

# 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  $\varepsilon$  are large with respect to  $\varepsilon$ .

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  $\text{O}_2$  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 Cl<sub>2</sub>

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

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

$$m_F = 18.998 \text{ amu} = 3.1547 \times 10^{-26} \text{ kg} \quad (28.14)$$

Since

$$\frac{1}{2} m_F u_{min}^2 = \frac{D_0}{N_A} \quad (28.15)$$

we have

$$u_{min} = \sqrt{\frac{2D_0}{mN_A}} = \sqrt{\frac{2 \times 435.6 \times 10^3}{3.1547 \times 10^{-26} \times N_A}} = 6772 \text{ m/s} \quad (28.16)$$

## 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（300 K）附近活化焓分别为 60, 80, 100 kJ · mol<sup>-1</sup> 时之反应比速及  $t_{1/2}$ 。

$$k(\Delta^\ddagger H^\circ) = \frac{k_B T}{h c^\circ} e^{-\Delta^\ddagger H^\circ / RT} \quad (28.17)$$

$$k(60 \text{ kJ/mol}) = \frac{k_B \times 300}{h \times 1} e^{-60000/R \times 300} = 223.47 \text{ s}^{-1} \quad (28.18)$$

$$k(80 \text{ kJ/mol}) = \frac{k_B \times 300}{h \times 1} e^{-80000/R \times 300} = 0.07362 \text{ s}^{-1} \quad (28.19)$$

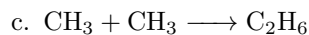
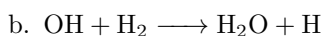
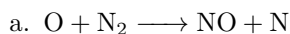
$$k(100 \text{ kJ/mol}) = \frac{k_B \times 300}{h \times 1} e^{-100000/R \times 300} = 2.425 \times 10^{-5} \text{ s}^{-1} \quad (28.20)$$

$$t_{1/2}(60 \text{ kJ/mol}) = \frac{\ln 2}{k(60 \text{ kJ/mol})} = \frac{\ln 2}{223.47} = 3.102 \times 10^{-3} \text{ s} \quad (28.21)$$

$$t_{1/2}(80 \text{ kJ/mol}) = \frac{\ln 2}{k(80 \text{ kJ/mol})} = \frac{\ln 2}{0.07362} = 9.416 \text{ s} \quad (28.22)$$

$$t_{1/2}(100 \text{ kJ/mol}) = \frac{\ln 2}{k(100 \text{ kJ/mol})} = \frac{\ln 2}{2.425 \times 10^{-5}} = 2.858 \times 10^4 \text{ s} \quad (28.23)$$

2 Use activated complex theory to determine the temperature dependence of the Arrhenius pre-exponential factors for the following three gas-phase reactions at constant  $T$  and  $P$ .



In other words, for  $A \propto T^n$ , find  $n$  for each equation. You may assume that the activated complex is linear for reaction (a) and nonlinear for reaction (b) and (c), and use the following formula to calculate the partition functions.

Hint:

$$q_{\text{vib}} \approx \frac{k_B T}{h\nu}; \quad q_{\text{elec}} \approx 1 \quad (28.24)$$

$$A \propto \frac{T q_{\text{int}}/V}{(q_A/V)(q_B/V)} \quad (28.25)$$