5.62 Physical Chemistry II
Spring 2008

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Transition State Theory. I.

Transition State Theory = Activated Complex Theory = Absolute Rate Theory

\[ H_2 + F \rightleftharpoons [H_2F]^+ \xrightarrow{k} HF + H \]

Assume equilibrium between reactants \( H_2 + F \) and the transition state.

\[ K^+ = \frac{[H_2F]^+}{[H_2][F]} \]

Treat the transition state as a molecule with structure that decays unimolecularly with rate constant \( k \).

\[ \frac{d[HF]}{dt} = k[H_2F]^+ = kK^+[H_2][F] \]

\( k \) has units of sec\(^{-1}\) (unimolecular decay). The motion along the reaction coordinate looks like an antisymmetric vibration of \( [H_2F]^+ \), one-half cycle of this vibration. Therefore \( k \) can be approximated by the frequency of the antisymmetric vibration \( \nu \) [sec\(^{-1}\)]

\[ k \approx \nu \equiv \text{frequency of antisymmetric vibration (bond formation and cleavage looks like antisymmetric vibration)} \]

\[ \frac{d[HF]}{dt} = \nu K^+ [H_2][F] \]

\[ \frac{d[HF]}{dt} = \nu \left( \frac{q^+}{N} \right) \left( \frac{q^2_{H_2}/N}{q^F/N} \right) e^{-E^\pm/kT} [H_2][F] \]

\[ K^+ = \left( \frac{q^\pm_{trans}/N}{q^H_{trans}/N} \right) \left( \frac{q^\pm/vib}{q^H_{vib}} \right) \frac{g^0_{H_2}g^0_{F}}{g^\pm_{H_2}g^\pm_{F}} e^{-E^\pm/kT} \]

Reaction coordinate is antisymmetric vibrational mode of \( H_2F^+ \). This vibration is fully excited (high T limit) because it leads to the cleavage of the H–H bond and the formation of the H–F bond. For a fully excited vibration

\[ \hbar \nu \ll kT \]

The vibrational partition function for the antisymmetric mode is
\[ q_{\text{vib}}^{*\text{asym}} = \frac{1}{1 - e^{-\hbar v/kT}} \cdot \frac{kT}{\hbar}, \] 

since \( e^{-\hbar v/kT} \approx 1 - \hbar v/kT \)

Note that this is an incredibly important simplification. The unknown \( v \) simply disappears! We do not need to estimate it!

\[
K^\ddagger = \frac{kT}{\hbar} \left[ \frac{q_{\text{trans}}^H / N}{(q_{\text{trans}}^H / N)(q_{\text{vib}}^\ddagger // q_{\text{vib}}^\downarrow)} \left( \frac{q_{\text{rot}}^\ddagger // q_{\text{rot}}^\downarrow}{q_{\text{rot}}^\ddagger // q_{\text{rot}}^\downarrow} \left( \frac{q_{\text{vib}}^\ddagger // q_{\text{vib}}^\downarrow}{q_{\text{vib}}^\ddagger // q_{\text{vib}}^\downarrow} \right) \right) e^{-E^\ddagger / kT} \right]
\]

where

\[
q_{\text{vib}}^{*\ddagger} = \prod_{i=1}^{3n-5-1} \frac{1}{1 - e^{-\hbar v_i/kT}} \quad \text{if transition state is linear}
\]

or

\[
q_{\text{vib}}^{*\ddagger} = \prod_{i=1}^{3n-6-1} \frac{1}{1 - e^{-\hbar v_i/kT}} \quad \text{if transition state is nonlinear}
\]

\( n \) is # of atoms in transition state

\( q_{\text{vib}}^{*\ddagger} \equiv \) partition function from which the antisymmetric vibrational mode is excluded; it has become the reaction coordinate

So

\[
K^\ddagger = K^\ddagger = \frac{kT}{\hbar} K^\ddagger' \quad K^\ddagger' = \text{“special” modification of } K^\ddagger
\]

that excludes the partition function for the antisymmetric vibrational mode

What is \( E^\ddagger ? \)
Since a molecule cannot have a vibrational energy lower than its zero point energy, the effective barrier along the reaction coordinate is

\[ E^\ddagger = V_0 + (\text{ZPE})_{\text{TS}} - (\text{ZPE})_R \]

\( V_0 \) is the potential energy difference between the bare barrier (saddle point) and the reactant bare minimum.

For linear \( H_2F^\ddagger \), \( n = 3 \), so \( 3n-5-1 = 3 \) regular vibrational modes, thus

\[ E^\ddagger = V_0 + \frac{1}{2} h \left[ v_{\text{sym.st.}}^\ddagger + 2v_{\text{bend}}^\ddagger - v_{H_2} \right] \]

**FORMULATION of \( k^{\text{TST}} \)**

\[ \frac{d[HF]}{dt} = v \frac{kT}{h} K^{\ddagger} [H_2][F] = \frac{kT}{h} K^{\ddagger} [H_2][F] = k^{\text{TST}} [H_2][F] \]

so

\[ k^{\text{TST}} = \frac{kT}{h} K^{\ddagger} \]

but not all reactant molecules make it all the way to products — some are reflected back to separated reactants.

Thus,

\[ k^{\text{TST}} = \kappa \frac{kT}{h} K^{\ddagger} \]

where \( \kappa \equiv \text{transmission coefficient (a fudge factor)} \)

**EVALUATION OF \( k^{\text{TST}} \)**

**POTENTIAL ENERGY SURFACE KNOWN:**

- \( E^\ddagger \) — directly from potential energy surface
- \( I^\ddagger \) — (moment of inertia of transition state)
  calculate from geometric structure of transition state
- \( v^\ddagger \) — analyze shape of potential in saddle point region
- \( \kappa \) — trajectory calculations — consider \( \kappa = 1 \) for now.
\[ \text{H}_2 + \text{F} \rightarrow \text{HF} + \text{H} \quad \text{T} = 300K \]

\[ m_{\text{H}_2} = 2 \quad m_{\text{F}} = 19 \]

**Translational part**

\[
\left[ \frac{\left(q_{\text{trans}}^H / N\right)}{\left(q_{\text{trans}}^F / N\right)} \right] = \frac{Nh^3}{(2\pi kT)^{3/2}} \left( \frac{m^i}{m_{\text{H}_2} m_{\text{F}}} \right)^{3/2} = 6 \times 10^{23} \text{ mol}^{-1} \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^3}{(2\pi \times 1.38 \times 10^{-23} \text{ J/K} \times 300 \text{ K})^{3/2}} \left( \frac{6 \times 10^{23} \times 0.021}{0.002 \times 0.019 \text{ kg}} \right)^{3/2} = 2.52 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}
\]

**Rotational part**

\[ \sigma_{\text{H}_2} = 2 \quad \sigma^i = 1 \quad q_{\text{rot}} = \frac{8\pi^2 l kT}{\hbar^2} \quad I_{\text{H}_2} = 4.56 \times 10^{-48} \text{ m}^2 \text{ kg} \quad I^i = 1.24 \times 10^{-46} \text{ m}^2 \text{ kg} \]

\[ \frac{q_{\text{rot}}^{i*}}{q_{\text{rot}}^{i}} = \frac{I^i}{I_{\text{H}_2}} \frac{\sigma_{\text{H}_2}}{\sigma^i} = 54.4 \]

**Vibrational Part**

\[ \text{H}_2\text{F}^i \text{ is a linear transition state (assumed)} \]

\[ 3n-5-1 = 3 \text{ vibrational degrees of freedom (one vibration is reaction coordinate)} \]

\[ \frac{h\nu_x^i}{k} = 5771 \text{ K} \text{ stretch} \quad \frac{h\nu_y^i}{k} = 573 \text{ K} \text{ (doubly degenerate) bend} \]

\[ h\nu_{\text{H}_2}/k = 6323 \text{ K} \]

\[ \frac{q_{\text{vib}}^{i*}}{q_{\text{vib}}^{\text{H}_2}} = \left(1 - e^{-h\nu_x^i/kT}\right)^{-1} \left(1 - e^{-h\nu_y^i/kT}\right)^{-2} \left(1 - e^{-h\nu_{\text{H}_2}/kT}\right)^{-1} = 1.38 \]

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Electronic part

\[ g_0^s = 2(S = 1/2) \quad g_0^F = 6(L = 1, S = 1/2) \quad g_0^{H_2} = 1 \]

(spin orbit splitting of F \(^2\)P\(_{1/2}\) - \(^2\)P\(_{3/2}\) is 404 cm\(^{-1}\))

\[ \frac{g_0^s}{g_0^{H_2}} = \frac{1}{3} \]

Calculate \(E^\pm\):

\[ V_0 = 3.8 \text{kJ mol}^{-1} \quad v_s^i = 1.2 \times 10^{14} \text{s}^{-1} \quad v_b^i = 1.19 \times 10^{13} \text{s}^{-1} \] (reasonable guesses)

(How do we guess values for \(v_s^i\) and \(v_b^i\)?)

\[ v_{H_2} = 1.32 \times 10^{14} \text{ s}^{-1} \]

\[ E^\pm = V_0 + \frac{1}{2} \hbar N \left[ v_s^i + 2v_b^i - v_{H_2} \right] = 6.1 \text{ kJ mol}^{-1} \]

Calculate \(kT/h\)

\[ kT/h = \frac{1.38 \times 10^{-23} \text{J/K} \times 300 \text{K}}{6.63 \times 10^{-34} \text{J} \cdot \text{s}} = 6.24 \times 10^{12} \text{ s}^{-1} \]

Putting it all together:

\[ k^{\text{TST}} = \kappa \frac{kT}{h} K^{k'p} \]

\[ = 1 \left( 6.24 \times 10^{12} \text{ s}^{-1} \right) \left( 2.52 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1} \right) \left( 54.4 \right) \left( 1.38 \right) \frac{1}{3} e^{-6.1/RT} \]

\[ = 3.93 \times 10^7 e^{-6.1/RT} \]

\[ k^{\text{TST}} = 3.40 \times 10^6 \text{m}^3 \text{mol}^{-1} \text{s}^{-1} \text{ at } 300 \text{K} \]

\[ k^{\text{EXP}} = 2.70 \times 10^6 \text{m}^3 \text{mol}^{-1} \text{s}^{-1} \quad \text{acceptable agreement} \]

Experimental value is smaller because \(\kappa\) is probably not 1. Sometimes \(k^{\text{TST}}\) will be smaller than \(k^{\text{EXP}}\) because of tunneling. This model for \(k^{\text{TST}}\) does not take the quantum mechanical phenomenon of tunneling into account. Tunneling can make the reaction rate become faster than the \(k^{\text{TST}}\) prediction.

If \(k^{\text{TST}} < k^{\text{EXP}}\), it may mean that there is some tunneling contribution.