

Advanced Physical Chemistry II

HW Part I

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25 The Kinetic Theory of Gases

2,3,17,26,27,35,37,42

25-2

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{28.02 \times 10^{-3}}} \quad (25.1)$$

thus

$$u_{\text{rms}}(200 \text{ K}) = 421.95 \text{ m/s} \quad (25.2)$$

$$u_{\text{rms}}(300 \text{ K}) = 516.78 \text{ m/s} \quad (25.3)$$

$$u_{\text{rms}}(500 \text{ K}) = 667.16 \text{ m/s} \quad (25.4)$$

$$u_{\text{rms}}(1000 \text{ K}) = 943.50 \text{ m/s} \quad (25.5)$$

25-3 Since

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (25.6)$$

The RMS speed is increased by $\sqrt{2}$.

25-17 Since

$$f(u_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mu_x^2/2k_B T} \quad (25.7)$$

when $u_x > 0$

$$\begin{aligned} \langle u_x \rangle &= \int_0^\infty u_x f(u_x) du_x = \sqrt{\frac{m}{2\pi k_B T}} \int_0^\infty u_x e^{-mu_x^2/2k_B T} du_x \\ &= \sqrt{\frac{m}{2\pi k_B T}} \left(-\frac{k_B T}{m} \right) (0 - 1) \\ &= \sqrt{\frac{k_B T}{2\pi m}} \end{aligned} \quad (25.8)$$

25-26 Since

$$F(\varepsilon) = \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/k_B T} \quad (25.9)$$

Let $\frac{dF}{d\varepsilon} = 0$, we have

$$\frac{1}{2} \varepsilon^{-1/2} e^{-\varepsilon/k_B T} + \varepsilon^{1/2} \left(-\frac{1}{k_B T} \right) e^{-\varepsilon/k_B T} = 0 \quad (25.10)$$

$$\varepsilon = \frac{k_B T}{2} \quad (25.11)$$

25-27

$$\begin{aligned}
\langle \varepsilon \rangle &= \int_0^\infty \varepsilon F(\varepsilon) d\varepsilon \\
&= \int_0^\infty \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{3/2} e^{-\varepsilon/k_B T} d\varepsilon \\
&= \frac{2\pi}{(\pi k_B T)^{3/2}} \frac{3}{4} (k_B T)^{5/2} \sqrt{\pi} \\
&= \frac{3}{2} k_B T
\end{aligned} \tag{25.12}$$

$$\begin{aligned}
\langle \varepsilon^2 \rangle &= \int_0^\infty \varepsilon^2 F(\varepsilon) d\varepsilon \\
&= \int_0^\infty \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{5/2} e^{-\varepsilon/k_B T} d\varepsilon \\
&= \frac{2\pi}{(\pi k_B T)^{3/2}} \frac{15}{8} (k_B T)^{7/2} \sqrt{\pi} \\
&= \frac{15}{4} (k_B T)^2
\end{aligned} \tag{25.13}$$

$$\sigma_\varepsilon^2 = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \frac{3}{2} (k_B T)^2 \tag{25.14}$$

thus

$$\frac{\sigma_\varepsilon}{\langle \varepsilon \rangle} = \sqrt{\frac{3}{2}} / \frac{3}{2} = \sqrt{\frac{2}{3}} \tag{25.15}$$

which means the fluctuations in ε are large with respect to ε .

25-35

$$\begin{aligned}
z_A &= \rho \sigma \sqrt{2} \sqrt{\frac{8RT}{\pi M}} = \frac{P N_A}{RT} \sigma \cdot 4 \sqrt{\frac{RT}{\pi M}} \\
&= \frac{4 \sigma N_A}{\sqrt{\pi M R T}} P
\end{aligned} \tag{25.16}$$

where $\sigma = 0.230 \times 10^{-18} \text{ m}^2$

(a)

$$z_A = \frac{4 \times 0.230 \times 10^{-18} \times 6.022 \times 10^{23}}{\sqrt{\pi \times 2.016 \times 10^{-3} \times 8.3145 \times 298.15}} \times 133.32 = 1.86 \times 10^7 \text{ s}^{-1} \tag{25.17}$$

(b)

$$z_A = \frac{4 \times 0.230 \times 10^{-18} \times 6.022 \times 10^{23}}{\sqrt{\pi \times 2.016 \times 10^{-3} \times 8.3145 \times 298.15}} \times 1 \times 10^5 = 1.40 \times 10^{10} \text{ Hz} \tag{25.18}$$

25-37 The probability that an O_2 molecule will travel distance d without a collision is

$$\begin{aligned}
P(d) &= 1 - \int_0^d p(x) dx = 1 - \int_0^d \frac{1}{l} e^{-x/l} dx \\
&= 1 - \frac{1}{l} (-l e^{-x/l}) \Big|_0^d \\
&= 1 + (e^{-d/l} - 1) \\
&= e^{-d/l}
\end{aligned} \tag{25.19}$$

Since the MFP

$$l = \frac{1}{\sqrt{2} \rho \sigma} = \frac{k_B T}{\sqrt{2} \sigma P}$$

$$\begin{aligned}
&= \frac{1.38 \times 10^{-23} \times 298.15}{\sqrt{2} \times 0.410 \times 10^{-18} \times 1 \times 10^5} \\
&= 7.10 \times 10^{-8} \text{ m} = 7.10 \times 10^{-5} \text{ mm}
\end{aligned} \tag{25.20}$$

we get

$$(a) \quad P(1.00 \times 10^{-5} \text{ mm}) = e^{-1.00 \times 10^{-5} / 7.10 \times 10^{-5}} = 0.869 \tag{25.21}$$

$$(b) \quad P(1.00 \times 10^{-3} \text{ mm}) = e^{-1.00 \times 10^{-3} / 7.10 \times 10^{-5}} = 7.63 \times 10^{-7} \tag{25.22}$$

$$(c) \quad P(1.00 \text{ mm}) = e^{-1.00 / 7.10 \times 10^{-5}} = 4.20 \times 10^{-6118} \tag{25.23}$$

25-42 Since

$$l = \frac{1}{\sqrt{2}\rho\sigma} = \frac{k_B T}{\sqrt{2}\sigma P} \tag{25.24}$$

we have

$$P(l) = \frac{k_B T}{\sqrt{2}\sigma l} \tag{25.25}$$

where $\sigma = 0.230 \times 10^{-18} \text{ m}^2$, $T = 293.15 \text{ K}$.
thus

$$\begin{aligned}
P(100 \mu\text{m}) &= 124 \text{ Pa} \\
P(1.00 \text{ mm}) &= 12.4 \text{ Pa} \\
P(1.00 \text{ m}) &= 0.0124 \text{ Pa}
\end{aligned} \tag{25.26}$$

26 Chemical Kinetics I: Rate Laws

26-47

$$\begin{aligned}
\Delta^\ddagger G^\circ &= \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ \\
&= 31.38 - 325 \times 16.74 \times 10^{-3} \\
&= 25.94 \text{ kJ/mol}
\end{aligned} \tag{26.1}$$

$$\begin{aligned}
k &= \frac{k_B T}{h c^\circ} e^{-\Delta^\ddagger G^\circ / RT} \\
&= \frac{1.38 \times 10^{-23} \times 325}{6.626e - 34 \times 1} e^{-25.94 \times 10^3 / 8.314 \times 325} \\
&= 4.59 \text{ s}^{-1}
\end{aligned} \tag{26.2}$$

28 The Rate of a Bimolecular Gas-Phase Reaction

1,4,6,10

28-1 The cross section between NO and Cl₂

$$\sigma = \pi d^2 = \pi \left(\frac{370 + 540}{2} \right) = 6.50 \times 10^5 \text{ pm}^2 = 6.50 \times 10^{-19} \text{ m}^2 \quad (28.1)$$

the reduced mass

$$\mu = \frac{m_{\text{NO}} \times m_{\text{Cl}_2}}{m_{\text{NO}} + m_{\text{Cl}_2}} = \frac{70.906 \times 30.006}{70.906 + 30.006} = 21.0838 \text{ amu} = 3.5010 \times 10^{-26} \text{ kg} \quad (28.2)$$

thus

$$\langle u_r \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi\mu}} = \sqrt{\frac{8 \times k_{\text{B}} \times 300}{\pi \times 3.5010 \times 10^{-26}}} = 548.88 \text{ m/s} \quad (28.3)$$

the hard-sphere collision theory rate constant is

$$\begin{aligned} k_{\text{theo}} &= \sigma N_{\text{A}} \langle u_r \rangle \\ &= 6.50 \times 10^{-19} \times 6.022 \times 10^{23} \times 548.88 \\ &= 2.15 \times 10^8 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} = 2.15 \times 10^{11} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \end{aligned} \quad (28.4)$$

and the experimental rate constant is

$$\begin{aligned} k_{\text{exp}} &= A e^{-E_a/RT} \\ &= 3.981 \times 10^9 e^{-84900/(8.3145 \times 300)} \\ &= 6.57 \times 10^{-6} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \end{aligned} \quad (28.5)$$

the ratio

$$\frac{k_{\text{theo}}}{k_{\text{exp}}} = \frac{2.15 \times 10^{11}}{6.57 \times 10^{-6}} = 3.27 \times 10^{13} \quad (28.6)$$

28-4 The threshold energy

$$\begin{aligned} E_0 &= E_a - \frac{1}{2}RT \\ &= 10.5 - \frac{1}{2} \times 8.3145 \times 10^{-3} \times 1000 \\ &= 6.34 \text{ kJ/mol} \end{aligned} \quad (28.7)$$

Since

$$\mu = \frac{30.006 \times 47.998}{30.006 + 47.998} = 18.4635 \text{ amu} = 3.0659 \times 10^{-26} \text{ kg} \quad (28.8)$$

$$\begin{aligned} \langle u_r \rangle &= \sqrt{\frac{8k_{\text{B}}T}{\pi\mu}} = \sqrt{\frac{8k_{\text{B}} \times 1000}{\pi \times 3.0659 \times 10^{-26}}} \\ &= 1070.8 \text{ m/s} \end{aligned} \quad (28.9)$$

the hard-sphere reaction cross section is

$$\sigma = \frac{A}{\langle u_r \rangle N_{\text{A}} \sqrt{e}} = \frac{7.94 \times 10^6}{\sqrt{e} \times N_{\text{A}} \times 1070.8} = 7.47 \times 10^{-21} \text{ m}^2 \quad (28.10)$$

28-6

$$E_0 = 70.0 \text{ KJ/mol} = 5851 \text{ cm}^{-1} \quad (28.11)$$

Since

$$G(v) = \tilde{\nu}_e(v + 1/2) - \tilde{x}_e \tilde{\nu}_e(v + 1/2)^2 \quad (28.12)$$

Let

$$5851 < 2321.7(v + 1/2) - 66.2(v + 1/2)^2 \quad (28.13)$$

we get $2.23 < v < 31.8$, thus $v_{\text{min}} = 3$

28-10 Additional Problems

1. 对于单分子气相反应，活化熵变往往可忽略不计，试计算按室温 (200 K) 附近活化焓分别为 60,80,100 kJ · mol⁻¹ 时之反应比速及 $t_{1/2}$ 。

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