Physical and Chemical Kinetics
Final Examination
07-11-2013

Please use the provided paper sheets to write down the solutions of the problems. Write your name and student ID number on a first page and enumerate all subsequent pages. Do not forget to hand in your paperwork after the examination.

Problem 1

Two interacting hydrogen atoms have laboratory velocities with (x, y, z) components of (1×10^3 m/s, 0, 0) and (0, 1×10^3 m/s, 0).

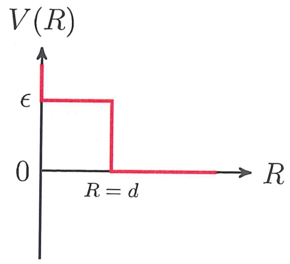
a. Find velocities of the atoms in the center-of-mass frame of reference.

b. Find the kinetic energy of relative movement of the hydrogen atoms.

c. Find the total angular momentum of hydrogen atoms relative to the origin of the center-of-mass frame of reference when distance between atoms $\mathbf{r} = (1\,\mathrm{cm}, 1\,\mathrm{cm}, 0)$.

Problem 2

Interaction of particles is described by a repulsive square-well potential with height ϵ at a distance d between particles (see fig.). The relative velocity of the particles before collision is v, impact parameter is b and their relative mass is μ.



a. What is magnitude of the relative velocity after collision?

b. Sketch the trajectory of the particle moving in a field with this potential.

c. Find the distance of the closest approach between the particles as a function of v, b, μ, ϵ, and d.

Problem 3

Consider nitrogen at temperature $T = 500\,\mathrm{K}$. Molecular weight of nitrogen is $28\,\mathrm{g/mol}$.

a. Find the most probable magnitude of the velocity of nitrogen molecules at this temperature.

b. What is larger - the most probable velocity or the average velocity? Explain why these velocities are not the same.

c. Find the sound velocity of nitrogen gas at this temperature.

Problem 4

Formation of the nitrogen oxide proceeds through the Zeldovich mechanism:

$$\mathrm{N_2 + O \xrightarrow{k_1} NO + N}$$

$$\mathrm{N + O_2 \xrightarrow{k_2} NO + O}$$

a. Assuming that rate coefficient k_2 is much larger than k_1, derive the expression for the rate of formation of the nitric oxide.

b. Dissociation of oxygen molecules is sufficient fast that it is possible to assume that this reaction in equilibrium with the equilibrium constant K_d. Express the rate of formation of NO through the concentration of oxygen and nitrogen molecules

c. Find the mole fraction of NO molecules at exit of a combustion chamber. The combustion gases can be treated as air at temperature $2000\,\mathrm{K}$ and pressure $10\,\mathrm{atm} \approx 1 \times 10^6\,\mathrm{Pa}$. The residence time of combustion products in the chamber is $\sim 1\,\mathrm{ms}$. The rate coefficient $k_1 = 1.8 \times 10^8 e^{-38370/T}\ \mathrm{m^3/mol\,s}$ and the equilibrium constant $k_d = 3.97 \times 10^5 T^{-1/2}[\mathrm{O_2}]^{1/2} e^{-31090/T} \mathrm{mol/m^3}$, where T is in K. Molecular weight of air is $29\,\mathrm{g/mole}$.

Physical constants

Electron mass	$m_e = 9.109\,39 \times 10^{-28}$ g
Proton mass	$m_p = 1.672\,62 \times 10^{-24}$ g
Atomic unit of mass	$m_a = \frac{1}{12}m(^{12}\mathrm{C}) = 1.660\,54 \times 10^{-24}$ g
Planck constant	$h = 6.626\,19 \times 10^{-27}$ erg cm
	$\hbar = 1.054\,57 \times 10^{-27}$ erg cm
Light velocity	$c = 2.997\,92 \times 10^{10}$ cm/s
Electron charge	$e = 1.602\,19 \times 10^{-19}$ C
Avogadro number	$N_A = 6.022\,14 \times 10^{23}$ mol^{-1}
Molar volume	$V_m = 22.414$ l/mol
Universal gas constant	$R = 8.314 \times 10^{7}$ erg/mol K
Boltzmann constant	$k = R/N_A = 1.3807 \times 10^{-16}$ erg/K

1 Molecular Motion and Collisions

$$m_1 + m_2 = m_1' + m_2' \tag{1.1}$$

$$m_1\mathbf{v_1} + m_2\mathbf{v_2} = m_1\mathbf{v_1'} + m_2\mathbf{v_2'} \tag{1.2}$$

$$\frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2 = \frac{1}{2}m_1 v_1'^2 + \frac{1}{2}m_2 v_2'^2 \tag{1.3}$$

$$m_1[\mathbf{r_1} \times \mathbf{v_1}] + m_2[\mathbf{r_2} \times \mathbf{v_2}] = m_1[\mathbf{r_2'} \times \mathbf{v_1'}] + m_2[\mathbf{r_2'} \times \mathbf{v_2'}] \tag{1.4}$$

$$m_1\frac{\mathrm{d}^2\mathbf{r_1}}{\mathrm{d}t^2} = \mathbf{F_{21}} \text{ and } m_2\frac{\mathrm{d}^2\mathbf{r_2}}{\mathrm{d}t^2} = \mathbf{F_{12}} \tag{1.5}$$

$$\begin{aligned} \mathbf{r} &= \mathbf{r_2} - \mathbf{r_1} \\ \mathbf{R} &= \frac{m_1\mathbf{r_1} + m_2\mathbf{r_2}}{m_1 + m_2} \end{aligned} \tag{1.6}$$

$$\begin{aligned} \mathbf{v} &= \mathbf{v_2} - \mathbf{v_1} \\ \mathbf{V} &= \frac{m_1\mathbf{v_1} + m_2\mathbf{v_2}}{m_1 + m_2} \end{aligned} \tag{1.7}$$

$$\begin{aligned} (m_1 + m_2)\frac{\mathrm{d}^2\mathbf{R}}{\mathrm{d}t^2} &= 0 \\ \mu\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} &= \mathbf{F} \end{aligned} \tag{1.8}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{1.9}$$

$$\begin{aligned} \mathbf{v_1} &= \mathbf{V} - \frac{m_2}{m_1 + m_2}\mathbf{v} \\ \mathbf{v_2} &= \mathbf{V} + \frac{m_1}{m_1 + m_2}\mathbf{v} \end{aligned} \tag{1.10}$$

$$\mu[\mathbf{r} \times \mathbf{v}] = \mu[\mathbf{r'} \times \mathbf{v'}] \tag{1.11}$$

$$\frac{\mu v^2}{2} + V(r) = const \tag{1.12}$$

$$\mathbf{L} = \mu \mathbf{r} \times \mathbf{v} = const \tag{1.13}$$

$$b = d \cos \frac{\chi}{2}, \text{ when } b \leq d \tag{1.14}$$

$$V(d) = E\left(1 - \frac{b^2}{d^2}\right) \tag{1.15}$$

$$E = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu \dot{r}^2 + \frac{1}{2}\mu r^2 \dot{\theta}^2 + V(r) \tag{1.16}$$

$$\mu v b = \mu r^2 \dot{\theta} \tag{1.17}$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}r} = \frac{b}{r^2 \sqrt{1 - \frac{b^2}{r^2} - \frac{V(r)}{\frac{1}{2}\mu}}} \tag{1.18}$$

$$1 - \frac{b^2}{r_0^2} = \frac{V(r_0)}{E} \tag{1.19}$$

$$\chi = \pi - 2b \int_{r_0}^{\infty} \frac{\mathrm{d}r}{r^2 \sqrt{1 - \frac{b^2}{r^2} - \frac{V(r)}{E}}} \tag{1.20}$$

$$b = \frac{A}{2E} \cot\left(\frac{\chi}{2}\right) \tag{1.21}$$

$$\mathrm{d}N_{Ar}(v, \alpha, \beta) = \sigma(v, \alpha, \beta) v n_1(v_1) n_2(v_2) \tau \mathrm{d}\Omega' \tag{1.22}$$

$$\mathrm{d}N_{Ar}(v, \chi, \phi) = \sigma(v, \chi) v n_1(v_1) n_2(v_2) \sin \chi \mathrm{d}\chi \mathrm{d}\phi \tag{1.23}$$

$$\sigma(v, \alpha, \beta) \sin \alpha \mathrm{d}\alpha \mathrm{d}\beta = \sigma(v, \chi) \sin \chi \mathrm{d}\chi \mathrm{d}\phi \tag{1.24}$$

$$\sigma(v) = \int_{\alpha=0}^{\pi} \int_{\beta=0}^{2\pi} \sigma(v, \alpha, \beta) \sin \alpha \mathrm{d}\alpha \mathrm{d}\beta \tag{1.25}$$

$$\sigma(v, \chi) = \frac{b}{\sin \chi} \left| \frac{\mathrm{d}b}{\mathrm{d}\chi} \right| \tag{1.26}$$

$$\sigma(v, \chi) = \frac{d^2}{2} \cos \frac{\chi}{2} \sin \frac{\chi}{2} \frac{1}{2 \sin \chi} = \frac{d^2}{4} \tag{1.27}$$

$$\sigma(v, \chi) = \left(\frac{A}{4E}\right)^2 \frac{1}{2 \sin^4 \left(\frac{\chi}{2}\right)} \tag{1.28}$$

$$\sigma(\theta, E = \frac{\hbar^2 k^2}{2\mu}) = |f(\theta, E|^2 \tag{1.29}$$

2 The Kinetic Theory of Gases

$$N = \int_{v_x=-\infty}^{v_x=\infty} \int_{v_y=-\infty}^{v_y=\infty} \int_{v_z=-\infty}^{v_z=\infty} \iiint\limits_V f(\mathbf{r}, \mathbf{v}, t)\, \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z \tag{2.1}$$

$$\mathfrak{f}(\mathbf{r}, \mathbf{v}, t) = \frac{f(\mathbf{r}, \mathbf{v}, t)}{N} \tag{2.2}$$

$$1 = \int_{v_x=-\infty}^{v_x=\infty} \int_{v_y=-\infty}^{v_y=\infty} \int_{v_z=-\infty}^{v_z=\infty} \iiint\limits_V \mathfrak{f}(\mathbf{r}, \mathbf{v}, t)\, \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z \tag{2.3}$$

$$f(\mathbf{v}, t) = \iiint\limits_V f(\mathbf{r}, \mathbf{v}, t)\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z \tag{2.4}$$

$$\mathfrak{f}(\mathbf{v}, t) = \iiint\limits_V \mathfrak{f}(\mathbf{r}, \mathbf{v}, t)\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z \tag{2.5}$$

$$\begin{aligned} v_x &= v \sin\theta \cos\phi \\ v_y &= v \sin\theta \sin\phi \\ v_z &= v cos\theta \end{aligned} \tag{2.6}$$

$$\mathrm{d}\mathbf{v} = \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z = v^2\, \mathrm{d}v \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi \tag{2.7}$$

$$\mathfrak{f}(\mathbf{v}, t)\mathrm{d}\mathbf{v} = \mathfrak{f}(v, \theta, \phi, t) v^2 \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi\, \mathrm{d}v \tag{2.8}$$

$$\mathfrak{f}(v, t) = v^2 \mathfrak{f}(\mathbf{v}, t) \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi = 4\pi v^2 \mathfrak{f}(\mathbf{v}, t) \tag{2.9}$$

$$N = \sum_{j=0}^{g-1} f(j, t) \tag{2.10}$$

$$1 = \sum_{j=0}^{g-1} \mathfrak{f}(j, t) \tag{2.11}$$

$$\tau Z_{12}(\mathbf{v_1}, \mathbf{v_2}) = 2\pi \int_{\chi=0}^{\pi} v\sigma(v, \chi) n_1 n_2 \mathfrak{f}_1(\mathbf{v_1}, t) \mathfrak{f}_2(\mathbf{v_2}, t) \tau\, \mathrm{d}\mathbf{v_1}\, \mathrm{d}\mathbf{v_2} \sin\chi\, \mathrm{d}\chi \tag{2.12}$$

$$Z_{12} = 2\pi n_1 n_2 \int\limits_{\mathbf{v_1}} \int\limits_{\mathbf{v_2}} \int_{\chi=0}^{\pi} v\sigma(v, \chi) \mathfrak{f}(\mathbf{v_1}, t) \mathfrak{f}(\mathbf{v_2}, t)\, \mathrm{d}\mathbf{v_1}\, \mathrm{d}\mathbf{v_2} \sin\chi\, \mathrm{d}\chi \tag{2.13}$$

$$\frac{\partial(n\mathfrak{f})}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla}(n\mathfrak{f}) + \frac{\mathbf{F}}{m} \cdot \boldsymbol{\nabla}_v(n\mathfrak{f}) = S_{col} \tag{2.14}$$

$$\begin{aligned} \mathrm{d}\mathbf{v}'_1\, \mathrm{d}\mathbf{v}'_2 &= \mathrm{d}\mathbf{V}'\, \mathrm{d}\mathbf{v}' \\ \mathrm{d}\mathbf{v_1}\, \mathrm{d}\mathbf{v_2} &= \mathrm{d}\mathbf{V}\, \mathrm{d}\mathbf{v} \end{aligned} \tag{2.15}$$

$$\begin{aligned} \mathbf{v}'_1 &= \mathbf{v_1} + \Delta\mathbf{v_1}(v, \chi) \\ \mathbf{v}'_2 &= \mathbf{v_2} + \Delta\mathbf{v_2}(v, \chi), \end{aligned} \tag{2.16}$$

$$S_{col} = 2\pi n^2 \int\limits_{\chi}\int\limits_{\mathbf{v_2}} v\sigma(v,\chi) \times \left\{ f(\mathbf{v_1}+\Delta\mathbf{v_1},t)f(\mathbf{v_2}+\Delta\mathbf{v_2},t) - f(\mathbf{v_1},t)f(\mathbf{v_2},t)\right\} \mathrm{d}\mathbf{v_2} \sin\chi \,\mathrm{d}\chi \tag{2.17}$$

$$f(\mathbf{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} \tag{2.18}$$

$$f(\mathbf{v}) = f(v_x)f(v_y)f(v_z), \tag{2.19}$$

$$f(v_x)\mathrm{d}v_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv_x^2}{2kT}} \mathrm{d}v_x \tag{2.20}$$

$$\langle \mathbf{v}\rangle = \int_{\mathbf{v}} \mathbf{v} f(\mathbf{v})\mathrm{d}\mathbf{v} \tag{2.21}$$

$$f(v) = 4\pi \left(\tfrac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} \tag{2.22}$$

$$\langle v\rangle = \int_{v=0}^{\infty} v f(v)\,\mathrm{d}v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_{v=0}^{\infty} v^3 e^{-\frac{mv^2}{2kT}}\,\mathrm{d}v = \left(\frac{8kT}{\pi m}\right)^{1/2} \tag{2.23}$$

$$\left\langle \frac{1}{2}mv^2 \right\rangle = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_{0}^{\infty} \left(\frac{1}{2}mv^2\right) v^2 e^{-\frac{mv^2}{2kT}}\,\mathrm{d}v = \frac{3}{2}kT \tag{2.24}$$

$$Z_{12} = \pi d^2 n_1 n_2 \left(\frac{8kT}{\pi\mu_{12}}\right)^{1/2} = \pi d^2 n_1 n_2 \langle v_{12}\rangle \tag{2.25}$$

$$Z = \frac{\pi d^2}{\sqrt{2}} n^2 \langle v\rangle \tag{2.26}$$

$$l = \frac{\langle v\rangle t}{\pi d^2 \langle v_{12}\rangle t} = \frac{1}{\sqrt{2}\pi d^2 n} \tag{2.27}$$

$$\Gamma_n(\mathbf{r},t) = \int\limits_{\mathbf{v}} v\cos\theta f(\mathbf{r},\mathbf{v},t)\,\mathrm{d}\mathbf{v} = \int\limits_{\mathbf{v}} \mathbf{v}\cdot\mathbf{k} f(\mathbf{r},\mathbf{v},t)\,\mathrm{d}\mathbf{v} \tag{2.28}$$

$$\boldsymbol{\Gamma_n} = \int\limits_{\mathbf{v}} \mathbf{v} f(\mathbf{r},\mathbf{v},t)\,\mathrm{d}\mathbf{v} \tag{2.29}$$

$$\Gamma_m = m\Gamma_n \tag{2.30}$$

$$\Gamma_E(\mathbf{r},t) = \frac{m}{2}\int\limits_{\mathbf{v}} v^3\cos\theta f(\mathbf{r},\mathbf{v},t)\,\mathrm{d}\mathbf{v} = \frac{m}{2}\int\limits_{\mathbf{v}} v^2\mathbf{v}\cdot\mathbf{k} f(\mathbf{r},\mathbf{v},t)\,\mathrm{d}\mathbf{v} \tag{2.31}$$

$$\boldsymbol{\Gamma_E} = \frac{m}{2}\int\limits_{\mathbf{v}} v^2\mathbf{v} f(\mathbf{r},\mathbf{v},t)\,\mathrm{d}\mathbf{v} \tag{2.32}$$

$$\Gamma_{m\mathbf{v}} = m\int\limits_{\mathbf{v}} \mathbf{v}\mathbf{v} f(\mathbf{r},\mathbf{v},t)\,\mathrm{d}\mathbf{v} \tag{2.33}$$

$$\Gamma_n = \frac{1}{4} n \langle v\rangle \tag{2.34}$$

$$\Gamma_\psi = -\frac{\langle v \rangle}{3} l \left(\frac{\mathrm{d} \langle \psi n \rangle}{\mathrm{d}z} \right)_{z=0} \tag{2.35}$$

$$D = \frac{1}{3} \langle v \rangle l$$
$$\eta = \frac{1}{3} nm \langle v \rangle l \tag{2.36}$$
$$\lambda = \frac{1}{3} n C_v \langle v \rangle l$$

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \langle \mathbf{v} \rangle) = R_{col} \tag{2.37}$$

$$\frac{\partial \rho \langle \mathbf{v} \rangle_\alpha}{\partial t} + \frac{\partial \Gamma_{\alpha\beta}}{\partial x_\beta} + n F_\alpha = 0 \tag{2.38}$$

$$\frac{\partial \left(n \left\langle \frac{mv^2}{2} \right\rangle \right)}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{\Gamma_E} + n \mathbf{F} \cdot \mathbf{v} = 0 \tag{2.39}$$

$$\left(\frac{\partial \rho}{\partial t} \right)_x + \left[\frac{\partial (\rho u)}{\partial x} \right]_t = 0 \tag{2.40}$$

$$\left(\frac{\partial p}{\partial x} \right)_t + \rho \left(\frac{\partial u}{\partial t} \right)_x + \rho u \left(\frac{\partial u}{\partial x} \right)_t = 0 \tag{2.41}$$

$$c^2 = \frac{\omega^2}{k^2} = \left(\frac{\partial p}{\partial \rho} \right)_T + \frac{M p_0}{C_V \rho_0^2} \left(\frac{\partial p}{\partial T} \right)_\rho \tag{2.42}$$

$$c^2 = \frac{p_0}{\rho_0} \left(1 + \frac{R}{C_V} \right) = \frac{p_0}{\rho_0} \gamma, \quad \left(\gamma = \frac{C_p}{C_V} \right) \tag{2.43}$$

$$c^2 = \frac{\omega^2}{k^2} = c_0^2 + \frac{4}{3} \frac{i \eta \omega}{\rho_0} \tag{2.44}$$

3 The Kinetic Theory of Dense Phases

$$P(n_1, N) = \frac{N!}{n_1!(N - n_1)!} p^{n_1} q^{N - n_1} \tag{3.1}$$

$$P(n_1; N) = \frac{1}{\sqrt{2\pi N p q}} e^{\frac{-(n_1 - n^*)^2}{2Npq}} \tag{3.2}$$

$$\left\langle (\Delta n_1)^2 \right\rangle = Npq \tag{3.3}$$

$$P(n_1; N) = \frac{1}{\sqrt{2\pi \left\langle (\Delta n_1)^2 \right\rangle}} e^{-\frac{(n_1 - n_1^*)^2}{2\left\langle (\Delta n_1)^2 \right\rangle}} = \frac{1}{\sqrt{2\pi N p q}} e^{-\frac{(n_1 - n_1^*)^2}{2Npq}} \tag{3.4}$$

$$\left\langle (\Delta x)^2 \right\rangle = 2Dt \tag{3.5}$$

$$m \frac{\mathrm{d}v}{\mathrm{d}t} = -\zeta v + f(t) \tag{3.6}$$

$$m\frac{\mathrm{d}\langle v\rangle}{\mathrm{d}t} = -\zeta\langle v\rangle \tag{3.7}$$

$$\langle x^2\rangle = \frac{2kT}{\zeta}\left[t - \frac{m}{\zeta}\left(1 - e^{-\zeta t/m}\right)\right] \tag{3.8}$$

$$\langle x^2\rangle = \frac{kT}{m}t^2 \tag{3.9}$$

$$\langle x^2\rangle = \frac{2kT}{\zeta}t \tag{3.10}$$

$$D = \frac{kT}{\zeta} \tag{3.11}$$

$$D = \frac{kT}{6\pi\eta a} \tag{3.12}$$

$$\frac{\langle K\rangle}{D} = \frac{q}{kT} \tag{3.13}$$

$$D = \int_0^\infty \mathrm{d}\sigma\,\langle v(0)v(\sigma)\rangle \tag{3.14}$$

$$\langle v(0)v(\sigma)\rangle = \langle v(0)^2\rangle e^{-\zeta t/m} = \frac{kT}{m}e^{-\zeta\sigma/m} \tag{3.15}$$

4 Chemical Kinetics

$$\sum \nu_i X_i = 0 \tag{4.1}$$

$$\dot{\xi} = \frac{1}{\nu_i}\frac{\mathrm{d}n_i}{\mathrm{d}t} \tag{4.2}$$

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A]^\alpha[B]^\beta[C]^\gamma\ldots, \tag{4.3}$$

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A] \tag{4.4}$$

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A]^2 \tag{4.5}$$

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A][B] \tag{4.6}$$

$$\frac{[A]}{[B]} = \frac{[A]_0}{[B]_0}e^{(b[A]_0 - a[B]_0)kt} \tag{4.7}$$

$$\sigma_R(E) = \pi p d^2\left(1 - \frac{\Delta E_f^*}{E}\right) \tag{4.8}$$

$$\left(\frac{\mathrm{d}n_C}{\mathrm{d}t}\right)_f = n_A n_B \int_{\alpha,\beta}\int_{\mathbf{v}_A}\int_{\mathbf{v}_B} \sigma_R(v,\alpha,\beta)v f_A(\mathbf{v}_A)f(\mathbf{v}_B)\,\mathrm{d}\mathbf{v}_A\,\mathrm{d}\mathbf{v}_B\,\mathrm{d}\Omega' \tag{4.9}$$

$$\left(\frac{\mathrm{d}n_C}{\mathrm{d}t}\right)_f = k_f n_A n_B \tag{4.10}$$

$$k_f = \int_{\mathbf{v}_A}\int_{\mathbf{v}_B} \sigma_R(v) v f_A(\mathbf{v}_A) f_B(\mathbf{v}_B)\,\mathrm{d}\mathbf{v}_A\,\mathrm{d}\mathbf{v}_B \tag{4.11}$$

$$k_f = \pi p d^2 \left(\frac{8kT}{\pi\mu_{AB}}\right)^{1/2} e^{-\Delta E_f^*/kT} \tag{4.12}$$

$$k = Ae^{-E_a/RT} \tag{4.13}$$

$$k = AT^n e^{-E_a/RT} \tag{4.14}$$

$$k_f = \kappa\frac{kT}{h}\left(K_V^{\ddagger}\right)' \tag{4.15}$$

$$\left(K_V^{\ddagger}\right)' = N_A \frac{q_1[(AB)^{\ddagger}]}{q_1(A)q_2(B)} e^{-\Delta(E_0^0)^{\ddagger}/RT} \tag{4.16}$$

$$\frac{k_f}{k_r} = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}} = K_V \tag{4.17}$$

$$\Delta G^{0\ddagger} = \Delta H^{0\ddagger} - T\Delta S^{0\ddagger} = RT\ln K^{\ddagger} \tag{4.18}$$

$$E_a = \Delta H^{0\ddagger} + RT \tag{4.19}$$

$$k_f = \kappa\frac{kT}{h} N_A \frac{q_1(AB)^{\ddagger}}{q_1(A)q_1(B)} e^{-\Delta E_0^{0\ddagger}/RT} \tag{4.20}$$

$$\Delta E_0^{0\ddagger}(m) = E_a - mRT \tag{4.21}$$

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A][B][C] \tag{4.22}$$

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = -\frac{\mathrm{d[A]}}{\mathrm{d}t} = \frac{k_1[\mathrm{A}][\mathrm{M}]}{k_2[\mathrm{M}] + k_3} \tag{4.23}$$

$$[\mathrm{NO}_2^*]_s = \frac{k_1 I_0[\mathrm{NO}_2]}{k_F + (k_{Q_1} + k_2)[\mathrm{NO}_2] + k_{Q_2}[\mathrm{Xe}]} \tag{4.24}$$

$$\Phi_F = \frac{I_F}{k_1 I_0[\mathrm{NO}_2]} = \frac{k_F}{k_F + (k_{Q_1} + k_2)[\mathrm{NO}_2] + k_{Q_2}[\mathrm{Xe}]} \tag{4.25}$$

$$\Phi(\mathrm{O}_2) = \frac{\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t}{k_1 I_0[\mathrm{NO}_2]} = \frac{k_2[\mathrm{NO}_2^*]_s[\mathrm{NO}_2]}{k_1 I_0[\mathrm{NO}_2]} = \frac{k_2[\mathrm{NO}_2]}{k_f + (k_{Q1} + k_2)[\mathrm{NO}_2] + k_{Q2}[\mathrm{Xe}]} \tag{4.26}$$