Dougherty Valley • AP Chemistry [Keep for Reference]

Chemical Kinetics: Rates of Reaction

STUDY INFO From Paul Groves

**Three Ways to Speed Up a Reaction**

**Temperature** (more and harder collisions)

**Concentration** (more collisions)

increase ***concentration*** (of solutions)

increase ***partial pressure*** (of gases)

increase ***surface area*** (different phases)

**Catalyst** (more effective collisions)

***homogeneous*** (used & reformed)

***heterogeneous*** (surface catalyst)

[catalyst provides an alternate mechanism that requires lower energy collision or  
 ensures that correct particles collide]

**Converting Rates**

Reaction: 2A + 3B → 4C

** =  = **

**NOTE:** The Rate Law **CANNOT** be determined from the overall reaction. It MUST be determined **experimentally** because the rate law reflects only the “rate determining step.”

**Rate Law matches the Rate Determining Step**

Examples for: 2A + 3B → C

|  |  |
| --- | --- |
| Rate Law matches | Rate Determining Step  in the mechanism |
| Rate = k [A][B] | A + B → X (slow) |
| Rate = k [A]2 | A + A → X (slow) |
| Rate = k [A]2[B] | A + A  X (fast)  B + X → Y (slow) |
| Rate = k | This could be a mechanism that depends on an enzyme. Concentrations do not matter. |

**Graphical Method of Order of Reaction**

|  |  |  |
| --- | --- | --- |
| **order** | **straight-line plot** | **Slope** |
| 0 | [R]t vs. t | -k |
| 1 | ln[R]t vs. t | -k |
| 2 | 1/[R]t vs. t | k |

**Two Important Diagrams**

**PE energy profile** of a reaction



Exothermic, downhill, negative ΔH

Endothermic, uphill, positive ΔH

activation energy (Ea) = energy barrier

• activated complex (at the peak)

• whether a reaction is fast or slow depends on the activation energy in the PE profile

• PE profile does not change with change in temperature of the reactants?

• adding a catalyst lowers the Ea

The **KE** **distribution** of a substance



- **temperature** is the **average** KE

-increasing temperature spreads out curve to the right, increases average KE



- adding a **catalyst** moves the threshold energy to the left.



**Reaction mechanisms**

Overall:

4 HBr + O2 → 2 Br2 + 2 H2O

Mechanism:

HBr + O2 → HOOBr

HOOBr + HBr → 2 HOBr

2HOBr + 2HBr → 2Br2 + 2H2O

[NOTE: HOOBr and HOBr are “intermediates”]

**Chain Reactions**

H2 + Cl2 → 2HCl

* initiation steps

Cl2 → 2Cl•

* propagation steps

Cl• + H2 → HCl + H•

H• + Cl2 → HCl + Cl•

* termination step

Cl• + Cl• → Cl2

2O3 → 3O2

* initiation step

F2CCl2 + UV light → F2CCl• + Cl•

* propagation steps

Cl• + O3 → O2 + ClO•

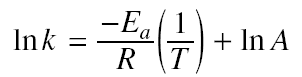
ClO• + O3 → 2O2 + Cl•

* termination step

Cl• + Cl• → Cl2

One Cl• can destroy 100,000 O3 molecules.

**Arrhenius Equation**



R = 8.31 J mol-1 K-1 (Units: Ea is in kJ mol-1)

Use the rate law to calculate the rate constant, k, at two different temperatures.

Determine activation energy, Ea, using the Arrhenius Equation. Since the above equation fits the “y = mx + b” expression, you can plot a graph of ln *k* (y-axis) vs. 1/T (x-axis). The slope of the line is –Ea/R.

Here is how the **equations** are given on the AP Exam and how they will appear on your chapter test:

These are the first order integrated rate law, the second order integrated rate law, and the Arrhenius Equation.

