Class 9.2

Chemical Kinetics

CHEM 102H

T. Hughbanks

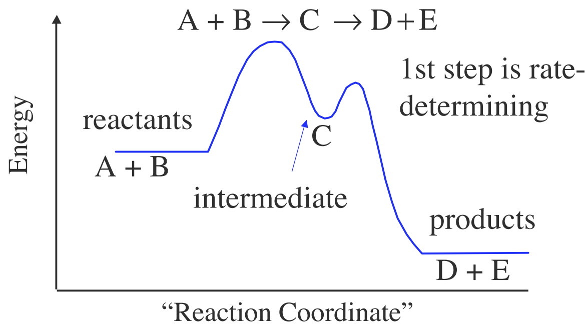
Rate laws & mechanisms

- Start with overall reaction
- Guess some mechanism(s)
- Derive corresponding rate laws
- Compare with experiments
- Repeat as needed
- **We need to relate rates of individual steps to the overall, observable rate laws.**

Rate Determining Steps

- If a single step in a reaction mechanism is much slower than the other steps, then the rate of the slow step is crucial in determining overall rate.
- The rate determining step (RDS) can be thought of as a “bottleneck” in the formation of products. Steps that follow the RDS have negligible effect on the overall rate of reaction.

A reaction profile



Example: rates & mechanisms

$$2\,NO_2 \rightarrow 2\,NO + O_2$$

- 2 possible mechanisms for this:

1. $NO_2 \rightarrow NO + O$ (slow)
   $O + NO_2 \rightarrow O_2 + NO$ (fast)
2. $2\,NO_2 \rightarrow NO_3 + NO$ (slow)
   $NO_3 \rightarrow NO + O_2$ (fast)

Example: rates & mechanisms

- experimental rate law is:

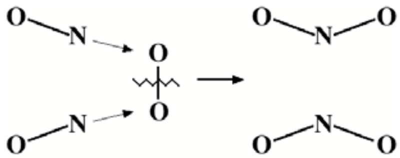
$$\text{rate} = k[NO_2]^2$$

1. $NO_2 \rightarrow NO + O$ (slow)
   $O + NO_2 \rightarrow O_2 + NO$ (fast)
   rate = ?
2. $2\,NO_2 \rightarrow NO_3 + NO$ (slow)
   $NO_3 \rightarrow NO + O_2$ (fast)
   rate = ?

Rate Laws Can Prove a Mechanism is Wrong but Can't Prove one Right!

$2\ NO + O_2 \rightarrow 2NO_2$ rate = $k[NO]^2[O_2]$

A single step mechanism?



Rate Law is consistent.

Rate Laws ... Proof?

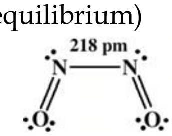
$2\ NO + O_2 \rightarrow 2NO_2$

rate = $k[NO]^2[O_2]$

Two-step mechanism?

(1) $NO + NO \rightleftarrows N_2O_2$ (fast equilibrium)

(2) $N_2O_2 + O_2 \rightarrow 2NO_2$ (slow)



Rate Law for this mechanism?

Mechanism & Rate

(1) $NO + NO \rightleftarrows N_2O_2$ (fast equilibrium)

(2) $N_2O_2 + O_2 \rightarrow 2NO_2$ (slow)

- rate = rate of slow step = $k_2[N_2O_2][O_2]$
- N_2O_2 is NOT a reactant or a product. We should eliminate it from the rate law.

Equilibrium: $2\ NO \rightleftarrows N_2O_2$

- The interconversion of products and reactants are an example of <u>equilibrium</u>
- Set: rate forward = rate backward

  $k_f[NO]^2 = k_r[N_2O_2]$
- Thus, the Equilibrium Constant, K_{eq}, is:

$$\frac{k_f}{k_r} = \frac{[N_2O_2]}{[NO]^2} = K_{eq}$$

Reversible Step: $2\ NO \rightleftarrows N_2O_2$

$$2\ NO \rightleftarrows N_2O_2 \quad \text{(fast)}$$

- Rates of forward and backward reactions will quickly become equal.
- Set: rate forward = rate backward

  $k_f[NO]^2 = k_r[N_2O_2]$
- From this:

  $[N_2O_2] = (k_f / k_r)[NO]^2$

$2\ NO_2 + O_2 \rightarrow 2\ NO_2$, cont...

$$2\ NO \rightleftarrows N_2O_2 \quad \text{(fast)}$$
$$N_2O_2 + O_2 \rightarrow 2NO_2 \quad \text{(slow)}$$

- rate = rate of slow step = $k_2[N_2O_2][O_2]$
- $[N_2O_2] = (k_f / k_r)[NO]^2$
- So:

  rate = $k_2[N_2O_2][O_2] = k_2(k_f/k_r)[NO]^2[O_2]$

  $= k_{\text{observed}}[NO]^2[O_2] = k_2 K_{eq}[NO]^2[O_2]$