} - 2p_{z6}) & E_4 &= \alpha - \beta \\
\psi_5 &= \tfrac{1}{\sqrt{3}}(2p_{z1} - \tfrac{1}{2}2p_{z2} - \tfrac{1}{2}2p_{z3} + 2p_{z4} - \tfrac{1}{2}2p_{z5} - \tfrac{1}{2}2p_{z6}) & E_5 &= \alpha - \beta \\
\psi_6 &= \tfrac{1}{\sqrt{6}}(2p_{z1} - 2p_{z2} + 2p_{z3} - 2p_{z4} + 2p_{z5} - 2p_{z6}) & E_6 &= \alpha - 2\beta
\end{aligned} \tag{10.31}$$

Chapter 11

Computational Quantum Chemistry

$$\psi(1,2,\ldots,N) = \frac{1}{N!}\begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \cdots & \psi_{N/2}(1)\alpha(1) & \psi_{N/2}(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \cdots & \psi_{N/2}(2)\alpha(2) & \psi_{N/2}(2)\beta(2) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(N)\alpha(N) & \psi_1(N)\beta(N) & \cdots & \psi_{N/2}(N)\alpha(N) & \psi_{N/2}(N)\beta(N) \end{vmatrix} \quad (11.1)$$

$$S_{nlm}(r,\theta,\phi) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} Y_l^m(\theta,\phi) \quad (11.2)$$

$$G_{nlm}(r,\theta,\phi) = N_n r^{n-1} e^{-\alpha r^2} Y_l^m(\theta,\phi) \quad (11.3)$$

$$\phi_{1s}(r) = \phi_{1s}^{\mathrm{STO}}(r, 1.24) \quad (11.4)$$

$$\phi_{1s}(r) = \phi_{1s}^{\mathrm{GF}}(r, 0.4166) \quad (11.5)$$

$$\phi_{1s}^{\mathrm{STO}}(r,\zeta) = S_{100}(r,\zeta) = \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta r} \quad (11.6)$$

$$\phi_{1s}^{\mathrm{GF}}(r,\alpha) = G_{100}(r,\alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2} \quad (11.7)$$

$$\begin{aligned}\phi_{1s}(r) &= \sum_{i=1}^{3} d_{1si}\phi_{1s}^{\mathrm{GF}}(r,\alpha_{1si}) \\ &= 0.4446\phi_{1s}^{\mathrm{GF}}(r,0.1688) + 0.5353\phi_{1s}^{\mathrm{GF}}(r,0.6239) + 0.1543\phi_{1s}^{\mathrm{GF}}(r,3.425)\end{aligned} \tag{11.8}$$

$$\psi_i = \sum_{k=1}^{M} c_{ki}\phi_k \tag{11.9}$$

$$\sum_{j=1}^{N}(F_{ij} - E_i S_{ij})c_{ji} = 0 \tag{11.10}$$

$$|F_{ij} - E_i S_{ij}| = 0 \tag{11.11}$$

$$\phi_{2s}(r) = \phi_{2s}^{\mathrm{STO}}(r,\zeta_1) + d\phi_{2s}^{\mathrm{STO}}(r,\zeta_2) \tag{11.12}$$

$$\psi_{\mathrm{MO}} = 1s_A(1)1s_{\mathrm{B}}(2)+1s_A(2)1s_{\mathrm{B}}(1)+1s_A(1)1s_{\mathrm{A}}(2)+1s_B(1)1s_{\mathrm{B}}(2) \tag{11.13}$$

Chapter 12

Group Theory: The Exploitation of Symmetry

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{12.1}$$

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \tag{12.2}$$

$$\begin{aligned} \phi_1 &= \frac{1}{\sqrt{6}}(\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6) \\ \phi_2 &= \frac{1}{\sqrt{6}}(\psi_1 - \psi_2 + \psi_3 - \psi_4 + \psi_5 - \psi_6) \\ \phi_3 &= \frac{1}{\sqrt{12}}(2\psi_1 + \psi_2 - \psi_3 - 2\psi_4 - \psi_5 + \psi_6) \\ \phi_4 &= \frac{1}{\sqrt{12}}(\psi_1 + 2\psi_2 + \psi_3 - \psi_4 - 2\psi_5 - \psi_6) \\ \phi_5 &= \frac{1}{\sqrt{12}}(2\psi_1 - \psi_2 - \psi_3 + 2\psi_4 - \psi_5 - \psi_6) \\ \phi_6 &= \frac{1}{\sqrt{12}}(-\psi_1 + 2\psi_2 - \psi_3 - \psi_4 + 2\psi_5 - \psi_6) \end{aligned} \tag{12.3}$$

$$\begin{vmatrix} x+2 & | & 0 & & 0 & 0 & & 0 & 0 \\ --- & - & --- & & & & & & \\ 0 & | & x-2 & | & 0 & 0 & & 0 & 0 \\ & & --- & - & --- & --- & & & \\ 0 & & 0 & | & x+1 & \frac{x+1}{2} & | & 0 & 0 \\ 0 & & 0 & | & \frac{x+1}{2} & x+1 & | & 0 & 0 \\ & & & & --- & --- & - & --- & --- \\ 0 & & 0 & & 0 & 0 & | & x-1 & \frac{1-x}{2} \\ 0 & & 0 & & 0 & 0 & | & \frac{1-x}{2} & x-1 \end{vmatrix} = 0 \tag{12.4}$$

$$(x+2)(x-2)\begin{vmatrix} x+1 & \frac{x+1}{2} \\ \frac{x+1}{2} & x+1 \end{vmatrix}\begin{vmatrix} x-1 & \frac{1-x}{2} \\ \frac{1-x}{2} & x-1 \end{vmatrix} = 0 \tag{12.5}$$

$$\frac{9}{16}(x+2)(x-2)(x+1)^2(x-1)^2 = 0 \tag{12.6}$$

$$\sum_{j=1}^{N} d_j^2 = h \tag{12.7}$$

$$\sum_{j=1}^{N} d_j^2 = h \tag{12.8}$$

$$\sum_{j=1}^{N} [\chi_j(\hat{E})]^2 = h \tag{12.9}$$

$$\mathbf{u} \cdot \mathbf{v} = |u||v| \cos\theta \tag{12.10}$$

$$\mathbf{u} \cdot \mathbf{v} = u_1 v_1 + u_2 v_2 + u_3 v_3 \tag{12.11}$$

$$\mathbf{u} \cdot \mathbf{v} = u_1 v_1 + u_2 v_2 + u_3 v_3 = 0 \tag{12.12}$$

$$\mathbf{u} \cdot \mathbf{v} = \sum_{k=1}^{n} u_k v_k \tag{12.13}$$

$$\sum_{\hat{R}} \chi_i(\hat{R}) \chi_j(\hat{R}) = 0 \qquad i \neq j \tag{12.14}$$

$$\sum_{\text{classes}} n(\hat{R}) \chi_i(\hat{R}) \chi_j(\hat{R}) = 0 \qquad i \neq j \tag{12.15}$$

$$\sum_{\hat{R}} \chi_j(\hat{R}) = \sum_{\text{classes}} n(\hat{R}) \chi_j(\hat{R}) = 0 \qquad j \neq A_1 \tag{12.16}$$

$$(\text{length})^2 = \sum_{\hat{R}} [\chi_j(\hat{R})]^2 \tag{12.17}$$

$$\sum_{\hat{R}} [\chi_j(\hat{R})]^2 = h \tag{12.18}$$

$$\sum_{\text{classes}} n(\hat{R}) [\chi_j(\hat{R})]^2 = h \tag{12.19}$$

$$\sum_{\hat{R}} \chi_i(\hat{R}) \chi_j(\hat{R}) = \sum_{\text{classes}} n(\hat{R}) \chi_i(\hat{R}) \chi_j(\hat{R}) = h\delta_{ij} \tag{12.20}$$

$$\chi(\hat{R}) = \sum_{j} a_j \chi_j(\hat{R}) \tag{12.21}$$

$$a_i = \frac{1}{h} \sum_{\hat{R}} \chi(\hat{R}) \chi_i(\hat{R}) \tag{12.22}$$

$$a_i = \frac{1}{h} \sum_{\hat{R}} \chi(\hat{R}) \chi_i(\hat{R}) = \frac{1}{h} \sum_{\text{classes}} n(\hat{R}) \chi(\hat{R}) \chi_i(\hat{R}) \tag{12.23}$$

$$H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau \quad \text{and} \quad S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.24}$$

$$S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.25}$$

$$\hat{R} S_{ij} = \int \hat{R} \phi_i^* \hat{R} \phi_j d\tau = S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.26}$$

$$\hat{R} \phi_i^* = \chi_a(\hat{R}) \phi_i^* \quad \text{and} \quad \hat{R} \phi_j = \chi_b(\hat{R}) \phi_j \tag{12.27}$$

$$S_{ij} = \chi_a(\hat{R})\chi_b(\hat{R}) \int \phi_i^* \phi_j d\tau = \chi_a(\hat{R})\chi_b(\hat{R}) S_{ij} \tag{12.28}$$

$$\chi_a(\hat{R})\chi_b(\hat{R}) = 1 \qquad \text{for all } \hat{R} \tag{12.29}$$

$$\begin{aligned} \hat{R}H_{ij} &= \int (\hat{R}\phi_i^*)(\hat{R}\hat{H})(\hat{R}\phi_j) d\tau = H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau \\ &= \chi_a(\hat{R})\chi_{A_1}(\hat{R})\chi_b(\hat{R}) H_{ij} \end{aligned} \tag{12.30}$$

$$\chi_a(\hat{R})\chi_{A_1}(\hat{R})\chi_b(\hat{R}) = 1 \qquad \text{for all } \hat{R} \tag{12.31}$$

$$\hat{P}_j = \frac{l_j}{h} \sum_{\hat{R}} \chi_j(\hat{R}) \hat{R} \tag{12.32}$$

$$\begin{aligned} \hat{P}_{B_g}\psi_1 &= \tfrac{1}{4}(\psi_1 - \psi_4 - \psi_4 + \psi_1) \propto \psi_1 - \psi_4 \\ \hat{P}_{B_g}\psi_2 &= \tfrac{1}{4}(\psi_2 - \psi_3 - \psi_3 + \psi_2) \propto \psi_2 - \psi_3 \\ \hat{P}_{A_u}\psi_1 &= \tfrac{1}{4}(\psi_1 + \psi_4 + \psi_4 + \psi_1) \propto \psi_1 + \psi_4 \\ \hat{P}_{A_u}\psi_2 &= \tfrac{1}{4}(\psi_2 + \psi_3 + \psi_3 + \psi_2) \propto \psi_2 + \psi_3 \\ \hat{P}_{B_u}\psi_1 &= \hat{P}_{B_u}\psi_2 = 0 \end{aligned} \tag{12.33}$$

$$(x^2 + x - 1)(x^2 - x - 1) = 0 \tag{12.34}$$

Chapter 13

Molecular Spectroscopy

$$\Delta E = E_u - E_l = h\nu \tag{13.1}$$

$$E_v = (v + \tfrac{1}{2})h\nu \qquad v = 0,\ 1,\ 2,\ \ldots \tag{13.2}$$

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \tag{13.3}$$

$$G(v) = \left(v + \frac{1}{2}\right)\tilde{\nu} \tag{13.4}$$

$$\tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{13.5}$$

$$E_J = \frac{\hbar^2}{2I}J(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots \tag{13.6}$$

$$g_J = 2J + 1 \tag{13.7}$$

$$F(J) = \tilde{B}J(J+1) \tag{13.8}$$

$$\tilde{B} = \frac{h}{8\pi^2 cI} \tag{13.9}$$

$$\tilde{E}_{v,J} = G(v) + F(J) = (v + \tfrac{1}{2})\tilde{\nu} + \tilde{B}J(J+1) \qquad \begin{matrix} v = 0,\ 1,\ 2,\ \ldots \\ J = 0,\ 1,\ 2,\ \ldots \end{matrix} \tag{13.10}$$

$$\begin{aligned} \Delta v &= +1 \qquad \text{(absorption)} \\ \Delta J &= \pm 1 \end{aligned} \tag{13.11}$$

$$\begin{aligned} \tilde{\nu}_{\text{obs}}(\Delta J = +1) &= \tilde{E}_{v+1,J+1} - \tilde{E}_{v,J} \\ &= \left(v + \frac{3}{2}\right)\tilde{\nu} + \tilde{B}(J+1)(J+2) - \left(v + \frac{1}{2}\right)\tilde{\nu} + \tilde{B}J(J+1) \\ &= \tilde{\nu} + 2\tilde{B}(J+1) \qquad J = 0,\ 1,\ 2,\ \ldots \end{aligned} \tag{13.12}$$

$$\tilde{\nu}_{\text{obs}}(\Delta J = -1) = \tilde{E}_{v+1,J-1} - \tilde{E}_{v,J} = \tilde{\nu} - 2\tilde{B}J \qquad J = 1,\ 2,\ \ldots \tag{13.13}$$

$$\tilde{E}_{v,J} = \tilde{\nu}(v + \tfrac{1}{2}) + \tilde{B}_v J(J+1) \tag{13.14}$$

$$\begin{aligned} \tilde{\nu}_R(\Delta J = +1) &= E_{1,J+1} - E_{0,J} \\ &= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} + \tilde{B}_0 J(J+1) \\ &= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \quad J = 0,\ 1,\ 2,\ \ldots \end{aligned} \tag{13.15}$$

$$\tilde{\nu}_P(\Delta J = -1) = E_{1,J-1} - E_{0,J} = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \quad J = 1,\ 2,\ 3,\ \ldots \tag{13.16}$$

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e(v + \tfrac{1}{2}) \tag{13.17}$$

$$F(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2 \tag{13.18}$$

$$\begin{aligned} \tilde{\nu} &= F(J+1) - F(J) \\ &= 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3 \qquad J = 0,\ 1,\ 2,\ \ldots \end{aligned} \tag{13.19}$$

$$V(R) - V(R_e) = \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \cdots$$
$$= \frac{k}{2}x^2 + \frac{\gamma_3}{6}x^3 + \frac{\gamma_4}{24}x^4 + \cdots \qquad (13.20)$$

$$G(v) = \tilde{\nu}_e(v+\tfrac{1}{2}) - \tilde{x}_e\tilde{\nu}_e(v+\tfrac{1}{2})^2 + \cdots \qquad v = 0,\ 1,\ 2,\ \ldots \qquad (13.21)$$

$$\tilde{\nu}_{\text{obs}} = G(v) - G(0) = \tilde{\nu}_e v - \tilde{x}_e\tilde{\nu}_e v(v+1) \qquad v = 1,\ 2,\ \ldots \qquad (13.22)$$

$$\tilde{E}_{\text{total}} = \tilde{\nu}_{\text{el}} + G(v) + F(J)$$
$$= \tilde{\nu}_{\text{el}} + \tilde{\nu}_e(v+\tfrac{1}{2}) - \tilde{x}_e\tilde{\nu}_e(v+\tfrac{1}{2})^2 + \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2 \qquad (13.23)$$

$$\tilde{\nu}_{\text{obs}} = \tilde{T}_e + (\tfrac{1}{2}\tilde{\nu}'_e - \tfrac{1}{4}\tilde{x}'_e\tilde{\nu}'_e) - (\tfrac{1}{2}\tilde{\nu}''_e - \tfrac{1}{4}\tilde{x}''_e\tilde{\nu}''_e) + \tilde{\nu}'_e v' - \tilde{x}'_e\tilde{\nu}'_e v'(v'+1) \qquad (13.24)$$

$$\tilde{\nu}_{\text{obs}} = \tilde{\nu}_{0,0} + \tilde{\nu}'_e v' - \tilde{x}'_e\tilde{\nu}'_e v'(v'+1) \qquad v' = 0,\ 1,\ 2,\ \ldots \qquad (13.25)$$

$$I_{xx} = \sum_{j=1}^{N} m_j[(y_j - y_{cm})^2 + (z_j - z_{cm})^2]$$
$$I_{yy} = \sum_{j=1}^{N} m_j[(x_j - x_{cm})^2 + (z_j - z_{cm})^2] \qquad (13.26)$$
$$I_{zz} = \sum_{j=1}^{N} m_j[(x_j - x_{cm})^2 + (y_j - y_{cm})^2]$$

$$\tilde{A} = \frac{h}{8\pi^2 c I_A}, \qquad \tilde{B} = \frac{h}{8\pi^2 c I_B}, \quad \text{and} \quad \tilde{C} = \frac{h}{8\pi^2 c I_C} \qquad (13.27)$$

$$F(J,K) = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2 \tag{13.28}$$

$$F(J,K) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2 \tag{13.29}$$

$$\begin{array}{lll} \Delta J = 0, \pm 1 & \Delta K = 0 & \text{for } K \neq 0 \\ \Delta J = \pm 1 & \Delta K = 0 & \text{for } K = 0 \end{array} \tag{13.30}$$

$$\tilde{\nu} = 2\tilde{B}(J+1) \tag{13.31}$$

$$\tilde{\nu} = 2\tilde{B}(J+1) - 2\tilde{D}_{JK}K^2(J+1) - 4\tilde{D}_J(J+1)^3 \tag{13.32}$$

$$\begin{aligned} \Delta V &= V(q_1, q_2, \ldots, q_{N_{\text{vib}}}) - V(0,0,\ldots,0) = \frac{1}{2}\sum_{i=1}^{N_{\text{vib}}}\sum_{j=1}^{N_{\text{vib}}}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right) q_i q_j + \cdots \\ &= \frac{1}{2}\sum_{i=1}^{N_{\text{vib}}}\sum_{j=1}^{N_{\text{vib}}} f_{ij} q_i q_j + \cdots \end{aligned} \tag{13.33}$$

$$\Delta V = \frac{1}{2}\sum_{j=1}^{N_{\text{vib}}} F_j Q_j^2 \tag{13.34}$$

$$\hat{H}_{\text{vib}} = -\sum_{j=1}^{N_{\text{vib}}} \frac{\hbar^2}{2\mu_j}\frac{d^2}{dQ_j^2} + \frac{1}{2}\sum_{j=1}^{N_{\text{vib}}} F_j Q_j^2 \tag{13.35}$$

$$\begin{gathered} \hat{H}_{\text{vib}} = \sum_{j=1}^{N_{\text{vib}}} \hat{H}_{\text{vib},j} = \sum_{j=1}^{N_{\text{vib}}} \left(-\frac{\hbar^2}{2\mu_j}\frac{d^2}{dQ_j^2} + \frac{1}{2}F_j Q_j^2\right) \\ \psi_{\text{vib}}(Q_1, Q_2, \ldots, Q_{\text{vib}}) = \psi_{\text{vib},1}(Q_1)\psi_{\text{vib},2}(Q_2)\cdots\psi_{\text{vib},N_{\text{vib}}}(Q_{N_{\text{vib}}}) \end{gathered} \tag{13.36}$$

$$E_{\text{vib}} = \sum_{j=1}^{N_{\text{vib}}} h\nu_j(v_j + \tfrac{1}{2}) \qquad \text{each } v_j = 0,\ 1,\ 2,\ \ldots \tag{13.37}$$

$$\hat{H}\Psi = i\hbar\frac{\partial \Psi}{\partial t} \tag{13.38}$$

$$\mathbf{E} = \mathbf{E}_0 \cos 2\pi\nu t \tag{13.39}$$

$$\hat{H}^{(1)} = -\boldsymbol{\mu} \cdot \mathbf{E} = -\boldsymbol{\mu} \cdot \mathbf{E}_0 \cos 2\pi\nu t \tag{13.40}$$

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{13.41}$$

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} = \hat{H}^{(0)} - \boldsymbol{\mu} \cdot \mathbf{E}_0 \cos 2\pi\nu t \tag{13.42}$$

$$\hat{H}^{(0)}\psi = i\hbar \frac{\partial \psi}{\partial t} \tag{13.43}$$

$$\Psi_1(t) = \psi_1 e^{-iE_1 t/\hbar} \text{ and } \Psi_2(t) = \psi_2 e^{-iE_2 t/\hbar} \tag{13.44}$$

$$\Psi(t) = a_1(t)\Psi_1(t) + a_2(t)\Psi_2(t) \tag{13.45}$$

$$\begin{aligned} &a_1(t)\hat{H}^{(0)}\Psi_1 + a_2(t)\hat{H}^{(0)}\Psi_2 + a_1(t)\hat{H}^{(1)}\Psi_1 + a_2(t)\hat{H}^{(1)}\Psi_2 \\ &\qquad = a_1(t) i\hbar \frac{\partial \Psi_1}{dt} + a_2(t) i\hbar \frac{\partial \Psi_2}{dt} + i\hbar \Psi_1 \frac{da_1}{dt} + i\hbar \Psi_2 \frac{da_2}{dt} \end{aligned} \tag{13.46}$$

$$a_1(t)\hat{H}^{(1)}\Psi_1 + a_2(t)\hat{H}^{(1)}\Psi_2 = i\hbar \Psi_1 \frac{da_1}{dt} + i\hbar \Psi_2 \frac{da_2}{dt} \tag{13.47}$$

$$\begin{aligned} &a_1(t) \textstyle\int \psi_2^* \hat{H}^{(1)} \Psi_1 d\tau + a_2(t) \textstyle\int \psi_2^* \hat{H}^{(1)} \Psi_2 d\tau \\ &\qquad = i\hbar \frac{da_1}{dt} \int \psi_2^* \Psi_1 d\tau + i\hbar \frac{da_2}{dt} \int \psi_2^* \Psi_2 d\tau \end{aligned} \tag{13.48}$$

$$i\hbar \frac{da_2}{dt} = a_1(t) \exp\left[\frac{-i(E_1 - E_2)t}{\hbar}\right] \int \psi_2^* \hat{H}^{(1)} \psi_1 d\tau + a_2(t) \int \psi_2^* \hat{H}^{(1)} \psi_2 d\tau \tag{13.49}$$

$$a_1(0) = 1 \quad \text{and} \quad a_2(0) = 0 \tag{13.50}$$

$$i\hbar \frac{da_2}{dt} = \exp\left[\frac{-i(E_1 - E_2)t}{\hbar}\right] \int \psi_2^* \hat{H}^{(1)} \psi_1 d\tau \tag{13.51}$$

$$\frac{da_2}{dt} \propto (\mu_z)_{12}\mathrm{E}_{0z}\left\{\exp\left[\frac{i(E_2 - E_1 + h\nu)t}{\hbar}\right] + \exp\left[\frac{i(E_2 - E_1 - h\nu)t}{\hbar}\right]\right\} \tag{13.52}$$

$$(\mu_z)_{12} = \int \psi_2^* \mu_z \psi_1 d\tau \tag{13.53}$$

$$\begin{aligned} a_2(t) \quad &\propto \quad (\mu_z)_{12}\mathrm{E}_{0z} \\ &\times \left\{\frac{1 - \exp[i(E_2 - E_1 + h\nu)t/\hbar]}{E_2 - E_1 + h\nu} + \frac{1 - \exp[i(E_2 - E_1 - h\nu)t/\hbar]}{E_2 - E_1 - h\nu}\right\} \end{aligned} \tag{13.54}$$

$$E_2 - E_1 \approx h\nu \tag{13.55}$$

$$a_2^*(t)a_2(t) \propto \frac{\sin^2[(E_2 - E_1 - \hbar\omega)/2\hbar]}{(E_2 - E_1 - \hbar\omega)^2} \tag{13.56}$$

$$(\mu_z)_{J,M,J',M'} = \mu \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta,\phi)^* Y_J^M(\theta,\phi) \cos\theta \sin\theta d\theta d\phi \tag{13.57}$$

$$Y_J^M(\theta,\phi) = N_{JM} P_J^{|M|}(\cos\theta) e^{iM\phi} \tag{13.58}$$

$$(\mu_z)_{J,M;J',M'} = \mu N_{J,M} N_{J',M'} \int_0^{2\pi} d\phi e^{i(M-M')\phi} \int_{-1}^{1} dx\; x P_{J'}^{|M'|}(x) P_J^{|M|}(x) \tag{13.59}$$

$$(\mu_z)_{J,M;J',M'} = 2\pi\mu N_{JM} N_{J'M} \int_{-1}^{1} dx x P_{J'}^{|M|}(x) P_J^{|M|}(x) \tag{13.60}$$

$$(2J+1)xP_J^{|M|}(x) = (J - |M| + 1)P_{J+1}^{|M|}(x) + (J + |M|)P_{J-1}^{|M|}(x) \tag{13.61}$$

$$\psi_v(q) = N_v H_v(\alpha^{1/2} q) e^{-\alpha q^2/2} \tag{13.62}$$

$$(\mu_z)_{v,v'} = \int_{-\infty}^{\infty} N_v N_{v'} H_{v'}(\alpha^{1/2}q)e^{-\alpha q^2/2}\mu_z(q)H_v(\alpha^{1/2}q)e^{-\alpha q^2/2}dq \quad (13.63)$$

$$\mu_z(q) = \mu_0 + \left(\frac{d\mu}{dq}\right)_0 q + \cdots \quad (13.64)$$

$$\begin{aligned}(\mu_z)_{v,v'} &= N_v N_{v'}\mu_0 \int_{-\infty}^{\infty} H_{v'}(\alpha^{1/2}q)H_v(\alpha^{1/2}q)e^{-\alpha q^2}dq \\ &+ N_v N_{v'}\left(\frac{d\mu}{dq}\right)_0 \int_{-\infty}^{\infty} H_{v'}(\alpha^{1/2}q)qH_v(\alpha^{1/2}q)e^{-\alpha q^2}dq\end{aligned} \quad (13.65)$$

$$\xi H_v(\xi) = vH_{v-1}(\xi) + \tfrac{1}{2}H_{v+1}(\xi) \quad (13.66)$$

$$(\mu_z)_{v,v'} = \frac{N_v N_{v'}}{\alpha}\left(\frac{d\mu}{dq}\right)_0 \int_{-\infty}^{\infty} H_{v'}(\xi)\left[nH_{v-1}(\xi) + \frac{1}{2}H_{v+1}(\xi)\right]e^{-\xi^2}d\xi \quad (13.67)$$

$$I_{0\to 1} = \int \psi_0(Q_1, Q_2, \ldots, Q_{N_{\mathrm{vib}}})\left\{\begin{array}{c}\mu_x\\ \mu_y\\ \mu_z\end{array}\right\}\psi_1(Q_1, Q_2, \ldots, Q_{N_{\mathrm{vib}}})dQ_1, Q_2, \ldots, Q_{N_{\mathrm{vib}}} \quad (13.68)$$

$$\psi_0(Q_1, Q_2, \ldots, Q_{N_{\mathrm{vib}}}) = ce^{-\alpha_1 Q_1^2 - \alpha_2 Q_2^2 - \cdots - \alpha_{N_{\mathrm{vib}}} Q_{N_{\mathrm{vib}}}^2} \quad (13.69)$$

$$\hat{R}\psi_0(Q_1, Q_2, \ldots, Q_{N_{\mathrm{vib}}}) = \psi_0(Q_1, Q_2, \ldots, Q_{N_{\mathrm{vib}}}) \quad (13.70)$$

$$\begin{aligned}\psi_1(Q_1, Q_2, \ldots, Q_{N_{\mathrm{vib}}}) &= \psi_0(Q_1)\psi_0(Q_2)\cdots\psi_0(Q_{j-1})\psi_1(Q_j)\psi_0(Q_{j+1})\cdots\psi_0(Q_{\mathrm{vib}}) \\ &= c'Q_j e^{-\alpha_1 Q_1^2 - \alpha_2 Q_2^2 - \cdots - \alpha_{N_{\mathrm{vib}}} Q_{N_{\mathrm{vib}}}^2}\end{aligned} \quad (13.71)$$

$$\hat{R}\psi_1(Q_1, Q_2, \ldots, Q_{N_{\mathrm{vib}}}) = \chi_{Q_j}(\hat{R})\psi_1(Q_1, Q_2, \ldots, Q_{N_{\mathrm{vib}}}) \quad (13.72)$$

$$
\begin{aligned}
\hat{R}I_{0\to1} = I_{0\to1} &= \int (\hat{R}\psi_0)(\hat{R}\mu_x)(\hat{R}\psi_1)dQ_1dQ_2\ldots dQ_{\mathrm{vib}} \\
&= \chi_{A_1}(\hat{R})\chi_{\mu_x}(\hat{R})\chi_{Q_j}(\hat{R})\int \psi_0\mu_x\psi_1 dQ_1dQ_2\ldots dQ_{\mathrm{vib}} \\
&= \chi_{A_1}(\hat{R})\chi_{\mu_x}(\hat{R})\chi_{Q_j}(\hat{R})I_{0\to1} \qquad (13.73)
\end{aligned}
$$

Chapter 14

Nuclear Magnetic Resonance Spectroscopy

$$\hat{S}^2\alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\alpha \qquad \hat{S}^2\beta = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\beta$$
$$\hat{S}_z\alpha = \frac{1}{2}\hbar\alpha \qquad \hat{S}_z\beta = -\frac{1}{2}\hbar\beta \tag{14.1}$$

$$\int \alpha^*(\sigma)\alpha(\sigma)d\sigma = \int \beta^*(\sigma)\beta(\sigma)d\sigma = 1$$
$$\int \alpha^*(\sigma)\beta(\sigma)d\sigma = \int \alpha(\sigma)\beta^*(\sigma)d\sigma = 0 \tag{14.2}$$

$$\mu = iA \tag{14.3}$$

$$i = \frac{qv}{2\pi r} \tag{14.4}$$

$$\mu = \frac{qrv}{2} \tag{14.5}$$

$$\boldsymbol{\mu} = \frac{q(\mathbf{r}\times\mathbf{v})}{2} \tag{14.6}$$

$$\boldsymbol{\mu} = \frac{q}{2m}\mathbf{L} \tag{14.7}$$

$$\boldsymbol{\mu} = g_{\mathrm{N}}\frac{q}{2m_{\mathrm{N}}}\mathbf{I} = g_{\mathrm{N}}\beta_{\mathrm{N}}\mathbf{I} = \gamma\mathbf{I} \tag{14.8}$$

$$V = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{14.9}$$

$$\mathbf{F} = q(\mathbf{v} \times \mathbf{B}) \tag{14.10}$$

$$V = -\mu_z B_z \tag{14.11}$$

$$V = -\gamma B_z I_z \tag{14.12}$$

$$\hat{H} = -\gamma B_z \hat{I}_z \tag{14.13}$$

$$\hat{H}\psi = -\gamma B_z \hat{I}_z \psi = E\psi \tag{14.14}$$

$$E = -\hbar\gamma m_I B_z \tag{14.15}$$

$$\Delta E = E(m_I = -1/2) - E(m_I = 1/2) = \hbar\gamma B_z \tag{14.16}$$

$$\nu = \frac{\gamma B_z}{2\pi} \qquad \text{(Hz)} \tag{14.17}$$

$$\omega = \gamma B_z \qquad (\text{rad}\cdot\text{s}^{-1}) \tag{14.18}$$

$$B_{\text{elec}} = -\sigma B_0 \tag{14.19}$$

$$B_0 = \frac{2\pi\nu}{\gamma(1-\sigma)} = \frac{\omega}{\gamma(1-\sigma)} \tag{14.20}$$

$$\nu_{\text{H}} = \frac{\gamma B_0}{2\pi}(1 - \sigma_{\text{H}}) \tag{14.21}$$

$$\begin{aligned} \delta_{\text{H}} &= \frac{\text{resonance frequency of nucleus H relative to TMS}}{\text{spectrometer frequency}} \times 10^6 \\ &= \left(\frac{\nu_{\text{H}} - \nu_{\text{TMS}}}{\nu_{\text{spectrometer}}}\right) \times 10^6 \end{aligned} \tag{14.22}$$

$$\delta_1 - \delta_2 = \left(\frac{\nu_1 - \nu_2}{\nu_{\text{spectrometer}}}\right) \times 10^6 = \frac{\gamma B_0}{2\pi\nu_{\text{spectrometer}}}(\sigma_2 - \sigma_1) \times 10^6 \quad (14.23)$$

$$\delta_1 - \delta_2 = (\sigma_2 - \sigma_1) \times 10^6 \quad (14.24)$$

$$\hat{H} = -\gamma B_0(1-\sigma_1)\hat{I}_{z1} - \gamma B_0(1-\sigma_2)\hat{I}_{z2} \quad (14.25)$$

$$\hat{H} = -\gamma B_0(1-\sigma_1)\hat{I}_{z1} - \gamma B_0(1-\sigma_2)\hat{I}_{z2} + \frac{hJ_{12}}{\hbar^2}\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \quad (14.26)$$

$$\hat{H}^{(0)} = -\gamma B_0(1-\sigma_1)\hat{I}_{z1} - \gamma B_0(1-\sigma_2)\hat{I}_{z2} \quad (14.27)$$

$$\hat{H}^{(1)} = \frac{hJ_{12}}{\hbar^2}\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \quad (14.28)$$

$$\begin{array}{ll} \psi_1 = \alpha(1)\alpha(2) & \psi_3 = \beta(1)\alpha(2) \\ \psi_2 = \alpha(1)\beta(2) & \psi_4 = \beta(1)\beta(2) \end{array} \quad (14.29)$$

$$E_j = E_j^{(0)} + \int d\tau_1 d\tau_2 \psi_j^* \hat{H}^{(1)} \psi_j \quad (14.30)$$

$$\hat{H}^{(0)}\psi_j = E_j^{(0)}\psi_j \quad (14.31)$$

$$\begin{aligned} \hat{H}^{(0)}\psi_1 &= \hat{H}^{(0)}\alpha(1)\alpha(2) \\ &= -\gamma B_0(1-\sigma_1)\hat{I}_{z1}\alpha(1)\alpha(2) - \gamma B_0(1-\sigma_2)\hat{I}_{z2}\alpha(1)\alpha(2) \\ &= -\frac{\hbar\gamma B_0(1-\sigma_1)}{2}\alpha(1)\alpha(2) - \frac{\hbar\gamma B_0(1-\sigma_2)}{2}\alpha(1)\alpha(2) \\ &= E^{(0)}\alpha(1)\alpha(2) = E^{(0)}\psi_1 \end{aligned} \quad (14.32)$$

$$E_1^{(0)} = -\hbar\gamma B_0\left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) \quad (14.33)$$

$$E_2^{(0)} = \frac{\hbar\gamma B_0}{2}(\sigma_1 - \sigma_2) \quad (14.34)$$

$$E_3^{(0)} = \frac{\hbar\gamma B_0}{2}(\sigma_2 - \sigma_1) \tag{14.35}$$

$$E_4^{(0)} = \hbar\gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) \tag{14.36}$$

$$\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 = \hat{I}_{x1}\hat{I}_{x2} + \hat{I}_{y1}\hat{I}_{y2} + \hat{I}_{z1}\hat{I}_{z2} \tag{14.37}$$

$$\begin{aligned} H_{z,11} &= \frac{hJ_{12}}{\hbar^2}\int d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)\hat{I}_{z1}\hat{I}_{z2}\alpha(1)\alpha(2) \\ &= \frac{hJ_{12}}{\hbar^2}\frac{\hbar^2}{4}\int d\tau_1 \alpha^*(1)\alpha(1)\int d\tau_2 \alpha^*(2)\alpha(2) \\ &= \frac{hJ_{12}}{4} \end{aligned} \tag{14.38}$$

$$H_{z,22} = H_{z,33} = -\frac{hJ_{12}}{4} \tag{14.39}$$

$$H_{z,44} = \frac{hJ_{12}}{4} \tag{14.40}$$

$$\begin{aligned} \hat{I}_x\alpha &= \frac{\hbar}{2}\beta & \hat{I}_y\alpha &= \frac{i\hbar}{2}\beta \\ \hat{I}_x\beta &= \frac{\hbar}{2}\alpha & \hat{I}_y\beta &= -\frac{i\hbar}{2}\alpha \end{aligned} \tag{14.41}$$

$$\begin{aligned} E_1 &= -h\nu_0\left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) + \frac{hJ_{12}}{4} \\ E_2 &= \frac{h\nu_0}{2}(\sigma_1 - \sigma_2) - \frac{hJ_{12}}{4} \\ E_3 &= \frac{h\nu_0}{2}(\sigma_2 - \sigma_1) - \frac{hJ_{12}}{4} \\ E_4 &= h\nu_0\left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) + \frac{hJ_{12}}{4} \end{aligned} \tag{14.42}$$

$$\nu_0 = \frac{\gamma B_0}{2\pi} \tag{14.43}$$

$$\begin{aligned}\nu_{1\to 2} &= \nu_0(1-\sigma_2) - \frac{J_{12}}{2} \\ \nu_{1\to 3} &= \nu_0(1-\sigma_1) - \frac{J_{12}}{2} \\ \nu_{2\to 4} &= \nu_0(1-\sigma_1) + \frac{J_{12}}{2} \\ \nu_{3\to 4} &= \nu_0(1-\sigma_2) + \frac{J_{12}}{2}\end{aligned} \tag{14.44}$$

$$\hat{H} = -\gamma B_0(1-\sigma_A)\hat{I}_{z1} - \gamma B_0(1-\sigma_A)\hat{I}_{z2} + \frac{hJ_{AA}}{\hbar^2}\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \tag{14.45}$$

$$\hat{H}^{(0)} = -\gamma B_0(1-\sigma_A)(\hat{I}_{z1} + \hat{I}_{z2}) \tag{14.46}$$

$$\hat{H}^{(1)} = \frac{hJ_{AA}}{\hbar^2}\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \tag{14.47}$$

$$\begin{aligned}\phi_1 &= \alpha(1)\alpha(2) & \phi_2 &= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ \phi_3 &= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] & \phi_4 &= \beta(1)\beta(2)\end{aligned} \tag{14.48}$$

$$\begin{aligned}E_1 &= E_1^{(0)} + E_1^{(1)} \\ &= \int\int d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)\left[-\gamma B_0(1-\sigma_A)(\hat{I}_{z1} + \hat{I}_{z2})\right]\alpha(1)\alpha(2) \\ &\quad + \int\int d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)\frac{hJ_{AA}}{\hbar^2}(\hat{I}_{x1}\hat{I}_{x2} + \hat{I}_{y1}\hat{I}_{y2} + \hat{I}_{z1}\hat{I}_{z2})\alpha(1)\alpha(2)\end{aligned} \tag{14.49}$$

$$\begin{aligned}E_1 &= -\gamma B_0(1-\sigma_A)\left(\frac{\hbar}{2} + \frac{\hbar}{2}\right)\int d\tau_1 \alpha^*(1)\alpha(1)\int d\tau_2 \alpha^*(2)\alpha(2) \\ &\quad + \frac{hJ_{AA}}{\hbar^2}\frac{\hbar^2}{4}\int d\tau_1 \alpha^*(1)\alpha(1)\int d\tau_2 \alpha^*(2)\alpha(2) \\ &= -\hbar\gamma B_0(1-\sigma_A) + \frac{hJ_{AA}}{4}\end{aligned} \tag{14.50}$$

$$E_2 = E_2^{(1)} = -\frac{3hJ_{AA}}{4} \tag{14.51}$$

$$E_3 = \frac{hJ_{AA}}{4} \tag{14.52}$$

$$E_4 = \hbar\gamma B_0(1-\sigma_A) + \frac{hJ_{AA}}{4} \tag{14.53}$$

$$\hat{H} = -\gamma B_0(1-\sigma_1)\hat{I}_{z1} - \gamma B_0(1-\sigma_2)\hat{I}_{z2} + \frac{hJ_{12}}{\hbar^2}\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 \tag{14.54}$$

$$\begin{aligned} \phi_1 &= \alpha(1)\alpha(2) & \phi_2 &= \alpha(1)\beta(2) \\ \phi_3 &= \beta(1)\alpha(2) & \phi_4 &= \beta(1)\beta(2) \end{aligned} \tag{14.55}$$

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 \tag{14.56}$$

$$E = \frac{\int\int d\tau_1 d\tau_2 \psi^* \hat{H}\psi}{\int\int d\tau_1 d\tau_2 \psi^* \psi} \tag{14.57}$$

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} & H_{14} \\ H_{12} & H_{22}-E & H_{23} & H_{24} \\ H_{13} & H_{23} & H_{33}-E & H_{34} \\ H_{14} & H_{24} & H_{34} & H_{44}-E \end{vmatrix} = 0 \tag{14.58}$$

$$H_{ij} = \int\int d\tau_1 d\tau_2 \phi_i^* \hat{H} \phi_j \tag{14.59}$$

$$\begin{vmatrix} -d_1 - d_2 + \frac{hJ}{4} - E & 0 & 0 & 0 \\ 0 & -d_1 + d_2 - \frac{hJ}{4} - E & \frac{hJ}{2} & 0 \\ 0 & \frac{hJ}{2} & d_1 - d_2 - \frac{hJ}{4} - E & 0 \\ 0 & 0 & 0 & d_1 + d_2 + \frac{hJ}{4} - E \end{vmatrix} = 0 \tag{14.60}$$

$$
\begin{aligned}
E_1 &= -h\nu_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) + \frac{hJ}{4} \\
E_2 &= -\frac{hJ}{4} - \frac{h}{2}[\nu_0^2(\sigma_1 - \sigma_2)^2 + J^2]^{1/2} \\
E_3 &= -\frac{hJ}{4} + \frac{h}{2}[\nu_0^2(\sigma_1 - \sigma_2)^2 + J^2]^{1/2} \\
E_4 &= h\nu_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) + \frac{hJ}{4}
\end{aligned} \tag{14.61}
$$

$$
\begin{aligned}
\nu_{1\to 2} &= \nu_0(1 - \sigma_1) - \frac{J}{2} \\
\nu_{3\to 4} &= \nu_0(1 - \sigma_1) + \frac{J}{2} \\
\nu_{1\to 3} &= \nu_0(1 - \sigma_2) - \frac{J}{2} \\
\nu_{2\to 4} &= \nu_0(1 - \sigma_2) + \frac{J}{2}
\end{aligned} \tag{14.62}
$$

Chapter 15

Lasers, Laser Spectroscopy, and Photochemistry

$$\text{rate} = -\frac{dN_1(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) \tag{15.1}$$

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) \qquad \text{(absorption only)} \tag{15.2}$$

$$-\frac{dN_2(t)}{dt} = A_{21}N_2(t) \qquad \text{(spontaneous emission only)} \tag{15.3}$$

$$-\frac{dN_2(t)}{dt} = B_{21}\rho_\nu(\nu_{12})N_2(t) \qquad \text{(stimulated emission only)} \tag{15.4}$$

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho_\nu(\nu_{12})N_2(t) \tag{15.5}$$

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = 0 \tag{15.6}$$

$$\rho_\nu(\nu_{12}) = \frac{8\pi h}{c^3}\frac{\nu_{12}^3}{e^{h\nu_{12}/k_\mathrm{B}T} - 1} \tag{15.7}$$

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{(N_1/N_2)B_{12} - B_{21}} \tag{15.8}$$

$$N_j = ce^{-E_j/k_\mathrm{B}T} \tag{15.9}$$

$$\frac{N_2}{N_1} = e^{-(E_2-E_1)/k_\mathrm{B}T} = e^{-h\nu_{12}/k_\mathrm{B}T} \tag{15.10}$$

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{B_{12}e^{h\nu_{12}/k_\mathrm{B}T} - B_{21}} \tag{15.11}$$

$$B_{12} = B_{21} \tag{15.12}$$

$$A_{21} = \frac{8h\pi\nu_{12}^3}{c^3}B_{21} \tag{15.13}$$

$$B_{21}\rho_\nu(\nu_{12})N_2 > B_{12}\rho_\nu(\nu_{12})N_1 \tag{15.14}$$

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B\rho_\nu(\nu_{12})\{N_1(t) - N_2(t)\} - AN_2(t) \tag{15.15}$$

$$N_2(t) = \frac{B\rho_\nu(\nu_{12})N_\mathrm{total}}{A + 2B\rho_\nu(\nu_{12})}\{1 - e^{-[A+2B\rho_\nu(\nu_{12})]t}\} \tag{15.16}$$

$$\frac{N_2(t\to\infty)}{N_\mathrm{total}} = \frac{B\rho_\nu(\nu_{12})}{A + 2B\rho_\nu(\nu_{12})} \tag{15.17}$$

$$\frac{N_2}{N_\mathrm{total}} = \frac{N_2}{N_1 + N_2} < \frac{1}{2} \tag{15.18}$$

$$N_\mathrm{total} = N_1(t) + N_2(t) + N_3(t) \tag{15.19}$$

$$\frac{dN_2(t)}{dt} = 0 = A_{32}N_3 - A_{21}N_2 + \rho_\nu(\nu_{32})B_{32}N_3 - \rho_\nu(\nu_{32})B_{32}N_2 \tag{15.20}$$

$$N_3[A_{32} + B_{32}\rho_\nu(\nu_{32})] = N_2[A_{21} + B_{32}\rho_\nu(\nu_{32})] \tag{15.21}$$

$$\frac{N_3}{N_2} = \frac{A_{21} + B_{32}\rho_\nu(\nu_{32})}{A_{32} + B_{32}\rho_\nu(\nu_{32})} \tag{15.22}$$

$$\Phi = \frac{\text{number of molecules that undergo reaction}}{\text{number of photons absorbed}} \tag{15.23}$$

$$\mathrm{ICN(g)} + h\nu \longrightarrow \mathrm{I(g)} + \mathrm{CN(g)} \tag{15.24}$$

Chapter 16

The Properties of Gases

$$P = \frac{mg}{A} = \frac{\rho h A g}{A} = \rho h g \tag{16.1}$$

$$T = \lim_{P \to 0} \frac{P\overline{V}}{R} \tag{16.2}$$

$$t/^\circ\mathrm{C} = T/\mathrm{K} - 273.15 \tag{16.3}$$

$$\left(P + \frac{a}{\overline{V}^2}\right)(\overline{V} - b) = RT \tag{16.4}$$

$$Z = \frac{P\overline{V}}{RT} = \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}} \tag{16.5}$$

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}(\overline{V} + B)} \tag{16.6}$$

$$P = \frac{RT}{\overline{V} - \beta} - \frac{\alpha}{\overline{V}(\overline{V} + \beta) + \beta(\overline{V} - \beta)} \tag{16.7}$$

$$\overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)\overline{V} - \frac{AB}{T^{1/2}P} = 0 \tag{16.8}$$

$$\overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P} = 0 \tag{16.9}$$

$$\overline{V}^3 - 3\overline{V}_{\mathrm{c}}\overline{V}^2 + 3\overline{V}_{\mathrm{c}}^2\overline{V} - \overline{V}_{\mathrm{c}}^3 = 0 \tag{16.10}$$

$$3\overline{V}_{\mathrm{c}} = b + \frac{RT_{\mathrm{c}}}{P_{\mathrm{c}}}, \qquad 3\overline{V}_{\mathrm{c}}^2 = \frac{a}{P_{\mathrm{c}}}, \quad \text{and} \quad \overline{V}_{\mathrm{c}}^3 = \frac{ab}{P_{\mathrm{c}}} \tag{16.11}$$

$$\overline{V}_{\mathrm{c}} = 3.8473B, \quad P_{\mathrm{c}} = 0.029894\frac{A^{2/3}R^{1/3}}{B^{5/3}}, \text{ and } T_{\mathrm{c}} = 0.34504\left(\frac{A}{BR}\right)^{2/3} \tag{16.12}$$

$$\frac{P_{\mathrm{c}}\overline{V}_{\mathrm{c}}}{RT_{\mathrm{c}}} = \frac{1}{R}\left(\frac{a}{27b^2}\right)(3b)\left(\frac{27bR}{8a}\right) = \frac{3}{8} = 0.375 \tag{16.13}$$

$$\frac{P_{\mathrm{c}}\overline{V}_{\mathrm{c}}}{RT_{\mathrm{c}}} = \frac{1}{R}\left(\frac{0.029894A^{2/3}R^{1/3}}{B^{5/3}}\right)(3.8473\beta)\left(\frac{[BR]^{2/3}}{0.34504A^{2/3}}\right) = 0.33333 \tag{16.14}$$

$$a = \frac{27(RT_{\mathrm{c}})^2}{64P_{\mathrm{c}}} \quad \text{and} \quad b = \frac{RT_{\mathrm{c}}}{8P_{\mathrm{c}}} \tag{16.15}$$

$$A = 0.42748\frac{R^2T_{\mathrm{c}}^{5/2}}{P_{\mathrm{c}}} \quad \text{and} \quad B = 0.086640\frac{RT_{\mathrm{c}}}{P_{\mathrm{c}}} \tag{16.16}$$

$$\left(P_{\mathrm{R}} + \frac{3}{\overline{V}_{\mathrm{R}}^2}\right)\left(\overline{V}_{\mathrm{R}} - \frac{1}{3}\right) = \frac{8}{3}T_{\mathrm{R}} \tag{16.17}$$

$$Z = \frac{\overline{V}_{\mathrm{R}}}{\overline{V}_{\mathrm{R}} - \frac{1}{3}} - \frac{9}{8\overline{V}_{\mathrm{R}}T_{\mathrm{R}}} \tag{16.18}$$

$$Z = \frac{\overline{V}_R}{\overline{V}_R - 0.25992} - \frac{1.2824}{T_R^{3/2}(\overline{V}_R + 0.25992)} \tag{16.19}$$

$$Z = \frac{P\overline{V}}{RT} = 1 + \frac{B_{2V}(T)}{\overline{V}} + \frac{B_{3V}(T)}{\overline{V}^2} + \cdots \tag{16.20}$$

$$Z = \frac{P\overline{V}}{RT} = 1 + B_{2P}(T)P + B_{3P}(T)P^2 + \cdots \tag{16.21}$$

$$B_{2V}(T) = RTB_{2P}(T) \tag{16.22}$$

$$B_{2V}(T) = -2\pi N_{\mathrm{A}}\int_0^\infty [e^{-u(r)/k_{\mathrm{B}}T} - 1]r^2dr \tag{16.23}$$

$$u(r) \longrightarrow -\frac{c_6}{r^6} \tag{16.24}$$

$$u(r) \longrightarrow \frac{c_n}{r^n} \tag{16.25}$$

$$u(r) = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6} \tag{16.26}$$

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{16.27}$$

$$B_{2V}(T) = -2\pi N_{\mathrm{A}} \int_0^\infty \left[\exp\left\{ -\frac{4\varepsilon}{k_{\mathrm{B}}T} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \right\} - 1 \right] r^2 dr \tag{16.28}$$

$$B_{2V}^*(T^*) = -3 \int_0^\infty \left[\exp\left\{ -\frac{4}{T^*}(x^{-12} - x^{-6}) \right\} - 1 \right] x^2 dx \tag{16.29}$$

$$B_{2V}(T) = \overline{V} - \overline{V}_{\mathrm{ideal}} \tag{16.30}$$

$$u_{d.d}(r) = -\frac{2\mu_1^2\mu_2^2}{(4\pi\varepsilon_0)^2(3k_{\mathrm{B}}T)} \frac{1}{r^6} \tag{16.31}$$

$$\mu_{\mathrm{induced}} = \alpha E \tag{16.32}$$

$$u_{\mathrm{induced}}(r) = -\frac{\mu_1^2\alpha_2}{(4\pi\varepsilon_0)^2 r^6} - \frac{\mu_2^2\alpha_1}{(4\pi\varepsilon_0)^2 r^6} \tag{16.33}$$

$$u_{\mathrm{disp}}(r) = -\frac{3}{2}\left(\frac{I_1 I_2}{I_1 + I_2}\right) \frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2} \frac{1}{r^6} \tag{16.34}$$

$$C_6 = \frac{2\mu^4}{3(4\pi\varepsilon_0)^2 k_{\mathrm{B}}T} + \frac{2\alpha\mu^2}{(4\pi\varepsilon_0)^2} + \frac{3}{4}\frac{I\alpha^2}{(4\pi\varepsilon_0)^2} \tag{16.35}$$

$$u(r) = \begin{matrix} \infty & \quad r < \sigma \\ 0 & \quad r > \sigma \end{matrix} \tag{16.36}$$

$$
\begin{aligned}
B_{2V}(T) &= -2\pi N_{\mathrm{A}}\int_0^{\infty}[e^{-u(r)/k_{\mathrm{B}}T}-1]r^2dr \\
&= -2\pi N_{\mathrm{A}}\int_0^{\sigma}[0-1]r^2dr - 2\pi N_{\mathrm{A}}\int_{\sigma}^{\infty}[e^0-1]r^2dr \\
&= \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3} \qquad (16.37)
\end{aligned}
$$

$$
u(r) = \begin{matrix} \infty & r<\sigma \\ -\varepsilon & \sigma<r<\lambda\sigma \\ 0 & r>\lambda\sigma \end{matrix} \qquad (16.38)
$$

$$
\begin{aligned}
B_{2V}(T) &= -2\pi N_{\mathrm{A}}\int_0^{\sigma}[0-1]r^2dr - 2\pi N_{\mathrm{A}}\int_{\sigma}^{\lambda\sigma}[e^{\varepsilon/k_{\mathrm{B}}T}-1]r^2dr \\
&\qquad -2\pi N_{\mathrm{A}}\int_{\lambda\sigma}^{\infty}[e^0-1]r^2dr \\
&= \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3} - \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3}(\lambda^3-1)(e^{\varepsilon/k_{\mathrm{B}}T}-1) \\
&= \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3}[1-(\lambda^3-1)(e^{\varepsilon/k_{\mathrm{B}}T}-1)] \qquad (16.39)
\end{aligned}
$$

$$
\begin{aligned}
P &= \frac{RT}{\overline{V}-b} - \frac{a}{\overline{V}^2} \\
&= \frac{RT}{\overline{V}}\frac{1}{(1-\frac{b}{\overline{V}})} - \frac{a}{\overline{V}^2} \qquad (16.40)
\end{aligned}
$$

$$
B_{2V}(T) = b - \frac{a}{RT} \qquad (16.41)
$$

$$
u(r) = \begin{matrix} \infty & r<\sigma \\ -\frac{c_6}{r^6} & r>\sigma \end{matrix} \qquad (16.42)
$$

$$
\begin{aligned}
B_{2V}(T) &= \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3} - \frac{2\pi N_{\mathrm{A}} c_6}{k_{\mathrm{B}}T}\int_{\sigma}^{\infty}\frac{r^2dr}{r^6} \\
&= \frac{2\pi\sigma^3 N_{\mathrm{A}}}{3} - \frac{2\pi\sigma^3 N_{\mathrm{A}} c_6}{3k_{\mathrm{B}}T} \qquad (16.43)
\end{aligned}
$$

$$B_{2V}(T) = B - \frac{A}{RT^{3/2}} \tag{16.44}$$

$$B_{2V}(T) = \beta - \frac{\alpha}{RT} \tag{16.45}$$

Chapter 17

The Boltzmann Factor and Partition Functions

$$\hat{H}_N \Psi_j = E_j \Psi_j \qquad j = 1,\ 2,\ 3,\ \ldots \tag{17.1}$$

$$E_j(N,V) = \epsilon_1 + \epsilon_2 + \cdots + \epsilon_N \tag{17.2}$$

$$\epsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{17.3}$$

$$\frac{a_2}{a_1} = f(E_1, E_2) \tag{17.4}$$

$$f(E_1, E_2) = f(E_1 - E_2) \tag{17.5}$$

$$\frac{a_2}{a_1} = f(E_1 - E_2) \tag{17.6}$$

$$\frac{a_3}{a_2} = f(E_2 - E_3) \quad \text{and} \quad \frac{a_3}{a_1} = f(E_1 - E_3) \tag{17.7}$$

$$f(E_1 - E_3) = f(E_1 - E_2)\, f(E_2 - E_3) \tag{17.8}$$

$$\frac{a_2}{a_1} = e^{\beta(E_1 - E_2)} \tag{17.9}$$

$$\frac{a_l}{a_i} = e^{\beta(E_i - E_l)} \tag{17.10}$$

$$a_j = Ce^{-\beta E_j} \tag{17.11}$$

$$\frac{a_j}{\mathcal{A}} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \tag{17.12}$$

$$p_j = \frac{e^{-\beta E_j}}{\sum_i e^{-\beta E_i}} \tag{17.13}$$

$$Q(N, V, \beta) = \sum_i e^{-\beta E_i(N,V)} \tag{17.14}$$

$$p_j(N, V, \beta) = \frac{e^{-\beta E_j(N,V)}}{Q(N, V, \beta)} \tag{17.15}$$

$$\beta = \frac{1}{k_{\mathrm{B}} T} \tag{17.16}$$

$$p_j(N, V, T) = \frac{e^{-E_j(N,V)/k_{\mathrm{B}}T}}{Q(N, V, T)} \tag{17.17}$$

$$\langle E \rangle = \sum_j p_j(N, V, \beta) E_j(N, V) = \sum_j \frac{E_j(N, V) e^{-\beta E_j(N,V)}}{Q(N, V, \beta)} \tag{17.18}$$

$$\begin{aligned} \left(\frac{\partial \ln Q(N, V, \beta)}{\partial \beta}\right)_{N,V} &= \frac{1}{Q(N, V, \beta)} \left(\frac{\partial \sum e^{-\beta E_j(N,V)}}{\partial \beta}\right)_{N,V} \\ &= \frac{1}{Q(N, V, \beta)} \sum_j [-E_j(N, V)] e^{-\beta E_j(N,V)} \\ &= -\sum_j \frac{E_j(N, V) e^{-\beta E_j(N,V)}}{Q(N, V, \beta)} \end{aligned} \tag{17.19}$$

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} \tag{17.20}$$

$$\langle E \rangle = k_{\mathrm{B}} T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \tag{17.21}$$

$$Q(N, V, \beta) = \frac{[q(V, \beta)]^N}{N!} \tag{17.22}$$

$$q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V \tag{17.23}$$

$$\overline{U} = \frac{3}{2}RT + RT + \frac{N_\mathrm{A}h\nu}{2} + \frac{N_\mathrm{A}h\nu e^{-\beta h\nu}}{1-e^{-\beta h\nu}} \tag{17.24}$$

$$C_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} = \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{17.25}$$

$$\overline{C}_V = \tfrac{3}{2}R \qquad \left(\begin{array}{c}\text{monatomic}\\ \text{ideal gas}\end{array}\right) \tag{17.26}$$

$$\begin{aligned}
\overline{C}_V &= \frac{5}{2}R + N_\mathrm{A}h\nu\frac{\partial}{\partial T}\left(\frac{e^{-\beta h\nu}}{1-e^{-\beta h\nu}}\right) \\
&= \frac{5}{2}R - \frac{N_\mathrm{A}h\nu}{k_\mathrm{B}T^2}\frac{\partial}{\partial\beta}\left(\frac{e^{-\beta h\nu}}{1-e^{-\beta h\nu}}\right) \qquad \left(\begin{array}{c}\text{diatomic}\\ \text{ideal gas}\end{array}\right) \\
&= \frac{5}{2}R + R\left(\frac{h\nu}{k_\mathrm{B}T}\right)^2\frac{e^{-h\nu/k_\mathrm{B}T}}{(1-e^{-h\nu/k_\mathrm{B}T})^2}
\end{aligned} \tag{17.27}$$

$$Q = e^{-\beta U_0}\left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^{3N} \tag{17.28}$$

$$\overline{C}_V = 3R\left(\frac{h\nu}{k_\mathrm{B}T}\right)^2\frac{e^{-h\nu/k_\mathrm{B}T}}{(1-e^{-h\nu/k_\mathrm{B}T})^2} \tag{17.29}$$

$$P_j(N,V) = -\left(\frac{\partial E_j}{\partial V}\right)_N \tag{17.30}$$

$$\langle P\rangle = \sum_j p_j(N,V,\beta)\left(-\frac{\partial E_j}{\partial V}\right)_N = \sum_j\left(-\frac{\partial E_j}{\partial V}\right)_N\frac{e^{-\beta E_j(N,V)}}{Q(N,V,\beta)} \tag{17.31}$$

$$\langle P\rangle = k_\mathrm{B}T\left(\frac{\partial\ln Q}{\partial V}\right)_{N,\beta} \tag{17.32}$$

$$\begin{aligned}
Q(N,V,T) &= \sum_i e^{-\beta\varepsilon_i^a}\sum_j e^{-\beta\varepsilon_j^b}\sum_k e^{-\beta\varepsilon_k^c}\cdots \\
&= q_a(V,T)q_b(V,T)q_c(V,T)\cdots
\end{aligned} \tag{17.33}$$

$$q(V,T) = \sum_i e^{-\beta\varepsilon_i} = \sum_i e^{-\varepsilon_i/k_\mathrm{B}T} \tag{17.34}$$

$$Q(N,V,T) = [q(V,T)]^N \qquad \begin{pmatrix}\text{independent, distinguishable}\\ \text{atoms or molecules}\end{pmatrix} \tag{17.35}$$

$$Q = \left[e^{-\beta u_0}\left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^3\right]^N \tag{17.36}$$

$$Q(N,V,T) = \sum_{i,j,k,\ldots} e^{-\beta(\varepsilon_i+\varepsilon_j+\varepsilon_k+\cdots)} \tag{17.37}$$

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!} \qquad \begin{pmatrix}\text{independent, indistinguishable}\\ \text{atoms or molecules}\end{pmatrix} \tag{17.38}$$

$$q(V,T) = \sum_j e^{-\varepsilon_j/k_\mathrm{B}T} \tag{17.39}$$

$$\frac{N}{V}\left(\frac{h^2}{8mk_\mathrm{B}T}\right)^{3/2} \ll 1 \tag{17.40}$$

$$\begin{aligned}\langle E\rangle &= k_\mathrm{B}T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}\\ &= Nk_\mathrm{B}T^2\left(\frac{\partial \ln q}{\partial T}\right)_V\\ &= N\sum_j \varepsilon_j \frac{e^{-\varepsilon_j/k_\mathrm{B}T}}{q(V,T)}\end{aligned} \tag{17.41}$$

$$\langle E\rangle = N\langle\varepsilon\rangle \tag{17.42}$$

$$\langle\varepsilon\rangle = \sum_j \varepsilon_j \frac{e^{-\varepsilon_j/k_\mathrm{B}T}}{q(V,T)} \tag{17.43}$$

$$\pi_j = \frac{e^{-\varepsilon_j/k_\mathrm{B}T}}{q(V,T)} = \frac{e^{-\varepsilon_j/k_\mathrm{B}T}}{\sum_j e^{-\varepsilon_j/k_\mathrm{B}T}} \tag{17.44}$$

$$\varepsilon = \varepsilon_i^{\rm trans} + \varepsilon_j^{\rm rot} + \varepsilon_k^{\rm vib} + \varepsilon_l^{\rm elec} \tag{17.45}$$

$$q(V,T) = q_{\rm trans} q_{\rm rot} q_{\rm vib} q_{\rm elec} \tag{17.46}$$

$$q_{\rm trans} = \sum_j e^{-\varepsilon_j^{\rm trans}/k_{\rm B}T} \tag{17.47}$$

$$\pi_{ijkl} = \frac{e^{-\varepsilon_i^{\rm trans}/k_{\rm B}T} e^{-\varepsilon_j^{\rm rot}/k_{\rm B}T} e^{-\varepsilon_k^{\rm vib}/k_{\rm B}T} e^{-\varepsilon_l^{\rm elec}/k_{\rm B}T}}{q_{\rm trans} q_{\rm rot} q_{\rm vib} q_{\rm elec}} \tag{17.48}$$

$$\begin{aligned} \pi_k^{\rm vib} &= \sum_{i,j,l} \pi_{ijkl} = \frac{\left(\sum_i e^{-\varepsilon_i^{\rm trans}/k_{\rm B}T}\right)\left(\sum_j e^{-\varepsilon_j^{\rm rot}/k_{\rm B}T}\right)\left(\sum_l e^{-\varepsilon_l^{\rm elec}/k_{\rm B}T}\right) e^{-\varepsilon_k^{\rm vib}/k_{\rm B}T}}{q_{\rm trans} q_{\rm rot} q_{\rm vib} q_{\rm elec}} \\ &= \frac{e^{-\varepsilon_k^{\rm vib}/k_{\rm B}T}}{q_{\rm vib}} = \frac{e^{-\varepsilon_k^{\rm vib}/k_{\rm B}T}}{\sum_k e^{-\varepsilon_k^{\rm vib}/k_{\rm B}T}} \end{aligned} \tag{17.49}$$

$$\begin{aligned} \langle \varepsilon^{\rm vib} \rangle &= \sum_k \varepsilon_k^{\rm vib} \frac{e^{-\varepsilon_k^{\rm vib}/k_{\rm B}T}}{q_{\rm vib}} \\ &= k_{\rm B}T^2 \frac{\partial \ln q_{\rm vib}}{\partial T} = -\frac{\partial \ln q_{\rm vib}}{\partial \beta} \end{aligned} \tag{17.50}$$

$$\langle \varepsilon^{\rm trans} \rangle = k_{\rm B}T^2 \left(\frac{\partial \ln q_{\rm trans}}{\partial T}\right)_V = -\left(\frac{\partial \ln q_{\rm trans}}{\partial \beta}\right)_V \tag{17.51}$$

$$\langle \varepsilon^{\rm rot} \rangle = k_{\rm B}T^2 \frac{\partial \ln q_{\rm rot}}{\partial T} = -\frac{\partial \ln q_{\rm rot}}{\partial \beta} \tag{17.52}$$

$$q(V,T) = \sum_{\substack{j \\ \text{(states)}}} e^{-\varepsilon_j/k_{\rm B}T} \tag{17.53}$$

$$q(V,T) = \sum_{\substack{j \\ \text{(levels)}}} g_i e^{-\varepsilon_j/k_{\rm B}T} \tag{17.54}$$

$$q_{\rm rot}(T) = \sum_{J=0}^{\infty} (2J+1) e^{-\hbar^2 J(J+1)/2Ik_{\rm B}T} \tag{17.55}$$

Chapter 18

Partition Functions and Ideal Gases

$$q(V,T) = q_{\text{trans}}(V,T)q_{\text{elec}}(T) \tag{18.1}$$

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad n_x, n_y, n_z = 1,\ 2,\ \ldots \tag{18.2}$$

$$q_{\text{trans}} = \sum_{n_x,n_y,n_z=1}^{\infty} e^{-\beta\varepsilon_{n_x n_y n_z}} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left[-\frac{\beta h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)\right] \tag{18.3}$$

$$q_{\text{trans}}(V,T) = \left[\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right)\right]^3 \tag{18.4}$$

$$q_{\text{trans}}(V,T) = \left(\int_0^{\infty} e^{-\beta h^2 n^2/8ma^2}\, dn\right)^3 \tag{18.5}$$

$$q_{\text{trans}}(V,T) = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V \tag{18.6}$$

$$\begin{aligned}
\langle\varepsilon_{\text{trans}}\rangle &= k_{\text{B}}T^2\left(\frac{\partial \ln q_{\text{trans}}}{\partial T}\right)_V \\
&= k_{\text{B}}T^2\left(\frac{\partial}{\partial T}\left[\frac{3}{2}\ln T + \text{terms independent of } T\right]\right)_V \\
&= \tfrac{3}{2}k_{\text{B}}T
\end{aligned} \tag{18.7}$$

$$q_{\text{elec}} = \sum_i g_{ei} e^{-\beta\varepsilon_{ei}} \tag{18.8}$$

$$q_{\text{elec}}(T) = g_{e1} + g_{e2} e^{-\beta\varepsilon_{e2}} + \cdots \tag{18.9}$$

$$\begin{aligned} f_2 &= \frac{g_{e2} e^{-\beta\varepsilon_{e2}}}{q_{\text{elec}}(T)} \\ &= \frac{g_{e2} e^{-\beta\varepsilon_{e2}}}{g_{e1} + g_{e2} e^{-\beta\varepsilon_{e2}} + g_{e3} e^{-\beta\varepsilon_{e3}} + \cdots} \\ &= \frac{3e^{-\beta\varepsilon_{e2}}}{1 + 3e^{-\beta\varepsilon_{e2}} + 2e^{-\beta\varepsilon_{e3}} + \cdots} \end{aligned} \tag{18.10}$$

$$q_{\text{elec}}(T) \approx g_{e1} + g_{e2} e^{-\beta\varepsilon_{e2}} \tag{18.11}$$

$$Q(N, V, T) = \frac{(q_{\text{trans}} q_{\text{elec}})^N}{N!} \tag{18.12}$$

$$\begin{aligned} q_{\text{trans}}(V, T) &= \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V \\ q_{\text{elec}}(T) &= g_{e1} + g_{e2} e^{-\beta\varepsilon_{e2}} + \cdots \end{aligned} \tag{18.13}$$

$$U = k_{\text{B}} T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = N k_{\text{B}} T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V = \frac{3}{2} N k_{\text{B}} T + \frac{N g_{e2} \varepsilon_{e2} e^{-\beta\varepsilon_{e2}}}{q_{\text{elec}}} + \cdots \tag{18.14}$$

$$\begin{aligned} P &= k_{\text{B}} T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = N k_{\text{B}} T \left(\frac{\partial \ln q}{\partial V}\right)_T \\ &= N k_{\text{B}} T \left[\frac{\partial}{\partial V} (\ln V + \text{terms not involving } V)\right]_T \\ &= \frac{N k_{\text{B}} T}{V} \end{aligned} \tag{18.15}$$

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}} \tag{18.16}$$

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!} \tag{18.17}$$

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} \tag{18.18}$$

$$Q(N,V,T) = \frac{(q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}})^N}{N!} \tag{18.19}$$

$$q_{\text{trans}}(V,T) = \left[\frac{2\pi(m_1+m_2)k_{\text{B}}T}{h^2}\right]^{3/2} V \tag{18.20}$$

$$q_{\text{elec}} = g_{e1} e^{D_e/k_{\text{B}}T} + g_{e2} e^{-\varepsilon_{e2}/k_{\text{B}}T} \tag{18.21}$$

$$\varepsilon_v = \left(v + \frac{1}{2}\right) h\nu \qquad\qquad v = 0,\ 1,\ 2,\ \ldots \tag{18.22}$$

$$q_{\text{vib}}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \tag{18.23}$$

$$q_{\text{vib}}(T) = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} \tag{18.24}$$

$$\langle E_{\text{vib}} \rangle = N k_{\text{B}} T^2 \frac{d \ln q_{\text{vib}}}{dT} = N k_{\text{B}} \left(\frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1}\right) \tag{18.25}$$

$$\overline{C}_{\text{vib}} = \frac{d\langle \overline{E}_{\text{vib}} \rangle}{dT} = R \left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1 - e^{-\Theta_{\text{vib}}/T}\right)^2} \tag{18.26}$$

$$f_v = \frac{e^{-\beta h\nu(v+\frac{1}{2})}}{q_{\text{vib}}} \tag{18.27}$$

$$f_v = \left(1 - e^{-\beta h\nu}\right) e^{-\beta h\nu v} = \left(1 - e^{-\Theta_{\text{vib}}/T}\right) e^{-v\Theta_{\text{vib}}/T} \tag{18.28}$$

$$f_{v>0} = e^{-\Theta_{\text{vib}}/T} = e^{-\beta h\nu} \tag{18.29}$$

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1) e^{-\beta\hbar^2 J(J+1)/2I} \tag{18.30}$$

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_{\text{B}}} = \frac{h}{k_{\text{B}}B} \tag{18.31}$$

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty}(2J+1)e^{-\Theta_{\text{rot}}J(J+1)/T} \tag{18.32}$$

$$\begin{aligned} q_{\text{rot}}(T) &= \int_0^{\infty} e^{-\Theta_{\text{rot}}x/T}dx \\ &= \frac{T}{\Theta_{\text{rot}}} = \frac{8\pi^2 Ik_{\text{B}}T}{h^2} \qquad \Theta_{\text{rot}} \ll T \end{aligned} \tag{18.33}$$

$$\begin{aligned} f_J &= \frac{(2J+1)e^{-\Theta_{\text{rot}}J(J+1)/T}}{q_{\text{rot}}} \\ &= (2J+1)(\Theta_{\text{rot}}/T)e^{-\Theta_{\text{rot}}J(J+1)/T} \end{aligned} \tag{18.34}$$

$$J_{\text{mp}} \approx \left(\frac{T}{2\Theta_{\text{rot}}}\right)^{1/2} - \frac{1}{2} \tag{18.35}$$

$$q_{\text{rot}}(T) = \frac{T}{2\Theta_{\text{rot}}} \tag{18.36}$$

$$q_{\text{rot}}(T) = \frac{T}{\sigma\Theta_{\text{rot}}} \tag{18.37}$$

$$\begin{aligned} q(V,T) &= q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}} \\ &= \left(\frac{2\pi Mk_{\text{B}}T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma\Theta_{\text{rot}}} \cdot \frac{e^{-\Theta_{\text{vib}}/2T}}{1-e^{-\Theta_{\text{vib}}/T}} \cdot g_{e1}e^{D_e/k_{\text{B}}T} \end{aligned} \tag{18.38}$$

$$\overline{U} = \frac{3}{2}RT + RT + R\frac{\Theta_{\text{vib}}}{2} + R\frac{\Theta_{\text{vib}}e^{-\Theta_{\text{vib}}/T}}{1-e^{-\Theta_{\text{vib}}/T}} - N_{\text{A}}D_e \tag{18.39}$$

$$\frac{\overline{C}_V}{R} = \frac{5}{2} + \left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}T}}{(1-e^{-\Theta_{\text{vib}}T})^2} \tag{18.40}$$

$$Q(N,V,T) = \frac{(q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}})^N}{N!} \tag{18.41}$$

$$q_{\text{trans}}(V,T) = \left[\frac{2\pi M k_{\text{B}} T}{h^2}\right]^{3/2} V \tag{18.42}$$

$$q_{\text{elec}} = g_{e1} e^{D_e/k_{\text{B}}T} + \cdots \tag{18.43}$$

$$\varepsilon_{\text{vib}} = \sum_{j=1}^{\alpha} \left(v_j + \tfrac{1}{2}\right) h\nu_j \qquad v_j = 0,\ 1,\ 2,\ \ldots \tag{18.44}$$

$$q_{\text{vib}} = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{\text{vib},j}/2T}}{\left(1 - e^{-\Theta_{\text{vib},j}/T}\right)} \tag{18.45}$$

$$E_{\text{vib}} = N k_{\text{B}} \sum_{j=1}^{\alpha} \left(\frac{\Theta_{\text{vib},j}}{2} + \frac{\Theta_{\text{vib},j} e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}}\right) \tag{18.46}$$

$$C_{V,\text{vib}} = N k_{\text{B}} \sum_{j=1}^{\alpha} \left[\left(\frac{\Theta_{\text{vib},j}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{(1 - e^{-\Theta_{\text{vib},j}/T})^2}\right] \tag{18.47}$$

$$\Theta_{\text{vib},j} = \frac{h\nu_j}{k_{\text{B}}} \tag{18.48}$$

$$q_{\text{rot}} = \frac{8\pi^2 I k_{\text{B}} T}{\sigma h^2} = \frac{T}{\sigma \Theta_{\text{rot}}} \tag{18.49}$$

$$\Theta_{\text{r},j} = \frac{\hbar^2}{2 I_j k_{\text{B}}} \qquad j = \text{A},\ \text{B},\ \text{C} \tag{18.50}$$

$$\begin{aligned} \varepsilon_J &= \frac{J(J+1)\hbar^2}{2I} \\ g_J &= (2J+1)^2 \qquad\qquad J = 0,\ 1,\ 2,\ \ldots \end{aligned} \tag{18.51}$$

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1)^2 e^{-\hbar^2 J(J+1)/2I k_{\text{B}} T} \tag{18.52}$$

$$q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{\Theta_{\text{rot}}}\right)^{3/2} \qquad \text{spherical top} \tag{18.53}$$

$$q_{\mathrm{rot}}(T) = \frac{\pi^{1/2}}{\sigma}\left(\frac{T}{\Theta_{\mathrm{rot,A}}}\right)\left(\frac{T}{\Theta_{\mathrm{rot,C}}}\right)^{1/2} \quad \text{symmetric top} \tag{18.54}$$

$$q_{\mathrm{rot}}(T) = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_{\mathrm{rot,A}}\Theta_{\mathrm{rot,B}}\Theta_{rot,\mathrm{C}}}\right)^{1/2} \quad \text{asymmetric top} \tag{18.55}$$

$$q(V,T) = \left(\frac{2\pi M k_{\mathrm{B}} T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma\Theta_{\mathrm{rot}}} \cdot \left(\prod_{j=1}^{3n-5} \frac{e^{-\Theta_{\mathrm{vib},j}/2T}}{1-e^{-\Theta_{\mathrm{vib},j}/T}}\right) \cdot g_{e1} e^{D_e/k_{\mathrm{B}}T} \tag{18.56}$$

$$\frac{U}{Nk_{\mathrm{B}}T} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5}\left(\frac{\Theta_{\mathrm{vib},j}}{2T} + \frac{\Theta_{\mathrm{vib},j}/T}{e^{\Theta_{\mathrm{vib},j}/T}-1}\right) - \frac{D_e}{k_{\mathrm{B}}T} \tag{18.57}$$

$$\frac{C_V}{Nk_{\mathrm{B}}} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5}\left(\frac{\Theta_{\mathrm{vib},j}}{T}\right)^2 \frac{e^{\Theta_{\mathrm{vib},j}/T}}{(e^{\Theta_{\mathrm{vib},j}/T}-1)^2} \tag{18.58}$$

$$q(V,T) = \left(\frac{2\pi M k_{\mathrm{B}} T}{h^2}\right)^{3/2} V \cdot \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_{\mathrm{rot,A}}\Theta_{\mathrm{rot,B}}\Theta_{rot,\mathrm{C}}}\right)^{1/2} \cdot \left[\prod_{j=1}^{3n-6} \frac{e^{-\Theta_{\mathrm{vib},j}/2T}}{(1-e^{-\Theta_{\mathrm{vib},j}/T})}\right] \cdot g_{e1} e^{D_e/k_{\mathrm{B}}T} \tag{18.59}$$

$$\frac{U}{Nk_{\mathrm{B}}T} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6}\left(\frac{\Theta_{\mathrm{vib},j}}{2T} + \frac{\Theta_{\mathrm{vib},j}/T}{e^{\Theta_{\mathrm{vib},j}/T}-1}\right) - \frac{D_e}{k_{\mathrm{B}}T} \tag{18.60}$$

$$\frac{C_V}{Nk_{\mathrm{B}}} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6}\left(\frac{\Theta_{\mathrm{vib},j}}{T}\right)^2 \frac{e^{\Theta_{\mathrm{vib},j}/T}}{(e^{\Theta_{\mathrm{vib},j}/T}-1)^2} \tag{18.61}$$

$$\Delta = e^{-\alpha(n+1)^2} - e^{-\alpha n^2} = e^{-\alpha n^2}\left[e^{-\alpha(2n+1)} - 1\right] \tag{18.62}$$

Chapter 19

The First Law of Thermodynamics

$$w = -P_{\text{ext}}\Delta V \tag{19.1}$$

$$w = -\int_{\overline{V}_i}^{\overline{V}_f} P_{\text{ext}} dV \tag{19.2}$$

$$\int_1^2 dU = U_2 - U_1 = \Delta\overline{U} \tag{19.3}$$

$$\begin{aligned} w_{\text{rev}} &= -\int_1^2 P_{\text{gas}} dV = -\int_1^2 \frac{nRT}{V} dV = -nRT \int_1^2 \frac{dV}{V} \\ &= -nRT \ln \frac{\overline{V}_2}{\overline{V}_1} \end{aligned} \tag{19.4}$$

$$\int_1^2 \delta w = w \qquad (\text{not } \Delta w \text{ or } w_2 - w_1) \tag{19.5}$$

$$\int_1^2 dU = U_2 - U_1 = \Delta\overline{U} \qquad (U \text{ is a state function}) \tag{19.6}$$

$$\int_1^2 \delta w = w \quad (\text{not } w_2 - w_1) \qquad (\text{path function}) \tag{19.7}$$

$$\int_1^2 \delta q = q \qquad (\text{not } q_2 - q_1) \qquad\qquad (\text{path function}) \tag{19.8}$$

$$dU = \delta q + \delta w \tag{19.9}$$

$$\Delta\overline{U} = q + w \tag{19.10}$$

$$\Delta\overline{U}_{\mathrm{A}} = 0 \tag{19.11}$$

$$\delta w_{\mathrm{rev,A}} = -\delta q_{\mathrm{rev,A}} = -\frac{RT_1}{\overline{V}} d\overline{V} \tag{19.12}$$

$$w_{\mathrm{rev,A}} = -q_{\mathrm{rev,A}} = -RT_1 \int_{\overline{V}_1}^{\overline{V}_2} \frac{d\overline{V}}{\overline{V}} = -RT_1 \ln \frac{\overline{V}_2}{\overline{V}_1} \tag{19.13}$$

$$dU = \delta w \tag{19.14}$$

$$q_{\mathrm{rev,B}} = 0 \tag{19.15}$$

$$w_{\mathrm{rev,B}} = \Delta\overline{U}_{\mathrm{B}} = \int_{T_1}^{T_2} \left(\frac{\partial \overline{U}}{\partial T}\right)_V dT = \int_{T_1}^{T_2} \overline{C}_V(T) dT \tag{19.16}$$

$$q_{\mathrm{rev,C}} = \Delta\overline{U}_{\mathrm{C}} = \int_{T_2}^{T_1} \overline{C}_V(T) dT \tag{19.17}$$

$$\begin{aligned} q_{\mathrm{rev,B+C}} &= q_{\mathrm{rev,B}} + q_{\mathrm{rev,C}} = 0 + \int_{T_2}^{T_1} \overline{C}_V(T) dT \\ &= \int_{T_2}^{T_1} \overline{C}_V(T) dT \end{aligned} \tag{19.18}$$

$$\begin{aligned} w_{\mathrm{rev,B+C}} &= w_{\mathrm{rev,B}} + w_{\mathrm{rev,C}} = \int_{T_1}^{T_2} \overline{C}_V(T) dT + 0 \\ &= \int_{T_1}^{T_2} \overline{C}_V(T) dT \end{aligned} \tag{19.19}$$

$$\overline{C}_V(T)dT = -\frac{RT}{V}dV \tag{19.20}$$

$$\int_{T_1}^{T_2} \frac{\overline{C}_V(T)}{T}dT = -R\int_{\overline{V}_1}^{\overline{V}_2} \frac{dV}{V} = -R\ln\frac{\overline{V}_2}{\overline{V}_1} \tag{19.21}$$

$$\left(\frac{T_2}{T_1}\right)^{3/2} = \frac{\overline{V}_1}{\overline{V}_2} \qquad \begin{pmatrix}\text{monatomic}\\ \text{ideal gas}\end{pmatrix} \tag{19.22}$$

$$P_1\overline{V}_1^{5/3} = P_2\overline{V}_2^{5/3} \tag{19.23}$$

$$U = \sum_j p_j(N,V,\beta)E_j(N,V) \tag{19.24}$$

$$p_j(N,V,\beta) = \frac{e^{-\beta Ej(N,V)}}{Q(N,V,\beta)} \tag{19.25}$$

$$dU = \sum_j p_j dE_j + \sum_j E_j dp_j \tag{19.26}$$

$$dU = \sum_j p_j(N,V,\beta)\left(\frac{\partial E_j}{\partial V}\right)_N dV + \sum_j E_j(N,V)dp_j(N,V,\beta) \tag{19.27}$$

$$dU = \delta w_{\text{rev}} + \delta q_{\text{rev}} \tag{19.28}$$

$$\delta w_{\text{rev}} = \sum_j p_j(N,V,\beta)\left(\frac{\partial E_j}{\partial V}\right)_N dV \tag{19.29}$$

$$\delta q_{\text{rev}} = \sum_j E_j(N,V)dp_j(N,V,\beta) \tag{19.30}$$

$$P = -\sum_j p_j(N,V,\beta)\left(\frac{\partial E_j}{\partial V}\right)_N = -\left\langle\left(\frac{\partial E}{\partial V}\right)_N\right\rangle \tag{19.31}$$

$$\Delta\overline{U} = q + w = q - \int_{\overline{V}_1}^{\overline{V}_2} P_{\text{ext}}dV \tag{19.32}$$

$$\Delta\overline{U} = q_V \tag{19.33}$$

$$q_P = \Delta\overline{U} + P_{\mathrm{ext}} \int_{\overline{V}_1}^{\overline{V}_2} dV = \Delta\overline{U} + P_{\mathrm{ext}}\Delta V \tag{19.34}$$

$$H = U + PV \tag{19.35}$$

$$\Delta H = \Delta\overline{U} + P\Delta V \qquad \text{(constant pressure)} \tag{19.36}$$

$$q_P = \Delta H \tag{19.37}$$

$$\Delta H = \Delta\overline{U} + RT\Delta n_{\mathrm{gas}} \tag{19.38}$$

$$\overline{C}_V = \left(\frac{\partial U}{\partial T}\right)_V \approx \frac{\Delta\overline{U}}{\Delta T} = \frac{q_V}{\Delta T} \tag{19.39}$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \approx \frac{\Delta H}{\Delta T} = \frac{q_P}{\Delta T} \tag{19.40}$$

$$H = U + nRT \qquad \text{(ideal gas)} \tag{19.41}$$

$$\frac{dH}{dT} = \frac{dU}{dT} + nR \tag{19.42}$$

$$C_P - \overline{C}_V = nR \qquad \text{(ideal gas)} \tag{19.43}$$

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_P(T)dT \tag{19.44}$$

$$H(T) - H(0) = \int_0^T C_P(T')dT' \tag{19.45}$$

$$H(T) - H(0) = \int_0^{T_{\mathrm{fus}}} C_P^{\mathrm{s}}(T)dT + \Delta_{\mathrm{fus}}H + \int_{T_{\mathrm{fus}}}^T C_P^{\mathrm{l}}(T')dT' \tag{19.46}$$

$$\Delta_{\mathrm{r}}H = H_{\mathrm{prod}} - H_{\mathrm{react}} \tag{19.47}$$

$$\Delta_{\mathrm{r}}H(\text{reverse}) = -\Delta_{\mathrm{r}}H(\text{forward}) \tag{19.48}$$

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)} \tag{19.49}$$

$$\mathrm{2\,C(s) + 2\,O_2(g) \longrightarrow 2\,CO_2(g)} \tag{19.50}$$

$$\mathrm{2\,C(s) + H_2(g) \longrightarrow C_2H_2(g)} \tag{19.51}$$

$$\Delta_{\mathrm{r}} H = y\Delta_{\mathrm{f}} H^\circ[\mathrm{Y}] + z\Delta_{\mathrm{f}} H^\circ[\mathrm{Z}] - a\Delta_{\mathrm{f}} H^\circ[\mathrm{A}] - b\Delta_{\mathrm{f}} H^\circ[\mathrm{B}] \tag{19.52}$$

$$\begin{aligned} \Delta_{\mathrm{r}} H(T_2) &= y[H_Y(T_2) - H_Y(0)] + z[H_Z(T_2) - H_Z(0)] \\ &\quad - a[H_A(T_2) - H_A(0)] - b[H_B(T_2) - H_B(0)] \end{aligned} \tag{19.53}$$

$$H_X(T_2) - H_X(0) = \int_0^{T_2} C_{P,X}(T)dT \tag{19.54}$$

$$\begin{aligned} \Delta_{\mathrm{r}} H(T_1) &= y[H_Y(T_1) - H_Y(0)] + z[H_Z(T_2) - H_Z(0)] \\ &\quad -a[H_A(T_1) - H_A(0)] - b[H_B(T_1) - H_B(0)] \end{aligned} \tag{19.55}$$

$$H_X(T_1) - H_X(0) = \int_0^{T_1} C_{P,X}(T)dT \tag{19.56}$$

$$\Delta_{\mathrm{r}} H(T_2) = \Delta_{\mathrm{r}} H(T_1) + \int_{T_1}^{T_2} \Delta C_P(T)dT \tag{19.57}$$

$$\Delta C_P(T) = yC_{P,\mathrm{Y}}(T) + zC_{P,\mathrm{Z}}(T) - aC_{P,\mathrm{A}}(T) - bC_{P,\mathrm{B}}(T) \tag{19.58}$$

Chapter 20

Entropy and the Second Law of Thermodynamics

$$\begin{aligned}\delta q_{\text{rev}} &= dU - \delta w_{\text{rev}} = C_V(T)dT + PdV \\ &= C_V(T)dT + \frac{nRT}{V}dV \end{aligned} \tag{20.1}$$

$$\frac{\delta q_{\text{rev}}}{T} = \frac{C_V(T)dT}{T} + \frac{nR}{V}dV \tag{20.2}$$

$$dS = \frac{\delta q_{\text{rev}}}{T} \tag{20.3}$$

$$\oint dS = 0 \tag{20.4}$$

$$\oint \frac{\delta q_{\text{rev}}}{T} = 0 \tag{20.5}$$

$$\delta q_{\text{rev,A}} = \frac{RT_1}{V}dV \tag{20.6}$$

$$\delta q_{\text{rev,B}} = 0 \tag{20.7}$$

$$\int_{T_1}^{T_2} \frac{\overline{C}_V(T)}{T}dT = -R\ln\frac{V_2}{V_1} \tag{20.8}$$

$$\begin{aligned}\Delta S_A &= \int_1^2 \frac{\delta q_{\text{rev,A}}}{T_1} = \int_{V_1}^{V_2} \frac{1}{T_1}\frac{RT_1}{V}dV \\ &= R\int_{V_1}^{V_2}\frac{dV}{V} = R\ln\frac{V_2}{V_1}\end{aligned} \tag{20.9}$$

$$\Delta S_{B+C} = \Delta S_B + \Delta S_C = 0 + R\ln\frac{V_2}{V_1} = R\ln\frac{V_2}{V_1} \tag{20.10}$$

$$\delta q_{\text{rev},D} = dU_D - \delta w_{\text{rev},D} = \overline{C}_V(T)dT + P_1 dV \tag{20.11}$$

$$\delta q_{\text{rev},E} = dU_E = \overline{C}_V(T)dT \tag{20.12}$$

$$\begin{gathered} U_{\text{A}} + U_{\text{B}} = \text{constant} \\ V_{\text{A}} = \text{constant} \qquad V_{\text{B}} = \text{constant} \\ S = S_{\text{A}} + S_{\text{B}} \end{gathered} \tag{20.13}$$

$$\begin{aligned} dU_{\text{A}} &= \delta q_{\text{rev}} + \delta w_{\text{rev}} = T_{\text{A}} dS_{\text{A}} \\ dU_{\text{B}} &= \delta q_{\text{rev}} + \delta w_{\text{rev}} = T_{\text{B}} dS_{\text{B}} \end{aligned} \tag{20.14}$$

$$\begin{aligned} dS &= dS_{\text{A}} + dS_{\text{B}} \\ &= \frac{dU_{\text{A}}}{T_{\text{A}}} + \frac{dU_{\text{B}}}{T_{\text{B}}} \end{aligned} \tag{20.15}$$

$$dS = dU_{\text{B}}\left(\frac{1}{T_{\text{B}}} - \frac{1}{T_{\text{A}}}\right) \tag{20.16}$$

$$\begin{aligned} dS > 0 &\qquad \text{(spontaneous process in an isolated system)} \\ dS = 0 &\qquad \text{(reversible process in an isolated system)} \end{aligned} \tag{20.17}$$

$$\begin{aligned} dS &= dS_{\text{prod}} + dS_{\text{exch}} \\ &= dS_{\text{prod}} + \frac{\delta q}{T} \end{aligned} \tag{20.18}$$

$$dS = \frac{\delta q_{\rm rev}}{T} \tag{20.19}$$

$$dS > \frac{\delta q_{\rm irr}}{T} \tag{20.20}$$

$$dS \geq \frac{\delta q}{T} \tag{20.21}$$

$$\Delta S \geq \int \frac{\delta q}{T} \tag{20.22}$$

$$W(a_1, a_2, a_3, \ldots) = \frac{\mathcal{A}!}{a_1!a_2!a_3!\ldots} = \frac{\mathcal{A}!}{\prod_j a_j!} \tag{20.23}$$

$$S = k_{\rm B} \ln W \tag{20.24}$$

$$S = k_{\rm B} \ln \Omega \tag{20.25}$$

$$\Delta_{\rm mix}\overline{S}/R = -y_1 \ln y_1 - y_2 \ln y_2 \tag{20.26}$$

$$\Delta S = \int_1^2 \frac{\delta q_{\rm rev}}{T} \tag{20.27}$$

$$\Delta S = \int_1^2 \frac{\delta q_{\rm rev}}{T} = -\int_1^2 \frac{\delta w_{\rm rev}}{T} = nR\int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \frac{V_2}{V_1} \tag{20.28}$$

$$\Delta S = -n_{\rm N_2} R \ln \frac{n_{\rm N_2}}{n_{\rm N_2} + n_{\rm Br_2}} - n_{\rm Br_2} R \ln \frac{n_{\rm Br_2}}{n_{\rm N_2} + n_{\rm Br_2}} \tag{20.29}$$

$$\Delta_{\rm mix}\overline{S} = -R \sum_{j=1}^{N} y_j \ln y_j \tag{20.30}$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} \tag{20.31}$$

$$\begin{aligned} \Delta S &= \Delta S_{\rm h} + \Delta S_{\rm c} \\ &= C_V \ln \frac{(T_{\rm h} + T_{\rm c})^2}{4T_{\rm h}T_{\rm c}} \end{aligned} \tag{20.32}$$

$$\Delta U_{\text{engine}} = w + q_{\text{rev,h}} + q_{\text{rev,c}} = 0 \tag{20.33}$$

$$\Delta S_{\text{engine}} = \frac{\delta q_{\text{rev,h}}}{T_{\text{h}}} + \frac{\delta q_{\text{rev,c}}}{T_{\text{c}}} = 0 \tag{20.34}$$

$$\text{efficiency} = 1 - \frac{T_{\text{c}}}{T_{\text{h}}} = \frac{T_{\text{h}} - T_{\text{c}}}{T_{\text{h}}} \tag{20.35}$$

$$U = k_{\text{B}} T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} \tag{20.36}$$

$$P = k_{\text{B}} T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} \tag{20.37}$$

$$\begin{aligned} S_{\text{ensemble}} &= k_{\text{B}} \ln \frac{\mathcal{A}!}{\prod_j a_j!} = k_{\text{B}} \ln \mathcal{A}! - k_{\text{B}} \sum_j \ln a_j! \\ &= k_{\text{B}} \mathcal{A} \ln \mathcal{A} - k_{\text{B}} \mathcal{A} - k_{\text{B}} \sum_j a_j \ln a_j + k_{\text{B}} \sum_j a_j \\ &= k_{\text{B}} \mathcal{A} \ln \mathcal{A} - k_{\text{B}} \sum_j a_j \ln a_j \end{aligned} \tag{20.38}$$

$$\begin{aligned} S_{\text{ensemble}} &= k_{\text{B}} \mathcal{A} \ln \mathcal{A} - k_{\text{B}} \sum_j p_j \mathcal{A} \ln p_j \mathcal{A} \\ &= k_{\text{B}} \mathcal{A} \ln \mathcal{A} - k_{\text{B}} \sum_j p_j \mathcal{A} \ln p_j - k_{\text{B}} \sum_j p_j \mathcal{A} \ln \mathcal{A} \end{aligned} \tag{20.39}$$

$$S_{\text{system}} = -k_{\text{B}} \sum_j p_j \ln p_j \tag{20.40}$$

$$p_j(N, V, \beta) = \frac{e^{-\beta E_j(N,V)}}{Q(N, V, \beta)} \tag{20.41}$$

$$
\begin{aligned}
S &= -k_{\mathrm{B}} \sum_j p_j \ln p_j \\
&= -k_{\mathrm{B}} \sum_j \frac{e^{-\beta E_j}}{Q} \left(-\beta E_j - \ln Q\right) \\
&= \beta k_{\mathrm{B}} \sum_j \frac{E_j e^{-\beta E_j}}{Q} + \frac{k_{\mathrm{B}} \ln Q}{Q} \sum_j e^{-\beta E_j} \\
&= \frac{U}{T} + k_{\mathrm{B}} \ln Q
\end{aligned} \tag{20.42}
$$

$$
S = k_{\mathrm{B}} T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_{\mathrm{B}} \ln Q \tag{20.43}
$$

$$
\overline{S} = \frac{3}{2} R + R \ln \left[\left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{3/2} \overline{V}\right] - k_{\mathrm{B}} \ln N_{\mathrm{A}}! \tag{20.44}
$$

$$
\overline{S} = \frac{5}{2} R + R \ln \left[\left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_{\mathrm{A}}}\right] \tag{20.45}
$$

$$
dS = -k_{\mathrm{B}} \sum_j \ln p_j dp_j \tag{20.46}
$$

$$
dS = \beta k_{\mathrm{B}} \sum_j E_j(N, V) dp_j(N, V, \beta) \tag{20.47}
$$

$$
dS = \beta k_{\mathrm{B}} \delta q_{\mathrm{rev}} \tag{20.48}
$$

Chapter 21

Entropy and the Third Law of Thermodynamics

$$dU = TdS - PdV \tag{21.1}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \tag{21.2}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \tag{21.3}$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{21.4}$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_V(T)dT}{T} \qquad \text{(constant } V\text{)} \tag{21.5}$$

$$dH = TdS + VdP \tag{21.6}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P(T)}{T} \tag{21.7}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \tag{21.8}$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P(T)dT}{T} \qquad \text{(constant } P\text{)} \tag{21.9}$$

$$S(T) = S(T=0) + \int_0^T \frac{C_P(T')dT'}{T'} \qquad \text{(constant } P\text{)} \tag{21.10}$$

$$S = k_\mathrm{B} \ln W \tag{21.11}$$

$$S = -k_\mathrm{B} \sum_j p_j \ln p_j \tag{21.12}$$

$$S(0\ \mathrm{K}) = -k_\mathrm{B} \sum_{j=1}^{n} \frac{1}{n} \ln \frac{1}{n} = k_\mathrm{B} \ln n \tag{21.13}$$

$$S(T) = \int_0^T \frac{C_P(T')dT'}{T'} \tag{21.14}$$

$$\Delta_\mathrm{trs} S = \frac{q_\mathrm{rev}}{T_\mathrm{trs}} \tag{21.15}$$

$$\Delta_\mathrm{trs} S = \frac{\Delta_\mathrm{trs} H}{T_\mathrm{trs}} \tag{21.16}$$

$$\begin{aligned} S(T) &= \int_0^{T_\mathrm{fus}} \frac{C_P^\mathrm{s}(T)dT}{T} + \frac{\Delta_\mathrm{fus} H}{T_\mathrm{fus}} + \int_{T_\mathrm{fus}}^{T_\mathrm{vap}} \frac{C_P^\mathrm{l}(T)dT}{T} \\ &\quad + \frac{\Delta H_\mathrm{vap}}{T_\mathrm{vap}} + \int_{T_\mathrm{vap}}^{T} \frac{C_P^\mathrm{g}(T')dT'}{T'} \end{aligned} \tag{21.17}$$

$$\begin{aligned} \overline{S}(T) &= \int_0^T \frac{\overline{C}_P(T')dT'}{T'} = \frac{12\pi^4 R}{5\Theta_D^3} \int_0^T T'^2 dT' \\ &= \frac{12\pi^4 R}{5\Theta_D^3} \frac{T^3}{3} = \frac{\overline{C}_P(T)}{3} \end{aligned} \tag{21.18}$$

$$S = k_\mathrm{B} \ln Q + k_\mathrm{B} T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \tag{21.19}$$

$$Q(N,V,T) = \sum_j e^{-E_j(N,V)/k_\mathrm{B}T} \tag{21.20}$$

$$S = k_{\mathrm{B}} \ln \sum_j e^{-E_j/k_{\mathrm{B}}T} + \frac{1}{T} \frac{\sum_j E_j e^{-E_j/k_{\mathrm{B}}T}}{\sum_j e^{-E_j/k_{\mathrm{B}}T}} \tag{21.21}$$

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!} \tag{21.22}$$

$$q(V,T) = \left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \cdot g_{e1} \tag{21.23}$$

$$q(V,T) = \left(\frac{2\pi M k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma\Theta_{\mathrm{rot}}} \cdot \frac{e^{-\Theta_{\mathrm{vib}}/2T}}{1 - e^{-\Theta_{\mathrm{vib}}/T}} \cdot g_{e1} e^{D_e/k_{\mathrm{B}}T} \tag{21.24}$$

$$q(V,T) = \left(\frac{2\pi M k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma\Theta_{\mathrm{rot}}} \cdot \left[\prod_{j=1}^{3n-5} \frac{e^{-\Theta_{\mathrm{vib}}/2T}}{1 - e^{-\Theta_{\mathrm{vib}}/T}}\right] \cdot g_{e1} e^{D_e/k_{\mathrm{B}}T} \tag{21.25}$$

$$q(V,T) = \left(\frac{2\pi M k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2} \left[\prod_{j=1}^{3n-6} \frac{e^{-\Theta_{\mathrm{vib}}/2T}}{1 - e^{-\Theta_{\mathrm{vib}}/T}}\right] g_{e1} e^{D_e/k_{\mathrm{B}}T} \tag{21.26}$$

$$S = N k_{\mathrm{B}} + N k_{\mathrm{B}} \ln \left[\frac{q(V,T)}{N}\right] + N k_{\mathrm{B}} T \left(\frac{\partial \ln q}{\partial T}\right)_V \tag{21.27}$$

$$\begin{aligned} \frac{\overline{S}}{R} &= \ln \left[\left(\frac{2\pi M k_{\mathrm{B}}T}{h^2}\right)^{3/2} \frac{\overline{V} e^{5/2}}{N_{\mathrm{A}}}\right] + \ln \frac{Te}{2\Theta_{\mathrm{rot}}} - \ln(1 - e^{-\Theta_{\mathrm{vib}}/T}) \\ &\quad + \frac{\Theta_{\mathrm{vib}}/T}{e^{\Theta_{\mathrm{vib}}/T} - 1} + \ln g_{e1} \end{aligned} \tag{21.28}$$

Chapter 22

Helmholtz and Gibbs Energies

$$dU = \delta q + \delta w \tag{22.1}$$

$$dU \leq TdS \qquad \text{(constant } V\text{)} \tag{22.2}$$

$$d(U - TS) \leq 0 \qquad \text{(constant } T \text{ and } V\text{)} \tag{22.3}$$

$$A = U - TS \tag{22.4}$$

$$dA \leq 0 \qquad \text{(constant } T \text{ and } V\text{)} \tag{22.5}$$

$$\Delta A = \Delta U - T\Delta S \tag{22.6}$$

$$\Delta A = \Delta U - T\Delta S \leq 0 \qquad \text{(constant } T \text{ and } V\text{)} \tag{22.7}$$

$$\Delta A = \Delta U - T\Delta S \tag{22.8}$$

$$\Delta A = w_{\text{rev}} \qquad \text{(isothermal, reversible)} \tag{22.9}$$

$$d(U - TS + PV) \leq 0 \qquad \text{(constant } T \text{ and } P\text{)} \tag{22.10}$$

$$G = U - TS + PV \tag{22.11}$$

$$dG \leq 0 \qquad \text{(constant } T \text{ and } P\text{)} \tag{22.12}$$

$$G = H - TS \tag{22.13}$$

$$G = A + PV \tag{22.14}$$

$$\Delta G = \Delta H - T\Delta S \leq 0 \qquad \text{(constant } T \text{ and } P\text{)} \tag{22.15}$$

$$\Delta G = w_{nPV} \qquad \text{(reversible, constant } T \text{ and } P\text{)} \tag{22.16}$$

$$dA = -PdV - SdT \tag{22.17}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{22.18}$$

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV \qquad \text{(constant } T\text{)} \tag{22.19}$$

$$\Delta \overline{S} = R\int_{\overline{V}_1}^{\overline{V}_2} \frac{d\overline{V}}{\overline{V}} = R \ln \frac{\overline{V}_2}{\overline{V}_1} \qquad \text{(isothermal process)} \tag{22.20}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \tag{22.21}$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \tag{22.22}$$

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \tag{22.23}$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{22.24}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{22.25}$$

$$C_P - C_V = \frac{\alpha^2 TV}{\kappa} \tag{22.26}$$

$$\Delta A = -\int_{V_1}^{V_2} PdV \qquad \text{(constant } T\text{)} \tag{22.27}$$

$$\Delta A = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT\ln\frac{V_2}{V_1} \qquad \text{(constant } T\text{)} \tag{22.28}$$

$$dG = -SdT + VdP \tag{22.29}$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{22.30}$$

$$\Delta S = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{(constant } T\text{)} \tag{22.31}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{22.32}$$

$$dU = TdS - PdV \tag{22.33}$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{22.34}$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \tag{22.35}$$

$$dU = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV + C_V dT \tag{22.36}$$

$$dS = \frac{1}{T}dU + PdV \tag{22.37}$$

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_U = P \tag{22.38}$$

$$dH = TdS + VdP \tag{22.39}$$

$$dA = -SdT - PdV \tag{22.40}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \tag{22.41}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V \tag{22.42}$$

$$dG = -SdT + VdP \tag{22.43}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V \tag{22.44}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{22.45}$$

$$dU = TdS - PdV \tag{22.46}$$

$$dH = TdS + VdP \tag{22.47}$$

$$dA = -SdT - PdV \tag{22.48}$$

$$dG = -SdT + VdP \tag{22.49}$$

$$\begin{aligned} S(P^{\text{id}}) - S(1\ \text{bar}) &= -\int_{1\ \text{bar}}^{P^{\text{id}}} \left(\frac{\partial V}{\partial T}\right)_P dP \\ &= \int_{P^{\text{id}}}^{1\ \text{bar}} \left(\frac{\partial V}{\partial T}\right)_P dP \quad (\text{constant } T) \end{aligned} \tag{22.50}$$

$$S^{\circ}(1\ \text{bar}) - \overline{S}(P^{\text{id}}) = -\int_{P^{\text{id}}}^{1\ \text{bar}} \frac{R}{P} dP \tag{22.51}$$

$$S^\circ(\text{at 1 bar}) - \overline{S}(\text{at 1 bar}) = \int_{P^{\text{id}}}^{1\ \text{bar}} \left[\left(\frac{\partial \overline{V}}{\partial T} \right)_P - \frac{R}{P} \right] dP \tag{22.52}$$

$$\frac{P\overline{V}}{RT} = 1 + \frac{B_{2V}(T)}{RT} P + \cdots \tag{22.53}$$

$$S^\circ(\text{at 1 bar}) = S(\text{at 1 bar}) + \frac{dB_{2V}}{dT} \times (1\ \text{bar}) + \cdots \tag{22.54}$$

$$\Delta G = \int_{P_1}^{P_2} V\,dP \qquad (\text{constant } T) \tag{22.55}$$

$$\Delta \overline{G} = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1} \tag{22.56}$$

$$\overline{G}(T,P) = G^\circ(T) + RT \ln(P/1\ \text{bar}) \tag{22.57}$$

$$\left(\frac{\partial G/T}{\partial T} \right)_P = -\frac{H}{T^2} \tag{22.58}$$

$$\left(\frac{\partial \Delta G/T}{\partial T} \right)_P = -\frac{\Delta H}{T^2} \tag{22.59}$$

$$\begin{aligned} H(T) - H(0) &= \int_0^{T_{\text{fus}}} C_P^s(T) dT + \Delta_{\text{fus}} H \\ &\quad + \int_{T_{\text{fus}}}^{T_{\text{vap}}} C_P^l(T) dT + \Delta_{\text{vap}} H \\ &\quad + \int_{T_{\text{vap}}}^{T} C_P^g(T') dT' \end{aligned} \tag{22.60}$$

$$\begin{aligned} S(T) &= \int_0^{T_{\text{fus}}} \frac{C_P^s(T)}{T} dT + \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}} \\ &\quad + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \frac{C_P^l(T)}{T} dT + \frac{\Delta_{\text{vap}} H}{T_{\text{vap}}} \\ &\quad + \int_{T_{\text{vap}}}^{T} \frac{C_P^g(T')}{T'} dT' \end{aligned} \tag{22.61}$$

$$\overline{G}(T,P) = G^\circ(T) + RT \ln \frac{P}{P^\circ} \tag{22.62}$$

$$\left(\frac{\partial \overline{G}}{\partial P}\right)_T = \overline{V} \tag{22.63}$$

$$\overline{G}(T,P) = \overline{G}(P^{\text{id}},T) + RT\ln\frac{P}{P^{\text{id}}} + B_{2P}(T)P + \frac{B_{3P}(T)P^2}{2} + \cdots \tag{22.64}$$

$$\overline{G}(T,P) = G^\circ(T) + RT\ln\frac{P}{P^\circ} + B_{2P}(T)P + \frac{B_{3P}(T)P^2}{2} + \cdots \tag{22.65}$$

$$\overline{G}(T,P) = G^\circ(T) + RT\ln\frac{f}{f^\circ} \tag{22.66}$$

$$\frac{f(P,T)}{f^\circ} = \frac{P}{P^\circ}\exp\left[\frac{B_{2P}(T)P}{RT} + \frac{B_{3P}(T)P^2}{2RT} + \cdots\right] \tag{22.67}$$

$$\Delta\overline{G}_1 = \overline{G}^{\text{id}}(T,P) - \overline{G}(T,P) \tag{22.68}$$

$$\Delta\overline{G}_1 = RT\ln\frac{P}{f} \tag{22.69}$$

$$\ln\frac{f}{P} = \int_0^P \left(\frac{\overline{V}}{RT} - \frac{1}{P'}\right)dP' \tag{22.70}$$

$$\gamma = \frac{f}{P} \tag{22.71}$$

$$\ln\gamma = \int_0^P \frac{Z-1}{P'}dP' \tag{22.72}$$

$$\ln\gamma = \int_0^{P_{\text{R}}} \left(\frac{Z-1}{P'_{\text{R}}}\right)dP'_{\text{R}} \tag{22.73}$$

Chapter 23

Phase Equilibria

$$dG = \left(\frac{\partial G^{\mathrm{g}}}{\partial n^{\mathrm{g}}}\right)_{P,T} dn^{\mathrm{g}} + \left(\frac{\partial G^{\mathrm{l}}}{\partial n^{\mathrm{l}}}\right)_{P,T} dn^{\mathrm{l}} \tag{23.1}$$

$$dG = \left[\left(\frac{\partial G^{\mathrm{g}}}{\partial n^{\mathrm{g}}}\right)_{P,T} - \left(\frac{\partial G^{\mathrm{l}}}{\partial n^{\mathrm{l}}}\right)_{P,T}\right] dn^{\mathrm{g}} \tag{23.2}$$

$$\mu^{\mathrm{g}} = \left(\frac{\partial G^{\mathrm{g}}}{\partial n^{\mathrm{g}}}\right)_{P,T} \quad \text{and} \quad \mu^{\mathrm{l}} = \left(\frac{\partial G^{\mathrm{l}}}{\partial n^{\mathrm{l}}}\right)_{P,T} \tag{23.3}$$

$$dG = (\mu^{\mathrm{g}} - \mu^{\mathrm{l}}) dn^{\mathrm{g}} \tag{23.4}$$

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T} = \left(\frac{\partial n\mu(T,P)}{\partial n}\right)_{T,P} = \mu(T,P) \tag{23.5}$$

$$\mu^{\alpha}(T,P) = \mu^{\beta}(T,P) \qquad \text{(equilibrium between phases)} \tag{23.6}$$

$$\left(\frac{\partial \mu^{\alpha}}{\partial P}\right)_{T} dP + \left(\frac{\partial \mu^{\alpha}}{\partial T}\right)_{P} dT = \left(\frac{\partial \mu^{\beta}}{\partial P}\right)_{T} dP + \left(\frac{\partial \mu^{\beta}}{\partial T}\right)_{P} dT \tag{23.7}$$

$$\left(\frac{\partial \mu}{\partial P}\right)_{T} = \left(\frac{\partial \overline{G}}{\partial P}\right)_{T} = \overline{V} \quad \text{and} \quad \left(\frac{\partial \mu}{\partial T}\right)_{P} = \left(\frac{\partial \overline{G}}{\partial T}\right)_{P} = -\overline{S} \tag{23.8}$$

$$\frac{dP}{dT} = \frac{\overline{S}^{\beta} - \overline{S}^{\alpha}}{\overline{V}^{\beta} - \overline{V}^{\alpha}} = \frac{\Delta_{\mathrm{trs}}\overline{S}}{\Delta_{\mathrm{trs}}\overline{V}} \tag{23.9}$$

$$\frac{dP}{dT} = \frac{\Delta_{\mathrm{trs}}\overline{H}}{T\Delta_{\mathrm{trs}}\overline{V}} \tag{23.10}$$

$$\frac{dP}{dT} = \frac{\Delta_{\mathrm{vap}}\overline{H}}{T(\overline{V}^{\mathrm{g}} - \overline{V}^{\mathrm{l}})} \tag{23.11}$$

$$\frac{1}{P}\frac{dP}{dT} = \frac{d\ln P}{dT} = \frac{\Delta_{\mathrm{vap}}\overline{H}}{RT^2} \tag{23.12}$$

$$\ln\frac{P_2}{P_1} = -\frac{\Delta_{\mathrm{vap}}\overline{H}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{\Delta_{\mathrm{vap}}\overline{H}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \tag{23.13}$$

$$\ln P = -\frac{\Delta_{\mathrm{vap}}\overline{H}}{RT} + \mathrm{constant} \tag{23.14}$$

$$\ln P = -\frac{A}{RT} + \frac{B}{R}\ln T + \frac{C}{R}T + K + O(T^2) \tag{23.15}$$

$$\ln P(\mathrm{torr}) = -\frac{4124.4}{T} - 1.81630\ln T + 34.4834 \tag{23.16}$$

$$\frac{dP^{\mathrm{s}}}{dT} = P^{\mathrm{s}}\frac{\Delta_{\mathrm{sub}}\overline{H}}{RT^2} \tag{23.17}$$

$$\frac{dP^{\mathrm{l}}}{dT} = P^{\mathrm{l}}\frac{\Delta_{\mathrm{vap}}\overline{H}}{RT^2} \tag{23.18}$$

$$\frac{dP^{\mathrm{s}}/dT}{dP^{\mathrm{l}}/dT} = \frac{\Delta_{\mathrm{sub}}\overline{H}}{\Delta_{\mathrm{vap}}\overline{H}} \tag{23.19}$$

$$\Delta_{\mathrm{sub}}\overline{H} = \Delta_{\mathrm{fus}}\overline{H} + \Delta_{\mathrm{vap}}\overline{H} \tag{23.20}$$

$$U = k_{\mathrm{B}}T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \tag{23.21}$$

$$S = k_{\mathrm{B}}T\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_{\mathrm{B}}\ln Q \tag{23.22}$$

$$A = -k_{\mathrm{B}} T \ln Q \tag{23.23}$$

$$\begin{aligned} dA &= \left(\frac{\partial A}{\partial T}\right)_{N,V} dT + \left(\frac{\partial A}{\partial V}\right)_{N,T} dV + \left(\frac{\partial A}{\partial N}\right)_{T,V} dN \\ &= -SdT - PdV + \left(\frac{\partial A}{\partial N}\right)_{T,V} dN \end{aligned} \tag{23.24}$$

$$dA = -SdT - PdV + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn \tag{23.25}$$

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial A}{\partial n}\right)_{T,V} \tag{23.26}$$

$$\mu = -k_{\mathrm{B}} T \left(\frac{\partial \ln Q}{\partial n}\right)_{V,T} = -RT \left(\frac{\partial \ln Q}{\partial N}\right)_{V,T} \tag{23.27}$$

$$\begin{aligned} \mu &= -RT(\ln q - \ln N - 1 + 1) \\ &= -RT \ln \frac{q(V,T)}{N} \qquad \text{(ideal gas)} \end{aligned} \tag{23.28}$$

$$\mu = -RT \ln \left[\left(\frac{q}{V}\right) \frac{V}{N}\right] \tag{23.29}$$

$$\begin{aligned} \mu &= -RT \ln \left[\left(\frac{q}{V}\right) \frac{k_{\mathrm{B}} T}{P}\right] \\ &= -RT \ln \left[\left(\frac{q}{V}\right) k_{\mathrm{B}} T\right] + RT \ln P \end{aligned} \tag{23.30}$$

$$\mu(T,P) = \mu^{\circ}(T) + RT \ln P \tag{23.31}$$

$$\mu^{\circ}(T) = -RT \ln \left[\left(\frac{q}{V}\right) k_{\mathrm{B}} T\right] \tag{23.32}$$

$$\mu(T,P) = \mu^{\circ}(T) + RT \ln \frac{P}{P^{\circ}} \tag{23.33}$$

$$\begin{aligned}\mu^\circ &= -RT\ln\left[\left(\frac{q}{V}\right)k_\mathrm{B}T\right] + RT\ln P^\circ \\ &= -RT\ln\left[\left(\frac{q}{V}\right)\frac{k_\mathrm{B}T}{P^\circ}\right]\end{aligned} \tag{23.34}$$

$$\begin{aligned}q(V,T) &= e^{-\varepsilon_0/k_\mathrm{B}T}[1 + e^{-(\varepsilon_1-\varepsilon_0)/k_\mathrm{B}T} + e^{-(\varepsilon_2-\varepsilon_0)/k_\mathrm{B}T} + \cdots] \\ &= e^{-\varepsilon_0/k_\mathrm{B}T}q^0(V,T)\end{aligned} \tag{23.35}$$

$$\begin{aligned}\mu^\circ(T) - E_0 &= -RT\ln\left[\left(\frac{q^0}{V}\right)\frac{k_\mathrm{B}T}{P^\circ}\right] \\ &= -RT\ln\left[\left(\frac{q^0}{V}\right)\frac{RT}{N_\mathrm{A}P^\circ}\right]\end{aligned} \tag{23.36}$$

$$q^0(V,T) = \left(\frac{2\pi m k_\mathrm{B}T}{h^2}\right)^{3/2} V \cdot \frac{T}{\Theta_\mathrm{rot}} \cdot \frac{1}{1 - e^{-\Theta_\mathrm{vib}/T}} \tag{23.37}$$

Chapter 24

Solutions I: Liquid-Liquid Solutions

$$\begin{aligned} dG &= \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP \\ &\quad + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1} dn_2 \end{aligned} \tag{24.1}$$

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 \tag{24.2}$$

$$\mu_j = \mu_j(T, P, n_1, n_2) = \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_{i\neq j}} = \overline{G}_j \tag{24.3}$$

$$\overline{Y}_j = \overline{Y}_j(T, P, n_1, n_2) = \left(\frac{\partial Y}{\partial n_j}\right)_{T,P,n_{i\neq j}} \tag{24.4}$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \tag{24.5}$$

$$G(T, P, n_1, n_2) = \mu_1 n_1 + \mu_2 n_2 \tag{24.6}$$

$$V(T, P, n_1, n_2) = \overline{V}_1 n_1 + \overline{V}_2 n_2 \tag{24.7}$$

$$\mu_j = \overline{G}_j = \overline{H}_j - T\overline{S}_j \tag{24.8}$$

$$d\mu_j = -\overline{S}_j dT + \overline{V}_j dP \tag{24.9}$$

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \qquad \text{(constant } T \text{ and } P\text{)} \tag{24.10}$$

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \qquad \text{(constant } T \text{ and } P\text{)} \tag{24.11}$$

$$\mu_j^{\text{vap}} = \mu_j^{\text{sln}} \tag{24.12}$$

$$\mu_j^{\text{sln}} = \mu_j^{\text{vap}} = \mu_j^{\circ}(T) + RT \ln P_j \tag{24.13}$$

$$\mu_j^*(l) = \mu_j^*(\text{vap}) = \mu_j^{\circ}(T) + RT \ln P_j^* \tag{24.14}$$

$$\mu_j^{\text{sln}} = \mu_j^*(l) + RT \ln \frac{P_j}{P_j^*} \tag{24.15}$$

$$P_j = x_j P_j^* \tag{24.16}$$

$$\mu_j^{\text{sln}} = \mu_j^*(l) + RT \ln x_j \tag{24.17}$$

$$\begin{aligned} P_{\text{total}} &= P_1 + P_2 = x_1 P_1^* + x_2 P_2^* = (1 - x_2) P_1^* + x_2 P_2^* \\ &= P_1^* + x_2 (P_2^* - P_1^*) \end{aligned} \tag{24.18}$$

$$\frac{n^{\text{l}}}{n^{\text{vap}}} = \frac{y_2 - x_a}{x_a - x_2} \tag{24.19}$$

$$\Delta_{\text{mix}} G = G^{\text{sln}}(T, P, n_1, n_2) - G_1^*(T, P, n_1) - G_2^*(T, P, n_2) \tag{24.20}$$

$$\begin{aligned} \Delta_{\text{mix}} G^{\text{id}} &= n_1 \mu_1^{\text{sln}} + n_2 \mu_2^{\text{sln}} - n_1 \mu_1^* - n_2 \mu_2^* \\ &= RT (n_1 \ln x_1 + n_2 \ln x_2) \end{aligned} \tag{24.21}$$

$$\Delta_{\text{mix}} S^{\text{id}} = -\left(\frac{\partial \Delta_{\text{mix}} G^{\text{id}}}{\partial T}\right)_{P,n_1,n_2} = -R(n_1 \ln x_1 + n_2 \ln x_2) \tag{24.22}$$

$$\Delta_{\text{mix}} V^{\text{id}} = \left(\frac{\partial \Delta_{\text{mix}} G^{\text{id}}}{\partial P}\right)_{T,n_1,n_2} = 0 \tag{24.23}$$

$$\Delta_{\text{mix}} H^{\text{id}} = \Delta_{\text{mix}} G^{\text{id}} + T\Delta_{\text{mix}} S^{\text{id}} = 0 \tag{24.24}$$

$$P_1 \longrightarrow x_1 P_1^* \quad \text{as} \quad x_1 \longrightarrow 1 \tag{24.25}$$

$$P_1 \longrightarrow k_{\text{H},1} x_1 \quad \text{as} \quad x_1 \longrightarrow 0 \tag{24.26}$$

$$\begin{aligned} P_j &\longrightarrow x_j P_j^* \qquad \text{as} \qquad x_j \longrightarrow 1 \\ P_j &\longrightarrow x_j k_{\text{H},j} \qquad \text{as} \qquad x_j \longrightarrow 0 \end{aligned} \tag{24.27}$$

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1}\right)_{T,P} dx_1 + x_2 \left(\frac{\partial \ln P_2}{\partial x_2}\right)_{T,P} dx_2 = 0 \tag{24.28}$$

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1}\right)_{T,P} = x_2 \left(\frac{\partial \ln P_2}{\partial x_2}\right)_{T,P} \tag{24.29}$$

$$\frac{n'}{n''} = \frac{n_1' + n_2'}{n_1'' + n_2''} = \frac{x_2'' - x_2}{x_2 - x_2'} \tag{24.30}$$

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln \frac{P_j}{P_j^*} \tag{24.31}$$

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln x_j \quad \text{(ideal solution)} \tag{24.32}$$

$$P_1 = x_1 P_1^* \exp(\alpha x_2^2 + \beta x_2^3 + \cdots) \tag{24.33}$$

$$\mu_1 = \mu_1^* + RT \ln x_1 + \alpha RT x_2^2 + \beta RT x_2^3 + \cdots \tag{24.34}$$

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln a_j \tag{24.35}$$

$$a_j = \frac{P_j}{P_j^*} \qquad \text{(ideal vapor)} \tag{24.36}$$

$$\gamma_j = \frac{a_j}{x_j} \tag{24.37}$$

$$x_1 d \ln a_1 + x_2 d \ln a_2 = 0 \tag{24.38}$$

$$a_j = \frac{P_j}{P_j^*} \qquad \text{(ideal vapor)} \tag{24.39}$$

$$\mu_j^{\mathrm{sln}} = \mu_j^* + RT \ln \frac{P_j}{P_j^*} \tag{24.40}$$

$$\begin{aligned} \mu_j^{\mathrm{sln}} &= \mu_j^* + RT \ln \frac{x_j k_{\mathrm{H},j}}{P_j^*} \qquad (x_j \to 0) \\ &= \mu_j^* + RT \ln \frac{k_{\mathrm{H},j}}{P_j^*} + RT x_j \qquad (x_j \to 0) \end{aligned} \tag{24.41}$$

$$\mu_j^{\mathrm{sln}} = \mu_j^* + RT \ln \frac{k_{\mathrm{H},j}}{P_j^*} + RT \ln a_j \tag{24.42}$$

$$a_j = \frac{P_j}{k_{\mathrm{H},j}} \qquad \text{(ideal vapor)} \tag{24.43}$$

$$\mu_j^{\mathrm{sln}} = \mu_j^* + RT \ln a_j = \mu_j^* + RT \ln x_j + RT \ln \gamma_j \tag{24.44}$$

$$\Delta_{\mathrm{mix}} G/RT = n_1 \ln x_1 + n_2 \ln x_2 + n_1 \ln \gamma_1 + n_2 \ln \gamma_2 \tag{24.45}$$

$$\Delta_{\mathrm{mix}} \overline{G}/RT = x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{24.46}$$

$$\Delta_{\mathrm{mix}} \overline{G}/RT = x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2 \tag{24.47}$$

$$\frac{\Delta_{\mathrm{mix}} \overline{G}}{w} = \frac{RT}{w}(x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2 \tag{24.48}$$

$$\frac{\partial(\Delta_{\text{mix}}\overline{G}/w)}{\partial x_1} = \frac{RT}{w}[\ln x_1 - \ln(1-x_1)] + (1-2x_1) = 0 \tag{24.49}$$

$$G^{\text{E}} = \Delta_{\text{mix}}G - \Delta_{\text{mix}}G^{\text{id}} \tag{24.50}$$

$$\overline{G}^{\text{E}}/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{24.51}$$

$$\overline{G}^{\text{E}}/RT = \alpha x_1 x_2 \tag{24.52}$$

$$P_1 = x_1 P_1^* e^{\alpha x_2^2} \qquad P_2 = x_2 P_2^* e^{\alpha x_1^2} \tag{24.53}$$

$$U = \frac{zN_1^2}{2(N_1+N_2)}\epsilon_{11} + \frac{zN_2^2}{2(N_1+N_2)}\epsilon_{22} + \frac{zN_1N_2}{N_1+N_2}\epsilon_{12} \tag{24.54}$$

$$w = zN_{\text{A}}[\epsilon_{12} - \frac{1}{2}(\epsilon_{11}+\epsilon_{22})] \tag{24.55}$$

$$U = \frac{z\epsilon_{11}N_1}{2} + \frac{z\epsilon_{22}N_2}{2} - \frac{wN_1N_2}{N_{\text{A}}(N_1+N_2)} \tag{24.56}$$

$$G_{\text{soln}} = G_{\text{ideal}} + \frac{wN_1N_2}{N_{\text{A}}(N_1+N_2)} \tag{24.57}$$

$$G_{\text{soln}} = G_{\text{ideal}} - \frac{wN_{\text{A}}n_1n_2}{(n_1+n_2)} \tag{24.58}$$

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} = \left(\frac{\partial G_{\text{ideal}}}{\partial n_1}\right)_{T,P,n_2} + w\left(\frac{\partial n_1 n_2/(n_1+n_2)}{\partial n_1}\right)_{n_2} \tag{24.59}$$

$$\begin{aligned}\mu_1 &= \mu_1^* + RT\ln x_1 + wx_2^2 \\ &= \mu_1^* + RT\ln(x_1 e^{wx_2^2/RT})\end{aligned} \tag{24.60}$$

$$P_1 = x_1 P_1^* e^{wx_2^2/RT} \tag{24.61}$$

$$P_2 = x_2 P_2^* e^{w x_1^2/RT} \tag{24.62}$$

$$\Delta_{\text{mix}} G = n_1 RT \ln x_1 + n_2 RT \ln x_2 - \frac{z w N_{\text{A}}}{2}(n_2 x_1^2 + n_1 x_2^2) \tag{24.63}$$

$$\frac{\Delta_{\text{mix}} G}{(n_1 + n_2)RT} = x_1 \ln x_1 + x_2 \ln x_2 - \frac{z w x_1 x_2}{2 k_{\text{B}} T} \tag{24.64}$$

$$\frac{\Delta_{\text{mix}} S}{(n_1 + n_2)R} = -x_1 \ln x_1 - x_2 \ln x_2 \tag{24.65}$$

$$\frac{\Delta_{\text{mix}} H}{(n_1 + n_2)RT} = -\frac{z w x_1 x_2}{2 k_{\text{B}} T} \tag{24.66}$$

Chapter 25

Solutions II: Solid-Liquid Solutions

$$a_1 = \frac{P_1}{P_1^*} \qquad \text{(Raoult's law standard state)} \tag{25.1}$$

$$a_{2x} = \frac{P_2}{k_{\mathrm{H},x}} \qquad \text{(Henry's law standard state)} \tag{25.2}$$

$$m = \frac{n_2}{1000 \text{ g solvent}} \tag{25.3}$$

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{m}{\dfrac{1000 \text{ g}\cdot\text{kg}^{-1}}{M_1} + m} \tag{25.4}$$

$$x_2 = \frac{m}{55.506 \text{ mol}\cdot\text{kg}^{-1} + m} \tag{25.5}$$

$$a_{2m} \longrightarrow m \quad \text{as} \quad m \longrightarrow 0 \tag{25.6}$$

$$a_{2m} = \frac{P_2}{k_{\mathrm{H},m}} \tag{25.7}$$

$$c = \frac{n_2}{1000 \text{ mL solution}} \tag{25.8}$$

$$a_{2c} \longrightarrow c \quad \text{as} \quad c \longrightarrow 0 \tag{25.9}$$

$$a_{2c} = \frac{P_2}{k_{\mathrm{H},c}} \tag{25.10}$$

$$\begin{aligned} x_2 &= \frac{n_2}{n_1+n_2} = \frac{c}{\dfrac{(1000\ \mathrm{mL})\rho - cM_2}{M_1} + c} \\ &= \frac{cM_1}{(1000\ \mathrm{mL})\rho + c(M_1 - M_2)} \end{aligned} \tag{25.11}$$

$$\ln a_1 = \ln x_1 = \ln(1 - x_2) \approx -x_2 \approx -\frac{m}{55.506\ \mathrm{mol{\cdot}kg^{-1}}} \tag{25.12}$$

$$\ln a_1 = -\frac{m\phi}{55.506\ \mathrm{mol{\cdot}kg^{-1}}} \tag{25.13}$$

$$(55.506\ \mathrm{mol{\cdot}kg^{-1}})d\ln a_1 + md\ln a_2 = 0 \tag{25.14}$$

$$\ln \gamma_{2m} = \phi - 1 + \int_0^m \left(\frac{\phi - 1}{m'}\right) dm' \tag{25.15}$$

$$\ln a_1 = \frac{\mu_1^{\mathrm{s}} - \mu_1^{\mathrm{l}}}{RT} \tag{25.16}$$

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_{P,x_1} = \frac{\overline{H}_1^{\mathrm{l}} - \overline{H}_1^{\mathrm{s}}}{RT^2} = \frac{\Delta_{\mathrm{fus}}\overline{H}}{RT^2} \tag{25.17}$$

$$\ln a_1 = \int_{T_{\mathrm{fus}}^*}^{T_{\mathrm{fus}}} \frac{\Delta_{\mathrm{fus}}\overline{H}}{RT^2} dT \tag{25.18}$$

$$\Delta T_{\mathrm{fus}} = K_{\mathrm{f}} m \tag{25.19}$$

$$\begin{aligned} -x_2 &= \frac{\Delta_{\mathrm{fus}}\overline{H}}{R} \int_{T_{\mathrm{fus}}^*}^{T_{\mathrm{fus}}} \frac{dT}{T^2} = \frac{\Delta_{\mathrm{fus}}\overline{H}}{R}\left(\frac{1}{T_{\mathrm{fus}}^*} - \frac{1}{T_{\mathrm{fus}}}\right) \\ &= \frac{\Delta_{\mathrm{fus}}\overline{H}}{R}\left(\frac{T_{\mathrm{fus}} - T_{\mathrm{fus}}^*}{T_{\mathrm{fus}}T_{\mathrm{fus}}^*}\right) \end{aligned} \tag{25.20}$$

$$x_2 = \frac{m}{\frac{1000\ \text{g}\cdot\text{kg}^{-1}}{M_1} + m} \approx \frac{M_1 m}{1000\ \text{g}\cdot\text{kg}^{-1}} \tag{25.21}$$

$$\Delta T_{\text{fus}} = T^*_{\text{fus}} - T_{\text{fus}} = K_{\text{f}} m \tag{25.22}$$

$$K_{\text{f}} = \frac{M_1}{1000\ \text{g}\cdot\text{kg}^{-1}} \frac{R(T^*_{\text{fus}})^2}{\Delta_{\text{fus}}\overline{H}} \tag{25.23}$$

$$\Delta T_{\text{vap}} = T_{\text{vap}} - T^*_{\text{vap}} = K_{\text{b}} m \tag{25.24}$$

$$K_{\text{b}} = \frac{M_1}{1000\ \text{g}\cdot\text{kg}^{-1}} \frac{R(T^*_{\text{vap}})^2}{\Delta_{\text{vap}}\overline{H}} \tag{25.25}$$

$$\mu_1^*(T, P) = \mu_1^{\text{sln}}(T, P + \Pi, a_1) \tag{25.26}$$

$$\left(\frac{\partial \mu_1^*}{\partial P}\right)_T = \overline{V}_1^* \tag{25.27}$$

$$\mu_1^*(T, P) = \mu_1^{\text{sln}}(T, P + \Pi, a_1) = \mu_1^*(T, P + \Pi) + RT \ln a_1 \tag{25.28}$$

$$\int_P^{P+\Pi} \overline{V}^* dP + RT \ln a_1 = 0 \tag{25.29}$$

$$\Pi \overline{V}^* + RT \ln a_1 = 0 \tag{25.30}$$

$$\Pi = cRT \tag{25.31}$$

$$\mu_2 = \nu_+ \mu_+ + \nu_- \mu_- \tag{25.32}$$

$$\mu_2 = \mu_2^\circ + RT \ln a_2 \tag{25.33}$$

$$\begin{aligned} \mu_+ &= \mu_+^\circ + RT \ln a_+ \\ \mu_- &= \mu_-^\circ + RT \ln a_- \end{aligned} \tag{25.34}$$

$$a_2 = a_+^{\nu_+} a_-^{\nu_-} \tag{25.35}$$

$$a_2 = a_\pm^{\nu} = a_+^{\nu_+} a_-^{\nu_-} \tag{25.36}$$

$$a_2 = a_\pm^{\nu} = (m_+^{\nu_+} m_-^{\nu_-})(\gamma_+^{\nu_+} \gamma_-^{\nu_-}) \tag{25.37}$$

$$m_\pm^{\nu} = m_+^{\nu_+} m_-^{\nu_-} \tag{25.38}$$

$$\gamma_\pm^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-} \tag{25.39}$$

$$a_2 = a_\pm^{\nu} = m_\pm^{\nu} \gamma_\pm^{\nu} \tag{25.40}$$

$$\ln a_1 = -\frac{\nu m \phi}{55.506} \tag{25.41}$$

$$\ln \gamma_\pm = \phi - 1 + \int_0^m \left(\frac{\phi - 1}{m'} \right) dm' \tag{25.42}$$

$$\begin{aligned} \phi \;=\; & 1 - (0.3920\ \mathrm{kg}^{1/2}{\cdot}\mathrm{mol}^{-1/2}) m^{1/2} + (0.7780\ \mathrm{kg}{\cdot}\mathrm{mol}^{-1}) m \\ & - (0.8374\ \mathrm{kg}^{3/2}{\cdot}\mathrm{mol}^{-3/2}) m^{3/2} + (0.5326\ \mathrm{kg}^{2}{\cdot}\mathrm{mol}^{-2}) m^{2} \\ & - (0.1673\ \mathrm{kg}^{5/2}{\cdot}\mathrm{mol}^{-5/2}) m^{5/2} + (0.0206\ \mathrm{kg}^{3}{\cdot}\mathrm{mol}^{-3}) m^{3} \\ & 0 \le m \le 5.0\ \mathrm{mol}{\cdot}\mathrm{kg}^{-1} \end{aligned} \tag{25.43}$$

$$x_2 = \frac{\nu m}{\dfrac{1000\ \mathrm{g}{\cdot}\mathrm{kg}^{-1}}{M_1} + \nu m} \approx \frac{\nu m M_1}{1000\ \mathrm{g}{\cdot}\mathrm{kg}^{-1}} \tag{25.44}$$

$$\Delta T_{\mathrm{fus}} = \nu K_{\mathrm{f}} m \tag{25.45}$$

$$\Delta T_{\mathrm{vap}} = \nu K_{\mathrm{b}} m \tag{25.46}$$

$$\Pi = \nu M R T \tag{25.47}$$

$$\ln \gamma_j = -\frac{\kappa q_j^2}{8\pi \varepsilon_0 \varepsilon_r k_\mathrm{B} T} \tag{25.48}$$

$$\ln \gamma_\pm = -|q_+ q_-| \frac{\kappa}{8\pi \varepsilon_0 \varepsilon_r k_\mathrm{B} T} \tag{25.49}$$

$$\kappa^2 = \sum_{j=1}^{s} \frac{q_j^2}{\varepsilon_0 \varepsilon_r k_\mathrm{B} T} \left(\frac{N_j}{V} \right) \tag{25.50}$$

$$\kappa^2 = N_A (1000 \ \mathrm{L{\cdot}m^{-3}}) \sum_{j=1}^{s} \frac{q_j^2 c_j}{\varepsilon_0 \varepsilon_r k_\mathrm{B} T} \tag{25.51}$$

$$I_c = \frac{1}{2} \sum_{j=1}^{s} z_j^2 c_j \tag{25.52}$$

$$\kappa^2 = \frac{2e^2 N_A (1000 \ \mathrm{L{\cdot}m^{-3}})}{\varepsilon_0 \varepsilon_r k_\mathrm{B} T} I_c/\mathrm{mol{\cdot}L^{-1}} \tag{25.53}$$

$$p_i(r)dr = -q_i \kappa^2 r e^{-\kappa r} dr \tag{25.54}$$

$$\frac{1}{\kappa} = \frac{304 \ \mathrm{pm}}{(c/\mathrm{mol{\cdot}L^{-1}})^{1/2}} \tag{25.55}$$

$$\ln \gamma_\pm = -1.173 |z_+ z_-| (I_c/\mathrm{mol{\cdot}L^{-1}})^{1/2} \tag{25.56}$$

$$\ln \gamma_\pm = -\frac{1.173 |z_+ z_-| (I_c/\mathrm{mol{\cdot}L^{-1}})^{1/2}}{1 + (I_c/\mathrm{mol{\cdot}L^{-1}})^{1/2}} \tag{25.57}$$

$$\ln \gamma_\pm = -\frac{1.173 |z_+ z_-| (I_c/\ \mathrm{mol{\cdot}L^{-1}})^{1/2}}{1 + (I_c/\ \mathrm{mol{\cdot}L^{-1}})^{1/2}} + Cm \tag{25.58}$$

$$\ln \gamma_\pm = \ln \gamma_\pm^\mathrm{el} + \ln \gamma^\mathrm{HS} \tag{25.59}$$

$$\ln \gamma_\pm^\mathrm{el} = \frac{x(1+2x)^{1/2} - x - x^2}{4\pi \rho d^3} \tag{25.60}$$

$$\ln \gamma^\mathrm{HS} = \frac{4y - \frac{9}{4} y^2 + \frac{3}{8} y^3}{\left(1 - \frac{y}{2}\right)^3} \tag{25.61}$$

Chapter 26

Chemical Equilibrium

$$\nu_{\mathrm{A}}\mathrm{A(g)} + \nu_{\mathrm{B}}\mathrm{B(g)} \rightleftharpoons \nu_{\mathrm{Y}}\mathrm{Y(g)} + \nu_{\mathrm{Z}}\mathrm{Z(g)} \tag{26.1}$$

$$\underbrace{\begin{aligned} dn_{\mathrm{A}} &= -\nu_{\mathrm{A}} d\xi \\ dn_{\mathrm{B}} &= -\nu_{\mathrm{B}} d\xi \end{aligned}}_{\text{reactants}} \qquad \underbrace{\begin{aligned} dn_{\mathrm{Y}} &= \nu_{\mathrm{Y}} d\xi \\ dn_{\mathrm{Z}} &= \nu_{\mathrm{Z}} d\xi \end{aligned}}_{\text{products}} \tag{26.2}$$

$$dG = \sum_j \mu_j dn_j = \mu_{\mathrm{A}} dn_{\mathrm{A}} + \mu_{\mathrm{B}} dn_{\mathrm{B}} + \mu_{\mathrm{Y}} dn_{\mathrm{Y}} + \mu_{\mathrm{Z}} dn_{\mathrm{Z}} \quad (\text{constant } T \text{ and } P) \tag{26.3}$$

$$\begin{aligned} dG &= -\nu_{\mathrm{A}}\mu_{\mathrm{A}} d\xi - \nu_{\mathrm{B}}\mu_{\mathrm{B}} d\xi + \nu_{\mathrm{Y}}\mu_{\mathrm{Y}} d\xi + \nu_{\mathrm{Z}}\mu_{\mathrm{Z}} d\xi \\ &= (\nu_{\mathrm{Y}}\mu_{\mathrm{Y}} + \nu_{\mathrm{Z}}\mu_{\mathrm{Z}} - \nu_{\mathrm{A}}\mu_{\mathrm{A}} - \nu_{\mathrm{B}}\mu_{\mathrm{B}}) d\xi \quad (\text{constant } T \text{ and } P) \end{aligned} \tag{26.4}$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \nu_{\mathrm{Y}}\mu_{\mathrm{Y}} + \nu_{\mathrm{Z}}\mu_{\mathrm{Z}} - \nu_{\mathrm{A}}\mu_{\mathrm{A}} - \nu_{\mathrm{B}}\mu_{\mathrm{B}} \tag{26.5}$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_{\mathrm{r}} G = \nu_{\mathrm{Y}}\mu_{\mathrm{Y}} + \nu_{\mathrm{Z}}\mu_{\mathrm{Z}} - \nu_{\mathrm{A}}\mu_{\mathrm{A}} - \nu_{\mathrm{B}}\mu_{\mathrm{B}} \tag{26.6}$$

$$\Delta_{\mathrm{r}} G = \Delta_{\mathrm{r}} G^\circ + RT \ln Q \tag{26.7}$$

$$\Delta_{\mathrm{r}} G^\circ(T) = \nu_{\mathrm{Y}}\mu_{\mathrm{Y}}^\circ(T) + \nu_{\mathrm{Z}}\mu_{\mathrm{Z}}^\circ(T) - \nu_{\mathrm{A}}\mu_{\mathrm{A}}^\circ(T) - \nu_{\mathrm{B}}\mu_{\mathrm{B}}^\circ(T) \tag{26.8}$$

$$Q = \frac{(P_{\mathrm{Y}}/P^{\circ})^{\nu_{\mathrm{Y}}}(P_{\mathrm{Z}}/P^{\circ})^{\nu_{\mathrm{Z}}}}{(P_{\mathrm{A}}/P^{\circ})^{\nu_{\mathrm{A}}}(P_{\mathrm{B}}/P^{\circ})^{\nu_{\mathrm{B}}}} \tag{26.9}$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_{\mathrm{r}} G = 0 \tag{26.10}$$

$$\Delta_{\mathrm{r}} G^{\circ}(T) = -RT \ln \left(\frac{P_{\mathrm{Y}}^{\nu_{\mathrm{Y}}} P_{\mathrm{Z}}^{\nu_{\mathrm{Z}}}}{P_{\mathrm{A}}^{\nu_{\mathrm{A}}} P_{\mathrm{B}}^{\nu_{\mathrm{B}}}}\right)_{\mathrm{eq}} = -RT \ln K_P(T) \tag{26.11}$$

$$K_P(T) = \left(\frac{P_{\mathrm{Y}}^{\nu_{\mathrm{Y}}} P_{\mathrm{Z}}^{\nu_{\mathrm{Z}}}}{P_{\mathrm{A}}^{\nu_{\mathrm{A}}} P_{\mathrm{B}}^{\nu_{\mathrm{B}}}}\right)_{\mathrm{eq}} \tag{26.12}$$

$$\mathrm{PCl_5(g)} \rightleftharpoons \mathrm{PCl_3(g)} + \mathrm{Cl_2(g)} \tag{26.13}$$

$$K_P(T) = \frac{P_{\mathrm{PCl_3}} P_{\mathrm{Cl_2}}}{P_{\mathrm{PCl_5}}} \tag{26.14}$$

$$K_P(T) = \frac{\xi_{\mathrm{eq}}^2}{1 - \xi_{\mathrm{eq}}^2} P \tag{26.15}$$

$$P = cRT \qquad \text{and} \qquad P^{\circ} = c^{\circ} RT \tag{26.16}$$

$$\begin{aligned} K_P &= \frac{(P_{\mathrm{Y}}/P^{\circ})^{\nu_{\mathrm{Y}}}(P_{\mathrm{Z}}/P^{\circ})^{\nu_{\mathrm{Z}}}}{(P_{\mathrm{A}}/P^{\circ})^{\nu_{\mathrm{A}}}(P_{\mathrm{B}}/P^{\circ})^{\nu_{\mathrm{B}}}} \\ &= \frac{(c_{\mathrm{Y}}/c^{\circ})^{\nu_{\mathrm{Y}}}(c_{\mathrm{Z}}/c^{\circ})^{\nu_{\mathrm{Z}}}}{(c_{\mathrm{A}}/c^{\circ})^{\nu_{\mathrm{A}}}(c_{\mathrm{B}}/c^{\circ})^{\nu_{\mathrm{B}}}} \cdot (RT)^{\nu_{\mathrm{Y}}+\nu_{\mathrm{Z}}-\nu_{\mathrm{A}}-\nu_{\mathrm{B}}} \\ &= K_c (RT)^{\nu_{\mathrm{Y}}+\nu_{\mathrm{Z}}-\nu_{\mathrm{A}}-\nu_{\mathrm{B}}} \end{aligned} \tag{26.17}$$

$$K_c = \frac{(c_{\mathrm{Y}}/c^{\circ})^{\nu_{\mathrm{Y}}}(c_{\mathrm{Z}}/c^{\circ})^{\nu_{\mathrm{Z}}}}{(c_{\mathrm{A}}/c^{\circ})^{\nu_{\mathrm{A}}}(c_{\mathrm{B}}/c^{\circ})^{\nu_{\mathrm{B}}}} \tag{26.18}$$

$$\Delta_{\mathrm{r}} G^{\circ} = \nu_{\mathrm{Y}} \Delta_{\mathrm{f}} G^{\circ}[\mathrm{Y}] + \nu_{\mathrm{Z}} \Delta_{\mathrm{f}} G^{\circ}[\mathrm{Z}] - \nu_{\mathrm{A}} \Delta_{\mathrm{f}} G^{\circ}[\mathrm{A}] - \nu_{\mathrm{B}} \Delta_{\mathrm{f}} G^{\circ}[\mathrm{B}] \tag{26.19}$$

$$\begin{aligned} G(\xi) &= (1-\xi)\overline{G}_{\mathrm{N_2O_4}} + 2\xi \overline{G}_{\mathrm{NO_2}} \\ &= (1-\xi) G^{\circ}_{\mathrm{N_2O_4}} + 2\xi G^{\circ}_{\mathrm{NO_2}} + (1-\xi) RT \ln P_{\mathrm{N_2O_4}} + 2\xi RT \ln P_{\mathrm{NO_2}} \end{aligned} \tag{26.20}$$

$$G(\xi) = (1-\xi)G^\circ_{\mathrm{N_2O_4}} + 2\xi G^\circ_{\mathrm{NO_2}} + (1-\xi)RT\ln\frac{1-\xi}{1+\xi} + 2\xi RT\ln\frac{2\xi}{1+\xi} \quad (26.21)$$

$$\begin{aligned} G(\xi) &= (1-\xi)(97.787\ \mathrm{kJ\cdot mol^{-1}}) + 2\xi(51.258\ \mathrm{kJ\cdot mol^{-1}}) \\ &\quad + (1-\xi)RT\ln\frac{1-\xi}{1+\xi} + 2\xi RT\ln\frac{2\xi}{1+\xi} \end{aligned} \quad (26.22)$$

$$\begin{aligned} \left(\frac{\partial G}{\partial \xi}\right)_{T,P} &= (2)(51.258\ \mathrm{kJ\cdot mol^{-1}}) - 97.787\ \mathrm{kJ\cdot mol^{-1}} - RT\ln\frac{1-\xi}{1+\xi} \\ &\quad + 2RT\ln\frac{2\xi}{1+\xi} + (1-\xi)RT\left(\frac{1+\xi}{1-\xi}\right)\left[-\frac{1}{1+\xi} - \frac{1-\xi}{(1+\xi)^2}\right] \\ &\quad + 2\xi RT\left(\frac{1+\xi}{2\xi}\right)\left[\frac{2}{1+\xi} - \frac{2\xi}{(1+\xi)^2}\right] \end{aligned} \quad (26.23)$$

$$\Delta_\mathrm{r} G(T) = \Delta_\mathrm{r} G^\circ(T) + RT\ln\frac{P_\mathrm{Y}^{\nu_\mathrm{Y}} P_\mathrm{Z}^{\nu_\mathrm{Z}}}{P_\mathrm{A}^{\nu_\mathrm{A}} P_\mathrm{B}^{\nu_\mathrm{B}}} \quad (26.24)$$

$$Q_P = \frac{P_\mathrm{Y}^{\nu_\mathrm{Y}} P_\mathrm{Z}^{\nu_\mathrm{Z}}}{P_\mathrm{A}^{\nu_\mathrm{A}} P_\mathrm{B}^{\nu_\mathrm{B}}} \quad (26.25)$$

$$\begin{aligned} \Delta_\mathrm{r}\overline{G} &= -RT\ln K_P + RT\ln Q_P \\ &= RT\ln(Q_P/K_P) \end{aligned} \quad (26.26)$$

$$\begin{aligned} \Delta_\mathrm{r}\overline{G} &= \Delta_\mathrm{r} G^\circ + RT\ln Q_P \\ &= 4.729\ \mathrm{kJ\cdot mol^{-1}} + (2.479\ \mathrm{kJ\cdot mol^{-1}})\ln\frac{P^2_{\mathrm{NO_2}}}{P_{\mathrm{N_2O_4}}} \end{aligned} \quad (26.27)$$

$$\left(\frac{\partial \Delta G^\circ/T}{\partial T}\right)_P = -\frac{\Delta H^\circ}{T^2} \quad (26.28)$$

$$\left(\frac{\partial \ln K_P(T)}{\partial T}\right)_P = \frac{d\ln K_P(T)}{dT} = \frac{\Delta_\mathrm{r} H^\circ}{RT^2} \quad (26.29)$$

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T) dT}{RT^2} \tag{26.30}$$

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{26.31}$$

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_P^\circ(T) dT \tag{26.32}$$

$$\Delta_r H^\circ(T) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \cdots \tag{26.33}$$

$$\ln K_P(T) = -\frac{\alpha}{RT} + \frac{\beta}{R} \ln T + \frac{\gamma}{R} T + \frac{\delta T^2}{2R} + A \tag{26.34}$$

$$\ln K_P(T) = \ln K_P(T_1) + \int_{T_1}^{T} \frac{\Delta_r H^\circ(T) dT}{RT^2} \tag{26.35}$$

$$\nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B = 0 \tag{26.36}$$

$$\mu_A = -k_B T \left(\frac{\partial \ln Q}{\partial N_A} \right)_{N_j, V, T} = -k_B T \ln \frac{q_A(V,T)}{N_A} \tag{26.37}$$

$$\frac{N_Y^{\nu_Y} N_Z^{\nu_Z}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{q_Y^{\nu_Y} q_Z^{\nu_Z}}{q_A^{\nu_A} q_B^{\nu_B}} \tag{26.38}$$

$$K_c(T) = \frac{\rho_Y^{\nu_Y} \rho_Z^{\nu_Z}}{\rho_A^{\nu_A} \rho_B^{\nu_B}} = \frac{(q_Y/V)^{\nu_Y} (q_Z/V)^{\nu_Z}}{(q_A/V)^{\nu_A} (q_B/V)^{\nu_B}} \tag{26.39}$$

$$\begin{aligned} K(T) \quad = \quad & \left(\frac{m_{HI}^2}{m_{H_2} m_{I_2}} \right)^{3/2} \left(\frac{4 \Theta_r^{H_2} \Theta_r^{I_2}}{(\Theta_r^{HI})^2} \right) \frac{(1 - e^{-\Theta_v^{H_2}/T})(1 - e^{-\Theta_v^{I_2}/T})}{(1 - e^{-\Theta_v^{HI}/T})^2} \\ & \times \exp \frac{2 D_o^{HI} - D_o^{H_2} - D_o^{I_2}}{RT} \end{aligned} \tag{26.40}$$

$$K_P(T) = \frac{(q_{H_2O}/V)}{(k_B T)^{1/2} (q_{H_2}/V)(q_{O_2}/V)^{1/2}} \tag{26.41}$$

$$\begin{aligned}\frac{q_{\mathrm{H}_2}(T,V)}{V} &= \left(\frac{2\pi m_{\mathrm{H}_2} k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \left(\frac{T}{2\Theta_{\mathrm{r}}^{\mathrm{H}_2}}\right)(1-e^{-\Theta_{\mathrm{v}}^{\mathrm{H}_2}/T})^{-1} e^{D_o^{\mathrm{H}_2}/k_{\mathrm{B}}T} \\ &= 2.80\times 10^{32} e^{D_o^{\mathrm{H}_2}/k_{\mathrm{B}}T}\ \mathrm{m}^{-3} \qquad (26.42)\end{aligned}$$

$$\begin{aligned}\frac{q_{\mathrm{O}_2}(T,V)}{V} &= \left(\frac{2\pi m_{\mathrm{O}_2} k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \left(\frac{T}{2\Theta_{\mathrm{r}}^{\mathrm{O}_2}}\right)(1-e^{-\Theta_{\mathrm{v}}^{\mathrm{O}_2}/T})^{-1} 3 e^{D_o^{\mathrm{O}_2}/k_{\mathrm{B}}T} \\ &= 2.79\times 10^{36} e^{D_o^{\mathrm{O}_2}/k_{\mathrm{B}}T}\ \mathrm{m}^{-3} \qquad (26.43)\end{aligned}$$

$$\begin{aligned}\frac{q_{\mathrm{H_2O}}(T,V)}{V} &= \left(\frac{2\pi m_{\mathrm{H_2O}} k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A^{\mathrm{H_2O}}\Theta_B^{\mathrm{H_2O}}\Theta_C^{\mathrm{H_2O}}}\right)^{1/2} \\ &\qquad \times \prod_{j=1}^{3}(1-e^{-\Theta_{vj}^{\mathrm{H_2O}}/T})^{-1} e^{D_o^{\mathrm{H_2O}}/k_{\mathrm{B}}T} \\ &= 5.33\times 10^{35} e^{D_o^{\mathrm{H_2O}}/k_{\mathrm{B}}T}\ \mathrm{m}^{-3} \qquad (26.44)\end{aligned}$$

$$K_P = 5.18\times 10^{-5}\ \mathrm{Pa}^{-1} = 5.18\times 10^{5}\ \mathrm{bar}^{-1/2} \qquad (26.45)$$

$$\begin{aligned}q(V,T) &= \sum_j e^{-\varepsilon_j/k_{\mathrm{B}}T} = e^{-\varepsilon_0/k_{\mathrm{B}}T} + e^{-\varepsilon_1/k_{\mathrm{B}}T} + \cdots \\ &= e^{-\varepsilon_0/k_{\mathrm{B}}T}(1 + e^{-(\varepsilon_1-\varepsilon_0)/k_{\mathrm{B}}T} + \cdots) \\ &= e^{-\varepsilon_0/k_{\mathrm{B}}T} q^0(V,T) \qquad (26.46)\end{aligned}$$

$$\begin{aligned}U &= \langle E\rangle = Nk_{\mathrm{B}}T^2\left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= N\varepsilon_0 + Nk_{\mathrm{B}}T^2\left(\frac{\partial \ln q^0}{\partial T}\right)_V \qquad (26.47)\end{aligned}$$

$$\overline{H} = H^\circ(T) = H_0^\circ + RT^2\left(\frac{\partial \ln q^0}{\partial T}\right)_V + RT \qquad (26.48)$$

$$\mu^{\circ}(T) - E_0^{\circ} = -RT \ln \left\{ \left(\frac{q^0}{V} \right) \frac{RT}{N_{\mathrm{A}} P^{\circ}} \right\} \tag{26.49}$$

$$G^{\circ} - E_0^{\circ} = -RT \left\{ \left(\frac{q^0}{V} \right) \frac{RT}{N_{\mathrm{A}} P^{\circ}} \right\} \tag{26.50}$$

$$\mu(T, P) = \mu^{\circ}(T) + RT \ln \frac{f}{f^{\circ}} \tag{26.51}$$

$$\mu(T, P) = \mu^{\circ}(T) + RT \ln f \tag{26.52}$$

$$\mu_j(T, P) = \mu_j^{\circ}(T) + RT \ln f_j \tag{26.53}$$

$$\Delta_{\mathrm{r}} \overline{G} = \Delta_{\mathrm{r}} G^{\circ} + RT \ln \frac{f_{\mathrm{Y}}^{\nu_{\mathrm{Y}}} f_{\mathrm{Z}}^{\nu_{\mathrm{Z}}}}{f_{\mathrm{A}}^{\nu_{\mathrm{A}}} f_{\mathrm{B}}^{\nu_{\mathrm{B}}}} \tag{26.54}$$

$$\Delta_{\mathrm{r}} G^{\circ}(T) = -RT \ln K_f \tag{26.55}$$

$$K_f(T) = \left(\frac{f_{\mathrm{Y}}^{\nu_{\mathrm{Y}}} f_{\mathrm{Z}}^{\nu_{\mathrm{Z}}}}{f_{\mathrm{A}}^{\nu_{\mathrm{A}}} f_{\mathrm{B}}^{\nu_{\mathrm{B}}}} \right)_{\mathrm{eq}} \tag{26.56}$$

$$\mu_j = \mu_j^{\circ}(T) + RT \ln a_j \tag{26.57}$$

$$\Delta_{\mathrm{r}} \overline{G} = \Delta_{\mathrm{r}} G^{\circ} + RT \ln \frac{a_{\mathrm{Y}}^{\nu_{\mathrm{Y}}} a_{\mathrm{Z}}^{\nu_{\mathrm{Z}}}}{a_{\mathrm{A}}^{\nu_{\mathrm{A}}} a_{\mathrm{B}}^{\nu_{\mathrm{B}}}} \tag{26.58}$$

$$Q_a = \frac{a_{\mathrm{Y}}^{\nu_{\mathrm{Y}}} a_{\mathrm{Z}}^{\nu_{\mathrm{Z}}}}{a_{\mathrm{A}}^{\nu_{\mathrm{A}}} a_{\mathrm{B}}^{\nu_{\mathrm{B}}}} \tag{26.59}$$

$$\Delta_{\mathrm{r}} \overline{G} = \Delta_{\mathrm{r}} G^{\circ} + RT \ln Q_a \tag{26.60}$$

$$\Delta_{\mathrm{r}} G^{\circ} = -RT \ln Q_{a,\mathrm{eq}} \tag{26.61}$$

$$K_a = \left(\frac{a_{\mathrm{Y}}^{\nu_{\mathrm{Y}}} a_{\mathrm{Z}}^{\nu_{\mathrm{Z}}}}{a_{\mathrm{A}}^{\nu_{\mathrm{A}}} a_{\mathrm{B}}^{\nu_{\mathrm{B}}}} \right)_{\mathrm{eq}} \tag{26.62}$$

$$\Delta_{\mathrm{r}} G^{\circ} = -RT \ln K_a \tag{26.63}$$

$$\left(\frac{\partial\mu}{\partial P}\right)_T = \bar{V} \tag{26.64}$$

$$d\mu = RT d\ln a \qquad \text{(constant } T\text{)} \tag{26.65}$$

$$\ln a = \frac{1}{RT}\int_1^P \bar{V} dP' \qquad \text{(constant } T\text{)} \tag{26.66}$$

$$\ln a = \frac{\overline{V}}{RT}(P-1) \tag{26.67}$$

$$K_a = \frac{a_{\mathrm{H_3O^+}} a_{\mathrm{CH_3COO^-}}}{a_{\mathrm{CH_3COOH}} a_{\mathrm{H_2O}}} = \frac{a_{\mathrm{H_3O^+}} a_{\mathrm{CH_3COO^-}}}{a_{\mathrm{CH_3COOH}}} = 1.74 \times 10^{-5} \tag{26.68}$$

$$\frac{c_{\mathrm{H_3O^+}} c_{\mathrm{CH_3COO^-}}}{c_{\mathrm{CH_3COOH}}} = \frac{1.74 \times 10^{-5}}{\gamma_\pm^2} \tag{26.69}$$

$$c_{\mathrm{Ba^{2+}}} c_{\mathrm{F^-}}^2 = \frac{1.7 \times 10^{-6}\ \mathrm{mol^3 \cdot L^{-3}}}{\gamma_\pm^3} \tag{26.70}$$

Chapter 27

The Kinetic Theory of Gases

$$\frac{\Delta(mu_{1x})}{\Delta t} = \frac{2mu_{1x}}{2a/u_{1x}} = \frac{mu_{1x}^2}{a} \tag{27.1}$$

$$P_1 = \frac{F_1}{bc} = \frac{mu_{1x}^2}{abc} = \frac{mu_{1x}^2}{V} \tag{27.2}$$

$$P = \sum_{j=1}^{N} P_j = \sum_{j=1}^{N} \frac{mu_{jx}^2}{V} = \frac{m}{V}\sum_{j=1}^{N} u_{jx}^2 \tag{27.3}$$

$$\langle u_x^2 \rangle = \frac{1}{N}\sum_{j=1}^{N} u_{jx}^2 \tag{27.4}$$

$$PV = Nm\langle u_x^2 \rangle \tag{27.5}$$

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle \tag{27.6}$$

$$\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle \tag{27.7}$$

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle = \frac{1}{3}\langle u^2 \rangle \tag{27.8}$$

$$PV = \frac{1}{3}Nm\langle u^2 \rangle \tag{27.9}$$

$$\frac{1}{2}N_{\mathrm{A}}m\langle u^2 \rangle = \frac{3}{2}RT \tag{27.10}$$

$$\frac{1}{3}M\langle u^2\rangle = RT \tag{27.11}$$

$$\langle u^2\rangle = \frac{3RT}{M} \tag{27.12}$$

$$\langle u^2\rangle^{1/2} = \left(\frac{3RT}{M}\right)^{1/2} \tag{27.13}$$

$$u_{\mathrm{rms}} = \left(\frac{3RT}{M}\right)^{1/2} \tag{27.14}$$

$$u_{\mathrm{sound}} = \left(\frac{5RT}{3M}\right)^{1/2} \tag{27.15}$$

$$h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z) \tag{27.16}$$

$$\mathbf{u}\cdot\mathbf{u} = u^2 = u_x^2 + u_y^2 + u_z^2 \tag{27.17}$$

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z) \tag{27.18}$$

$$\ln h(u) = \ln f(u_x) + \ln f(u_y) + \ln f(u_z) \tag{27.19}$$

$$\left(\frac{\partial \ln h(u)}{\partial u_x}\right)_{u_y,u_z} = \frac{d\ln f(u_x)}{du_x} \tag{27.20}$$

$$\left(\frac{\partial \ln h}{\partial u_x}\right)_{u_y,u_z} = \frac{d\ln h}{du}\left(\frac{\partial u}{\partial u_x}\right)_{u_y,u_z} = \frac{u_x}{u}\frac{d\ln h}{du} \tag{27.21}$$

$$\frac{d\ln h(u)}{udu} = \frac{d\ln f(u_x)}{u_x du_x} = \frac{d\ln f(u_y)}{u_y du_y} = \frac{d\ln f(u_z)}{u_z du_z} \tag{27.22}$$

$$\frac{d\ln f(u_j)}{u_j du_j} = -\gamma \qquad j = x, y, z \tag{27.23}$$

$$f(u_j) = Ae^{-\gamma u_j^2} \qquad j = x, y, z \tag{27.24}$$

$$\int_{-\infty}^{\infty} f(u_x)du_x = 1 \tag{27.25}$$

$$A\int_{-\infty}^{\infty} e^{-\gamma u_x^2} du_x = 1 \tag{27.26}$$

$$A\int_{-\infty}^{\infty} e^{-\gamma u_x^2} du_x = 2A\int_{0}^{\infty} e^{-\gamma u_x^2} du_x \tag{27.27}$$

$$A\int_{-\infty}^{\infty} e^{-\gamma u_x^2} du_x = 2A\int_{0}^{\infty} e^{-\gamma u_x^2} du_x = 2A\left(\frac{\pi}{4\gamma}\right)^{1/2} = 1 \tag{27.28}$$

$$f(u_x) = \left(\frac{\gamma}{\pi}\right)^{1/2} e^{-\gamma u_x^2} \tag{27.29}$$

$$\langle u_x^2 \rangle = \frac{RT}{M} = \int_{-\infty}^{\infty} u_x^2 f(u_x) du_x = \left(\frac{\gamma}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} u_x^2 e^{-\gamma u_x^2} du_x \tag{27.30}$$

$$\langle u_x^2 \rangle = \frac{RT}{M} = 2\int_{0}^{\infty} u_x^2 f(u_x) du_x = 2\left(\frac{\gamma}{\pi}\right)^{1/2} \int_{0}^{\infty} u_x^2 e^{-\gamma u_x^2} du_x \tag{27.31}$$

$$f(u_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-Mu_x^2/2RT} \tag{27.32}$$

$$f(u_x) = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{1/2} e^{-mu_x^2/2k_{\mathrm{B}}T} \tag{27.33}$$

$$\langle u_x \rangle = \int_{-\infty}^{\infty} u_x f(u_x) du_x = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{1/2} \int_{-\infty}^{\infty} u_x e^{-mu_x^2/2k_{\mathrm{B}}T} du_x \tag{27.34}$$

$$\frac{1}{2}m\langle u_x^2 \rangle = \frac{1}{2}k_{\mathrm{B}}T \tag{27.35}$$

$$\nu \approx \nu_o\left(1 + \frac{u_x}{c}\right) \tag{27.36}$$

$$I(\nu) \propto e^{-mc^2(\nu-\nu_o)^2/2\nu_o^2 k_{\mathrm{B}}T} \tag{27.37}$$

$$F(u)du = f(u_x)du_x f(u_y)du_y f(u_z)du_z \tag{27.38}$$

$$F(u)du = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} e^{-m(u_x^2+u_y^2+u_z^2)/2k_{\mathrm{B}}T} du_x du_y du_z \tag{27.39}$$

$$F(u)du = 4\pi \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} u^2 e^{-mu^2/2k_{\mathrm{B}}T} du \tag{27.40}$$

$$\langle u \rangle = \int_0^\infty uF(u)du = 4\pi \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} \int_0^\infty u^3 e^{-mu^2/2k_{\mathrm{B}}T} du \tag{27.41}$$

$$\langle u \rangle = 4\pi \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} \cdot \frac{1!}{2} \left(\frac{2k_{\mathrm{B}}T}{m}\right)^2 = \left(\frac{8k_{\mathrm{B}}T}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{27.42}$$

$$u_{\mathrm{mp}} = \left(\frac{2k_{\mathrm{B}}T}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2} \tag{27.43}$$

$$\begin{aligned} F(\epsilon)d\epsilon &= 4\pi \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} \cdot \frac{2\epsilon}{m} \cdot e^{-\epsilon/k_{\mathrm{B}}T} \frac{d\epsilon}{(2m\epsilon)^{1/2}} \\ &= \frac{2\pi}{(\pi k_{\mathrm{B}}T)^{3/2}} \epsilon^{1/2} e^{-\epsilon/k_{\mathrm{B}}T} d\epsilon \end{aligned} \tag{27.44}$$

$$dN = \rho(Audt)\cos\theta \cdot F(u)du \cdot \frac{\sin\theta d\theta d\phi}{4\pi} \tag{27.45}$$

$$dz_{\mathrm{coll}} = \rho \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} u^3 e^{-mu^2/2k_{\mathrm{B}}T} du \cdot \cos\theta \sin\theta d\theta d\phi \tag{27.46}$$

$$z_{\mathrm{coll}} = \frac{\rho}{4\pi} \int_0^\infty uF(u)du \int_0^{\pi/2} \cos\theta \sin\theta d\theta \int_0^{2\pi} d\phi \tag{27.47}$$

$$z_{\mathrm{coll}} = \frac{1}{A}\frac{dN}{dt} = \rho \frac{\langle u \rangle}{4} \tag{27.48}$$

$$z_{\mathrm{A}} = \frac{dN}{dt} = \rho\sigma\langle u \rangle = \rho\sigma \left(\frac{8k_{\mathrm{B}}T}{\pi m}\right)^{1/2} \tag{27.49}$$

$$z_{\mathrm{A}} = \rho\sigma\langle u_{\mathrm{r}}\rangle = 2^{1/2}\rho\sigma\langle u\rangle \tag{27.50}$$

$$l = \frac{RT}{2^{1/2}N_{\mathrm{A}}\sigma P} \tag{27.51}$$

$$\text{probability of a collision} = \sigma\rho dx \tag{27.52}$$

$$n(x) = n_o e^{-\sigma\rho x} \tag{27.53}$$

$$n(x) = n_o e^{-x/l} \tag{27.54}$$

$$\begin{aligned} p(x)dx &= \frac{n(x) - n(x+dx)}{n_o} = -\frac{1}{n_o}\frac{dn}{dx}dx \\ &= \frac{1}{l}e^{-x/l}dx \end{aligned} \tag{27.55}$$

$$Z_{\mathrm{AA}} = \frac{1}{2}\rho z_{\mathrm{A}} = \frac{1}{2}\sigma\langle u_{\mathrm{r}}\rangle\rho^2 = \frac{\sigma\langle u\rangle}{2^{1/2}}\rho^2 \tag{27.56}$$

$$Z_{\mathrm{AB}} = \sigma_{\mathrm{AB}}\langle u_{\mathrm{r}}\rangle\rho_{\mathrm{A}}\rho_{\mathrm{B}} \tag{27.57}$$

$$\sigma_{\mathrm{AB}} = \frac{1}{2}(\sigma_{\mathrm{A}} + \sigma_{\mathrm{B}}) \qquad \text{and} \qquad \langle u_{\mathrm{r}}\rangle = (8k_{\mathrm{B}}T/\pi\mu)^{1/2} \tag{27.58}$$

$$\begin{aligned} dZ_{\mathrm{AB}} &\propto u_r^3 e^{-\mu u_r^2/2k_{\mathrm{B}}T} du_r \\ &= A u_r^3 e^{-\mu u_r^2/2k_{\mathrm{B}}T} \end{aligned} \tag{27.59}$$

$$\begin{aligned} \sigma_{\mathrm{AB}}\rho_{\mathrm{A}}\rho_{\mathrm{B}}\left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2} &= A\int_0^\infty u_r^3 e^{-\mu u_r^2/2k_{\mathrm{B}}T} du_r \\ &= 2A\left(\frac{k_{\mathrm{B}}T}{\mu}\right)^2 \end{aligned} \tag{27.60}$$

$$dZ_{\mathrm{AB}} = \sigma_{\mathrm{AB}}\rho_{\mathrm{A}}\rho_{\mathrm{B}}\left(\frac{\mu}{k_{\mathrm{B}}T}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} e^{-\mu u_r^2/2k_{\mathrm{B}}T} u_r^3 du_r \tag{27.61}$$

$$dZ_{\mathrm{AB}} = \sigma_{\mathrm{AB}}\rho_{\mathrm{A}}\rho_{\mathrm{B}}\left(\frac{8}{\pi\mu}\right)^{1/2}\left(\frac{1}{k_{\mathrm{B}}T}\right)^{3/2} \epsilon_r e^{-\epsilon_r/k_{\mathrm{B}}T} d\epsilon_r \tag{27.62}$$

$$Z_{\mathrm{AB}}(\epsilon_r > \epsilon_c) = \sigma_{\mathrm{AB}}\rho_{\mathrm{A}}\rho_{\mathrm{B}}\left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2}\left(1 + \frac{\epsilon_c}{k_{\mathrm{B}}T}\right) e^{-\epsilon_c/k_{\mathrm{B}}T} \tag{27.63}$$

Chapter 28

Chemical Kinetics I: Rate Laws

$$\nu_A A + \nu_B B \longrightarrow \nu_Y Y + \nu_Z Z \tag{28.1}$$

$$\begin{aligned} dn_A &= -\nu_A d\xi & dn_B &= -\nu_B d\xi \\ dn_Y &= \nu_Y d\xi & dn_Z &= \nu_Z d\xi \end{aligned} \tag{28.2}$$

$$\begin{aligned} n_A(t) &= n_A(0) - \nu_A \xi(t) & n_B(t) &= n_B(0) - \nu_B \xi(t) \\ n_Y(t) &= n_Y(0) + \nu_Y \xi(t) & n_Z(t) &= n_Z(0) + \nu_Z \xi(t) \end{aligned} \tag{28.3}$$

$$\begin{aligned} \frac{dn_A(t)}{dt} &= -\nu_A \frac{d\xi(t)}{dt} & \frac{dn_B(t)}{dt} &= -\nu_B \frac{d\xi(t)}{dt} \\ \frac{dn_Y(t)}{dt} &= \nu_Y \frac{d\xi(t)}{dt} & \frac{dn_Z(t)}{dt} &= \nu_Z \frac{d\xi(t)}{dt} \end{aligned} \tag{28.4}$$

$$\begin{aligned} \frac{1}{V}\frac{dn_A(t)}{dt} &= \frac{d[A]}{dt} = -\frac{\nu_A}{V}\frac{d\xi(t)}{dt} & \frac{1}{V}\frac{dn_B(t)}{dt} &= \frac{d[B]}{dt} = -\frac{\nu_B}{V}\frac{d\xi(t)}{dt} \\ \frac{1}{V}\frac{dn_Y(t)}{dt} &= \frac{d[Y]}{dt} = \frac{\nu_Y}{V}\frac{d\xi(t)}{dt} & \frac{1}{V}\frac{dn_Z(t)}{dt} &= \frac{d[Z]}{dt} = \frac{\nu_Z}{V}\frac{d\xi(t)}{dt} \end{aligned} \tag{28.5}$$

$$v(t) = -\frac{1}{\nu_A}\frac{d[A]}{dt} = -\frac{1}{\nu_B}\frac{d[B]}{dt} = \frac{1}{\nu_Y}\frac{d[Y]}{dt} = \frac{1}{\nu_Z}\frac{d[Z]}{dt} = \frac{1}{V}\frac{d\xi}{dt} \tag{28.6}$$

$$v(t) = k[\mathrm{NO}]^2[\mathrm{O_2}] \tag{28.7}$$

$$v(t) = k[\mathrm{A}]^{m_\mathrm{A}}[\mathrm{B}]^{m_\mathrm{B}}\cdots \tag{28.8}$$

$$\mathrm{H_2(g)} + \mathrm{Br_2(g)} \xrightarrow{k} 2\,\mathrm{HBr(g)} \tag{28.9}$$

$$v(t) = \frac{k'[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k''[\mathrm{HBr}][\mathrm{Br_2}]^{-1}} \tag{28.10}$$

$$\nu_\mathrm{A}\,\mathrm{A} + \nu_\mathrm{B}\,\mathrm{B} \xrightarrow{k} \nu_\mathrm{Y}\,\mathrm{Y} + \nu_\mathrm{Z}\,\mathrm{Z} \tag{28.11}$$

$$v = k[\mathrm{A}]^{m_\mathrm{A}}[\mathrm{B}]^{m_\mathrm{B}} \tag{28.12}$$

$$v = k'[\mathrm{B}]^{m_\mathrm{B}} \tag{28.13}$$

$$v = k''[\mathrm{A}]^{m_\mathrm{A}} \tag{28.14}$$

$$v = -\frac{d[\mathrm{A}]}{\nu_\mathrm{A}dt} \approx -\frac{\Delta[\mathrm{A}]}{\nu_\mathrm{A}\Delta t} = k[\mathrm{A}]^{m_\mathrm{A}}[\mathrm{B}]^{m_\mathrm{B}} \tag{28.15}$$

$$v_1 = -\frac{1}{\nu_\mathrm{A}}\left(\frac{\Delta[\mathrm{A}]}{\Delta t}\right)_1 = k[\mathrm{A}]^{m_\mathrm{A}}[\mathrm{B}]_1^{m_\mathrm{B}} \tag{28.16}$$

$$v_2 = -\frac{1}{\nu_\mathrm{A}}\left(\frac{\Delta[\mathrm{A}]}{\Delta t}\right)_2 = k[\mathrm{A}]^{m_\mathrm{A}}[\mathrm{B}]_2^{m_\mathrm{B}} \tag{28.17}$$

$$m_\mathrm{B} = \frac{\ln\dfrac{v_1}{v_2}}{\ln\dfrac{[\mathrm{B}]_1}{[\mathrm{B}]_2}} \tag{28.18}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \text{products} \tag{28.19}$$

$$v(t) = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}] \tag{28.20}$$

$$\ln \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt \tag{28.21}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-kt} \tag{28.22}$$

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt \tag{28.23}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \tag{28.24}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \text{products} \tag{28.25}$$

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2 \tag{28.26}$$

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt \tag{28.27}$$

$$t_{1/2} = \frac{1}{k[\mathrm{A}]_0} \tag{28.28}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \text{products} \tag{28.29}$$

$$-\frac{d[\mathrm{A}]}{dt} = -\frac{d[\mathrm{B}]}{dt} = k[\mathrm{A}][\mathrm{B}] \tag{28.30}$$

$$kt = \frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \ln \frac{[\mathrm{A}][\mathrm{B}]_0}{[\mathrm{B}][\mathrm{A}]_0} \tag{28.31}$$

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt \quad \text{or} \quad \frac{1}{[\mathrm{B}]} = \frac{1}{[\mathrm{B}]_0} + kt \tag{28.32}$$

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{kt[\mathrm{A}]_0 + 1} \tag{28.33}$$

$$\frac{t}{P} = \frac{nt}{2} + \frac{1}{k[\mathrm{A}]_0^{n-1}} \tag{28.34}$$

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{28.35}$$

$$-\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{B}]}{dt} = 0 \tag{28.36}$$

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] \tag{28.37}$$

$$-\frac{d[\mathrm{A}]}{dt} = (k_1 + k_{-1})[\mathrm{A}] - k_{-1}[\mathrm{A}]_0 \tag{28.38}$$

$$[\mathrm{A}] = ([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}})e^{-(k_1+k_{-1})t} + [\mathrm{A}]_{\mathrm{eq}} \tag{28.39}$$

$$\ln([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}) = \ln([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}) - (k_1 + k_{-1})t \tag{28.40}$$

$$\frac{k_1}{k_{-1}} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_c \tag{28.41}$$

$$\mathrm{H}^+(\mathrm{aq}) + \mathrm{OH}^-(\mathrm{aq}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{H_2O(l)} \tag{28.42}$$

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{28.43}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] \tag{28.44}$$

$$\begin{aligned} [\mathrm{A}] &= [\mathrm{A}]_{\mathrm{eq}} + \Delta[\mathrm{A}] \\ [\mathrm{B}] &= [\mathrm{B}]_{\mathrm{eq}} + \Delta[\mathrm{B}] \end{aligned} \tag{28.45}$$

$$\frac{d\Delta[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_{\mathrm{eq}} + k_1\Delta[\mathrm{A}] - k_{-1}[\mathrm{B}]_{\mathrm{eq}} - k_{-1}\Delta[\mathrm{B}] \tag{28.46}$$

$$\frac{d\Delta[\mathrm{B}]}{dt} = -(k_1 + k_{-1})\Delta[\mathrm{B}] \tag{28.47}$$

$$\Delta[\mathrm{B}] = \Delta[\mathrm{B}]_0 e^{-(k_1+k_{-1})t} = \Delta[\mathrm{B}]_0 e^{-t/\tau} \tag{28.48}$$

$$\tau = \frac{1}{k_1 + k_{-1}} \tag{28.49}$$

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{P} \tag{28.50}$$

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{A}][\mathrm{B}] - k_{-1}[\mathrm{P}] \tag{28.51}$$

$$\Delta[\mathrm{P}] = \Delta[\mathrm{P}]_0 e^{-t/\tau} \tag{28.52}$$

$$\tau = \frac{1}{k_1([\mathrm{A}]_{2,\mathrm{eq}} + [\mathrm{B}]_{2,\mathrm{eq}}) + k_{-1}} \tag{28.53}$$

$$\frac{d\ln k}{dT} = \frac{E_\mathrm{a}}{RT^2} \tag{28.54}$$

$$\ln k = \ln A - \frac{E_\mathrm{a}}{RT} \tag{28.55}$$

$$k = Ae^{-E_\mathrm{a}/RT} \tag{28.56}$$

$$k = aT^m e^{-E'/RT} \tag{28.57}$$

$$E_\mathrm{a} = RT^2 \frac{d\ln k}{dT} \tag{28.58}$$

$$\frac{dP}{dt} = k[\mathrm{A}][\mathrm{B}] \tag{28.59}$$

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}^\ddagger \longrightarrow \mathrm{P} \tag{28.60}$$

$$K_c^\ddagger = \frac{[\mathrm{AB}^\ddagger]/c^\circ}{[\mathrm{A}]/c^\circ[\mathrm{B}]/c^\circ} = \frac{[\mathrm{AB}^\ddagger]c^\circ}{[\mathrm{A}][\mathrm{B}]} \tag{28.61}$$

$$K_c^{\ddagger} = \frac{(q^{\ddagger}/V)c^{\circ}}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)} \tag{28.62}$$

$$\frac{dP}{dt} = \nu_{\mathrm{c}}[\mathrm{AB}^{\ddagger}] \tag{28.63}$$

$$k = \frac{\nu_{\mathrm{c}} K_c^{\ddagger}}{c^{\circ}} \tag{28.64}$$

$$q_{\mathrm{trans}} = \frac{(2\pi m^{\ddagger} k_{\mathrm{B}} T)^{1/2}}{h}\delta \tag{28.65}$$

$$K_c^{\ddagger} = \frac{(2\pi m^{\ddagger} k_{\mathrm{B}} T)^{1/2}}{h}\delta \frac{(q_{\mathrm{int}}^{\ddagger}/V)c^{\circ}}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)} \tag{28.66}$$

$$k = \nu_{\mathrm{c}} \frac{(2\pi m^{\ddagger} k_{\mathrm{B}} T)^{1/2}}{hc^{\circ}}\delta \frac{(q_{\mathrm{int}}^{\ddagger}/V)c^{\circ}}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)} \tag{28.67}$$

$$\langle u_{\mathrm{ac}} \rangle = \int_0^{\infty} u f(u) du = \left(\frac{m^{\ddagger}}{2\pi k_{\mathrm{B}} T}\right)^{1/2} \int_0^{\infty} u e^{-m^{\ddagger} u^2 / 2 k_{\mathrm{B}} T} du = \left(\frac{k_{\mathrm{B}} T}{2\pi m^{\ddagger}}\right)^{1/2} \tag{28.68}$$

$$k = \frac{k_{\mathrm{B}} T}{hc^{\circ}} \frac{(q_{\mathrm{int}}^{\ddagger}/V)c^{\circ}}{(q_{\mathrm{A}}/V)(q_{\mathrm{B}}/V)} = \frac{k_{\mathrm{B}} T}{hc^{\circ}} K_c^{\ddagger} \tag{28.69}$$

$$\Delta^{\ddagger} G^{\circ} = -RT \ln K_c^{\ddagger} \tag{28.70}$$

$$k(T) = \frac{k_{\mathrm{B}} T}{hc^{\circ}} e^{-\Delta^{\ddagger} G^{\circ}/RT} \tag{28.71}$$

$$\Delta^{\ddagger} G^{\circ} = \Delta^{\ddagger} H^{\circ} - T\Delta^{\ddagger} S^{\circ} \tag{28.72}$$

$$k(T) = \frac{k_{\mathrm{B}} T}{hc^{\circ}} e^{\Delta^{\ddagger} S^{\circ}/R} e^{-\Delta^{\ddagger} H^{\circ}/RT} \tag{28.73}$$

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_c^{\ddagger}}{dT} \tag{28.74}$$

$$\frac{d\ln k}{dT} = \frac{1}{T} + \frac{\Delta^{\ddagger}U^{\circ}}{RT^{2}} \tag{28.75}$$

$$\frac{d\ln k}{dT} = \frac{\Delta^{\ddagger}H^{\circ} + 2RT}{RT^{2}} \tag{28.76}$$

$$E_{\mathrm{a}} = \Delta^{\ddagger}H^{\circ} + 2RT \tag{28.77}$$

$$k(T) = \frac{e^{2}k_{\mathrm{B}}T}{hc^{\circ}}e^{\Delta^{\ddagger}S^{\circ}/R}e^{-E_{\mathrm{a}}/RT} \tag{28.78}$$

$$A = \frac{e^{2}k_{\mathrm{B}}T}{hc^{\circ}}e^{\Delta^{\ddagger}S^{\circ}/R} \tag{28.79}$$

Chapter 29

Chemical Kinetics II: Reaction Mechanisms

$$NO_2(g) + CO(g) \xrightarrow{k_{obs}} NO(g) + CO_2(g) \tag{29.1}$$

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g) \tag{29.2}$$

$$NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g) \tag{29.3}$$

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D \tag{29.4}$$

$$k_1[A]_{eq}[B]_{eq} = k_{-1}[C]_{eq}[D]_{eq} \tag{29.5}$$

$$\frac{k_1}{k_{-1}} = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}} = K_c \tag{29.6}$$

$$A \rightleftharpoons B \tag{29.7}$$

$$A + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + C \tag{29.8}$$

$$A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B \tag{29.9}$$

$$v_1 = k_1[\mathrm{A}]_{\mathrm{eq}}[\mathrm{C}]_{\mathrm{eq}} = v_{-1} = k_{-1}[\mathrm{B}]_{\mathrm{eq}}[\mathrm{C}]_{\mathrm{eq}} \tag{29.10}$$

$$v_2 = k_2[\mathrm{A}]_{\mathrm{eq}} = v_{-2} = k_{-2}[\mathrm{B}]_{\mathrm{eq}} \tag{29.11}$$

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_c = \frac{k_1}{k_{-1}} \tag{29.12}$$

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_c = \frac{k_2}{k_{-2}} \tag{29.13}$$

$$\frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}} \tag{29.14}$$

$$v_1 + v_2 = v_{-1} + v_{-2} \tag{29.15}$$

$$\mathrm{OClO(g)} \rightleftharpoons \mathrm{Cl(g)} + \mathrm{O_2(g)} \tag{29.16}$$

$$\begin{gathered}\mathrm{OClO(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ClOO(g)} \\ \mathrm{ClOO(g)} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Cl(g)} + \mathrm{O_2(g)}\end{gathered} \tag{29.17}$$

$$\mathrm{A} \xrightarrow{k_{\mathrm{obs}}} \mathrm{P} \tag{29.18}$$

$$\mathrm{A} \overset{k_1}{\Longrightarrow} \mathrm{I} \tag{29.19}$$

$$\mathrm{I} \overset{k_2}{\Longrightarrow} \mathrm{P} \tag{29.20}$$

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] \tag{29.21}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{I}] \tag{29.22}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{29.23}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t} \tag{29.24}$$

$$[\mathrm{I}] = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{29.25}$$

$$[\mathrm{P}] = [\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{I}] = [\mathrm{A}]_0 \left\{ 1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\} \tag{29.26}$$

$$[\mathrm{P}] = [\mathrm{A}]_0(1 - e^{-k_1 t}) \tag{29.27}$$

$$\mathrm{A} \xRightarrow{k_1} \mathrm{I} \xRightarrow{k_2} \mathrm{P} \tag{29.28}$$

$$[\mathrm{I}]_{\mathrm{ss}} = \frac{k_1[\mathrm{A}]}{k_2} \tag{29.29}$$

$$[\mathrm{I}] = \frac{k_1}{k_2}[\mathrm{A}]_0 e^{-k_1 t} \tag{29.30}$$

$$\frac{d[\mathrm{I}]_{\mathrm{ss}}}{dt} = -\frac{k_1^2}{k_2}[\mathrm{A}]_0 e^{-k_1 t} \tag{29.31}$$

$$[\mathrm{P}] = [\mathrm{A}]_0(1 - e^{-k_1 t}) \tag{29.32}$$

$$2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \xrightarrow{k_{\mathrm{obs}}} 2\,\mathrm{NO_2(g)} \tag{29.33}$$

$$\frac{1}{2}\frac{d[\mathrm{NO_2}]}{dt} = k_{\mathrm{obs}}[\mathrm{NO}]^2[\mathrm{O_2}] \tag{29.34}$$

$$\mathrm{NO(g)} + \mathrm{O_2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO_3(g)} \qquad \text{fast equilibrium} \tag{29.35}$$

$$\mathrm{NO_3(g)} + \mathrm{NO(g)} \xRightarrow{k_2} 2\,\mathrm{NO_2(g)} \qquad \text{rate determining} \tag{29.36}$$

$$K_{c,1} = \frac{k_1}{k_{-1}} = \frac{[\mathrm{NO_3}]}{[\mathrm{NO}][\mathrm{O_2}]} \tag{29.37}$$

$$\frac{1}{2}\frac{d[NO_2]}{dt} = k_2[NO_3][NO] \tag{29.38}$$

$$\frac{1}{2}\frac{d[NO_2]}{dt} = k_2 K_{c,1}[NO]^2[O_2] \tag{29.39}$$

$$NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g) \quad N_2O_2(g) \text{ is in steady state} \tag{29.40}$$

$$N_2O_2(g) + O_2(g) \xrightarrow{k_2} 2\,NO_2(g) \tag{29.41}$$

$$\frac{1}{2}\frac{d[NO]}{dt} = -k_1[NO]^2 + k_{-1}[N_2O_2] \tag{29.42}$$

$$\frac{d[N_2O_2]}{dt} = -k_{-1}[N_2O_2] - k_2[N_2O_2][O_2] + k_1[NO]^2 \tag{29.43}$$

$$\frac{1}{2}\frac{d[NO_2]}{dt} = k_2[N_2O_2][O_2] \tag{29.44}$$

$$[N_2O_2] = \frac{k_1[NO]^2}{k_{-1} + k_2[O_2]} \tag{29.45}$$

$$\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{k_2 k_1}{k_{-1}}[NO]^2[O_2] = k_2 K_{c,1}[NO]^2[O_2] \tag{29.46}$$

$$CH_3NC(g) \xrightarrow{k_{\text{obs}}} CH_3CN(g) \tag{29.47}$$

$$\frac{d[CH_3NC]}{dt} = -k_{\text{obs}}[CH_3NC] \tag{29.48}$$

$$\frac{d[CH_3NC]}{dt} = -k'_{\text{obs}}[CH_3NC]^2 \tag{29.49}$$

$$A(g) + M(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A(g)^* + M(g) \tag{29.50}$$

$$A(g)^* \xrightarrow{k_2} B(g) \tag{29.51}$$

$$\frac{d[\mathrm{B}]}{dt} = k_2[\mathrm{A}^*] \tag{29.52}$$

$$\frac{d[\mathrm{A}^*]}{dt} = 0 = k_1[\mathrm{A}][\mathrm{M}] - k_{-1}[\mathrm{A}^*][\mathrm{M}] - k_2[\mathrm{A}^*] \tag{29.53}$$

$$[\mathrm{A}^*] = \frac{k_1[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{29.54}$$

$$\frac{d[\mathrm{B}]}{dt} = -\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} = k_{\mathrm{obs}}[\mathrm{A}] \tag{29.55}$$

$$k_{\mathrm{obs}} = \frac{k_1 k_2[\mathrm{M}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{29.56}$$

$$k_{\mathrm{obs}} = \frac{k_1 k_2}{k_{-1}} \tag{29.57}$$

$$k_{\mathrm{obs}} = k_1[\mathrm{M}] \tag{29.58}$$

$$\mathrm{H_2(g)} + \mathrm{Br_2} \rightleftharpoons 2\,\mathrm{HBr(g)} \tag{29.59}$$

$$\frac{1}{2}\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k'[\mathrm{HBr}][\mathrm{Br_2}]^{-1}} \tag{29.60}$$

$$\frac{d[\mathrm{HBr}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br_2}] \tag{29.61}$$

$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{Br_2}] \tag{29.62}$$

$$\frac{d[\mathrm{Br}]}{dt} = 2k_1[\mathrm{Br_2}][\mathrm{M}] - 2k_{-1}[\mathrm{Br}]^2[\mathrm{M}] - k_2[\mathrm{Br}][\mathrm{H_2}] + k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br_2}] \tag{29.63}$$

$$\frac{d[\mathrm{H}]}{dt} = 0 = k_2[\mathrm{Br}][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{Br_2}] \tag{29.64}$$

$$\frac{d[\mathrm{Br}]}{dt} = 0 = 2k_1[\mathrm{Br_2}][\mathrm{M}] - 2k_{-1}[\mathrm{Br}]^2[\mathrm{M}] - k_2[\mathrm{Br}][\mathrm{H_2}] + k_{-2}[\mathrm{HBr}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{Br_2}] \tag{29.65}$$

$$[\mathrm{Br}] = \sqrt{\frac{k_1}{k_{-1}}}[\mathrm{Br}_2]^{1/2} = \sqrt{K_{c,1}}[\mathrm{Br}_2]^{1/2} \tag{29.66}$$

$$[\mathrm{H}] = \frac{k_2\sqrt{K_{c,1}}[\mathrm{H}_2][\mathrm{Br}_2]^{1/2}}{k_2[\mathrm{HBr}] + k_{-3}[\mathrm{Br}_2]} \tag{29.67}$$

$$\frac{1}{2}\frac{d[\mathrm{HBr}]}{dt} = \frac{k_2\sqrt{K_{c,1}}[\mathrm{H}_2][\mathrm{Br}_2]^{1/2}}{1 + (k_{-2}/k_3)[\mathrm{HBr}][\mathrm{Br}_2]^{-1}} \tag{29.68}$$

$$-\frac{d[\mathrm{S}]}{dt} = \frac{k[\mathrm{S}]}{K + [\mathrm{S}]} \tag{29.69}$$

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{E} + \mathrm{P} \tag{29.70}$$

$$-\frac{d[\mathrm{S}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] \tag{29.71}$$

$$-\frac{d[\mathrm{ES}]}{dt} = (k_2 + k_{-1})[\mathrm{ES}] - k_1[\mathrm{E}][\mathrm{S}] - k_{-2}[\mathrm{E}][\mathrm{P}] \tag{29.72}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] - k_{-2}[\mathrm{E}][\mathrm{P}] \tag{29.73}$$

$$[\mathrm{E}]_0 = [\mathrm{ES}] + [\mathrm{E}] \tag{29.74}$$

$$-\frac{d[\mathrm{ES}]}{dt} = [\mathrm{ES}](k_1[\mathrm{S}] + k_{-1} + k_2 + k_{-2}[\mathrm{P}]) - k_1[\mathrm{S}][\mathrm{E}]_0 - k_{-2}[\mathrm{P}][\mathrm{E}]_0 \tag{29.75}$$

$$[\mathrm{ES}] = \frac{k_1[\mathrm{S}] + k_{-2}[\mathrm{P}]}{k_1[\mathrm{S}] + k_{-2}[\mathrm{P}] + k_{-1} + k_2}[\mathrm{E}]_0 \tag{29.76}$$

$$v = -\frac{d[\mathrm{S}]}{dt} = \frac{k_1k_2[\mathrm{S}] - k_{-1}k_{-2}[\mathrm{P}]}{k_1[\mathrm{S}] + k_{-2}[\mathrm{P}] + k_{-1} + k_2}[\mathrm{E}]_0 \tag{29.77}$$

$$v = -\frac{d[\mathrm{S}]}{dt} = \frac{k_1k_2[\mathrm{S}]_0[\mathrm{E}]_0}{k_1[\mathrm{S}]_0 + k_{-1} + k_2} = \frac{k_2[\mathrm{S}]_0[\mathrm{E}]_0}{K_m + [\mathrm{S}]_0} \tag{29.78}$$

$$-\frac{d[\mathrm{S}]}{dt} = k_2[\mathrm{E}]_0 \tag{29.79}$$

Chapter 30

Gas-Phase Reaction Dynamics

$$\mathrm{A} + \mathrm{B} \overset{k}{\Longrightarrow} \text{products} \tag{30.1}$$

$$v = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}] \tag{30.2}$$

$$v = Z_{\mathrm{AB}} = \sigma\langle u_{\mathrm{r}}\rangle \rho_{\mathrm{A}}\rho_{\mathrm{B}} \tag{30.3}$$

$$k = \sigma\langle u_{\mathrm{r}}\rangle \tag{30.4}$$

$$k = (1000\ \mathrm{dm}^3{\cdot}\mathrm{m}^{-3})N_{\mathrm{A}}\sigma\langle u_{\mathrm{r}}\rangle \tag{30.5}$$

$$k(u_{\mathrm{r}}) = u_{\mathrm{r}}\sigma_{\mathrm{r}}(u_{\mathrm{r}}) \tag{30.6}$$

$$k = \int_0^\infty du_{\mathrm{r}} f(u_{\mathrm{r}})k(u_{\mathrm{r}}) = \int_0^\infty du_{\mathrm{r}} u_{\mathrm{r}} f(u_{\mathrm{r}})\sigma_{\mathrm{r}}(u_{\mathrm{r}}) \tag{30.7}$$

$$u_{\mathrm{r}} f(u_{\mathrm{r}})du_{\mathrm{r}} = \left(\frac{\mu}{k_{\mathrm{B}}T}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} u_{\mathrm{r}}^3 e^{-\mu u_{\mathrm{r}}^2/2k_{\mathrm{B}}T} du_{\mathrm{r}} \tag{30.8}$$

$$u_{\mathrm{r}} = \left(\frac{2E_{\mathrm{r}}}{\mu}\right)^{1/2} \quad \text{and} \quad du_{\mathrm{r}} = \left(\frac{1}{2\mu E_{\mathrm{r}}}\right)^{1/2} dE_{\mathrm{r}} \tag{30.9}$$

$$u_\mathrm{r} f(u_\mathrm{r}) du_\mathrm{r} = \left(\frac{2}{k_\mathrm{B}T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} E_\mathrm{r} e^{-E_\mathrm{r}/k_\mathrm{B}T} dE_\mathrm{r} \tag{30.10}$$

$$k = \left(\frac{2}{k_\mathrm{B}T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} \int_0^\infty dE_\mathrm{r} E_\mathrm{r} e^{-E_\mathrm{r}/k_\mathrm{B}T} \sigma_\mathrm{r}(E_\mathrm{r}) \tag{30.11}$$

$$\sigma_\mathrm{r}(E_\mathrm{r}) = \begin{cases} 0 & E_\mathrm{r} < E_0 \\ \pi d_\mathrm{AB}^2 & E_\mathrm{r} \geq E_0 \end{cases} \tag{30.12}$$

$$\begin{aligned} k &= \left(\frac{2}{k_\mathrm{B}T}\right)^{3/2} \left(\frac{1}{\mu\pi}\right)^{1/2} \int_{E_0}^\infty dE_\mathrm{r} E_\mathrm{r} e^{-E_\mathrm{r}/k_\mathrm{B}T} \pi d_\mathrm{AB}^2 \\ &= \left(\frac{8k_\mathrm{B}T}{\mu\pi}\right)^{1/2} \pi d_\mathrm{AB}^2 e^{-E_0/k_\mathrm{B}T} \left(1 + \frac{E_0}{k_\mathrm{B}T}\right) \\ &= \langle u_\mathrm{r} \rangle \sigma e^{-E_0/k_\mathrm{B}T} \left(1 + \frac{E_0}{k_\mathrm{B}T}\right) \end{aligned} \tag{30.13}$$

$$\sigma_\mathrm{r}(E_\mathrm{r}) = \begin{cases} 0 & E_\mathrm{r} < E_0 \\ \pi d_\mathrm{AB}^2 \left(1 - \frac{E_0}{E_\mathrm{r}}\right) & E_\mathrm{r} \geq E_0 \end{cases} \tag{30.14}$$

$$k = \left(\frac{8k_\mathrm{AB}T}{\mu\pi}\right)^{1/2} \pi d_\mathrm{AB}^2 e^{-E_0/k_\mathrm{B}T} = \langle u_\mathrm{r} \rangle \sigma e^{-E_0/k_\mathrm{B}T} \tag{30.15}$$

$$\mathbf{R} = \frac{m_\mathrm{A}\mathbf{r}_\mathrm{A} + m_\mathrm{B}\mathbf{r}_\mathrm{B}}{M} \tag{30.16}$$

$$\mathbf{u}_\mathrm{cm} = \frac{m_\mathrm{A}\mathbf{u}_\mathrm{A} + m_\mathrm{B}\mathbf{u}_\mathrm{B}}{M} \tag{30.17}$$

$$\mathrm{KE}_\mathrm{react} = \frac{1}{2} m_\mathrm{A} u_\mathrm{A}^2 + \frac{1}{2} m_\mathrm{B} u_\mathrm{B}^2 \tag{30.18}$$

$$\mathrm{KE}_\mathrm{react} = \frac{1}{2} M u_\mathrm{cm}^2 + \frac{1}{2} \mu u_\mathrm{r}^2 \tag{30.19}$$

$$\mathbf{R} = \frac{m_\mathrm{C}\mathbf{r}_\mathrm{C} + m_\mathrm{D}\mathbf{r}_\mathrm{D}}{M} \tag{30.20}$$

$$\mathbf{u}_\mathrm{cm} = \frac{m_\mathrm{C}\mathbf{u}_\mathrm{C} + m_\mathrm{D}\mathbf{u}_\mathrm{D}}{M} \tag{30.21}$$

$$\mathrm{KE_{prod}} = \frac{1}{2}Mu_{\mathrm{cm}}^2 + \frac{1}{2}\mu' {u'_{\mathrm{r}}}^2 \tag{30.22}$$

$$m_{\mathrm{A}}\mathbf{u}_{\mathrm{A}} + m_{\mathrm{B}}\mathbf{u}_{\mathrm{B}} = m_{\mathrm{C}}\mathbf{u}_{\mathrm{C}} + m_{\mathrm{D}}\mathbf{u}_{\mathrm{D}} \tag{30.23}$$

$$\frac{1}{2}\mu' {u'_{\mathrm{r}}}^2 = \frac{1}{2}\mu u_{\mathrm{r}}^2 - \Delta E_0 \tag{30.24}$$

$$\mathrm{F(g)} + \mathrm{D_2(g)} \Longrightarrow \mathrm{DF(g)} + \mathrm{D(g)} \tag{30.25}$$

$$\mathrm{F(g)} + \mathrm{D_2}(v=0)\mathrm{(g)} \Longrightarrow \mathrm{DF}(v)\mathrm{(g)} + \mathrm{D(g)} \tag{30.26}$$

$$E_{\mathrm{tot}} = E_{\mathrm{trans}} + E_{\mathrm{int}} = E'_{\mathrm{trans}} + E'_{\mathrm{int}} \tag{30.27}$$

$$E_{\mathrm{tot}} = E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{vib}} + E_{\mathrm{elec}} = E'_{\mathrm{trans}} + E'_{\mathrm{rot}} + E'_{\mathrm{vib}} + E'_{\mathrm{elec}} \tag{30.28}$$

$$E_{\mathrm{loc}} = \frac{1}{2}\mu u_{\mathrm{r,loc}}^2 = \frac{1}{2}\mu u_{\mathrm{r}}^2 \cos^2\chi \tag{30.29}$$

$$E_{\mathrm{loc}} = \frac{1}{2}\mu u_{\mathrm{r}}^2 \left(1 - \frac{b^2}{d_{\mathrm{AB}}^2}\right) \tag{30.30}$$

$$E_{\mathrm{loc}} = E_{\mathrm{r}} \left(1 - \frac{b^2}{d_{\mathrm{AB}}^2}\right) \tag{30.31}$$

$$E_0 = E_{\mathrm{r}} \left(1 - \frac{b^2}{d_{\mathrm{AB}}^2}\right) \tag{30.32}$$

$$b_{\mathrm{max}}^2 = d_{\mathrm{AB}}^2 \left(1 - \frac{E_0}{E_{\mathrm{r}}}\right) \tag{30.33}$$

$$\frac{E_{\mathrm{loc}}}{E_0} = \frac{1 - b^2/d_{\mathrm{AB}}^2}{1 - b_{\mathrm{max}}^2/d_{\mathrm{AB}}^2} \tag{30.34}$$

Chapter 31

Solids and Surface Chemistry

$$h = \frac{a}{a'} \qquad k = \frac{b}{b'} \qquad l = \frac{c}{c'} \tag{31.1}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{31.2}$$

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \tag{31.3}$$

$$\Delta = \overline{\mathrm{A_1C}} - \overline{\mathrm{A_2B}} \tag{31.4}$$

$$\Delta = a'(\cos\alpha - \cos\alpha_0) = n\lambda \tag{31.5}$$

$$a(\cos\alpha - \cos\alpha_0) = nh\lambda \tag{31.6}$$

$$b(\cos\beta - \cos\beta_0) = k\lambda \tag{31.7}$$

$$c(\cos\gamma - \cos\gamma_0) = l\lambda \tag{31.8}$$

$$a\cos\alpha = h\lambda \tag{31.9}$$

$$a(\cos\beta - \cos\beta_0) = k\lambda \tag{31.10}$$

$$a(\cos\gamma - \cos\gamma_0) = l\lambda \tag{31.11}$$

$$\lambda = 2\left(\frac{d}{n}\right)\sin\theta \tag{31.12}$$

$$\sin^2\theta = \frac{n^2\lambda^2}{4a^2(h^2+k^2+l^2)} \tag{31.13}$$

$$f = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} \rho(r)\frac{\sin kr}{kr} r^2 dr = 4\pi \int_0^{\infty} \rho(r)\frac{\sin kr}{kr} r^2 dr \tag{31.14}$$

$$\Delta_{11} = \Delta_{22} = \frac{a}{h}(\cos\alpha - \cos\alpha_0) = \lambda \tag{31.15}$$

$$\Delta_{12} = x(\cos\alpha - \cos\alpha_0) \tag{31.16}$$

$$\Delta_{12} = \frac{\lambda h x}{a} \tag{31.17}$$

$$\phi = 2\pi\frac{\Delta_{12}}{\lambda} = 2\pi\frac{\lambda hx/a}{\lambda} = \frac{2\pi hx}{a} \tag{31.18}$$

$$A = f_1\cos\omega t + f_2\cos(\omega t + \phi) \tag{31.19}$$

$$A = f_1 e^{i\omega t} + f_2 e^{i(\omega t+\phi)} \tag{31.20}$$

$$\begin{aligned} I \propto |A|^2 &= [f_1 e^{i\omega t} + f_2 e^{i(\omega t+\phi)}][f_1 e^{-i\omega t} + f_2 e^{-i(\omega t+\phi)}] \\ &= f_1^2 + f_1 f_2 e^{i\phi} + f_1 f_2 e^{-i\phi} + f_2^2 \\ &= f_1^2 + f_2^2 + 2f_1 f_2\cos\phi \end{aligned} \tag{31.21}$$

$$F(h) = f_1 + f_2 e^{i\phi} = f_1 + f_2 e^{2\pi i h x/a} \tag{31.22}$$

$$F(hkl) = \sum_j f_j e^{2\pi i(hx_j/a + ky_j/b + lz_j/c)} \tag{31.23}$$

$$F(hkl) = \sum_j f_j e^{2\pi i(hx'_j + ky'_j + lz'_j)} \tag{31.24}$$

$$\begin{aligned} F(hkl) &= f_+[1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}] \\ &\quad + f_-[(-1)^{h+k+l} + (-1)^h + (-1)^k + (-1)^l] \end{aligned} \tag{31.25}$$

$$\begin{aligned} F(hkl) &= 4(f_+ + f_-) \qquad h, k, \text{ and } l \text{ are all even} \\ F(hkl) &= 4(f_+ - f_-) \qquad h, k, \text{ and } l \text{ are all odd} \end{aligned} \tag{31.26}$$

$$F(hkl) = \int_0^a \int_0^b \int_0^c \rho(x, y, z) e^{2\pi i(hx/a + ky/b + lz/c)} dxdydz \tag{31.27}$$

$$F(hkl) \propto \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x, y, z) e^{2\pi i(hx/a + ky/b + lz/c)} dxdydz \tag{31.28}$$

$$\rho(x, y, z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F(hkl) e^{-2\pi i(hx/a + ky/b + lz/c)} \tag{31.29}$$

$$F(hkl) = A(hkl) + iB(hkl) \tag{31.30}$$

$$\begin{aligned} I(hkl) \propto |F(hkl)|^2 &= [A(hkl) + iB(hkl)][A(hkl) - iB(hkl)] \\ &= [A(hkl)]^2 + [B(hkl)]^2 \end{aligned} \tag{31.31}$$

$$k_{\mathrm{d}} = \tau_0^{-1} e^{-\Delta_{\mathrm{ads}} H/RT} \tag{31.32}$$

$$\tau = \tau_0 e^{\Delta_{\mathrm{ads}} H/RT} \tag{31.33}$$

$$A(g) + S(s) \underset{k_d}{\overset{k_a}{\rightleftarrows}} A\text{–}S(s) \qquad K_c = \frac{k_a}{k_d} = \frac{[\text{ A–S}]}{[A][S]} \tag{31.34}$$

$$\text{rate of desorption} = v_d = k_d \theta \sigma_0 \tag{31.35}$$

$$\text{rate of absorption} = v_a = k_a (1 - \theta) \sigma_0 [A] \tag{31.36}$$

$$\frac{1}{\theta} = 1 + \frac{1}{K_c[A]} \tag{31.37}$$

$$\frac{1}{\theta} = 1 + \frac{1}{bP_A} \tag{31.38}$$

$$\frac{d[B]}{dt} = k_{obs} P_A \tag{31.39}$$

$$\frac{d[B]}{dt} = k_1 [A(ads)] = k_1 \sigma_A \tag{31.40}$$

$$\frac{d[B]}{dt} = k_1 \frac{\sigma_0 K_c [A]}{1 + K_c[A]} = k_1 \frac{\sigma_0 b P_A}{1 + bP_A} \tag{31.41}$$

$$\frac{d[B]}{dt} = k_1 \sigma_0 b P_A = k_{obs} P_A \tag{31.42}$$

$$\frac{d[B]}{dt} = k_1 \sigma_0 = k_{obs} \tag{31.43}$$

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g) \tag{31.44}$$

$$v = \frac{k_3 b_{CO} b_{O_2}^{1/2} P_{CO} P_{O_2}^{1/2}}{(1 + b_{O_2}^{1/2} P_{O_2}^{1/2} + b_{CO} P_{CO})^2} \tag{31.45}$$

$$v = \frac{k_3 b_{CO} b_{O_2}^{1/2} P_{CO} P_{O_2}^{1/2}}{1 + b_{O_2}^{1/2} P_{O_2}^{1/2} + b_{CO} P_{CO}} \tag{31.46}$$

$$CO(g) + 3\,H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g) \tag{31.47}$$

$$D = D_0 e^{-\Delta E_{\mathrm{D}}/RT} \tag{31.48}$$

$$r_{\mathrm{rms}} = (4Dt)^{1/2} \tag{31.49}$$