LINDEMANN THEORY AND ITS LIMITATIONS

SOLUTION TO PROBLEM #1

- Hard spheres can only put energy into one place → translations (i.e. they can just move faster.)
- Molecules can put energy into lots of different places, the different degrees of freedom ← 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 "modes") into the relevant mode. Meaning that:

$$k(\text{expt}) > k(\text{SCT})$$

→ 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.

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

$e^{-E^0/RT}$ ↑ SCT

$\frac{1}{(s-1)!}\left(\frac{E^0}{RT}\right)^{s-1}$ ↳ correction. From statistical mechanics.

as s↑, then this ↑ and k↑, as expected (trust me.)

SOLUTION TO PROBLEM #2

- Distinguish an excited molecule, A^* (just hot and bothered), from an activated molecule $A^\ddagger$ (Also hot and bothered but in a productive, angry way.). i.e.:

$$A^* \xrightarrow{k_2} A^\ddagger \xrightarrow{k^\ddagger} P$$

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

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

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

$\left(\frac{E-E^0}{E}\right)$ ↳ i.e. how much excess energy is there to turn A^* into $A^\ddagger$.

This is RRK Theory

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