

# LINDEMANN THEORY AND ITS LIMITATIONS

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## SOLUTION TO PROBLEM #1

i.e. they can just move faster.

- Hard spheres can only put energy into one place  $\rightarrow$  translation
- Molecules can put energy into lots of different places, the different degrees of freedom  $\leftarrow$  i.e. translation, rotation, vibration.
- Even if a collision occurs with insufficient energy for a direct reaction, the energy could redistribute from other degrees of freedom (or "nodes") into the relevant mode. Meaning that:

$$k(\text{expt}) > k(\text{SCT}) \rightarrow \text{more molecules have enough energy to react in reality than predicted by SCT.}$$

Solution is to correct the energy factor ( $e^{-E^0/RT}$ ) to account for the # of different degrees of freedom, s. i.e.

$$e^{-E^0/RT} \xrightarrow{\text{SCT}} \frac{1}{(s-1)!} \left( \frac{E^0}{RT} \right)^{s-1} \times e^{-E^0/RT}$$

$\rightarrow$  correction. From statistical mechanics.

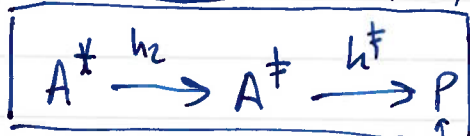
$\rightarrow$   $s \uparrow$ , then this  $\uparrow$  and  $k \uparrow$ , as expected.

## SOLUTION TO PROBLEM #2

- Distinguish an excited molecule,  $A^*$ , from an activated molecule  $A^\ddagger$ . i.e.:

just hot and too there.

Also hot and too there but in a productive way.



② Activated molecule can then form products. (in  $k^\ddagger$ ).

① Excited molecule has to redistribute energy to become activated (in  $k_2$ ).

This is RRK Theory

$$k_2 = k^\ddagger \left( \frac{E - E^0}{E} \right)^{s-1}$$

$\rightarrow$  i.e. how much excess energy is there to turn  $A^*$  into  $A^\ddagger$ .

$k_2 \ll k^\ddagger$  once a complex forms, it falls apart v. prob. e.g.  $A^* \rightarrow A^\ddagger$  (slow)  $A^\ddagger \rightarrow P$  (fast).