

CHEMICAL KINETICS

Rate of Reaction

- For a reaction, $aA + bB \rightarrow xX + yY$

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{x} \frac{d[X]}{dt} = +\frac{1}{y} \frac{d[Y]}{dt}$$
- Greater the concentration of reactants, faster is the reaction.
- Rate becomes double for every 10° rise in temperature.
- Greater the surface area of reactants, faster is the reaction.

Order and Molecularity

- For a rate law equation, $\text{rate} = k[A]^a[B]^b$
 Order of reaction = $a + b$.
- Molecularity** is the number of atoms, ions or molecules that must collide simultaneously with one another to result into a chemical reaction.

Integrated Rate Equation and Half-Life

Order	Integrated rate equation	Half-life $t_{1/2} =$
0	$[A]_t = -kt + [A]_0$	$[A]_0/2k$
1	$\ln[A]_t = -kt + \ln[A]_0$	$0.693/k$
2	$1/[A]_t = kt + 1/[A]_0$	$1/k[A]_0$
2	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	-
n	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$	$\frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$

- Relationship between time for different fractions of a first order reaction to complete,
 $t_{3/4}$ or $t_{75\%} = 2t_{1/2}$
 $t_{87.5\%} = 3t_{1/2} = \frac{3}{2}t_{75\%}$
 $t_{93.75\%} = 4t_{1/2} = 2t_{75\%}$
 $t_{96.87\%} = 5t_{1/2}$
 $t_{99.9\%} = 10t_{1/2}$

Temperature Dependence of Rate of Reaction and Effect of Catalyst

- Arrhenius equation** : $k = Ae^{-E_a/RT}$
 or $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$
- Activation energy
 = Threshold energy - Average kinetic energy of reactants
- Collision theory** : $k = PZe^{-E_a/RT}$
 where P is steric factor and Z is collision frequency.
- Catalyst** increases the rate of a reaction without itself undergoing any permanent chemical change.

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Keith J. Laidler



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