

Chemical Reactions, Rates and the Reaction Rate Constant

John W. Daily

Basic Concepts

- What is a chemical reaction? A collisional process in which the atomic composition of atoms/molecules change.

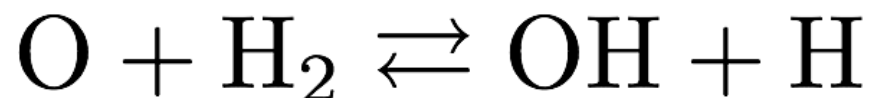


- Stoichiometric Coefficients and conservation of atoms

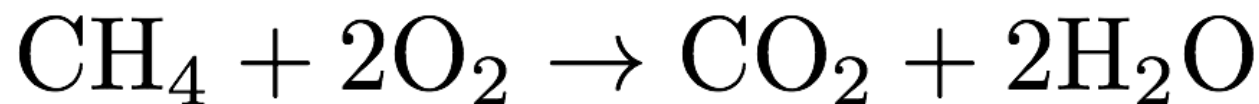
Atom	No. in Reactants	No. in Products
C	1	1
H	4	4
M	1	1

Elementary vs Global

- Elementary – Reactions that actually occur in a single step.

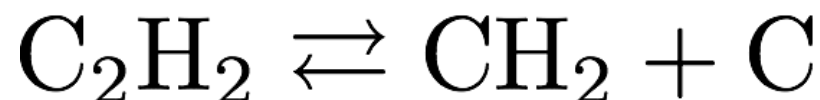


- Global – An overall reaction that involves multiple elementary reactions.

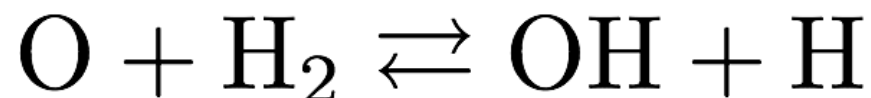


Examples of Elementary Reactions

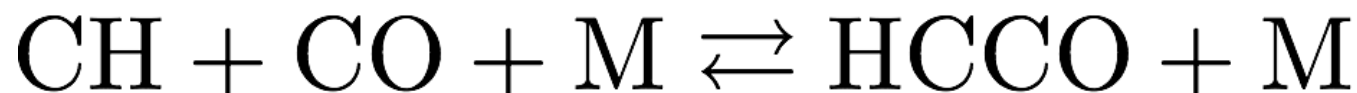
- Unimolecular



- Bimolecular

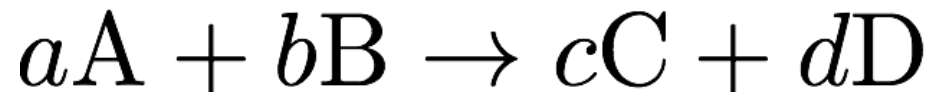


- Trimolecular



Higher order reactions not typically seen in practice.

Rate of Reaction



$$R = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Notation for concentration is $[A]$ = amount of material per unit volume.

Amount can be number density or moles.

So dimension of R is concentration per unit time.



Reaction Rate

- Reaction rate can be shown to usually depend on the concentration of the reactants. Most commonly:

$$R = k[A]^m[B]^n$$

- This is called a rate equation or rate expression. Generally:

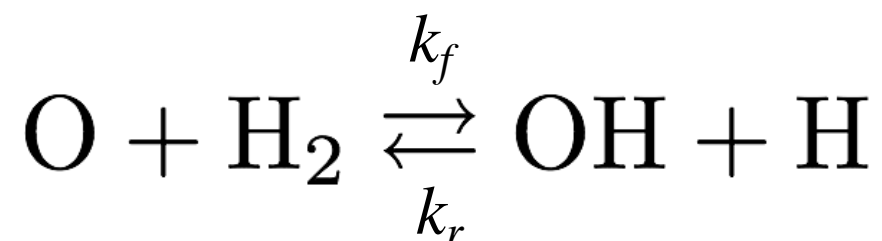
$$R = k \prod_{i=1}^K c_i^{n_i}$$

- k is the reaction rate constant



Elementary Reaction Example

- Reaction



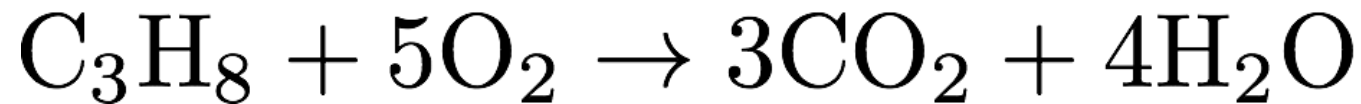
- Rate expression

$$\frac{d[\text{O}]}{dt} = -k_f [\text{O}][\text{H}_2] + k_r [\text{OH}][\text{H}]$$



Global Reaction Example

- Reaction



- Rate expression

$$\frac{d[\text{C}_3\text{H}_8]}{dt} = -k[\text{C}_3\text{H}_8]^{0.1}[\text{O}_2]^{1.63}$$



Reaction Rate Constant

- The reaction rate is determined by the rate at which reactants collide times the probability that a reaction will occur. Experiment shows that many rate constants are of the form:

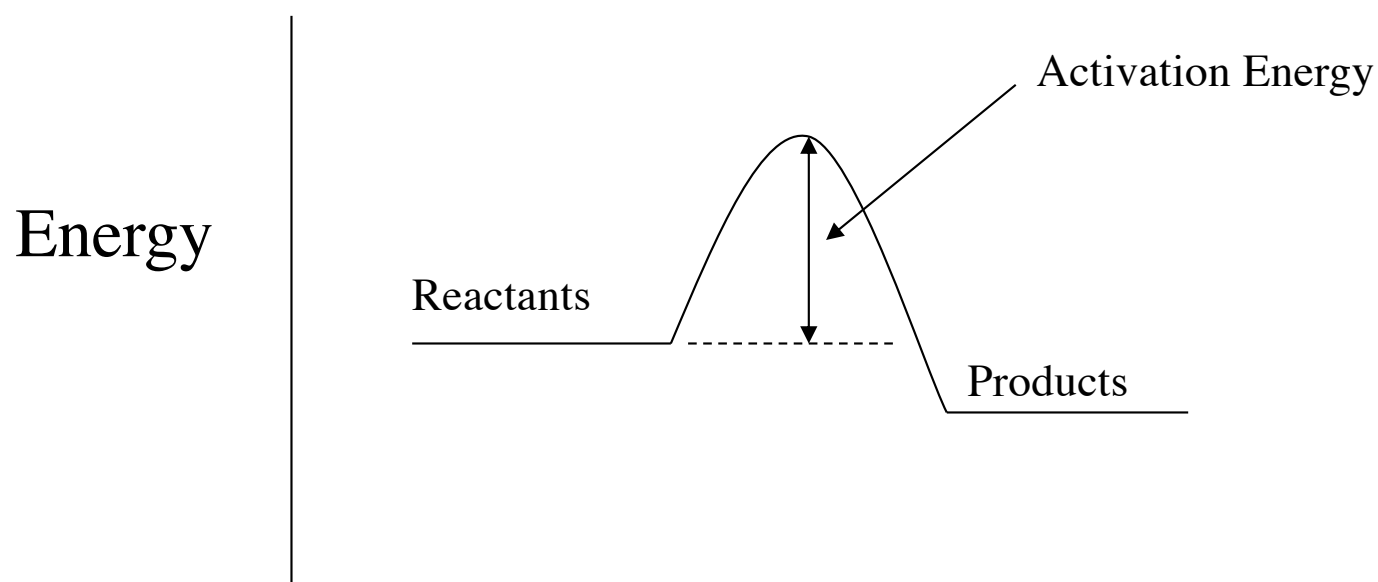
$$k = AT^n \exp(-E_{act} / RT)$$

Arrhenius
first developed

- A is called the pre-exponential or frequency factor. It can be a function of temperature.
- E_{act} is called the activation energy, and is approximately the collision energy required for a reaction to occur.



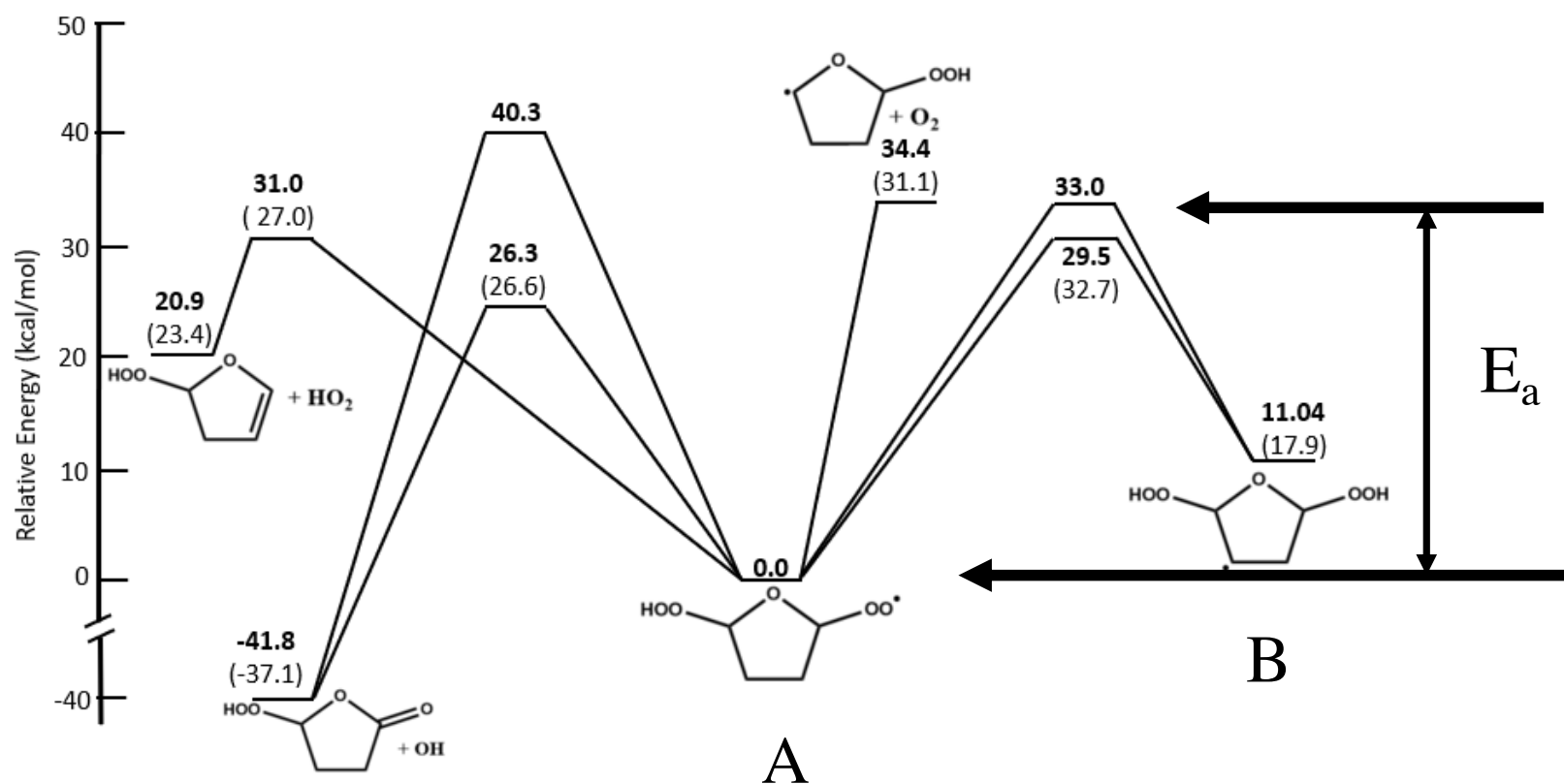
Reaction Rate Constant



Note that if the activation energy is zero, then the exponential Term disappears.



Example of an Potential Energy Surface



Simplification Due To Detailed Balance

- If we assume that the reaction rate constants are functions only of molecular properties and that local thermodynamic equilibrium applies, then detailed balance applies regardless of whether there is chemical equilibrium.

$$\frac{k_f}{k_r} = K_c(T)$$

- Thus, in practical calculation we only need to specify one of the two rate constants assuming we know the equilibrium constant (which will be a function of T).

