

Kinetics

I. Kinetics - branch of chemistry concerned with the rate of chemical reactions and the mechanisms by which chemical reactions occur

A. Rate of chemical reaction - # moles consumed or formed per unit volume per unit time.

B. Energy in Reactions

1. Activation Energy - minimum energy required needed to start a reaction

a. forms an activation complex (temporary) – a transitional structure that results from an effective collision and that persists while old bonds are breaking and new bonds are forming

b. Appears as "hill" in potential energy diagram

2. Heat of Reaction (ΔH) = enthalpy (Chart I)

a. heat energy released or absorbed in the course of a reaction

1. Exothermic reactions

a. energy is released (liberated)

b. products have less energy (potential) than reactants

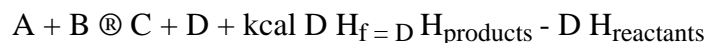
i. $\Delta H = - \text{kJ}$

c. forms more stable products than reactants

i. more negative the value, more stable the product

d. self sustaining - reaction releases enough energy to keep it going

e. Reaction: $A + B \rightarrow C + D$ $\Delta H = - \text{kcal}$ or



2. Endothermic reactions

a. energy is absorbed (decomposition reactions - reverse values on chart G)

b. reactants have less energy than products

c. $\Delta H = +\text{kcal}$

d. form less stable products in comparison to reactants

e. Not self sustaining - need added energy to keep the reaction going

f. Reaction: $A + B \rightarrow C + D$ $\Delta H = +\text{kcal}$ or



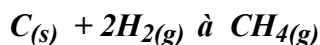
3. *Hess's Law of Constant Heat Summation*

a. *When a reaction can be expressed as the algebraic sum of two or more other reactions, then the heat of the reaction is the algebraic sum of the heats of these other reactions*

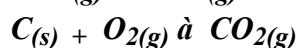
1. $\Delta H_f = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

b. *Heat of Summation – the overall heat of a reaction is the sum of any reactions which lead to the overall reaction.*

1. ex.

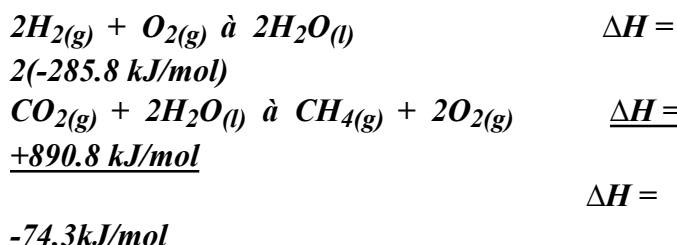


$$\Delta H = -74.3$$



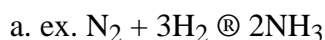
$$\Delta H =$$

$$-393.5 \text{ kJ/mol}$$



4. Heat of Formation - DH values expressed for 1mole of compound (usually products) formed from a synthesis reaction

1. causes the use of fractions in balancing of equations



b. $\frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightarrow \text{NH}_3$ *only 1 mole of compound

5. Factors Affecting the Rate of Reaction

a. Nature of the Reactants – type of substances will determine the rate of reaction

1. ionic substances dissolved in water tend to have the highest rate of reaction

a. ions are already split and only need to be recombined

2. Molecular substances have slower rates of reaction (ie. Organic compounds)

a. Molecules must be split first and then recombine

b. Catalyst

1. lowers activation energy required (speeds up rate of reaction)

a. Does Not affect amount of products or reactants formed

c. Increasing Concentration of Reactants

1. increases number of collisions which occur (increases reaction rate)

d. Increasing Temperature

1. increases rate of all reactions

a. increases number of collisions and effectiveness of collisions

e. Increase of Surface Area

1. increases number of molecules exposed for collisions (increases rate)

f. Increase Pressure (Gaseous Systems Only!)

1. moves molecules closer together (increases reaction rate)

6. Entropy - the amount of disorder, randomness or lack of organization of a system (D S).

Systems tend to change from a state of great order to a state of less order.

a. Solids have least entropy, gases have most

b. compounds have less entropy than free elements

c. a compound dissolved in water increases in entropy

1. ex. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$

B. Energy Changes favored in nature

1. *To go from high energy to low energy - DH (exothermic)*

a. *less stable to more stable*

2. *Entropy changes favor go from less entropy to more entropy +D S*

a. *less random to more random (solid → gas)*

3. *The difference between energy change and entropy change is the free energy change (D G) (Chart G)*

a. *Equation: $D G = D H - T D S$ (memorize)*

b. *- D G means a reaction is spontaneous*

c. *+D G means a reaction is not spontaneous*

- d. ***$\Delta G = 0$ indicates equilibrium***
- e. ***If energy change and entropy change are in conflict for a reaction, temperature determines direction of reaction***
 - 1. ***High temperature favors entropy (ΔS)***
 - 2. ***Low temperature favors energy change (ΔH)***