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Chemical Kinetic Modeling Reaction Principles

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Abstract

There are fundamental concepts or understandings involving chemical reactions which would be obvious to any scientist or engineer dealing with the subject on a routine basis. This may not be the case for the engineer which is assigned the task of developing a chemical reactor model including reactions for the first time. For this reason, these concepts dealing with energy, homogeneous and heterogeneous reactions, as well as the various types of possible reactions between compounds will be presented here without much mathematical foundations but illustrated with diagrams or example. Knowledge of the common reactions found in chemistry could be most useful in assembling elementary reactions for the detailed reaction model.

Keywords: Chemical kinetics; Energy barrier; Chemical reactions

Reaction Potential Energy Diagrams

Consider the hypothetical reaction in the gas phase between species A_2 (g) and B_2 (g) (or homogenous reaction).

$$A_2(g) + B_2(g) = 2\,AB\,(g) \quad (1)$$

The potential energy diagram for this reaction is shown in Figure 1. The reaction coordinate consists of the potential energy of reactants, an activated complex, and products.

For this reaction to take place, kinetic energy of the reactants is transformed into potential energy to overcome the activation energy barrier E_a, only to release excess energy to form the products or E_a' back in the form of kinetic energy [1,2].

Depending on conditions, only a fraction of all collisions between A_2 and B_2 result in reaction because (1) molecules of A_2 and B_2 are not properly aligned but what is most important, (2) the potential energy barrier for the encounter of the molecules is too high with only a fraction of the molecules possessing that energy or E_a (this is a consequence of the Kinetic Theory of Gases).

Figure 2 involves the same type of reaction but this time both catalyzed (a gas-phase or solid catalyst) and un-catalyzed paths are shown on the diagram. Note that (1) the height of the energy barrier has been reduced considerably both in the forward and reverse reactions with the use of a catalyst, and (2) The net energy ΔE of reaction remains the same. To keep in mind is that a catalyst is a substance that reduces the energy barrier for the reaction to take place.

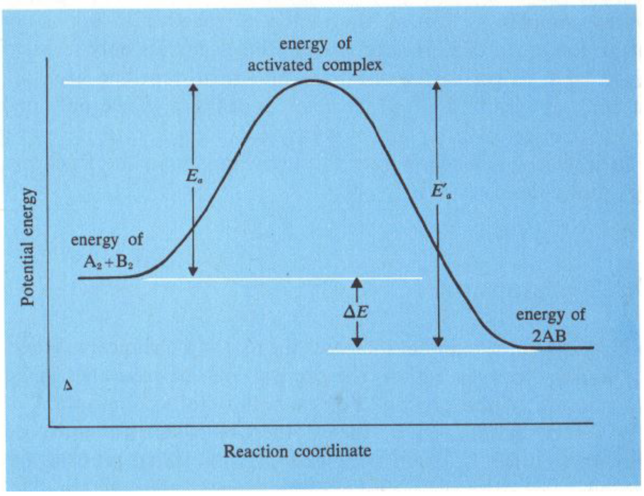

Figure 1: Reaction Potential Energy diagram [2].

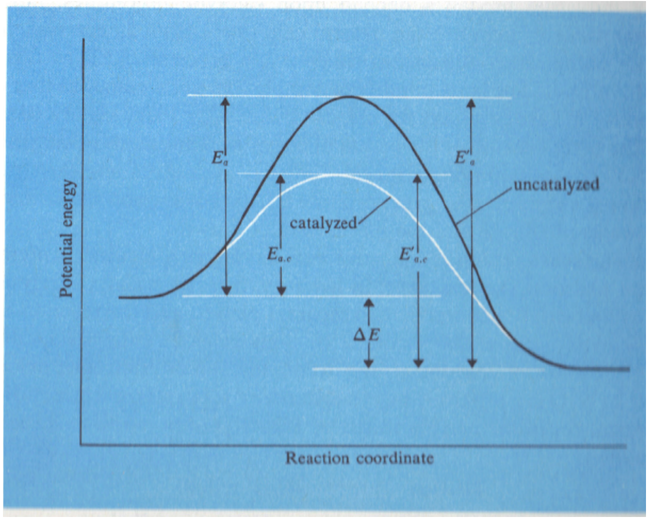

Figure 2: Reaction A_2+B_2 Potential Energy Diagram: Catalyzed vs. Uncatalyzed.

Reaction (1) is said to be homogeneous gas phase reaction. A heterogeneous reaction occur on a surface or phase boundary, hence the rate of such reaction can be greatly be increased if the active surface area is increased. For example, in a gas-solid reaction, the total number of collisions per unit time can be increased by pulverizing the solid.

The reaction between species involves the breaking of bonds, the

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partial formation of new bonds in the transition state, and finally the formation of products involving new molecular structures. The heat of reaction for the reaction depends on the strength of such bonds.

Using the Valance Bond approach, the bonds involve orbitals that resemble those corresponding to the Hydrogen atom (solutions to Quantum Chemistry Schrodinger equation) such as in Figure 3 for s, p, and d type orbitals. The valence shell orbitals are closely associated with each species in accordance to Valance Bond theory (in contrast to Molecular Orbital theory, where the orbital includes all atoms). Considering the overall reaction to form water from Hydrogen and Oxygen.

$H_2\,(g) + 1/2O_2\,(g) = H_2O\,(g)$

Referring to Figure 4, the molecular Hydrogen involves bonding between the 1s orbitals of the atoms. The molecular Oxygen is a sp2 Hybrid (involving 2s and three-2p orbitals of the single atoms) with a sigma bond, four lone pairs of electrons and a pi bond (the free p orbitals).

The final product of reaction or water is a sp3 hybrid with two lone pairs of electrons and two sigma bonds to hydrogen atoms. The heat of formation for the reaction (water) and since by definition the heat for Hydrogen and Oxygen is zero will depend on the relative strength of the bonding in each of the participants, for water the value is -248 kJ/mole or exothermic.

Kinds of chemical reactions

As it will be discussed in a later section, the assembly of elementary

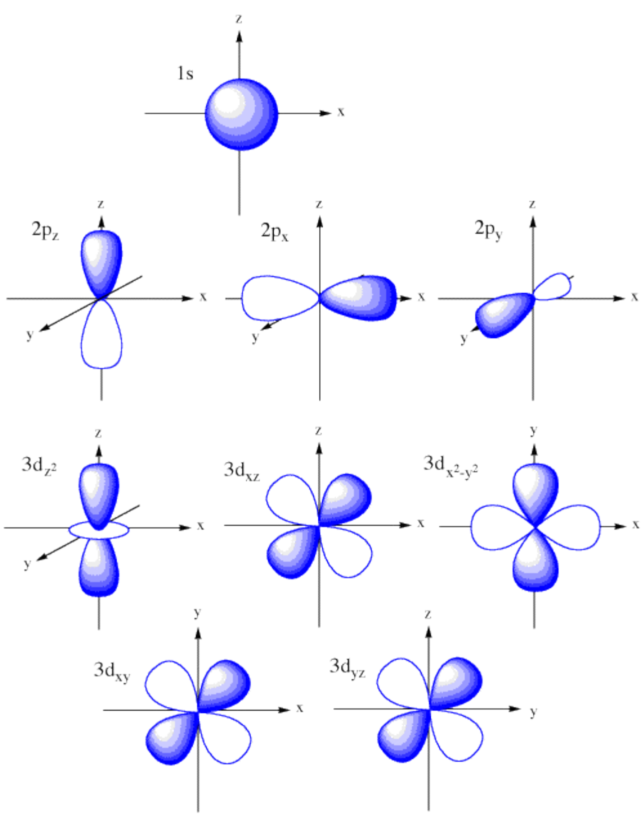

Figure 3: Atomic Orbitals (Quantum Chemistry solutions to the Hydrogen atom).

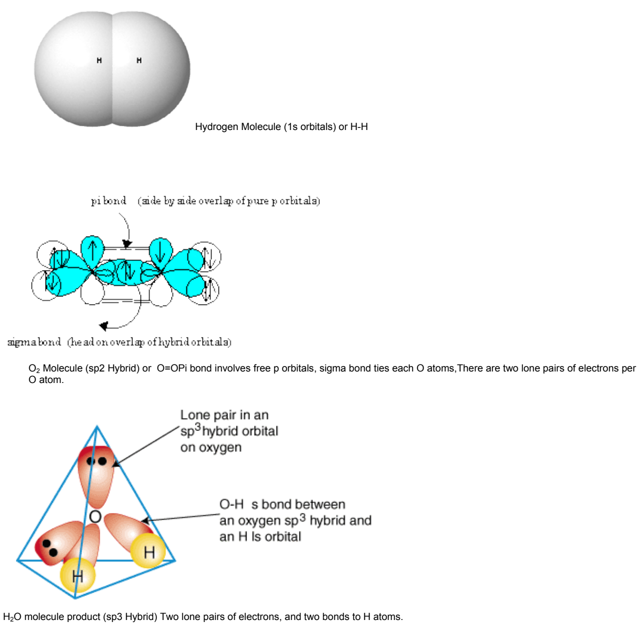

Figure 4: Formation of Water from Hydrogen/Oxygen: Valance Bond Diagrams for reactants and product.

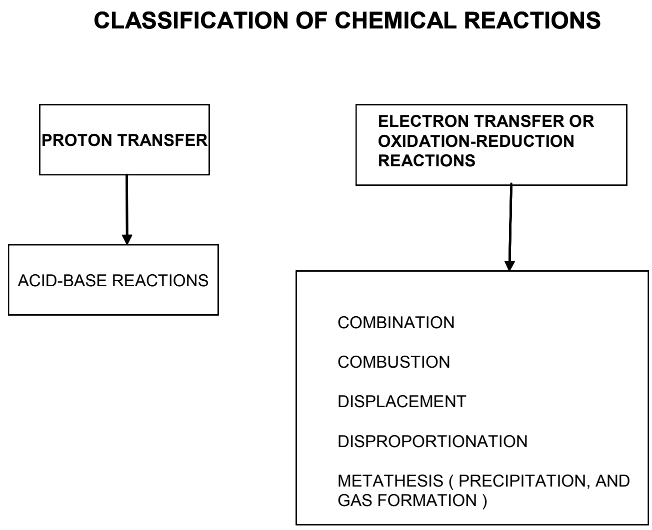

Figure 5: Types of Chemical Reactions.

reactions composing the detailed reaction model is one of the most important tasks. The model is as good as the chemical steps it is made of.

There are some basic types of reactions occurring in the physical world that can be used as guides in assembling possible reactions; these are depicted in Figure 5 below.

Proton transfer reactions occur in acid-base reactions. The H^+ ion in the acid reacts with the OH^- ion in the base to form water. An example involving hydrobromic acid follows:

$$HBr + NaOH = NaBr + H_2O \quad (3)$$

The most common reactions involve electron transfer or so called oxidation-reduction reactions. These are listed on Figure 5 on the right column.

Combination reactions involve two or more different substances that combine to produce a new substance, e.g.,

$$2Al(s) + 3\ Br_2\ (l) = 2AlBr_3\ (s) \quad (4)$$

Combustion reactions involve the reaction with oxygen with the release of heat and formation of flames, e.g.,

$$C_3H_8\ (g) + 5O_2\ (g) = 3CO_2(g) + 4H_2O\ (g) \quad (5)$$

Displacement reactions entails ion (atom) of one compound replacing ion (atom) in a second compound,

$$Cl_2(l) + 2INa(aq) = 2NaCl\ (aq) + I_2\ (g) \quad (6)$$

Disproportionation reactions involve the simultaneous oxidation and reduction of an element,

$$2H_2O_2(aq) = 2H_2O(l) + O_2(g) \quad (7)$$

Here the oxidation state of oxygen in peroxide is -1, and the products show oxygen in 2- state (water) and 0 state oxygen element.

In Methasis reactions, positive and negative ions in two compounds change partners to form two new compounds, such as in the precipitation reaction involving carbonate,

$$CaCl_2\ (aq) + Na_2CO_3\ (aq) = CaCO_3(s) + 2NaCl\ (aq) \quad (8)$$

This brings the discussion to the subject of radical species reactions which are outlined by Pryor [3,4]. As it will be fully discussed later, radical species are important in the modeling of many reactions at higher temperatures, specialty combustion modeling. Furthermore, combustion involves radical-chain reaction mechanisms. The radical reactions are grouped as follows.

- Hydrogen Abstraction
- Halogenation
- Addition Reactions
- Radical Polymerizations
- Aromatic Substitution
- Rearrangements
- Auto-oxidation
- Diradicals
- Termination Reactions

An example of Hydrogen Abstraction is the following,

$$CH_3\text{-} + RH = CH_4 + H \qquad R = \text{alkyl group} \quad (9)$$

Examining Figure 5 this is also a Displacement reaction by the methyl radical.

Halogenation involves Halogen Elements such as Chlorine, Fluorine. An example is

$$CH_3\text{-} + Cl_2\ (g) = CH_3Cl + Cl \quad (10)$$

Inspecting Figure 5 this can also be classified as a displacement reaction.

Addition reactions involve the addition of a radical species to a double bond or

$$Br\text{-} + CH_2{=}CH_2 = Br\text{-}CH_2\text{-}CH_2 \quad (11)$$

This is the equivalent of a combination reaction. The same can be said of polymerization reactions or,

$$nCH_2{=}CH_2 = (\text{-}CH_2\text{-}CH_2\text{-})n \quad (12)$$

Termination reactions involving radicals such as

$$R\text{-} + R'\text{-} = R\text{-}R \quad (13)$$

Fall in the category of combination reactions of Figure 5.

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