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Chapter 9

Kinetics and transport phenomena

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1. The kinetics of heterogeneous catalytic reactions

1.1. Definition and evaluation of reaction rate, mass balance equation, kinetic equation

The performance of a chemical reactor can be described by two kinds of equations: the mass balance and the kinetic equation. The mass balance equation referred to the time unit for the component i can be written as follows:

$$\underset{(1)}{\text{Input of } i \text{ mass}} = \underset{(2)}{\text{Output of } i \text{ mass}} + \underset{(3)}{\text{Mass of } i \text{ reacted}} + \underset{(4)}{\text{Accumulation}} \qquad (1)$$

Thus considering a reaction occurring without change in the number of moles, we can write the mole balance:

$$\underset{(1)}{Fc_i^e} = \underset{(2)}{Fc_i^u} + \underset{(3)}{wr_i} + \underset{(4)}{\frac{\mathrm{d}c_i}{\mathrm{d}t}} \qquad (2)$$

where: F is the volumetric feed rate; c_i^e and c_i^u are, respectively, the molar concentrations of i at the entrance and at the exit of the reactor; w is the catalyst weight; t the time; and r_i the reaction rate at which i appears (positive) or disappears (negative), expressed as moles of i per unit time per unit of catalyst weight; c_i is the i concentration in the reactor.

In the case of a continuous reactor operating in steady state conditions, term (4) of the mass balance can be ignored. On the contrary, in the case of a batch reactor, terms (1) and (2) must be neglected, while, in the case of a semibatch reactor term (2) is normally null. It is easy to recognize that the reaction rate contained in term (3) can be determined in different ways according to the type of reactor where it is measured. For a well mixed batch reactor we have, as a matter of fact:

$$r_i = \pm \frac{1}{W}\frac{\mathrm{d}c_i}{\mathrm{d}t} = \frac{\text{moles of i appeared/disappeared}}{\text{unit of catalyst weight} \times \text{unit of time}} \qquad (3)$$

while, for a well-mixed continuous reactor (CSTR), we will have:

$$r_i = \frac{F(c_i^e - c_i^u)}{W} \qquad (4)$$

In the case of a continuous tubular reactor, the reaction rate changes along the catalytic bed. Therefore, the mass balance must be applied, in this case, to an infinitesimal part of the reactor, that is for example dW. Then, we will have:

$$r_i = F\frac{\mathrm{d}c_i}{\mathrm{d}W} \qquad (5)$$

In each point of the reactor we can have a different reaction rate depending on the compo-

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sition of the reaction mixture and on the temperature at that point, that is:

$$r_i = f\,(\text{composition, temperature}) \tag{6}$$

This function is the kinetic equation or rate law indispensable for describing the behaviour of all the types of reactor mentioned and for modeling them. The kinetic equation for a given reaction can be determined only by collecting and processing experimental data under different operative conditions. However, before determining the kinetic equations of the reactions involved in a process, it is opportune to individuate the reaction scheme and the stoichiometry of each single reaction.

1.2. Reaction scheme, stoichiometry, thermodynamic constraints, analysis of the reaction networks

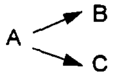
Two or more reagents put in a reactor could give more products than expected. We can identify the products by analysis and determine them quantitatively, however, often we don't know their origin, that is, we ignore how many and what kind of reactions have occurred. Therefore, the first step of a kinetic study must be the identification of the reaction scheme and, consequently, of the stoichiometry of each reaction. A reaction scheme could be very complex; however, it will always be recognizable as a combination of more single schemes of the type:

a) Single reactions $\mathrm{A} \rightarrow \mathrm{B}$ (7)

$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}$ (8)

b) Equilibrium reactions $\mathrm{A} \leftrightarrow \mathrm{B}$ (9)

c) Simultaneous reactions



(10)

d) Consecutive reactions $\mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{C}$ (11)

The stoichiometry of a single reaction allows the correlation of the rate of appearing or disappearing of any reagent or product with the kinetic equation. If we have, for example, the reaction

$$a\mathrm{A} + b\mathrm{B} \rightarrow m\mathrm{M} + n\mathrm{N} \tag{12}$$

The kinetic equation will be $r = f$ (composition temperature).

The rate of appearing products or disappearing reagents will be:

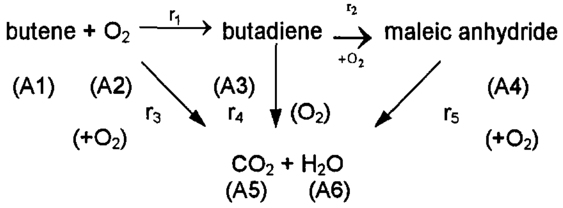
$$r_i = \alpha_i r \tag{13}$$

where α_i is the stoichiometry coefficient, positive for the products and negative for the reagents.

If products and reagents are involved in more than one reaction, each occurring with own rate and stoichiometry r_i becomes:

$$r_i = \sum_{i=1}^{j} \alpha_{ij} r_j \tag{14}$$

where, in this case, α_{ij} is the matrix of the stoichiometric coefficients. An example could be the oxidation of butene to maleic anhydride occurring with the following simplified scheme:



(15)

The matrix of the stoichiometric coefficients, α_{ij}, is:

$$\begin{array}{ccccccc}
j\backslash i & A_1 & A_2 & A_3 & A_4 & A_5 & A_6 \\
1 & -1 & -1/2 & 1 & 0 & 0 & 1 \\
2 & -1 & -6 & 0 & 0 & 4 & 4 \\
3 & 0 & -5/2 & -1 & 1 & 0 & 2 \\
4 & 0 & -11/2 & -1 & 0 & 4 & 3 \\
5 & 0 & -3 & 0 & -1 & 4 & 1
\end{array} \tag{16}$$

As a consequence, we can write:

$$\frac{\mathrm{d}p_{A_1}}{\mathrm{d}\tau} = -r_1 - r_2 \quad \frac{\mathrm{d}p_{A_2}}{\mathrm{d}\tau} = -\frac{1}{2}r_1 - 6r_2 - \frac{5}{2}r_3 - \frac{11}{2}r_4 - 3r_5$$

$$\frac{\mathrm{d}p_{A_3}}{\mathrm{d}\tau} = r_1 - r_3 - r_4 \quad \frac{\mathrm{d}p_{A_4}}{\mathrm{d}\tau} = r_3 - r_5 \quad \frac{\mathrm{d}p_{A_5}}{\mathrm{d}\tau} = 4(r_2 + r_4 + r_5)$$

$$\frac{\mathrm{d}p_{A_6}}{\mathrm{d}\tau} = r_1 + 4r_2 + 2r_3 + 3r_4 + r_5 \tag{17}$$

Where τ is a function of the residence time $= W/F$ and p_i are the partial pressures of the reaction components. As it can be seen, the problem comes back to the determination of the five kinetic equations $r_i = f$ (composition, temperature). If the kinetic equations r_1 to r_5 are known, it is possible to reproduce the evolution of any single specie along the catalyst bed by simultaneously integrating the system of differential Eqs. (17).

When in a reaction scheme, equilibrium reactions occurs, the yields of the products involved in these reactions are subjected to thermodynamic constraints. It is possible to define theoretically those yields also in the case of a complex reaction scheme. In this last case, we identify, with a simple procedure, the reactions that could be considered thermodynamically independent and that justify the presence of the observed products. Then, the equilibrium constants of the reactions are determined from data of free energies of reagents and products. The thermodynamic constraints must be introduced in the kinetic equation. For a second order reaction of the type A + B ↔ M + N, for example, we will write:

$$r = k_2 p_\mathrm{A} p_\mathrm{B} \left(1 - \frac{1}{K_\mathrm{e}} \frac{p_\mathrm{M} p_\mathrm{N}}{p_\mathrm{A} p_\mathrm{B}} \right) \tag{18}$$

where k_2 is the kinetic constant of direct reaction and K_e is the equilibrium constant of the reaction.

1.3. Diffusion, adsorption and surface reaction steps in the heterogeneous catalysis. The rate determining step and the steady state assumption applied to a reaction sequence

Reaction rates in heterogeneous catalysis can be affected by mass transfer or adsorption rates. As a matter of fact, the reactions normally occur between molecules adsorbed on the catalytic surface. Before and after the reaction, we can imagine the following steps:

(1) External diffusion of reagents (depends on the fluid dynamic characteristics of the system).

(2) Internal diffusion of reagents (depends on the porosity of the catalyst, on the size and shape of catalyst particles and occurs together with the surface reaction).

(3) Adsorption (depends on the possible interaction between molecules and the catalyst surface.

(4) Chemical reaction on the surface.

(5) Desorption (as in case c).

(6) Internal diffusion of products (as in case b).

(7) External diffusion of products (as in case a).

Each of the mentioned steps could affect reaction rates. In the experiments performed in laboratory reactor, operative conditions are normally selected in such a way to limit the effect of diffusion (steps 1, 2, 6, 7) at a negligible level. However, the effect of diffusion on kinetics will be examined in detail in a next chapter. It remains to analyze the contribution of steps 3, 4 and 5 to the reaction rate. First of all, it must be remarked that the surface chemical reaction normally occurs through a series of elementary steps (reaction mechanism) the slowest of which occur at the same rate of the overall reaction (rate determining step). In the reaction sequences of the mechanism different unstable species could be formed. These species quickly react and their concentrations remain rather low. It can be assumed that the concentration of these species is quite constant, that is, the rate of their formation is equal to that of disappearance. The assumptions of steady state conditions applied to unstable species and that of the rate determining step are very useful for obtaining kinetic equations based on the reaction mechanism, and containing concentrations of molecular species that can easily be determined by analysis. These two hypotheses are of general use and can also be extended to the adsorption and diffusion steps, as it will be seen.

1.4. Kinetic equation from the mechanisms of chemical adsorption and chemical surface reaction respectively. The Langmuir–Hinshelwood kinetic model

Chemical adsorption and desorption can be considered elementary steps that intervene before and after the reaction on the catalytic surface, respectively. We can write, for example, that the species A reacts with a free catalytic site, σ_f, as follows:

$$A + \sigma_f \overset{k_A}{\underset{k_{-A}}{\leftrightarrow}} \sigma_A \qquad (19)$$

being σ_A a site occupied by A as a consequence of the chemical adsorption.

The adsorption rate referred to the total number of sites will be:

$$r_A = k_A p_A \frac{\sigma_f}{\sigma_t} - k_{-A} \frac{\sigma_A}{\sigma_t} \qquad (20)$$

By introducing $\Theta_A = \sigma_A / \sigma_t =$ A coverage fraction and remembering that $\sigma_t = \sigma_A + \sigma_f$, we have $\sigma_f / \sigma_t = (1 - \Theta_A)$, hence:

$$r_A = k_A p_A (1 - \Theta_A) - k_{-A} \Theta_A \qquad (21)$$

At the equilibrium, this rate is null, therefore:

$$b_A = \frac{k_A}{k_{-A}} = \frac{\Theta_A}{p_A (1 - \Theta_A)} \text{ and } \Theta_A = \frac{b_A p_A}{1 + b_A p_A} \qquad (22)$$

b_A being the adsorption equilibrium constant. This constant depends on the temperature with a Van 't Hoff law type, that is, $b_A = b_A^{\circ} \exp(-\Delta H / RT)$.

Relation (22) is called the ‘adsorption isotherm of Langmuir’ and is valid rigorously for a homogeneous surface and for localized adsorption without lateral interactions between the adsorbed molecules. When these conditions are not present other isotherms must be considered such as that of Temkin, Freundlich, Fowler, etc. However, the Langmuir isotherm is particularly useful in kinetics because it well describes the competition of different molecules in adsorption. Suppose, for example, that two species, A and B, are involved in the adsorption. We will have, in this case:

$$r_A = k_A (1 - \Theta_A - \Theta_B) p_A - k_{-A} \Theta_A \qquad (23)$$

$$r_B = k_B (1 - \Theta_A - \Theta_B) p_B - k_{-B} \Theta_B \qquad (24)$$

At the equilibrium, both adsorption rates are null and hence:

$$\Theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B}$$

$$\Theta_B = \frac{b_B p_B}{1 + b_A p_A + b_B p_B} \qquad (25)$$

In the case of more components, for a generic i component, we can write:

$$\Theta_i = \frac{b_i p_i}{1 + \sum_{j=1}^{NC} {}_j b_j p_j} \qquad (26)$$

where NC is the number of components competing in adsorption. If the surface reaction is slow compared with adsorption steps we can consider these last at the equilibrium. Let us consider the surface reaction $A_{ads} \rightarrow B_{ads}$: the reaction rate will be proportional to the A coverage degree Θ_A, that is:

$$r = k\Theta_A \text{ and hence } r = k \frac{b_A p_A}{1 + b_A p_A} \qquad (27)$$

When $b_A p_A \ll 1$, at low coverage, $\Theta_A \rightarrow 0$, the reaction becomes pseudo first order, while if $b_A p_A \gg 1$ at high coverage, $\Theta_A \rightarrow 1$, the reaction becomes pseudo zero order.

In the intermediate cases, the reaction order appears a fractional number between 0 and 1. If other molecular species compete in the adsorption on the catalytic sites they show an inhibitory effect on the reaction and the reaction rate becomes:

$$r=\frac{kb_i p_i}{1+\sum_{j=1}^{NC} b_j p_j} \tag{28}$$

This kinetic equation derived from the assumption of the surface reaction as slow step and the adsorption at equilibrium, according to Langmuir, is called Langmuir–Hinshelwood (LH) kinetic model.

The same mechanism applied to a bimolecular reaction of the type A + B → C will show the following kinetic equation:

$$r=k_2\Theta_A\Theta_B=\frac{k_2 b_A b_B p_A p_B}{\left(1+\sum_{j=1}^{NC} b_j p_j\right)^2} \tag{29}$$

When the adsorption occurs with dissociation:

$$A_2+2\sigma_f \leftrightarrow 2\sigma_A \tag{30}$$

we will have:

$$r_A=k_A p_A(1-\Theta_A)^2-k_{-A}\Theta_A^2 \tag{31}$$

At equilibrium $r_A=0$, therefore:

$$\Theta_A=\frac{\sqrt{b_A p_A}}{1+\sqrt{b_A p_A}} \tag{32}$$

Consequently, the surface reaction rate (27) will change accordingly.

Another possibility is that a chemical species requires more than one catalytic site to give reaction, for example, two sites could be required and the adsorption on the second site is slow (dual site mechanism):

$$A+\sigma_f \leftrightarrow A\sigma \tag{33}$$

$$A\sigma+\sigma_f \rightarrow A\sigma_2 \tag{34}$$

In this case, we can write:

$$r=k_2\Theta_A\Theta_f=k_r\Theta_A(1-\Theta_A)=\frac{k_r b_A p_A}{(1+b_A p_A)^2} \tag{35}$$

When an adsorbed molecule reacts with another coming from the fluid phase we have the Rideal mechanism, that is:

$$A\sigma+B\rightarrow \text{products} \tag{36}$$

$$r=k_r\Theta_A p_B=\frac{k_r b_A p_A p_B}{1+b_A p_A} \tag{37}$$

Many catalytic oxidations occur through the redox mechanism in which the following reaction steps take place (Mars and Van Krevelen mechanism):

$$A+\Theta_{ox}\xrightarrow{k_1}P+\Theta_{red}$$

$$\Theta_{red}+\frac{1}{2}O_2\xrightarrow{k_2}\Theta_{ox} \tag{38}$$

where, Θ_{ox} and Θ_{red} are the fraction of oxidized and reduced sites, respectively. We can write $\Theta_{ox}+\Theta_{red}=1$, then, by introducing the steady state assumption, that is, $r_1=r_2$ we have

$$k_1 p_A\Theta_{ox}=k_2\Theta_{red}p_{O_2}^{1/2} \tag{39}$$

Remembering that $\Theta_{red}=(1-\Theta_{ox})$ it is possible to evaluate Θ_{ox} and then the reaction rate r_1:

$$r_1=\frac{k_1k_2p_A p_{O_2}^{1/2}}{k_1p_A+k_2p_{O_2}^{1/2}}=\frac{k_1p_A}{1+\left(\frac{k_1}{k_2}\frac{p_A}{p_{O_2}^{1/2}}\right)} \tag{40}$$

We can also have a mixed mechanism if the active sites are occupied by inactive molecules formed during the reaction, for example water. It is sufficient in this case to write $\Theta_{red}+\Theta_{ox}+\Theta_{occ}=1$. The reaction rate equation will become:

$$r=\frac{k_1p_A}{\left[1+\left(\frac{k_1}{k_2}\frac{p_A}{p_{O_2}^{1/2}}\right)\right]\left(1+\sum_j b_j p_j\right)} \tag{41}$$

1.5. Kinetics for complex reaction systems

In a complex reaction system, we can find: (i) equilibrium reactions, (ii) simultaneous reactions and (iii) consecutive reactions. The behaviour of the single reactions has already been described, let us now consider the equilibrium reactions and imagine the occurrence of the more simple equilibrium reaction

$$A \leftrightarrow B \tag{42}$$

if reaction rate is slow compared with adsorption and desorption rates:

$$r = k_r[\Theta_A - \Theta_B/K_S] \tag{43}$$

and consequently:

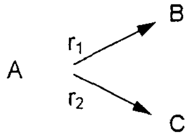
$$r = \frac{k_r b_A\left(p_A - \dfrac{p_B}{K_e}\right)}{1 + b_A p_A + b_B p_B} \tag{44}$$

where K_e is the equilibrium constant in the gas phase. Relation (49) can directly be obtained by introducing Θ_A and Θ_B derived from the Langmuir isotherm. In the same way for a reaction of the type $A + B \leftrightarrow C + D$ obeying to a second order law we obtain:

$$r = k_r \frac{b_A b_B p_A p_B\left(1 - \dfrac{1}{K_e}\dfrac{p_C p_D}{p_A p_B}\right)}{\left(1 + \sum_{j=1}^{NC}{}_j b_j p_j\right)^2} \tag{45}$$

When the reaction rate is comparable with the adsorption and desorption rate the kinetic equation becomes much more complicated.

In the case of simultaneous reaction we have:



(46)

where $r_A = -r_1 - r_2$; $r_B = r_1 = k_1\Theta_A$; $r_C = r_2 = k_2\Theta_A$ and

$$\Theta_A = \frac{b_A p_A}{1 + \Sigma_j b_j p_j} \tag{47}$$

These reactions are easily recognizable because $r_1/r_2 = k_1/k_2$.

In the case of consecutive reactions, we have, for example:

$$A \xrightarrow{r_1} B \xrightarrow{r_2} C \tag{48}$$

Hence:

$$r_A = -r_1 = -k_1\Theta_A \tag{49}$$

$$r_B = r_1 - r_2 = k_1\Theta_A - k_2\Theta_B \tag{50}$$

$$r_C = r_2 = k_2\Theta_B \tag{51}$$

Where $\Theta_A + \Theta_B + \Theta_C = 1$ and Θ_i can be expressed as in relation (26).

Consecutive reactions are recognizable because the concentration of the intermediate species such as B at different residence times, passes through a maximum.

1.6. The collection and processing of kinetic data with the aim of determining the kinetic equation

The main scope of the collection and processing of kinetic data is normally the evaluation of the kinetic equation, that is, the relation according to which the reaction rate depends on temperature and composition. Only when this equation is known, the parameters appearing in the equation can be determined. The two mentioned problems are different, it is opportune, therefore, to solve them with different approaches. Sequential experiences can be planned in order to determine the functional form of the kinetic equation by considering the influence of the different variables individually. In particular, experiences are useful in differential tubular reactors, continuous stirred tank reactor (CSTR) or tubular reactors with external recirculation because they allow a simple elaboration of the reaction rate data. However, also the integral tubular reactor can usefully been used with some difficulty. In this case, the conversion data must be related to the residence time, W/F, in polynomial relations of the type:

$$\lambda = a\left(\frac{W}{F}\right) + b\left(\frac{W}{F}\right)^2 + c\left(\frac{W}{F}\right)^3 + d\left(\frac{W}{F}\right)^4 \cdots \tag{52}$$

The parameters a, b, c, d, etc. can be evaluated by mathematical regression analysis of the experimental data. The derivative $d\lambda/d(W/F)$, corresponding to the reaction rates, can easily be calculated from relation (52) and applied to determine the exponent of a kinetic power law. For a reaction A + B → C the power law could be:

$$r = kp_A^{\alpha} p_B^{\beta} p_C^{\gamma} \tag{53}$$

where α, β, γ can be small integers, fractions, positive, negative or zero and give information on the form of the rate law.

The problem of the integral reactor is to achieve isothermal conditions in each point of the reactor.

A suitable experimental design (i.e. factorial, central composite, etc.) should be planned to allow a uniform exploration of the operating variables space and to obtain efficient estimates of the kinetic parameters by regression analysis.

Special techniques can be used to discriminate among rival models when present.

1.7. Determination of kinetic parameters

The kinetic equation must be derived from experimental data of reaction rates, measured under different operative conditions, after the introduction of a reliable hypothesis of a reaction mechanism and the assumption of a rate determining step. In this way, the kinetic equation has a physical meaning and the parameters appearing in the relation would obey to the thermodynamic constraints. Elementary steps, for example, cannot be trimolecular or more, activation energy must be a positive number in the range 5 to about 50 Kcal/mol corresponding to the strength of the chemical bonds. Values lower than 6–7 Kcal/mol suggest external diffusion limitation, as values greater than 50 Kcal/mol are suspected of the existence of thermal gradients. The pre-exponential factor would be inferior to the number of collisions of the molecules on the catalytic surface per time unit and per surface area unit. This number can easily be calculated with the aid of the kinetic theory of gases. Adsorption equilibrium parameters depend on the temperature as follows:

$$\begin{aligned} b_i &= b_i^{\circ}\exp(-\Delta H/RT) \\ &= \exp(\Delta S/R)\exp(-\Delta H/RT) \end{aligned} \tag{54}$$

The adsorption enthalpy change ΔH would be negative and falling in the range -5 to -50 Kcal, typical of the chemical bonds involved in the chemical adsorption. The adsorption entropy change ΔS would be greater than the translational entropy and smaller than the overall entropy of the molecule in the gas phase. Both values can easily be calculated. A mechanistic model should have physically meaningful parameters.

Any model can give support to a mechanistic theory but not demonstrate it. We can only state that a model is not in contrast with a theory or better that the particular experimental plan we did execute did not allow us to discard it.

1.8. Effects on kinetics of catalyst dispersion, sintering and poisoning

The specific surface area of a catalyst increases with dispersion. The dispersion of a metal on a support, for example can be defined as the ratio between the atoms on the surface and the total atoms of the metal. But the surface atoms have different positions and properties. We can have atoms on a vertex, atoms on a corner, atoms on a plane, adatoms and so on. The distribution of the different types of atoms can change strongly with the dispersion. Consequently, if a reaction is catalyzed on sites whose concentration strongly change with dispersion, specific activities for this reaction will strongly be affected from catalyst dispersion (reaction structure sensitive or demanding) while, on the contrary, when the reaction occurs on all the surface atoms, specific activities do not change with dispersion (reaction insensitive or facile). If more than one reaction occurs dispersion could affects selectivities, too. This fact, gives an explanation of the bed reproducibility in the behaviour of some catalysts and for the change in the activity and selectivity as a consequence of sintering.

Catalyst poisoning is another phenomenon responsible for changing activities and selectivities. Permanent poisons give strong chemical bonds with the catalytic sites and quickly decrease the activity to zero. This behaviour can successfully be applied to determine the density of active sites on a catalyst surface. Temporary poisons are, on the contrary, molecules competitively adsorbed with equilibrium on the catalytic sites. These molecules reduce more or less the activity according to the value of the adsorption equilibrium constant.

2. For further reading

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