Notes of **Advanced Physical Chemistry II**

hebrewsnabla

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Contents

25 The Kinetic Theory of Gases

25.1

25.2 Speed Distribution

$$f(u_x) = \sqrt{\frac{m}{2\pi k_\mathrm{B} T}}\, \mathrm{e}^{-m u_x^2/2k_\mathrm{B}T} \tag{25.1}$$

$$\langle u_x^2 \rangle = \frac{k_\mathrm{B} T}{m} = \frac{RT}{M} \tag{25.2}$$

25.3 Maxwell Distribution

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} \mathrm{e}^{-m u^2/2k_\mathrm{B}T} \tag{25.3}$$

$$\langle u \rangle = \sqrt{\frac{8 k_\mathrm{B} T}{\pi m}} \tag{25.4}$$

$$\langle u^2 \rangle = \frac{3 k_\mathrm{B} T}{m} \tag{25.5}$$

$$u_{mp} = \sqrt{\frac{2 k_\mathrm{B} T}{m}} \tag{25.6}$$

$$F(\varepsilon) = \frac{2\pi}{(\pi k_\mathrm{B} T)^{3/2}} \varepsilon^{1/2}\, \mathrm{e}^{-\varepsilon/k_\mathrm{B}T} \tag{25.7}$$

$$\langle \varepsilon \rangle = \frac{3}{2} k_\mathrm{B} T \tag{25.8}$$

25.4 The Frequency of Collisions with a Wall

$$\mathrm{d}z = \frac{1}{A} \frac{\mathrm{d}N}{\mathrm{d}t} \tag{25.9}$$

freq per area

$$z = \frac{\rho}{4} \langle u \rangle \tag{25.10}$$

25.5

25.6 Inter-collision and MFP

$$z_A = \rho\sigma \langle u_r \rangle = \rho\sigma\sqrt{2}\, \langle u \rangle \tag{25.11}$$

$$l = \frac{u}{z_A} = \frac{1}{\sqrt{2}\rho\sigma} \tag{25.12}$$

$$p(x)\mathrm{d}x = \frac{1}{l}\, \mathrm{e}^{-x/l}\, \mathrm{d}x \tag{25.13}$$

26 Chemical Kinetics I: Rate Laws

26.8 Reaction Rate Constants

$$k(T) = \frac{k_\mathrm{B} T}{h c^\circ}\, \mathrm{e}^{-\Delta^\ddagger G^\circ/RT} \tag{26.1}$$

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28 Gas Phase Reaction Dynamics

28.1 Hard-sphere Collision Theory

Naïve hard-sphere rate cons.

$$k = \sigma_{AB} N_\mathrm{A} \langle u_r \rangle \quad (\mathrm{dm^3\,mol^{-1}\,s^{-1}}) \tag{28.1}$$

experimental

$$k = A\,\mathrm{e}^{-E_a/RT} \tag{28.2}$$

Taking into account the dependence of the rate on $\langle u_r \rangle$

$$\sigma_r(E_r) = \begin{cases} 0 & E_r < E_0 \\ \pi d_{AB}^2 & E_r \geq E_0 \end{cases} \tag{28.3}$$

...

$$k = \sigma_{AB} N_\mathrm{A} \langle u_r \rangle\,\mathrm{e}^{-E_0/k_\mathrm{B}T} \left(1 + \frac{E_0}{k_\mathrm{B}T}\right) \tag{28.4}$$

28.2 Reaction Cross Section Depending on the Impact Parameter

line-of-centers model
energy dependence of the reaction CS

$$\sigma_r(E_r) = \begin{cases} 0 & E_r < E_0 \\ \pi d_{AB}^2 \left(1 - \dfrac{E_0}{E_r}\right) & E_r \geq E_0 \end{cases} \tag{28.5}$$

$$k = \sigma_{AB} N_\mathrm{A} \langle u_r \rangle\,\mathrm{e}^{-E_0/k_\mathrm{B}T} \tag{28.6}$$

Example 28-3

$$k = A\,\mathrm{e}^{-E_a/k_\mathrm{B}T} \;\Rightarrow\; E_a = k_\mathrm{B}T^2 \frac{\mathrm{d}\ln k}{\mathrm{d}T} \tag{28.7}$$

...

$$E_a = E_0 + \frac{1}{2}k_\mathrm{B}T \tag{28.8}$$

with (28.6),

$$\sigma_{AB} N_\mathrm{A} \langle u_r \rangle = A\,\mathrm{e}^{-1/2} \;\Rightarrow\; A = \sigma_{AB} N_\mathrm{A} \langle u_r \rangle\,\mathrm{e}^{1/2} \tag{28.9}$$

28.3

28.4 The Internal Energy of the Reactants

28.5 CoM Coordinate System

$$\mathrm{KE} = \frac{1}{2}m_A u_A^2 + \frac{1}{2}m_B u_B^2 = \frac{1}{2}M u_{CoM}^2 + \frac{1}{2}\mu u_r^2 \tag{28.10}$$

Since u_{CoM} is conserved,

$$U(R) + \frac{1}{2}\mu u_r^2(R) = U(P) + \frac{1}{2}\mu u_r^2(P) \tag{28.11}$$

28.6

28.7 Vibrationally Excited Products

$$E_{tot} = E_{trans} + E_{vib} + E_{elec} \tag{28.12}$$

$$E_{vib} = \tilde{\nu}_e(v + 1/2) - \tilde{\nu}_e\tilde{x}_e(v + 1/2)^2 \tag{28.13}$$

$$E_{rot} = [\tilde{B}_e - \tilde{\alpha}_e(v + 1/2)]J(J + 1) \tag{28.14}$$

28.8 Velocity and Angular Distribution

28.9

28.10