Principles of Chemical Engineering

Reaction Engineering

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Syllabus Contents

Chemical Kinetics - Elementary and non-elementary reactions - Effect of temperature on reaction rate
Thermodynamics - Heat of reaction - Feasibility of a chemical reaction

Chemical Kinetics

Chemical kinetics, also known as reaction kinetics is concerned with understanding the rates of chemical reactions.
According to the homogeneity of chemicals involved, reactions can be classified:

- homogeneous reactions—reactants and products are in a single phase as a homogeneous mixture.
- heterogeneous reactions—one ore more of the reactants / products / catalyst involved, is immiscible with the other components.

Rate of Reaction

The speed or rate of a chemical reaction is the change in amount (moles) of a reactant or product per unit time per unit volume of reactant.
Rate of consumption of a component i is given by,

$$-r_i = -\frac{1}{V}\frac{dN_i}{dt} \qquad \frac{\text{moles of } i \text{ consumed}}{\text{(volume of reactant)(time)}}$$

For constant volume systems (applicable for constant volume reactor and liquid systems), rate can be expressed in terms of concentration.

$$-r_i = -\frac{1}{V}\frac{dN_i}{dt} = -\frac{d(N_i/V)}{dt} = -\frac{dC_i}{dt}$$

C_i is the concentration of component i.

Rate Law

For,

$$A \rightarrow \text{product}$$

Power law model:

$$-r_A = kC_A^n$$

$$\begin{aligned} k &= \text{rate constant (depends on temperature)} \\ n &= \text{order of reaction} \\ C_A &= \text{concentration of the limiting reactant } A \end{aligned}$$

Rate of a reaction increases with increase in concentration of reactants and temperature of the system.

Order of reaction is always found by doing experiments. One can't deduce anything about the order of a reaction just by looking at the reaction stoichiometry.

Elementary and Non-elementary Reactions

- Reaction in which the rate law and stoichiometric equation have a direct correspondence is called an elementary reaction. For example,

$$
\begin{array}{lll}
1 & A + B \rightarrow R & -r_A = kC_AC_B \\
2 & A + 2B \rightarrow R & -r_A = kC_AC_B^2 \\
3 & 2A \rightarrow R & -r_A = kC_A^2
\end{array}
$$

- Certain reactions that do not hold any correspondence with the respective stoichiometry are called non-elementary reactions. For example,

$$
\begin{array}{lll}
1 & A + B \rightarrow R & -r_A = kC_A^2 \\
2 & A \rightarrow R & -r_A = \dfrac{k_1C_A}{1 + k_2C_A}
\end{array}
$$

Order of Reaction

- The powers to which the concentrations are raised in the rate law represent the order of reaction, with respect to that particular species. e.g.,

$$-r_A = kC_A^{\alpha} C_B^{\beta}$$

  The order of reaction is

$$\begin{aligned} \alpha & \quad \text{with respect to } A \\ \beta & \quad \text{with respect to } B \\ n & \quad \text{overall, } n = \alpha + \beta \end{aligned}$$

- The individual orders of reaction (α & β) are usually obtained from the experimental data. Hence, they need not be integers. Also, α & β need not have correspondence with stoichiometry.

Effect of Temperature on Rate of Reaction

- Chemical reactions typically occur faster at higher temperatures. Food spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days.
- We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures.
- In many cases, an increase in temperature of only $10^\circ\mathrm{C}$ will approximately double the rate of a reaction in a homogeneous system.

Effect of Temperature on Rate of Reaction

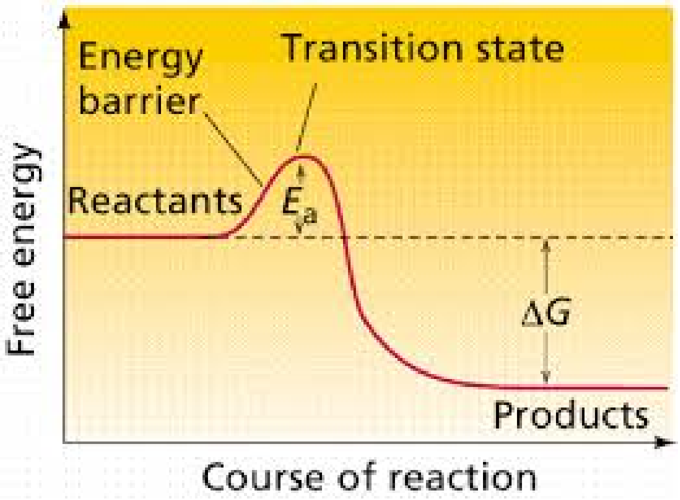
Effect of temperature (T) on the rate constant (k), and hence the rate of reaction is given by Arrhenius law as,

$$k = k_o e^{-E/(RT)}$$

where

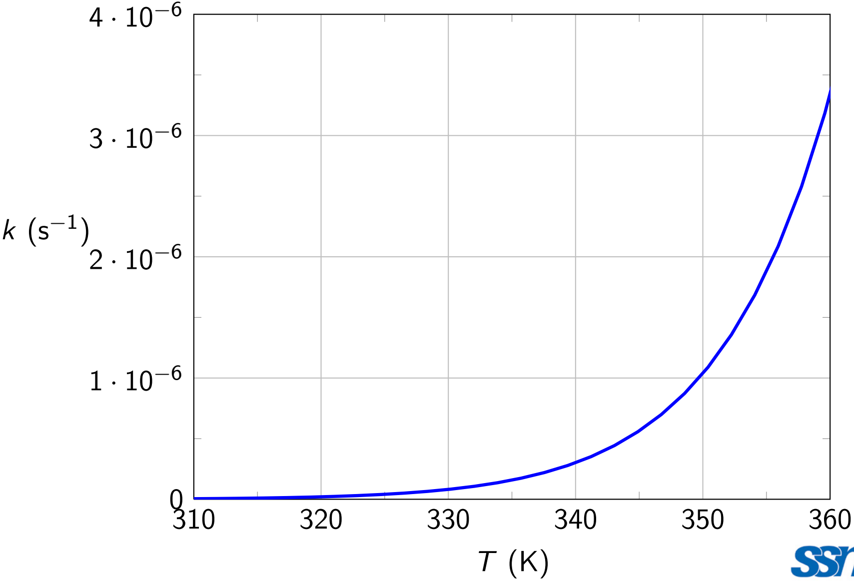
k	=	rate constant
E	=	activation energy of reaction
R	=	universal gas constant
T	=	temperature in absolute scale

Activation Energy



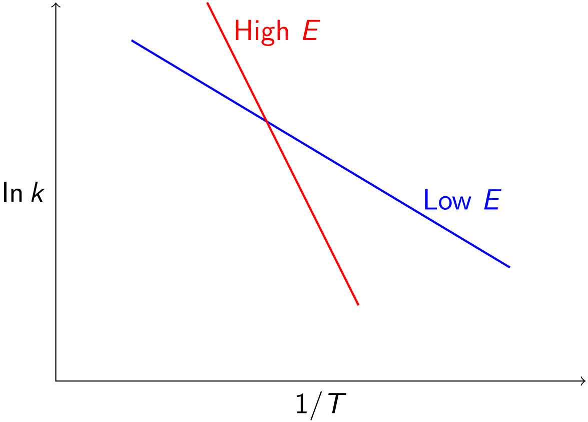
Effect of Temperature on Rate of Reaction (contd..)

Typical plot of k vs. T



Effect of Temperature on Rate of Reaction (contd..)

Plot of $\ln k$ vs. $1/T$



Slope $= -E/R$. Higher the activation energy (E) higher is the effect on rate, for a given change in T.

Role of Thermodynamics in Chemical Reactions

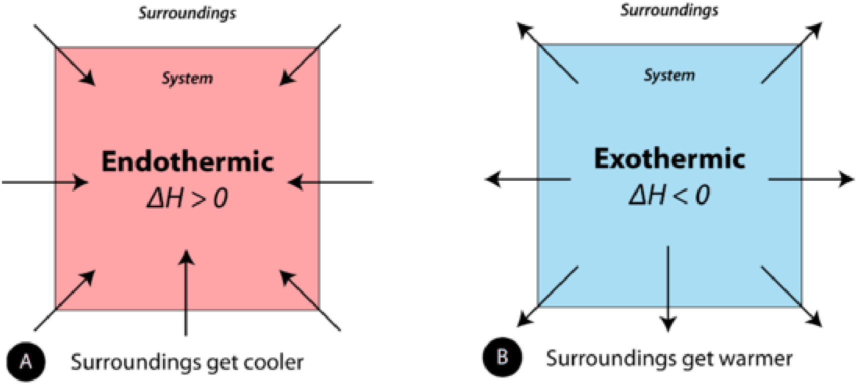
The concepts of thermodynamics provide three most important information regarding a chemical reaction:

- possibility of the reaction proceeding spontaneously.
- heat liberated or absorbed during the reaction.
- maximum possible conversion of a reaction and hence the concentration of reaction mixture.

Heat of Reaction

- The heat of reaction is the energy that is released or absorbed when chemicals are transformed in a chemical reaction. It describes the change of the energy content when reactants are converted into products.
- A reaction can be exothermic (heat releasing) or endothermic (heat absorbing).
- The quantity of heat of reaction depends on the nature of reactants and the products formed and is thus a function of the strength of the bonds between the atoms which are broken and newly formed.

Exothermic / Endothermic Reactions



Reversible Reaction

Consider the following elementary reversible reaction.

$$\alpha A + \beta B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \gamma C + \delta D$$

At equilibrium, rate of forward reaction equals that of the reverse reaction. Therefore,

$$k_1 C_A^\alpha C_B^\beta = k_2 C_C^\gamma C_D^\delta \qquad \Longrightarrow \qquad \frac{k_1}{k_2} = \frac{C_C^\gamma C_D^\delta}{C_A^\alpha C_B^\beta} = K$$

where K is the equilibrium constant. It is related with standard Gibbs free energy change (ΔG°) of reaction as

$$\Delta G^\circ = -RT \ln K$$

Equilibrium Constant

- The magnitude of the equilibrium constant, K, indicates the extent to which a reaction will proceed. If K is a large number, it means that the equilibrium concentration of the products is large. In this case, the reaction as written will proceed to the right (resulting in an increase in the concentration of products).
- Knowing the value of the equilibrium constant, K, will allow us to determine: (i) the direction a reaction will proceed to achieve equilibrium, and (ii) the ratios of the concentrations of reactants and products when equilibrium is reached.

Feasibility of a Chemical Reaction

- A reaction which can proceed in a given direction without the need of outside energy is called a spontaneous reaction.
- Enthalpy and entropy are the driving forces responsible for the spontaneity of chemical reactions.
    - Some reactions are spontaneous because they liberate energy in the form of heat ($\Delta H < 0$).
    - Some reactions are spontaneous since they lead to an increase in the disorder of the system ($\Delta S > 0$).

  The thermodynamic function, known as the Gibb's free energy (G, simply called 'free energy') is defined to determine the relative importance of the two driving forces behind a particular reaction. ΔG is defined, at constant T, as

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

Significance of Free Energy Calculations

Free energy calculations help to find the equilibrium compositions of chemical reactions. From free energy calculations, we can find the feasibility of a reaction.

- When $\Delta G_{T,P} = 0$, the reaction is in equilibrium and no further change may occur.
- When $\Delta G_{T,P} < 0$, the reaction is promising.
- For $0 < \Delta G < 40{,}000$ kJ/kmol, the reaction may or may not be possible and needs further study.
- When $\Delta G > 40{,}000$ kJ/kmol, the reaction is very unfavorable.
- For an impossible reaction, the value of K should be equal to zero or ΔG° should be infinite.

Quiz

1. Define 'rate' of a chemical reaction.
2. Write the rate of reaction in terms of its variables affecting.
3. What do you mean by an 'elementary reaction'?
4. Differentiate between elementary and non-elementary reactions.
5. What do mean by 'order of reaction'?
6. What is the effect of temperature on rate of a chemical reaction?
7. What information will be available from thermodynamics for understanding a chemical reaction?
8. How will you estimate the feasibility of a chemical reaction?