

## Transition-State Theory

A "good" theory must take into account the internal degrees of freedom of the reactants and their angle of approach. An approach known as transition state theory (=activated complex theory)(=absolute rate theory) does so in an approximate way.

### POTENTIAL ENERGY SURFACE

A correct theory must consider the internal structure of molecules and the forces acting on atoms in the molecules because bonds are being broken and formed during a reaction. During a reactive collision, the force on an atom depends on both intramolecular forces (forces between atoms in a molecule) and intermolecular forces (forces between molecules). Must treat the two colliding reactants as a single quantum mechanical system. This system exists only during collision process.

The system's potential energy is calculated the same way the potential energy for nuclear vibrational motion is calculated. Within the Born-Oppenheimer approximation, solve

$$H_{el} \Psi_{el} = E_{el} \Psi_{el}$$

at fixed nuclear configuration.

The resulting  $E_{el}$  is the potential energy at that nuclear configuration. Systematically vary the nuclear configuration (grid of points) to get potential energy as a function of nuclear coordinates.

Problem: too many nuclear coordinates! Can't plot potential energy as a function of more than 2 coordinates. A plot of potential energy versus 2 coordinates is a 3D plot where the potential energy is a SURFACE. Potential energy for more than 2 coordinates is still called a surface even though there are more than 2 coordinates.

EXAMPLE:  $\text{H}_2 + \text{F} \rightarrow \text{HF} + \text{H}$

For collinear approach: there are 2 independent variables  
 $R_{\text{HF}}$  and  $R_{\text{HH}}$  on which the potential depends

The potential energy of this system can be represented as a 3D surface as a function of  $R_{\text{HF}}$  and  $R_{\text{HH}}$ . The 3D surface can be represented as a 2D contour potential energy surface.

Lines on a contour map represent EQUIPOTENTIALS. Valleys correspond to initial and final states.

(To go from one valley to another requires crossing a saddle point)

### REACTION COORDINATE FOR F + H<sub>2</sub>

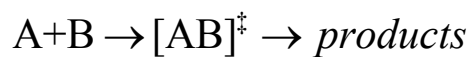
REACTION COORDINATE - *minimum energy path* along deepest part of potential energy surface

Note: reaction coordinate here corresponds to antisymmetric H<sub>2</sub>F vibration

TRANSITION STATE - transitory [H<sub>2</sub>F]<sup>‡</sup> complex with a definite structure - dissociates within one half antisymmetric vibration

### TRANSITION STATE THEORY

An approach to calculating a rate constant by reducing the dynamics of the reaction to an equilibrium between the reactants and the transition state along the reaction coordinate.



Uses statistical mechanics to treat the equilibrium. The reaction coordinate is the 1D antisymmetric vibration of the transition state.

### Transition State Theory

Transition state theory = Activated Complex Theory = Absolute Rate Theory



Assume equilibrium between reactants  $\text{H}_2 + \text{F}$  and the transition state. Treat the transition state as a molecule with structure which unimolecularly decays with rate constant  $k$ .

$$K^\ddagger = \frac{[\text{H}_2\text{F}]^\ddagger}{[\text{H}_2][\text{F}]}$$

$$\frac{d[\text{HF}]}{dt} = k[\text{H}_2\text{F}]^\ddagger = kK^\ddagger [\text{H}_2][\text{F}]$$

$k$  has units of  $\text{sec}^{-1}$  (unimolecularly decay). The motion along the reaction coordinate looks like an antisymmetric vibration of  $[\text{H}_2\text{F}]^\ddagger$ , one-half cycle of this vibration. Therefore  $k$  can be approximated by the frequency of the antisymmetric vibration  $\nu[\text{sec}^{-1}]$

$k = \nu =$  frequency of antisymmetric vibration (bond formation and cleavage looks like antisymmetric vibration)

$$\frac{d[\text{HF}]}{dt} = \nu K^\ddagger [\text{H}_2][\text{F}]$$

$$\frac{d[\text{HF}]}{dt} = \nu \left[ \frac{(q^{\ddagger*} / N)}{(q^{\text{H}_2^*} / N)(q^{\text{F}} / N)} \right] e^{-E^\ddagger / k_B T} [\text{H}_2][\text{F}]$$

$$K^\ddagger = \left[ \frac{(q_{\text{trans}}^\ddagger / N)}{(q_{\text{trans}}^{\text{H}_2} / N)(q_{\text{trans}}^{\text{F}} / N)} \right] \left( \frac{q_{\text{vib}}^{\ddagger*}}{q_{\text{vib}}^{\text{H}_2^*}} \right) \left( \frac{q_{\text{rot}}^\ddagger}{q_{\text{rot}}^{\text{H}_2}} \right) \left( \frac{g_0^\ddagger}{g_0^{\text{H}_2} g_0^{\text{F}}} \right) e^{-E^\ddagger / k_B T}$$

Reaction coordinate is antisymmetric vibrational mode of  $[\text{H}_2\text{F}]^\ddagger$ . This vibration is fully excited because it leads to the cleavage of the H-H bond and the formation of the H-F bond. For a fully excited vibration,

$$h\nu \ll k_B T$$

The vibrational partition function for the antisymmetric mode is

$$q_{vib}^{*,asym} = \frac{1}{1 - e^{-h\nu/k_B T}} \approx \frac{k_B T}{h\nu}, \text{ since } e^{-h\nu/k_B T} \approx 1 - \frac{h\nu}{k_B T}$$

$$K^\ddagger = \left[ \frac{(q_{trans}^\ddagger / N)}{(q_{trans}^{H_2} / N)(q_{trans}^F / N)} \right] \left( \frac{q_{vib}^{\ddagger*}}{q_{vib}^{H_2*}} \right) \left( \frac{q_{rot}^\ddagger}{q_{rot}^{H_2}} \right) \left( \frac{g_0^\ddagger}{g_0^{H_2} g_0^F} \right) e^{-E^\ddagger / k_B T}$$

where

$$q_{vib}^{\ddagger*} = \prod_{i=1}^{3n-5-1} \frac{1}{1 - e^{-h\nu_i/k_B T}} \text{ if the transition state is linear}$$

$$q_{vib}^{\ddagger*} = \prod_{i=1}^{3n-6-1} \frac{1}{1 - e^{-h\nu_i/k_B T}} \text{ if the transition state is linear}$$

(n = # atoms in transition state)

$q_{vib}^{\ddagger*}$  is the partition function from which the antisymmetric vibrational mode is excluded; it because the reaction coordinate

So

$$K^\ddagger = \frac{k_B T}{h\nu} K^{\ddagger*}$$

$K^{\ddagger*}$  is the special  $K^\ddagger$  excluding the partition function for the reaction coordinate

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

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

For linear  $\text{H}_2\text{F}^\ddagger$ ,  $n=3$ , so  $3n-5-1 = 3$  vibrational modes, thus

$$E^\ddagger = V_0 + \underbrace{\frac{h}{2} [v_{\text{sym.st.}}^\ddagger + 2v_{\text{bend}}^\ddagger - v_{\text{H}_2}]}_{\text{difference in ZPE}}$$

### FORMULATION OF $k^{\text{TST}}$

$$k^{\text{TST}} = \frac{k_B T}{h} K^\ddagger,$$

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

Thus,

$$k^{\text{TST}} = \kappa \frac{k_B T}{h} K^\ddagger, \text{ where } \kappa = \text{transmission coefficient}$$

### EVALUATION OF $k^{\text{TST}}$

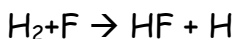
#### POTENTIAL ENERGY SURFACE KNOWN:

$E^\ddagger$  - directly from potential energy surface

$I^\ddagger$  - 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)



$$T=300\text{K}, m_{\text{H}_2} = 2 \text{ amu}, m_{\text{F}} = 19 \text{ amu}$$

Translational part

$$\left[ \frac{(q_{trans}^\ddagger / N)}{(q_{H_2} / N)(q_F / N)} \right] = \frac{Nh^3}{(2\pi k_B T)^{3/2}} \left( \frac{m^\ddagger}{m_{H_2} m_F} \right)^{3/2}$$

$$= 6 \times 10^{23} \text{ mol}^{-1} \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^3}{(2\pi \times 1.38 \times 10^{-23} \text{ J/K} \times 300 \text{ K})^{3/2}} \left( \frac{6 \times 10^{23} \times 0.021}{0.002 \times 0.019 \text{ kg}} \right)^{3/2}$$

$$= 2.52 \times 10^{-7} \text{ m}^3 / \text{mol}$$

Rotational part

$$\sigma_{H_2} = 2 \quad \sigma^\ddagger = 1 \quad q_{rot} = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

$$I_{H_2} = 4.56 \times 10^{-48} \text{ m}^2 \text{ kg} \quad I^\ddagger = 1.24 \times 10^{-46} \text{ m}^2 \text{ kg}$$

(assume linear TS)

$$\frac{q_{rot}^\ddagger}{q_{rot}^{H_2}} = \frac{I^\ddagger}{I_{H_2}} \frac{\sigma^{H_2}}{\sigma^\ddagger} = 54.4$$

Vibrational part

$[\text{H}_2\text{F}]^\ddagger$  is a linear transition state

$3n-5-1 = 3$  vibrational degrees of freedom (one vibration is reaction coordinate)

$$\frac{h\nu_s^\ddagger}{k_B} = 5771 \text{ K (stretch)} \quad \frac{h\nu_b^\ddagger}{k_B} = 573 \text{ K (2x degen bend)}$$

$$\frac{h\nu_{H_2}^\ddagger}{k_B} = 6323 \text{ K}$$



$$\frac{q_{vib}^{\ddagger*}}{q_{vib}^{*H_2}} = \frac{\left(1 - e^{-hv_s^\ddagger/k_B T}\right)^{-1} \left(1 - e^{-hv_b^\ddagger/k_B T}\right)^{-2}}{\left(1 - e^{-hv_{H_2}^\ddagger/k_B T}\right)^{-1}} = 1.38$$

Electronic part

$$g_0^\ddagger = 4 \quad g_0^F = 4 \quad g_0^{H_2} = 1 \quad \frac{g_0^\ddagger}{g_0^F g_0^{H_2}} = 1$$

Calculate  $E^\ddagger$ 

$$V_0 = 3.8 \text{ kJ/mol} \quad \nu_s^\ddagger = 1.20 \times 10^{14} \text{ s}^{-1} \quad \nu_b^\ddagger = 1.19 \times 10^{13} \text{ s}^{-1}$$

(How do we guess values for  $\nu_s^\ddagger$  and  $\nu_b^\ddagger$ ?)

$$\nu_{H_2}^\ddagger = 1.32 \times 10^{14} \text{ s}^{-1}$$

$$E^\ddagger = V_0 + \frac{1}{2} hN \left[ \nu_s^\ddagger + 2\nu_b^\ddagger - \nu_{H_2}^\ddagger \right] = 6.1 \text{ kJ/mol}$$

Calculate  $k_B T/h$ 

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

All together now

$$k^{TST} = \kappa \frac{k_B T}{h} K^\ddagger$$

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

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

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

$$k^{EXP} = 2.70 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ - NOT BAD AGREEMENT!}$$

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

If  $k^{TST} < k^{EXP}$ , it may mean that there is some tunneling contribution.

### Additional Material on TST

Want to get  $k^{TST}$  into Arrhenius form

$$k^{TST} = \kappa \frac{k_B T}{h} K^{\ddagger}$$

$$\text{but } K^{\ddagger} = e^{-G^{\ddagger}/RT} \rightarrow -RT \ln K^{\ddagger} = \Delta G^{\ddagger}$$

$$\text{so } k^{TST} = \kappa \frac{k_B T}{h} e^{-G^{\ddagger}/RT} = \kappa \frac{k_B T}{h} e^{-S^{\ddagger}/R} e^{-H^{\ddagger}/RT}$$

because  $G = H - TS$

$$\text{NOW: } H^{\ddagger} = E^{\ddagger} + \Delta n RT$$

Where  $\Delta n = \#$  molecules in TS - molecularity of reaction  
(molecularity: eg: unimolecular, bimolecular, etc)

$$\text{e.g.: } \Delta n = 1 - 2 = -1$$

$$\text{So: } k^{TST} = \kappa \underbrace{\frac{k_B T}{h} e^{-S^{\ddagger}/R}}_{BT^m} e^{-E^{\ddagger}/RT}$$

$$k^{TST} = BT^m e^{-E^{\ddagger}/RT}$$

(where  $m=1$ )

Again, theory predicts a temperature dependence to the pre-exponential factor which is difficult to observe experimentally unless the rate constant is measured over a wide temperature range (At least a factor of 5).

Now:

$$\frac{d \ln k^{TST}}{dT} = \frac{d \left( \ln \left[ \kappa \frac{k_B}{h} e^{S^\ddagger/R} e^1 \right] + \ln T + e^{-E^\ddagger/RT} \right)}{dT}$$

$$= \frac{1}{T} + \frac{E^\ddagger}{RT^2}$$

$$\text{Arrhenius: } \frac{d \ln k}{dT} = \frac{E_{act}}{RT^2}$$

$$\frac{d \ln k}{dT} = \frac{d \ln k^{TST}}{dT}$$

$$\frac{E_{act}}{RT^2} = \frac{1}{T} + \frac{E^\ddagger}{RT^2}$$

$$\therefore E_{act} = RT + E^\ddagger$$

Again, experimental  $E_{act}$  is larger than  $E^\ddagger$  because  $E_{act}$  is a difference between the average energy of molecules in the ensemble and the average energy of molecules that react, while  $E^\ddagger$  is a microscopic quantity, a threshold energy along PES. Notice  $E_{act}$  is not a barrier along PES.

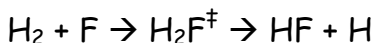
### COMPARISON OF TRANSITION STATE THEORY AND COLLISION THEORY

Calculate  $k^{TST}$  in the limit of the assumptions of collision theory (ie: simplified TST):

- 1) Collisions of hard spheres
- 2) Only translational degrees of freedom

Treat  $H_2$  as an atom - a hard sphere of mass 2 (no rotation, no vibration)

Treat  $H_2F^\ddagger$  as a diatomic molecule (One unknown parameter,  $d_{H_2-F}$ )



With these assumptions

$$k \approx \frac{k_B T}{h} \left[ \frac{(q_{trans}^\ddagger / N)}{(q_{trans}^{H_2} / N)(q_{trans}^F / N)} \right] q_{rot}^\ddagger e^{-E^\ddagger / RT}$$

Note: no vibrational partition function for  $H_2F^\ddagger$  is included because the one vibrational mode for the pseudo diatomic molecule transition state has become the reaction coordinate.

$$k \approx \frac{k_B T}{h} \left\{ \frac{\left[ \frac{2\pi(m_{H_2} + m_F)k_B T}{h^3 N} \right]^{3/2}}{\left[ \frac{2\pi m_{H_2} k_B T}{h^3 N} \right]^{3/2} \left[ \frac{2\pi m_F k_B T}{h^3 N} \right]^{3/2}} \right\} \frac{8\pi^2 I^\ddagger k_B T}{\sigma h^2} e^{-E^\ddagger / RT}$$

The reason there is no rotational or vibrational partition function for  $H_2$  is not that we are assuming the high-T limit, but rather  $H_2$  is treated as if it were an atom.

Now

$$I^\ddagger = \mu d_{H_2-F}^2, \quad \mu = \frac{m_{H_2} m_F}{m_{H_2} + m_F}$$

$$k = N \left[ \frac{8k_B T}{\pi} \left( \frac{m_{H_2} + m_F}{m_{H_2} m_F} \right) \right]^{1/2} \frac{\pi d_{H_2-F}^2}{\sigma} e^{-E^\ddagger / RT}$$

This looks identical to the collision theory result. Collision theory is not based on thermodynamics.

$$k^{CT} = \left[ \frac{8k_B T}{\pi\mu} \right]^{1/2} \pi d_{AB}^2 e^{-E_0/RT}$$

Calculate value for  $k^{TST}$  in limit of collision theory assumptions (ie: what fraction of collisions are effective because they have sufficient translational energy along the line of centers?):

$$\sigma = 1 \quad \pi d_{H_2-F}^2 = 3 \times 10^{19} m^2 \quad k = 3.4 \times 10^8 e^{-E^\ddagger/RT} m^3 / mol \cdot s$$

Compare to  $k^{TST}$

$$k^{TST} = 3.9 \times 10^7 e^{-E^\ddagger/RT} m^3 / mol \cdot s$$

$k^{TST}$  is smaller because it reflects the more restrictive collinear steric requirement.  $k^{CT}$  is an upper bound because collision theory treats reactants as spheres with no favored direction of approach (but with explicit requirement of the effective collision energy).