

$$\Delta H^{\circ}_{\text{rxn}} = \sum n_{\text{p-products}} \Delta H^{\circ}_{\text{f-products}} - \sum n_{\text{reactants}} \Delta H^{\circ}_{\text{f-reactants}}$$

$$= [2 \text{ moles } (-46.19 \text{ kJ/mole}) -$$

$$[1 \text{ mole } (0 \text{ kJ/mole}) + 3 \text{ moles } (0 \text{ kJ/mole})]$$

$$= -92.38 \text{ kJ}$$

The bond enthalpy method gives slightly more exothermic values, most likely due to the effect of averaging the 3 N-H bonds.

9:1:A

KINETICS:

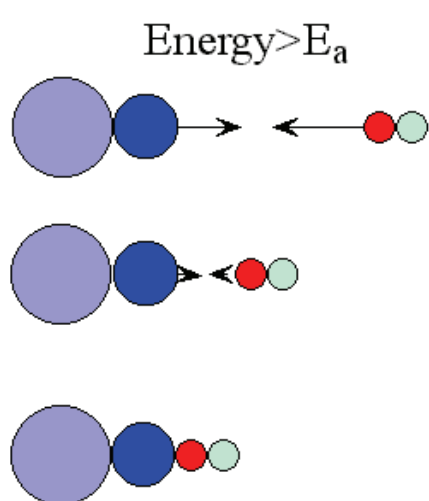
Kinetics is the study of the rates, or speeds of chemical reactions. These rates can be nearly instantaneous (combustion reactions) or can take millions of years (formation of diamonds from graphite). The rate of reaction is not the same thing as the spontaneity of a reaction—spontaneity refers only to the energy requirement, that is, a spontaneous reaction requires no additional energy to proceed

COLLISION THEORY:

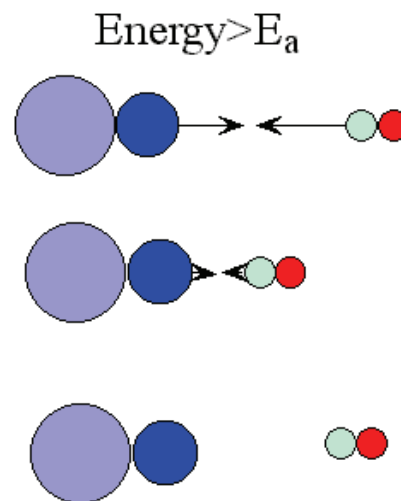
There are three basic concepts involved in the collision theory:

- 1) Atoms or molecules must physically collide in order for bonds to be formed.
- 2) The atoms or molecules must collide with sufficient energy to overcome the activation energy—the energy barrier to new bond formation.
- 3) The atoms or molecules must collide with a proper 3-dimensional orientation—in other words, the appropriate portions of the atoms or molecules must be facing each other in the correct manner.

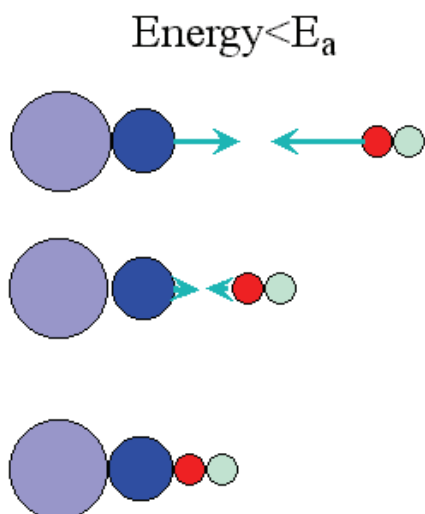
Figure 1:



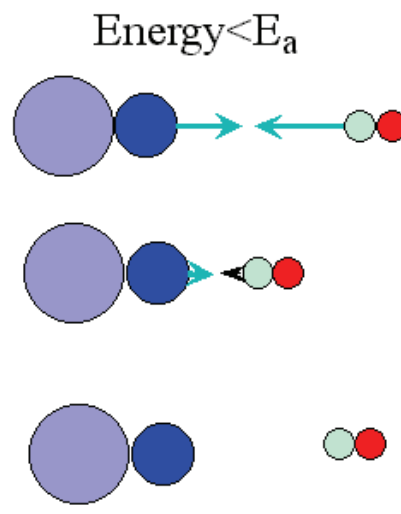
Reaction: Sufficient energy and proper orientation



No Reaction: Sufficient energy, incorrect orientation



No Reaction: Insufficient energy, correct orientation



No Reaction: Insufficient energy, incorrect orientation

THE DRIVING FORCES BEHIND REACTIONS

Whether or not a reaction takes place depends on the thermodynamics of the reaction. In general, nature tends to favor exothermic reactions ($-\Delta H$) resulting in an increase in entropy ($+\Delta S$). The spontaneity of a reaction is determined by the sign of the Gibb's free energy (ΔG) and must be negative. The relationship of these factors is given by the equation:

$$\Delta G = \Delta H - T\Delta S$$

REACTION RATES

The rate of any reaction is defined as the change (usually in the molar concentration of the reactants or products) over time.

For a general reaction: $aA + bB \rightarrow cC + dD$

The rate can be expressed **either** as the **decrease** in the concentration of A and B over time or the **increase** in the concentration of C and D over time. All these rates are equivalent.

$$\text{Average rate with respect to A} = -1/a \left[\frac{\Delta[A]}{\Delta t} \right]$$

$$= \text{Average rate with respect to B} = -1/b \left[\frac{\Delta[B]}{\Delta t} \right]$$

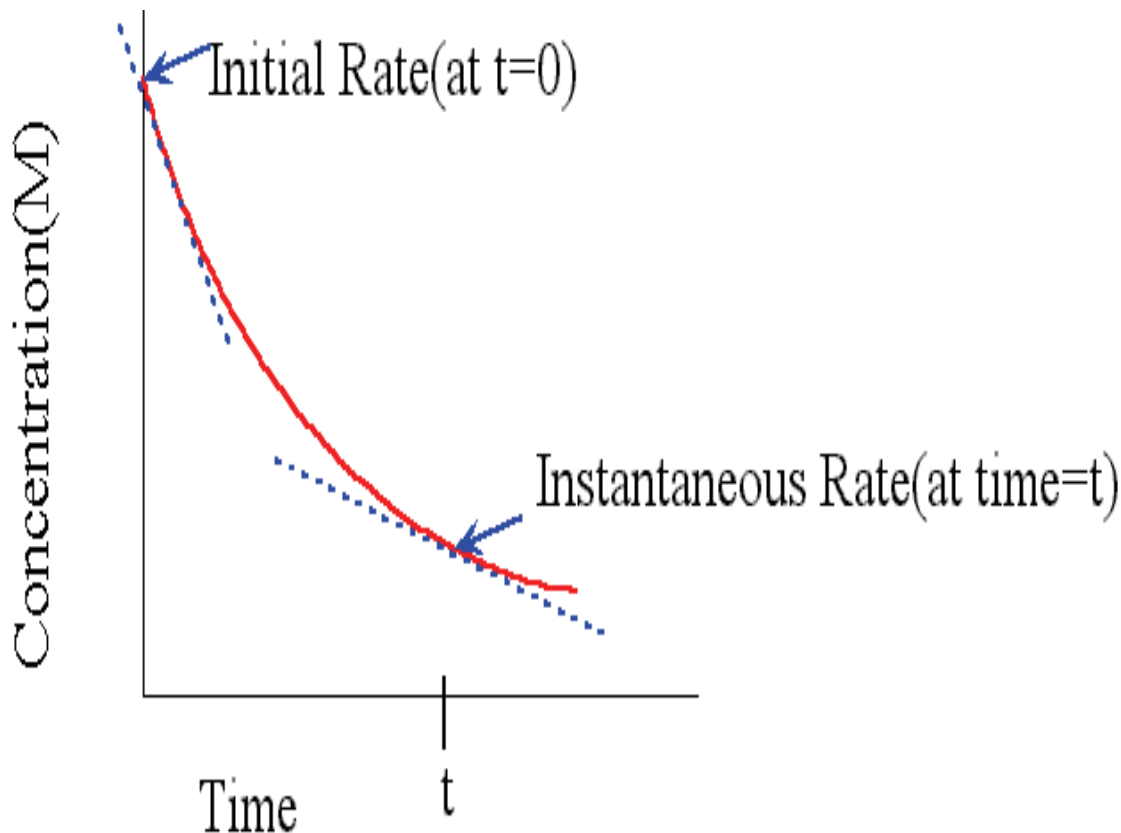
$$= \text{Average rate with respect to C} = +1/c \left[\frac{\Delta[C]}{\Delta t} \right]$$

$$= \text{Average rate with respect to D} = +1/d \left[\frac{\Delta[D]}{\Delta t} \right]$$

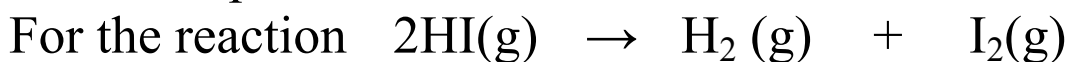
9:1:D

The concentrations can be plotted versus the time, and the instantaneous rate at any time “t” is the slope of the tangent to that point.

Figure 2



➤ Example:



$$\text{Rate} = \frac{+[\text{H}_2]}{\Delta t} = \frac{+[\text{I}_2]}{\Delta t} = \frac{-[\text{HI}]}{(2)\Delta t}$$

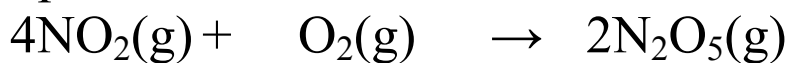
The **rate** of decrease in the concentration of HI is equal to $\frac{1}{2}$ that of the rate of increase in either H_2 or I_2 because for every 2 moles of HI that decompose, 1 mole of both H_2 and I_2 are produced.

9:1:E

If the rate of the disappearance of HI is $6 \times 10^{-3} \text{M/sec}$, what is the rate of appearance of H_2 and I_2 ?

Since: The rate of decrease of HI = $\frac{-[\text{HI}]}{(2)\Delta t} = \frac{+[\text{H}_2]}{\Delta t}$
 = $6 \times 10^{-3} \text{M/sec}$ and this is $\frac{1}{2}$ the rate of the appearance of H_2 and I_2 , the rates for the increase in both products equals $2 \times 6 \times 10^{-3} \text{M/sec}$
 = $1.2 \times 10^{-2} \text{M/sec}$.

➤ Example:



If the rate of the production of N_2O_5 is measured at $5.6 \times 10^{-6} \text{M/sec}$, what is the rate of the disappearance of NO_2 ?
 Of O_2 ?

Rate=

$$+1/2 \left[\frac{[\text{N}_2\text{O}_5]}{\Delta t} \right] = -1/4 \left[\frac{[\text{NO}_2]}{\Delta t} \right] = - \left[\frac{[\text{O}_2]}{\Delta t} \right]$$

$$= 5.6 \times 10^{-6} \text{M/sec}$$

Solving for each rate, the rate of disappearance of NO_2 is then $4/2$ or twice that of $\text{N}_2\text{O}_5 = 1.12 \times 10^{-5} \text{M/sec}$. The rate of disappearance of O_2 is $1/2$ that of the appearance of N_2O_5 and $= 2.8 \times 10^{-6} \text{M/sec}$.