P&S 5.3
The Lindemann mechanism for the gas phase isomerization of *cis* to *trans* but-2-ene is

\[
\text{cis but-2-ene} + \text{M} = \text{cis but-2-ene*} + \text{M} \quad k_{16}, k_{-16} \\
\text{cis but-2-ene*} = \text{trans but-2-ene} \quad k_{17}
\]

where *cis* but-2-ene* is an energized molecule of the olefin. Show that this mechanism leads to the following expression for the first order rate constant in pure *cis* but-2-ene:

\[
k = \frac{k_{16} k_{17} CM}{(k_{-16} M + k_{17})}
\]

The first-order rate constant for the isomerization of cis (C) to trans(T) at 742 K has the limiting high pressure value \( k_\infty = 1.9 \times 10^{-5} \text{s}^{-1} \). The half pressure for the reaction is 5 Pa. Taking \( k_{-16} \) to be \( 10^{14} \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \) estimate \( k_{16} \) and \( k_{17} \).

Denote cis by C and trans by T. Then

\[
\frac{dT}{dt} = -\frac{dC}{dt} = k_{17} C^* \\
\frac{dC^*}{dt} = k_{16} CM - k_{-16} C^* M - k_{17} C^* = 0
\]

\[
C^* = \frac{k_{16} CM}{k_{17} + k_{-16} M}
\]

and \( \frac{dT}{dt} = \frac{k_{17} k_{16} CM}{k_{17} + k_{-16} M} \) (misprint in book)
Chemistry 415 Fall 2014
Assignment 7 P&S 5: 3,5,9, & G

\[ k_i = \frac{rate}{C} = \frac{k_{17}k_{16}CM}{k_{17} + k_{16}M} = \frac{k_{17}k_{16}M}{k_{17} + k_{16}M} \]

\[ k_\infty = \frac{k_{17}k_{16}}{k_{17} + k_{16}} \quad \text{and if there is a pressure (M}_{1/2}\right) \text{ where } k_1 = k_{17}k_{16}M_{1/2}, \text{ then } k_i = \frac{k_{17}k_{16}M_{1/2}}{k_{17}M_{1/2} + k_{16}M_{1/2}} = \frac{k_\infty}{2} \]

\[ k_17 = k_{16}M_{1/2} \]

\[ M_{1/2} \Rightarrow 5Pa = \left[M_{1/2}\right]RT \]

\[ [M_{1/2}] = \frac{5}{8.31*742} = 8.11 \times 10^{-4} \text{mol/m}^3 = 8.11 \times 10^{-7} \text{mol/dm}^3 \]

\[ k_{17} = k_{16}M_{1/2} = 10^{14} \frac{dm^3}{mol \cdot s} \quad * \quad 8.11 \times 10^{-7} \text{mol/dm}^3 = 8.11 \times 10^{-7} \text{s}^{-1} \]

\[ k_\infty = \frac{k_{17}k_{16}}{k_{16}} = 1.9 \times 10^{-5} \text{s}^{-1} = \frac{8.11 \times 10^{-7} \text{s}^{-1} - k_{16}}{10^{14} \frac{dm^3}{mol \cdot s}} \]

\[ k_{16} = \frac{1.9 \times 10^{-5} \text{s}^{-1}}{8.11 \times 10^{-7} \text{s}^{-1}} \cdot 10^{14} \frac{dm^3}{mol \cdot s} = 23.4 \frac{dm^3}{mol \cdot s} \]

P&S 5.5 Methylene reacts with methane to form an excited ethane molecule which can decompose to form methy radicals. Using RRK theory estimate the rate of decomposition of the newly formed ethane. The activation energy for the decomposition of ethane is 200kJ/mole and the heats of formation of CH\(_2\), CH\(_4\), and C\(_2\)H\(_6\) are 380, -75, and -84 kJ/mol respectively.

\[ \text{CH}_2 + \text{CH}_4 = \text{C}_2\text{H}_6 \quad \Delta H = -84-(380-75) = -389 \text{ kJ.} \]

So C\(_2\)H\(_6\) * has 386 kJ of energy, dissociating with \(E_0 = 200\) kJ, so we’re 189 kJ above barrier.

\[ k = v \left( \frac{E - E_0}{E} \right)^{\nu-1} = 10^{13} \left( \frac{389 - 200}{389} \right)^{3N-7} = 10^{13} \left( \frac{389 - 200}{389} \right)^{17} = 4.7 \times 10^7 \text{s}^{-1} \]

P&S 5.9 Which of the rate coefficients for the following two reactions would you expect to reach the high pressure limit, \(k_\infty\), at the lower pressure. Why?

\[ \text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6 \]
\[ \text{CH}_3 + \text{H} = \text{CH}_4 \]

We expect the reactions to occur via the mechanisms

\[ \text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6^* \quad k_7, k_7 \quad \text{CH}_3 + \text{H} = \text{CH}_4^* \]

\[ \text{C}_2\text{H}_6^* + \text{M} = \text{C}_2\text{H}_6 + \text{M} \quad k_8 \quad \text{CH}_4^* + \text{M} = \text{CH}_4 + \text{M} \]
Using the steady state approximation for the excited molecule ($X^*$) we get
\[
\frac{dX^*}{dt} = k_1[X][Y] - k_\gamma[X^*] - k_8[X^*][M] = 0 \quad \text{so} \quad \frac{[X^*]}{[X]} = \frac{k_1[X][Y]}{k_\gamma + k_8[M]}
\]
the rate of formation of stable product is
\[
\frac{d[\text{Product}]}{dt} = k_8[X^*] = \frac{k_5k_1[X][Y]}{k_\gamma + k_8[M]}
\]
the high pressure limit occurs when $k_\gamma < k_8[M]$ or $[M] > \frac{k_\gamma}{k_8}$

$k_8$ (the rate of collisional deactivation) will be about the same for both, but $k_\gamma = \nu \left( \frac{\epsilon - \epsilon_c}{\epsilon} \right)^{3N-6}$ and this is smaller for $C_2H_6$ because N is larger. (This means that there are more internal degrees of freedom to store excess energy for $C_2H_6$ and its subsequent decay to reagents will be less likely).
So the high pressure limit is reached at lower pressure for the recombination of CH$_3$ radicals

G. The high pressure first-order rate constant for the decomposition of perchloric acid HOCIO$_3$ → OH + ClO$_3$ is

\[
k_\infty = 10^{14} \exp(-48,000/RT) \text{ sec}^{-1},
\]
where E is in cal/mole. Assume the collision frequency is $10^{14}$ cc mole$^{-1}$ sec$^{-1}$ and assume that one half of the normal modes of HOCIO$_3$ contribute to activation and that the steric factor for activation is unity. Estimate the pressure (in torr) at which the first order rate constant falls to 1/2 $k_\infty$ at 1000$^\circ$ K.

According to the Lindemann theory, $k_1 = \frac{k_9k_5[M]}{k_\gamma + k_8[M]}$ and $k_1 = \frac{k_\infty}{2}$ when $k_\gamma = k_8[M]$, so

\[
[M_{1/2}] = \frac{k_\gamma}{k_9} = \frac{k_\infty}{k_9}
\]

We expect $k_9$ to be given by $k_9 = \rho Z_{ab} e^{-\epsilon_c/kT} \left( \frac{\epsilon_c}{kT} \right)^{N-1} \frac{1}{(N-1)!}$

$Z_{ab} = 10^{14}$ cc mole$^{-1}$ sec$^{-1}$;

$\rho = 1$

$\epsilon_c = 48$ kcal/mol (strictly speaking, $\epsilon_c = E_a + (n-1)RT = 48 + 10 = 58$ kcal/mole)

$N=6$

$k_\infty = 10^{14} e^{-\epsilon_a/kT}$

so

\[
k_9 = \frac{1}{\rho} \left[ \frac{\epsilon_c}{kT} \right]^{N-1} \frac{1}{(N-1)!} = \frac{5!}{1 \times \frac{48000}{2 \times 1000}^5} = \frac{120}{245} = 0.5 \times 10^{-5} \text{ mole/cc}
\]

$[M_{1/2}] = 1.5 \times 10^{-5} \times 1000 \text{ moles/liter} = 1.5 \times 10^{-2} \text{ moles/liter}$

$P_{1/2} = 1.5 \times 10^{-2} \text{ RT} = 1.5 \times 10^{-2} \times 0.821 \times 1000 = 1.25 \text{ atm} = 950 \text{ Torr}$

(If $\epsilon_c = 58$ kcal, $P_{1/2} \approx 1.25 \text{ atm } \exp(5)(48/58)^5 = 72 \text{ atm}$)