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

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

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

25-27

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

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

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

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)

$$z_A = \frac{4\times0.230\times10^{-18}\times6.022\times10^{23}}{\sqrt{\pi\times2.016\times10^{-3}\times8.3145\times298.15}}\times133.32 = 1.86\times10^7\,\mathrm{s}^{-1}\tag{25.17}$$

(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

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

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

28 The Rate of a Bimolecular Gas-Phase Reaction

1,4,6,10

28-1 The cross section between NO and Cl_2

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

the reduced mass

$$\mu = \frac{m_{\mathrm{NO}} \times m_{\mathrm{Cl_2}}}{m_{\mathrm{NO}} + m_{\mathrm{Cl_2}}} = \frac{70.906 \times 30.006}{70.906 + 30.006} = 21.0838\,\mathrm{amu} = 3.5010 \times 10^{-26}\,\mathrm{kg} \tag{28.2}$$

thus

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

the hard-sphere collision theory rate constant is

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

and the experimental rate constant is

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

the ratio

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

28-4 The threshold energy

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

Since

$$\mu = \frac{30.006 \times 47.998}{30.006 + 47.998} = 18.4635\,\mathrm{amu} = 3.0659 \times 10^{-26}\,\mathrm{kg} \tag{28.8}$$

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

the hard-sphere reaction cross section is

$$\sigma = \frac{A}{\langle u_r \rangle N_{\mathrm{A}} \sqrt{\mathrm{e}}} = \frac{7.94 \times 10^6}{\sqrt{\mathrm{e}} \times N_{\mathrm{A}} \times 1070.8} = 7.47 \times 10^{-21}\,\mathrm{m}^2 \tag{28.10}$$

28-6

$$E_0 = 70.0\,\mathrm{KJ/mol} = 5851\,\mathrm{cm}^{-1} \tag{28.11}$$

Since

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

Let

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

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

28-10

$$m_{\mathrm{F}} = 18.998\,\mathrm{amu} = 3.1547 \times 10^{-26}\,\mathrm{kg} \tag{28.14}$$

Since

$$\frac{1}{2} m_{\mathrm{F}} u_{min}^2 = \frac{D_0}{N_{\mathrm{A}}} \tag{28.15}$$

we have

$$u_{min} = \sqrt{\frac{2D_0}{mN_{\mathrm{A}}}} = \sqrt{\frac{2 \times 435.6 \times 10^3}{3.1547 \times 10^{-26} \times N_{\mathrm{A}}}} = 6772\,\mathrm{m/s} \tag{28.16}$$

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