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

$$u_{\mathrm{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{28.02 \times 10^{-3}}} \tag{25.1}$$

thus

$$u_{\mathrm{rms}}(200\,\mathrm{K}) = 421.95\,\mathrm{m/s} \tag{25.2}$$
$$u_{\mathrm{rms}}(300\,\mathrm{K}) = 516.78\,\mathrm{m/s} \tag{25.3}$$
$$u_{\mathrm{rms}}(500\,\mathrm{K}) = 667.16\,\mathrm{m/s} \tag{25.4}$$
$$u_{\mathrm{rms}}(1000\,\mathrm{K}) = 943.50\,\mathrm{m/s} \tag{25.5}$$

25-3 Since

$$u_{\mathrm{rms}} = \sqrt{\frac{3RT}{M}} \tag{25.6}$$

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

25-17 Since

$$f(u_x) = \sqrt{\frac{m}{2\pi k_{\mathrm{B}}T}}\,\mathrm{e}^{-mu_x^2/2k_{\mathrm{B}}T} \tag{25.7}$$

when $u_x > 0$

$$\begin{aligned}\langle u_x \rangle &= \int_0^\infty u_x f(u_x)\mathrm{d}u_x = \sqrt{\frac{m}{2\pi k_{\mathrm{B}}T}} \int_0^\infty u_x\,\mathrm{e}^{-mu_x^2/2k_{\mathrm{B}}T}\,\mathrm{d}u_x \\ &= \sqrt{\frac{m}{2\pi k_{\mathrm{B}}T}}\left(-\frac{k_{\mathrm{B}}T}{m}\right)(0-1) \\ &= \sqrt{\frac{k_{\mathrm{B}}T}{2\pi m}}\end{aligned} \tag{25.8}$$

25-26 Since

$$F(\varepsilon) = \frac{2\pi}{(\pi k_{\mathrm{B}}T)^{3/2}}\varepsilon^{1/2}\,\mathrm{e}^{-\varepsilon/k_{\mathrm{B}}T} \tag{25.9}$$

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

$$\frac{1}{2}\varepsilon^{-1/2}\,\mathrm{e}^{-\varepsilon/k_{\mathrm{B}}T} + \varepsilon^{1/2}\left(-\frac{1}{k_{\mathrm{B}}T}\right)\mathrm{e}^{-\varepsilon/k_{\mathrm{B}}T} = 0 \tag{25.10}$$

$$\varepsilon = \frac{k_{\mathrm{B}}T}{2} \tag{25.11}$$

25-27

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

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

$$
\sigma_\varepsilon^2 = \left\langle\varepsilon^2\right\rangle - \langle\varepsilon\rangle^2 = \frac{3}{2}(k_\mathrm{B}T)^2 \tag{25.14}
$$

thus

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

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

25-35

$$
\begin{aligned}
z_A &= \rho\sigma\sqrt{2}\sqrt{\frac{8RT}{\pi M}} = \frac{PN_\mathrm{A}}{RT}\sigma\cdot 4\sqrt{\frac{RT}{\pi M}} \\
&= \frac{4\sigma N_\mathrm{A}}{\sqrt{\pi MRT}}P
\end{aligned}
\tag{25.16}
$$

where $\sigma = 0.230\times10^{-18}\,\mathrm{m}^2$

(a)

$$
z_A = \frac{4\times0.230\times10^{-18}\times6.022\times10^{23}}{\sqrt{\pi\times2.016\times10^{-3}\times8.3145\times298.15}}\times133.32 = 1.86\times10^7\,\mathrm{Hz} \tag{25.17}
$$

(b)

$$
z_A = \frac{4\times0.230\times10^{-18}\times6.022\times10^{23}}{\sqrt{\pi\times2.016\times10^{-3}\times8.3145\times298.15}}\times1\times10^5 = 1.40\times10^{10}\,\mathrm{Hz} \tag{25.18}
$$

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

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

Since the MFP

$$
l = \frac{1}{\sqrt{2}\rho\sigma} = \frac{k_\mathrm{B}T}{\sqrt{2}\sigma P}
$$

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

we get

(a)

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

(b)

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

(c)

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

25-42 Since

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

we have

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

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

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

26 Chemical Kinetics I: Rate Laws

26-47

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

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 60,80,100kJ $\cdot$ mol^{-1} 时之反应比速及 $t_{1/2}$。

2