

# Advanced Physical Chemistry II

## HW Part II

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### 28 The Rate of a Bimolecular Gas-Phase Reaction

15,18,21,22,23,27,28,29,30,32,33,34,37,43,44

28-15 For monatomic gas,

$$\gamma = \frac{5}{3} \quad (28.1)$$

thus

$$u_{\text{peak}}(\text{He}) = \sqrt{\frac{2 \times 8.3145 \times 300}{0.004003}} \sqrt{\frac{5/3}{5/3 - 1}} = 1765 \text{ m/s} \quad (28.2)$$

$$u_{\text{peak}}(\text{Ne}) = \sqrt{\frac{2 \times 8.3145 \times 300}{0.02018}} \sqrt{\frac{5/3}{5/3 - 1}} = 786.1 \text{ m/s} \quad (28.3)$$

28-18

- No vibrational motion:

Since

$$\frac{1}{2}\mu u_r^2(R) = E_{\text{int}}(P) + \frac{1}{2}\mu u_r^2(P) - E_{\text{int}}(R) \geq E_{\text{int}}(P) - E_{\text{int}}(R) \quad (28.4)$$

we have

$$\begin{aligned} u_{r,\min} &= \sqrt{\frac{2(E_{\text{int}}(P) - E_{\text{int}}(R))}{\mu}} \\ &= \sqrt{\frac{2 \times 12400}{\frac{35.453 \times 2.016}{35.453 + 2.016} \times 10^{-3}}} \\ &= 3606 \text{ m/s} \end{aligned} \quad (28.5)$$

- Hard-sphere harmonic oscillators:

$$\begin{aligned} \frac{1}{2}\mu u_r^2(R) &\geq E_{\text{int}}(P) - E_{\text{int}}(R) = D_e(\text{H}_2) - D_e(\text{HCl}) + E_{\text{vib}}(P) - E_{\text{vib}}(R) \\ &= 12.4 \text{ kJ/mol} + hcN_A(2886 \text{ cm}^{-1} - 4159 \text{ cm}^{-1})\frac{1}{2} \\ &= 4.79 \text{ kJ/mol} \end{aligned} \quad (28.6)$$

thus

$$\begin{aligned} u_{r,\min} &= \sqrt{\frac{2 \times 47900}{\frac{35.453 \times 2.016}{35.453 + 2.016} \times 10^{-3}}} \\ &= 2241 \text{ m/s} \end{aligned} \quad (28.7)$$

28-21

$$\begin{aligned}
 \frac{1}{2}\mu u_r^2(P) &= \frac{1}{2}\mu u_r^2(R) + E_{\text{vib}}(R) - E_{\text{vib}}(P) + D_e(\text{DF}) - D_e(\text{D}_2) \\
 &= 7.62 \text{ kJ/mol} + \frac{1}{2}hcN_A(2990 - 2907)\text{cm}^{-1} + 140 \text{ kJ/mol} \\
 &= 148 \text{ kJ/mol}
 \end{aligned} \tag{28.8}$$

thus

$$u_r(P) = \sqrt{\frac{2 \times 148 \times 10^3}{3.05 \times 10^{-27}}} = 1.27 \times 10^4 \text{ m/s} \tag{28.9}$$

thus  $|\mathbf{u}_{\text{DF}} - \mathbf{u}_{cm}|, |\mathbf{u}_{\text{D}} - \mathbf{u}_{cm}|$  remains the same as Example 28-5, as follows

$$|\mathbf{u}_{\text{DF}} - \mathbf{u}_{cm}| = \frac{m_{\text{D}}}{M} u_r(P) = 1.16 \times 10^3 \text{ m/s} \tag{28.10}$$

$$|\mathbf{u}_{\text{D}} - \mathbf{u}_{cm}| = \frac{m_{\text{DF}}}{M} u_r(P) = 1.21 \times 10^4 \text{ m/s} \tag{28.11}$$

28-22

$$E_{\text{vib}} = \tilde{\nu}_e(1/2) - \tilde{x}_e\tilde{\nu}_e(1/2)^2 = 1313.2 \text{ cm}^{-1} = 15.71 \text{ kJ/mol} \tag{28.12}$$

$\therefore$

$$E'_{\text{trans}} = E_{\text{trans}} + E_{\text{vib}} - E'_{\text{vib}} - [D_e(\text{HBr}) - D_e(\text{HCl})] > 0 \tag{28.13}$$

$$9.21 + 15.71 - E'_{\text{vib}} + 67.2 > 0 \tag{28.14}$$

$$E'_{\text{vib}} < 92.12 \text{ kJ/mol} = 7701.2 \text{ cm}^{-1} \tag{28.15}$$

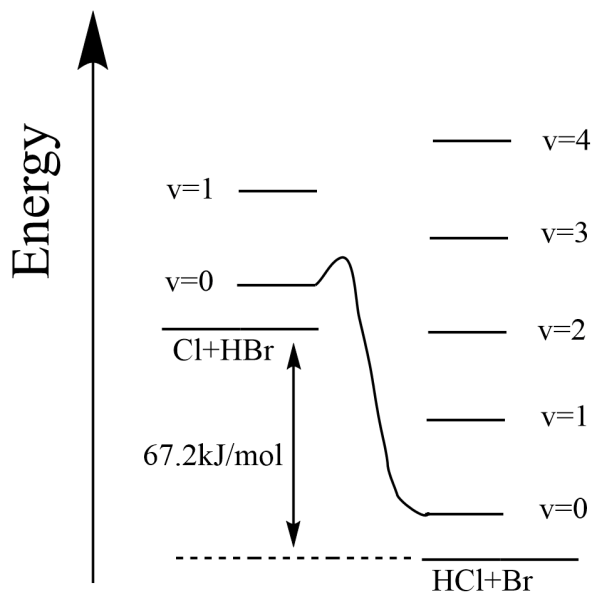
$\therefore$

$$2990.95(v + 1/2) - 52.82(v + 1/2)^2 < 7701.2 \tag{28.16}$$

$$v < 2.20 \tag{28.17}$$

i.e.  $v = 0, 1, 2$

The energy diagram is as follows



28-23 From 28-22, we have

$$E'_{\text{trans}} = E_{\text{trans}} + E_{\text{vib}} - E'_{\text{vib}} - [D_e(\text{HBr}) - D_e(\text{HCl})] = 92.12 \text{ kJ/mol} - E'_{\text{vib}} \quad (28.18)$$

thus

$$\begin{aligned} u'_r &= \sqrt{\frac{2[92120 - \tilde{\nu}_e(v + 1/2) + \tilde{\nu}_e \tilde{x}_e(v + 1/2)^2]}{\mu'}} \\ &= \sqrt{\frac{2[92120 - 35772(v + 1/2) + 631.7(v + 1/2)^2]}{2.504 \times 10^{-2}}} \text{ m/s} \end{aligned} \quad (28.19)$$

$$\begin{aligned} |\mathbf{u}_{\text{HCl}} - \mathbf{u}_{cm}| &= \frac{m_{\text{Br}}}{M} u'_r \\ &= \frac{79.904}{116.365} u'_r = 0.68667 u'_r \end{aligned} \quad (28.20)$$

∴

$v$	$u'_r / \text{ m/s}$	$ \mathbf{u}_{\text{HCl}} - \mathbf{u}_{cm}  / \text{ m/s}$
0	2438	1674
1	1785	1226
2	728.1	500.0

28-27

28-28

28-29

28-30

28-32

28-33

28-34

28-37

28-43

28-44

28-extra