

Notes of **Advanced Physical Chemistry II**

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Contents

25	The Kinetic Theory of Gases	2
25.1	2
25.2	Speed Distribution	2
25.3	Maxwell Distribution	2
25.4	The Frequency of Collisions with a Wall	2
25.5	2
25.6	Inter-collision and MFP	2
26	Chemical Kinetics I: Rate Laws	2
26.8	Reaction Rate Constants	2
27		3
28	Gas Phase Reaction Dynamics	3
28.1	Hard-sphere Collision Theory	3
28.2	Reaction Cross Section Depending on the Impact Parameter	3
	line-of-centers model	3
	Example 28-3	3
28.3	3
28.4	The Internal Energy of the Reactants	3
28.5	CoM Coordinate System	3
28.6	4
28.7	Vibrationally Excited Products	4
28.8	Velocity and Angular Distribution	4
28.9	4
28.10	4

25 The Kinetic Theory of Gases

25.1

25.2 Speed Distribution

$$f(u_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mu_x^2/2k_B T} \quad (25.1)$$

$$\langle u_x^2 \rangle = \frac{k_B T}{m} = \frac{RT}{M} \quad (25.2)$$

25.3 Maxwell Distribution

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mu^2/2k_B T} \quad (25.3)$$

$$\langle u \rangle = \sqrt{\frac{8k_B T}{\pi m}} \quad (25.4)$$

$$\langle u^2 \rangle = \frac{3k_B T}{m} \quad (25.5)$$

$$u_{mp} = \sqrt{\frac{2k_B T}{m}} \quad (25.6)$$

$$F(\varepsilon) = \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/k_B T} \quad (25.7)$$

$$\langle \varepsilon \rangle = \frac{3}{2} k_B T \quad (25.8)$$

25.4 The Frequency of Collisions with a Wall

$$dz = \frac{1}{A} \frac{dN}{dt} \quad (25.9)$$

freq per area

$$z = \frac{\rho}{4} \langle u \rangle \quad (25.10)$$

25.5

25.6 Inter-collision and MFP

$$z_A = \rho \sigma \langle u_r \rangle = \rho \sigma \sqrt{2} \langle u \rangle \quad (25.11)$$

$$l = \frac{u}{z_A} = \frac{1}{\sqrt{2} \rho \sigma} \quad (25.12)$$

$$p(x)dx = \frac{1}{l} e^{-x/l} dx \quad (25.13)$$

26 Chemical Kinetics I: Rate Laws

26.8 Reaction Rate Constants

$$k(T) = \frac{k_B T}{hc^\circ} e^{-\Delta^\ddagger G^\circ / RT} \quad (26.1)$$

28 Gas Phase Reaction Dynamics

28.1 Hard-sphere Collision Theory

Naïve hard-sphere rate cons.

$$k = \sigma_{AB} N_A \langle u_r \rangle \quad (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \quad (28.1)$$

experimental

$$k = A e^{-E_a/RT} \quad (28.2)$$

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

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

...

$$k = \sigma_{AB} N_A \langle u_r \rangle e^{-E_0/k_B T} \left(1 + \frac{E_0}{k_B T} \right) \quad (28.4)$$

28.2 Reaction Cross Section Depending on the Impact Parameter

line-of-centers model

energy dependence of the reaction CS

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

$$k = \sigma_{AB} N_A \langle u_r \rangle e^{-E_0/k_B T} \quad (28.6)$$

Example 28-3

$$k = A e^{-E_a/k_B T} \Rightarrow E_a = k_B T^2 \frac{d \ln k}{dT} \quad (28.7)$$

...

$$E_a = E_0 + \frac{1}{2} k_B T \quad (28.8)$$

with (28.6),

$$\sigma_{AB} N_A \langle u_r \rangle = A e^{-1/2} \Rightarrow A = \sigma_{AB} N_A \langle u_r \rangle e^{1/2} \quad (28.9)$$

28.3

28.4 The Internal Energy of the Reactants

28.5 CoM Coordinate System

$$\text{KE} = \frac{1}{2} m_A u_A^2 + \frac{1}{2} m_B u_B^2 = \frac{1}{2} M u_{CoM}^2 + \frac{1}{2} \mu u_r^2 \quad (28.10)$$

Since u_{CoM} is conserved,

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

28.6

28.7 Vibrationally Excited Products

$$E_{tot} = E_{trans} + E_{vib} + E_{elec} \quad (28.12)$$

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

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

28.8 Velocity and Angular Distribution

28.9

28.10

29 Solids and Surface Chemistry

29.1

29.2 Miller Indices

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (29.1)$$