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,

$$\gamma = \frac{5}{3} \tag{28.1}$$

thus

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

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

28-18

- No vibrational motion:

Since

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

we have

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

- Hard-sphere harmonic oscillators:

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

thus

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

28-21

$$\frac{1}{2}\mu u_r^2(P) = \frac{1}{2}\mu u_r^2(R) + E_{\mathrm{vib}}(R) - E_{\mathrm{vib}}(P) + D_e(\mathrm{DF}) - D_e(\mathrm{D_2})$$
$$= 7.62\,\mathrm{kJ/mol} + \frac{1}{2}hcN_{\mathrm{A}}(2990 - 2907)\mathrm{cm}^{-1} + 140\,\mathrm{kJ/mol}$$
$$= 148\,\mathrm{kJ/mol} \tag{28.8}$$

thus

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

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

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

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

28-22

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

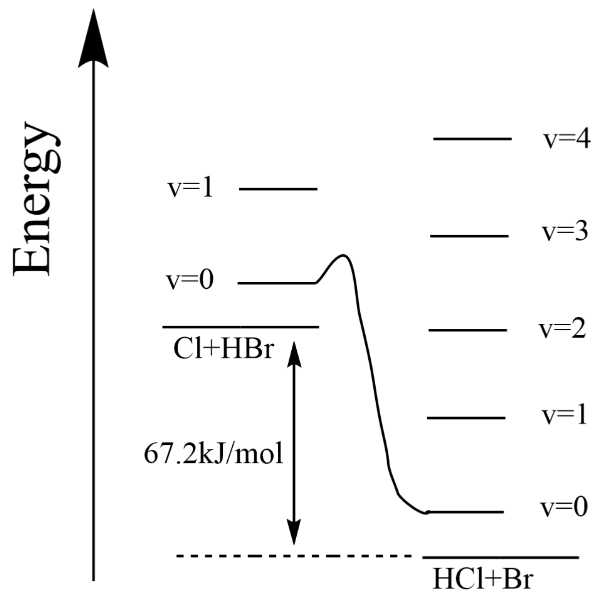
$\therefore$

$$E'_{\mathrm{trans}} = E_{\mathrm{trans}} + E_{\mathrm{vib}} - E'_{\mathrm{vib}} - [D_e(\mathrm{HBr}) - D_e(\mathrm{HCl})] > 0 \tag{28.13}$$
$$9.21 + 15.71 - E'_{\mathrm{vib}} + 67.2 > 0 \tag{28.14}$$
$$E'_{\mathrm{vib}} < 92.12\,\mathrm{kJ/mol} = 7701.2\,\mathrm{cm}^{-1} \tag{28.15}$$

$\therefore$

$$2990.95(v + 1/2) - 52.82(v + 1/2)^2 < 7701.2 \tag{28.16}$$
$$v < 2.20 \tag{28.17}$$

i.e. $v = 0, 1, 2$
The energy diagram is as follows



28-23 From 28-22, we have

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

thus

$$\begin{aligned} u'_r &= \sqrt{\frac{2[92120 - \tilde{\nu}_e(v+1/2) + \tilde{\nu}_e\tilde{x}_e(v+1/2)^2}{\mu'}} \\ &= \sqrt{\frac{2[92120 - 35772(v+1/2) + 631.7(v+1/2)^2}{2.504\times10^{-2}}}\text{m/s} \end{aligned} \tag{28.19}$$

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

$\therefore$

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

28-27 They will increase.
Since $u_r \propto \sqrt{E_{\text{trans}}}$, the radius will increase by $\sqrt{2}$.

28-28

$$\begin{aligned} E'_{\text{rot}} &= \tilde{\nu}_e\left(\frac{7}{2}-\frac{5}{2}\right) - \tilde{\nu}_e\tilde{x}_e\left[\left(\frac{7}{2}\right)^2 - \left(\frac{5}{2}\right)^2\right] \\ &= 2998.3\times1 - 45.71\times6\text{cm}^{-1} \\ &= 2724.0\,\text{cm}^{-1} \end{aligned} \tag{28.21}$$

while

$$E'_{\text{rot}} = [\tilde{B}_e - \tilde{\alpha}_e(v+1/2)]J(J+1) \tag{28.22}$$

we have

$$2724.0 = [11.007 - 0.293\times(5/2)]J(J+1) \tag{28.23}$$

$$J = 15.8 \approx 16 \tag{28.24}$$

which is too large, so there could not be a problem encountered in the analysis of the scatttering data.

28-29

$$E_{vib} = \tilde{\nu}_e(v+1/2) - \tilde{\nu}_e\tilde{x}_e(v+1/2)^2 = 13\,917.82\,\text{cm}^{-1} \tag{28.25}$$

$$E'_{\text{trans}} = E_{\text{trans}} + E_{\text{vib}} - [D_e(\text{H}_2) - D_e(\text{HCl})] > 0 \tag{28.26}$$

$\therefore$

$$703.91 + 13917.82 - 1036.64 - E'_{\text{vib}} > 0 \tag{28.27}$$

$$2990.95(v+1/2) - 52.82(v+1/2)^2 < 13585.90 \tag{28.28}$$

$$v < 4.5 \tag{28.29}$$

thus $v = 0, 1, 2, 3, 4$.

28-30 From 28-29, we have

$$2990.95(4+1/2) - 52.82(4+1/2)^2 + [\tilde{B}_e - \tilde{\alpha}_e(4+1/2)]J(J+1) < 13585.90 \tag{28.30}$$

$$2990.95(4+1/2) - 52.82(4+1/2)^2 + [10.59 - 0.307(4+1/2)]J(J+1) < 13585.90 \tag{28.31}$$

$$J < 10.9 \tag{28.32}$$

thus $J_{max} = 10$.

28-32 stripping, because the scattering is localized in the forward direction.

28-33 More low relative velocity products in (b) have internal energy that are greater than $D_e(\mathrm{N_2D^+})$.

28-34

$$\sigma = \pi\left(\frac{200+740}{2}\right)^2 = 6.94\times10^5\,\mathrm{pm}^2 \tag{28.33}$$

which is smaller than the measured cross section, which means a harpoon mechanism.

28-37 The PES is 4-dimensional for the first reaction, and 9-dimensional for the second.