

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)

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

(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

26 Chemical Kinetics I: Rate Laws

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28 The Rate of a Bimolecular Gas-Phase Reaction

1,4,6,10

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 时的反应比速及 $t_{1/2}$ 。

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