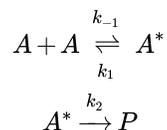


## 12.7: The Lindemann Mechanism

The **Lindemann mechanism** (Lindemann, Arrhenius, Langmuir, Dhar, Perrin, & Lewis, 1922) is a useful one to demonstrate some of the techniques we use for relating chemical mechanisms to rate laws. In this mechanism, a reactant is collisionally activated to a highly energetic form that can then go on to react to form products.



If the steady state approximation is applied to the intermediate  $A^*$

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] \approx 0$$

an expression can be derived for  $[A^*]$ .

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

Substituting this into an expression for the rate of the production of the product  $P$

$$\frac{d[P]}{dt} = k_2[A^*]$$

yields

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [A]^2}{k_{-1}[A] + k_2}$$

In the limit that  $k_{-1}[A] \ll k_2$ , the rate law becomes first order in  $[A]$  since  $k_{-1}[A] + k_2 \approx k_2$ .

$$\frac{d[P]}{dt} = \frac{k_2 k_1}{k_{-1}} [A]$$

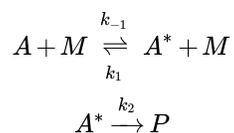
This will happen if the second step is very slow (and is the rate determining step), such that the reverse of the first step “wins” in the competition for  $[A^*]$ . However, in the other limit, that  $k_2 \gg k_{-1}[A]$ , the reaction becomes second order in  $[A]$  since  $k_{-1}[A] + k_2 \approx k_{-1}[A]$ .

$$\frac{d[P]}{dt} = k_1[A]^2$$

which is consistent with the forward reaction of the first step being the rate determining step, since  $A^*$  is removed from the reaction (through the formation of products) very quickly as soon as it is formed.

### Third-body Collisions

Sometimes, the **third-body collision** is provided by an inert species  $M$ , perhaps by filling the reaction chamber with a heavy non-reactive species, such as Ar. In this case, the mechanism becomes



And in the limit that  $[A^*]$  can be treated using the steady state approximation, the rate of production of the product becomes

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2}$$

And if the concentration of the third body collider is constant, it is convenient to define an **effective rate constant**,  $k_{uni}$ .

$$k_{uni} = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2}$$

The utility is that important information about the individual step rate constants can be extracted by plotting  $1/k_{uni}$  as a function of  $1/[M]$ .

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_2 k_1} + k_2 \left( \frac{1}{[M]} \right)$$

The plot should yield a straight line, the slope of which gives the value of  $k_2$ , and the intercept gives  $(k_{-1}/k_2 k_1)$ .

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