

AB^\ddagger is the transition state (or activated complex.)

Transition state theory assumes that the transition state and reactants are in equilibrium with each other, and uses concepts from **chemical equilibrium** and **statistical mechanics** to find kinetic info such as rate constants!

Eyring Equation (key to transition-state theory)

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

$$K^\ddagger = e^{-\Delta G^\ddagger / RT}$$

Change in Gibbs energy from reactants to TS

So...

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT} \xrightarrow{\Delta G = \Delta H - T\Delta S} k = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

Entropy of activation

Enthalpy of activation



$$E_a = RT + \Delta U^\ddagger \quad \text{and} \quad \Delta U^\ddagger = \Delta H^\ddagger - RT\Delta^\ddagger n_g$$

so
$$E_a = RT + \Delta H^\ddagger - RT\Delta^\ddagger n$$

Unimolecular Gas Phase Reaction

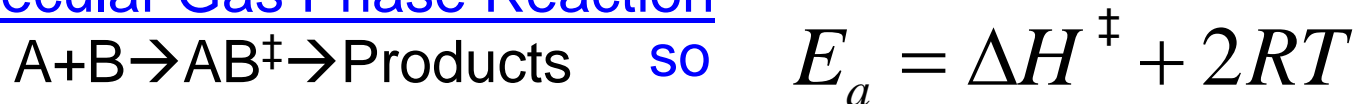


$$k = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

$$k = e \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-E_a / RT}$$

Same for
reactions
in solution

Bimolecular Gas Phase Reaction



$$k = e^2 \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-E_a / RT}$$



In the NMR/N,N-DMA Paper, Gasparro et al. found an activation energy of 70.3 kJ/mol and a pre-factor of $1.87 \times 10^{10} \text{ s}^{-1}$. Using these values, and a temperature of 298 K, find...

$$\Delta H^\ddagger \quad \Delta S^\ddagger \quad \Delta G^\ddagger$$

Why is TST important?

1. Provides details of a reaction on the molecular scale.
2. Connects quantum mechanics and kinetics.
3. Currently used for many computational studies on reaction rates.

