KINETICS AND MECHANISM OF CATALYTIC REACTIONS

PROF. ALEXANDER ELIYAS

INSTITUTE OF CATALYSIS, BULGARIAN ACADEMY OF SCIENCES

The modeling of kinetics of catalytic reactions has two main aspects – revealing some details about the mechanism of the catalytic reaction, which is of fundamental importance and at the same time enabling the design of catalytic reactors, the optimization of their configuration and the input parameters, which the operator is changing – this is of practical importance. The second aspect concerns not only laboratory catalytic reactors, but also pilot plant installations and large scale industrial catalytic reactors.

The Russian leading scientists in the field of kinetics of catalytic reactions – Prof. Kiperman [1] and Prof. Temkin [2] developed the basic aspects and the fundamentals of this research methodology – mainly modeling of steady state kinetics, while their most brilliant student – Yurii Matros made the next step in the USA – the company "Matros Technologies" – non-steady state kinetics developing the reverse flow reactor [3]. This type of reactor first feeds reactant flow from top to bottom and then it is reversing the reactant flow from bottom to the top. It provides more details about the catalytic reaction mechanism but the interpretation of the data is much more difficult and it requires additional equipment and training.

To begin at the beginning – the simplest case for kinetic modeling is the case of monomolecular reaction – for example isomerization reaction – A isomerizes into B – which has only 3 elementary steps:

1. Adsorption of reactant A on vacant site Z – formation of adsorbate $A+Z \leftrightarrow AZ$
2. Surface reaction adsorbed AZ isomerizes into BZ in adsorbed state $AZ \leftrightarrow BZ$
3. Desorption of product B from adsorbed state BZ liberating B molecule $BZ \leftrightarrow B + Z$

Hougen and Watson [4] derived the kinetic model for this simplest case, assuming that there is one slowest step – the so called "**rate limiting step**". If we assume that the surface reaction step 2 is rate limiting with rate constant $\mathbf{k_2}$, then we can accept that other two steps – adsorption and desorption are fast steps at equilibrium, described by their adsorption-desorption equilibrium constants $\mathbf{K_a}$ and $\mathbf{K_b}$. In this case the kinetic model acquires the following form for the rate of the catalytic reaction **R** includes the outlet partial pressures **Pa** and **Pb** :

$$R = k_2K_aP_a / (1 + K_aP_a + K_bP_b) \qquad (1)$$

The assumption that there is a rate-limiting step is not always justified. Temkin and Kiperman [1,2] developed a more general approach for the case when there is no rate limiting step – all elementary steps contribute to the overall reaction rate as their rates are practically commensurable. Therefore deriving the kinetic equation we should take into account all the rate constants of elementary steps or combinations of several rate constants of elementary steps. This approach leads to the so called **mechanistic kinetic model** of the catalytic reaction – this is the highest level in modeling kinetics. This approach leads to lengthy mathematical expressions and long lasting computational procedures. Mathematically the problem is already solved but it requires expenses for commercially available software POLYMATH or MINITAB, if funds are available. Most often one uses self-made **empirical kinetic models** – in this case the procedure is faster but the evaluated kinetic constants cannot always be attributed to specific elementary steps. More often these are combinations of several rate constants.

In both cases – mechanistic or empirical models the first thing that one has to do is to derive the **matrix of stoichiometric coefficients**, knowing analytically what are the reaction products and writing down the respective catalytic reactions leading to those products. Then one has to determine the rank of the matrix of stoichiometric coefficients – what is the biggest minor i.e. the biggest determinant different from zero – the rank gives the number of linearly independent routes. When you describe the occurring catalytic reactions sometimes you make combinations – adding or subtracting reactions and the reaction network can grow up but sometimes such addition or subtraction does not provide additional information. The linearly independent routes are the smallest number of reactions that describe uniquely the conversion in the catalytic reactor. Here the problem arises – we determine experimentally the rates for consumption (disappearance) of reagents and the rates of formation of reaction products $\mathbf{W_i}$ -how can we determine from them the rates along linearly independent routs $\mathbf{Rj}$ in the kinetic equation? In the case of gradientless reactor $\mathbf{W_i}$ are determined by simple algebraic formula – dividing the conversion degree $\mathbf{X_i}$ by the contact time $\boldsymbol{\tau_i}$:

$$\mathbf{W_i = X_i / \tau_i} \qquad (2)$$

Whereupon the contact time (or residence time) $\boldsymbol{\tau_i}$ of the reagent **i** is defined on the basis of the mass (the weight) of the catalyst bed **M** (g-cat) and the feed flow rate $\mathbf{F_i}$ of the same reactant **i** (mole/hour):

$$\boldsymbol{\tau_i} \mathbf{= M / F_i} \qquad (3)$$

$$\begin{aligned} W_O &= -0.5\,R(I) - 3\,R(II) \\ W_E &= -\,R(I) - R(II) \\ W_{EO} &= R(I) \qquad (4) \\ W_{CO} &= 2\,R(II) \\ W_{HO} &= 2\,R(II) \end{aligned}$$

It seem very easy – the rate along the first route ***R(I)*** in the case of selective oxidation of ethylene (let us assume that this is the rate of partial oxidation of ethylene to ethylene oxide over silver catalyst $\mathbf{W_{EO}}$). Then the rate of complete oxidation of ethylene ***R(II)*** to CO_2 and H_2O can be taken simply to be ***R(II)* = $\mathbf{W_{CO}}$ /2** or ***R(II)* = $\mathbf{W_{HO}}$ */2* –** however these two values are different because of the experimental error:

$R(II) = 0.5\ \mathbf{W_{HO}} \neq R(II) = 0.5\ \mathbf{W_{CO}}$

It is known that in the case of gas chromatographic analysis the experimental error is 5%. The GC peaks of H_2O (on GC column Porapak Q) have long trailing tails and give much higher values (respectively greater error), than those of CO_2. In other words – mathematically formulated – the **system of equations (4) is overdetermined** and it has no exact solution. This fact imposes the search for approximate solution, whereupon one has to use the so called **„Chebyshev approximation"**, which is well known to the mathematicians long time ago. Mathematically the problem is reduced to finding such a vector R (R1,R2,…, Rn), which has a minimum of the maximal deviation, i.e. the problem is equivalent to that of the linear programming – minimum of σ with limitations:

$$\left| \Sigma\, Cij.Rj - Wi \right| \leq \sigma \qquad (5)$$

In case of small experimental errors the rates for reactants ***Wi*** can find their solution. The linear programming requires that the **condition of Haar** is observed – all the major minors of the matrix of the stoichiometric coefficients should be different from zero. In the case of the above reaction of selective oxidation of ethylene on silver catalyst this condition is not fulfilled and this fact creates a problem. The problem has been overcome by **Abdelmalek** [5] – his algorithm is valid also in the cases, when the condition of Haar is not fulfilled. The experiments having large error lead to implausible solutions. So this is an additional way to check the quality of the obtained experimental data.

The best result, when the law of distribution of the experimental error is not known, is provided by the non-linear programming and to be more specific this is the algorithm of **Nelder-Mead** [6], developed further by Olson [7]:

$$E = \min\max \left| Wi^{Th} - Wi^{Exp} \right| / Wi^{Exp} \qquad (6)$$

In case of small experimental errors the linear and non-linear programming give the same result. In this case one prefers the linear programming as the faster computational procedures.

For data sets of experimentally measured values having considerable error or when the law of distribution of the experimental error is unknown the algorithm of Nelder-Mead [6] exists in the form of a software package **NEM**, by means of which one selects the best kinetic equation (in view of describing the obtained data set) between several different possible kinetic equations, available in the current literature, describing the rate of the specific catalytic reactions. The mass of accumulated data on the rate refers to different experimental conditions – various catalyst bed temperatures, various compositions of the feed reaction mixture at the inlet of the catalytic reactor i.e. different partial pressures of the reactants and products and various feed ratios between the reactants, as well as different flow rates of the inlet mixture i.e. various contact times (residence times). All these data are input into the NEM program and in addition also the experimentally determined rates, corresponding to a given set of variable input parameters. For this purpose the software package NEM includes one more program LINF, which calculates the rates along the linearly independent routes ***R(J),*** on the basis of the rates for reactants ***Wi***. The program NEM uses as criterion the minimization of the sum of the squares of the absolute errors over the entire experimental data set:

$$E_i = \Sigma^N{}_i\, (R(J)^{Th}{}_i - R(J)^{Exp}{}_i)^2 \tag{7}$$

Where N is the total number of experiments at different catalyst bed temperatures, while $R(J)^{Th}{}_i$ are the values, which are predicted by the tested kinetic equation. On the basis of these values one can calculate the model deviation of the equation D_m:

$$D_m = (\Sigma^N{}_i\, \left| R(J)^{Th}{}_i - R(J)^{Exp}{}_i) \right| .100/\, R(J)^{Exp}{}_i)\, .\, 1/N \tag{8}$$

The best kinetic equation is the one, which has the lowest values of the criterion of minimization E_i (7) and of the model deviation D_m (8), but they should have plausible values of the activation energy Ea within the interval $5 \leq Ea \leq 60$ kcal/mol. This energy of activation Ea appears in the kinetic equation in the form of the temperature dependence of the rate constant κ in the equation:

$$\kappa = \kappa_0\, .\, exp(Ea/RT) \tag{9}$$

The program NEM is varying both the pre-exponential factors κ_0, as well as Ea until it finds either a local minimum or the absolute minimum in the space pattern of the parameters $R(J)$, P_i, T_i, κ_0 and Ea. The most important aspect in the course of searching for the best kinetic model is the fact, that it enables us to draw conclusions about the mechanism of the catalytic reaction on the basis of a kinetic study only. In the case of the industrial process of selective oxidation of ethylene to ethylene oxide over silver catalyst the best kinetic equation following from our kinetic modeling [8] is:

$$\begin{aligned} R(1) &= a_1P_oP_e/(1+a_3P_o + a_4P_e) \\ R(2) &= a_2P_oP_e/(1+a_3Po + a_4Pe) \end{aligned} \tag{10}$$

The kinetic model (10) of the catalytic reaction provides kinetic evidence about the actual mechanism of the reaction:

$$\begin{array}{lcc} & \underline{I} & \underline{II} \\ 1)\ Z + O_2 \leftrightarrow ZO_2 & 2 & 0 \\ 2)\ ZO_2 + C_2H_4 \rightarrow ZO + C_2H_4O & 2 & 0 \\ 3)\ 2\ ZO \leftrightarrow 2\ Z + O_2 & 1 & -3 \\ 4)\ C_2H_4 + 6\ ZO \rightarrow 2\ CO_2 + 2\ H_2O + 6\ Z & 0 & 1 \end{array} \tag{11}$$

Analyzing the matrix of the stoichiometric coefficients (11) we find that the rank of the matrix is 2 (greatest minor equal to 2, i.e. the greatest determinant different from zero is determinant 2x2). Therefore we have 2 linearly independent routes out of 3 occurring reaction: partial and complete oxidation of ethylene C_2H_4 and complete oxidation of ethylene oxide C_2H_4O i.e. the reaction scheme is triangular parallel-consecutive, but if we subtract from reaction 2) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ reaction 1) $C_2H_4 + 1/2\ O_2 \rightarrow C_2H_4O$ we obtain the reaction 3) $C_2H_4O + 2.5O_2 \rightarrow 2CO_2 + 2H_2O$. Such combinations – adding or subtracting reactions does not provide new information – in our case it is sufficient to consider 2 reactions to describe in an unique way what occurs in the catalytic reactor i.e. the chemical transformation – we chose the following 2 reactions, but of course another choice of two other reactions is possible:

I) $\mathbf{2\ C_2H_4 + O_2 = 2\ C_2H_4O}$ (12)

II) $\mathbf{C_2H_4 + 3\ O_2 = 2\ CO_2 + 2\ H_2O}$

The so obtained kinetic data show that the partial oxidation of ethylene to ethylene oxide occurs involving the participation of molecularly adsorbed oxygen (non-dissociated O_2 molecule), while the complete oxidation of ethylene to CO_2 and H_2O proceeds involving the participation of atomically adsorbed oxygen (the O_2 molecule is dissociated into 2 adsorbed O atoms). It is not clear whether in the second case an ensemble of 6 neighboring adsorbed oxygen atoms or (more probably) this elementary step combines 6 consecutive fast elementary steps. Much to our regret the kinetic data cannot provide such information and what is the exact nature of the active site Z – the so called „Z approximation" approach indicates that in our case – in the specific case of this catalytic reaction there exists only one type of adsorption active sites on the surface of the silver, while the support corundum α-Al_2O_3 is catalytically inactive.

Reactor of Berty with internal recirculation

The catalytic autoclave reactor of Berty (Fig. 1) differs from the flow-circulation catalytic reactor of Temkin-Kiperman (Fig, 2) for laboratory testing of the catalytic activity of laboratory synthesized catalyst samples in a fixed bed in one major aspect – the ideal mixing of the reactant mixture requires intensive recirculation to pass several time through the catalyst bed – in the first case (Fig. 1) Berty [9] („Union Carbide Co.") uses internal recirculation with a fan, mounted inside the reactor, while in the second case (Fig. 2) Temkin and Kiperman applied external recirculation of the reactant mixture using a gas circulation pump, connected to the reactor in a circulation contour [1,2,10]. Berty reactor enables catalytic activity testing at high pressure similar to the conditions of the respective industrial process. Both types of reactors are gradientless i.e. there is no temperature or concentration gradient in the catalyst bed. Berty reactor enables also scaling-up of the data for larger size reactors. Both types of reactors allow kinetic modeling as the catalytic reaction proceeds in the kinetic region without any diffusion retardation effect. It is known that the “Theory of Similarity” [10] warns about the risk of transferring small scale laboratory reactors (grams of catalyst) to larger scale catalytic reactors (pilot plant installations with kilograms of catalysts and industrial reactors having tons of catalysts). The practice has shown that upon scaling up the catalytic reaction indices are deteriorated considerably. The “Theory of Similarity” recommends using dimensionless characteristic quantities [10] to estimate the degree of similarity – geometrical, flow indices, thermal and kinematic indices – for example the size of the catalyst granules in laboratory and industrial reactors should be the same, in order to have similarity. If we disregard the geometrical similarity (i.e. the laboratory and the industrial reactor have quite different sizes), then by all means we should maintain identical flow characteristics, thermal and kinetic regimes, in order to achieve similarity between laboratory and industrial reactors.

The above considerations, applied in the design of the reactor of Berty[9], are dictated entirely by engineering chemistry concepts – this is the practical aspect of the methods for studying the kinetics of catalytic reactions – the options for application and utilization of kinetic investigations. The fundamental aspect is already clear – obtaining information about the mechanism of occurring of the catalytic reaction and its elementary steps. The practical aspect of the design of catalytic reactors, as in the case of Berty reactor [9[, requires considering chemical kinetics in its interconnection with mass transfer phenomena (diffusion and convection) on one side, while on the other side – the chemical kinetics in interconnection with heat transfer phenomena i.e. kinetics ↔ thermodynamics. These two aspects deserve special attention to elucidate the special terms in this respect.

Reynolds number and Thiele modulus, effectiveness factor

Irrespective of our choice – which type of reactor we shall prefer – internal or external circulation – in both cases the very first thing, that we ought to do in the course of the experimental work is to establish whether the reaction occurs in the kinetic region or in the diffusion region. This means to check which is the slowest step – the so called „***rate determining step***”. If this is the interaction between reactant molecules, adsorbed on the surface of the catalyst, then the reaction is proceeding in the kinetic region, so we have the right to start with the modeling of the kinetics and to derive a kinetic model, further drawing conclusions about the mechanism of the catalytic reaction. To the contrary – if this is not the case – for example the case of continuous flow reactors without any circulation or mixing the reactants – then the ideal mixing of the reactants is missing and then we have the case of ***plug flow reactor***. Considering the fixed catalyst bed layer-by-layer the composition of the reactant mixture is different inside the separate layers and the catalytic reaction is occurring in the diffusion region i.e. the slowest and rate limiting step is the diffusion supply of reactants. The catalyst bed could be able to convert larger number of molecules of the reactants, but they are reaching slowly the active sites and not all the active sites are functioning. In this case we have no right to make comparison between the different catalyst samples and to draw conclusion which one is better. The good catalyst sample and the bad one perform in similar way and the rate of formation of products depends on the rate of diffusion.

In the case of continuous flow reactor (without circulation) the retardation effect could be due to external diffusion (from the bulk phase of the gaseous mixture to the surface of the catalyst granules), as well as due to internal diffusion (inside the pores of the catalyst granule). Considering these two cases we use the terms external diffusion region and respectively pore diffusion region of carrying out the catalytic reaction. These regions supply insufficient information and do not allow comparison of the activities of the synthesized catalyst samples, developing a kinetic model and drawing conclusions about the elementary steps in the mechanism of the reaction. Regrettably, under the industrial conditions of operation the reactors are of the continuous flow type and the catalytic reaction is occurring in the diffusion region. Only under laboratory conditions we have the option to create a maximally favorable hydrodynamic regime and to saturate the entire external and internal surface area of the catalyst with molecules of the reactants and to observe the maximum of productivity of each sample, to make comparison between them and to select the best sample to be introduced into the industrial practice. This is achieved by means of elimination of the external diffusion retardation effect using recirculation and ideal mixing of the reaction mixture. The elimination of pore diffusion retardation effect is accomplished by grinding the tablets of the industrial catalyst into small particles of size < 1 mm, whereupon the entire internal surface area becomes accessible to reactant molecules i.e. all the active sites are accessible and give their contribution. In this respect we have to be well acquainted with the special terms (criteria) such as ***Reynolds number, Thiele modulus* and *Effectiveness factor*.**

Let us consider a fluid flow passing through a catalyst bed: it has fluid density denoted by ρ_F and fluid viscosity μ_F, while the diameter of the catalyst particles is d_g and the space velocity of the fluid is V_{SF}. Reynolds has formulated his criterion [1,2,11] for characterizing the hydrodynamics of convective flow by the following formula:

$$Re = d_g .\ V_{SF} .\ \rho_F / \mu_F \qquad (13)$$

It should be explained here, that upon crushing of the industrial catalysts pellets one obtains particles of irregular form – during the reactant flow around them one uses the term ***„effective diameter”*** i.e. the particle shape is approximated to spherical form, which has the same geometrical surface area and then we consider the diameter $\boldsymbol{d_g}$ of this sphere. The Reynolds criterion ***Re*** indicates by means of its numerical value whether we are having laminar flow, in which we are having uniformly ordered movement of all the particles of the inlet flow. In each point they have the same linear velocity, remaining constant with the time. In this case the cross section of the flow can be considered conditionally as unmovable medium. The transfer of particles from the flow to the particles below it in case of laminar regime is accomplished by diffusion. This regime corresponds to low values of ***Re*** and then the coefficient of mass transfer is not depending on the ***Re*** number.

Upon increasing the linear velocity of the flow there is increasing probability of appearance of turbulent movements, which are facilitated by the low viscosity of a gaseous mixture. Then a turbulent flow regime arises of disordered movement of the particles of the flow having non-stationary changing velocity and different linear velocity in the various sections of the flow. The diffusion of the reagents to the surface of the catalyst particle is accomplished through a boundary layer, whose thickness depends substantially on the degree of turbulence of the flow at high values of ***Re*** [11]. The criterion of Reynolds is the basic quantity, which is included in the expressions of a series of other criteria – for example the criteria of Nusselt and of Stanton [1,2], which have been proposed for separate specific cases, which shall not be considered here.

Checking the presence or the absence of diffusion resistance requires knowledge of the so called „***Thiele modulus”, Φ*** [11]:

$$\Phi = R^2/D\ [(-1/V_C).dn/dt]\ .\ 1/C_S \tag{14}$$

Here ***R*** is the radius of the particle (cm), ***D*** is the diffusion coefficient (cm^2/s), while $\boldsymbol{V_C}$ is the volume of the catalyst bed (cm^3), ***dn/dt*** is the rate of the catalytic reaction (mol/s), while $\boldsymbol{C_S}$ is the concentration of the reactant on the external surface of the catalyst particle (mol/cm^3). It follows from equation (4) that in fact the Thiele modulus, ***Φ***, interconnects i.e. it correlates the rate of the catalytic reaction ***dn/dt*** with the diffusion coefficient ***D***. This is the important significance of this module. The values of these two quantities in the general case (14) depend on the volume of the catalyst bed (having larger quantity of the catalyst we have larger number of active sites and therefore higher rate ***dn/dt***). On the other side the size of the catalyst particle (the radius ***R***) is influencing the value of the diffusion coefficient ***D*** – when the catalyst pellet is crushed into smaller particles, this fact decreases the pore diffusion resistance. This is reflected directly on the concentration of the reactant C_S in the surface layer. In some separate specific cases the equation (14) could acquire a more simple form [13]:

$$-\Phi_{P1} = L\,(k_V / De)^{1/2} \qquad (15)$$

The equation (15) considers the specific case of first order reaction on a flat catalyst layer, accessible only from the top without any flow through it (***infinite slab – one end open***). The authors from Bremen University used the formula (15) for the processing of the experimental data from the reaction of catalytic oxidation of formic acid vapors HCOOH on Pd catalyst [12-14]. The reaction was carried out in continuous flow oscillation reactor (without recirculation) and the catalyst film on silver plate (***flat-plate continuous-flow reactor***), which is sealed from the bottom and the gaseous mixture is washing the catalyst layer from above (vapors HCOOH + O_2 + N_2). This pattern is in exact correspondence with the specific case (15). At large stoichiometric excess of O_2 one could assume that its concentration remains practically the same and it is included in the value of the apparent rate constant k'_V :

$$r_V = k_V \,.\, C_{HCOOH} \,.\, C_{O2} = k'_V \,.\, C_{HCOOH} \qquad (16)$$

As one can see in equation (16) the rate of the reaction r_V, related to the volume V_{cat} of the catalyst layer of thickness L and by assuming the efficient rate constant $(k'_V = k_V \,.\, C_{O2})$ we are approximating this reaction of second order under the given conditions (excess of C_{O2}) to a first order reaction. The rate r_V is calculated based on the flow rate of HCOOH vapors (F_{HCOOH}), on the measured conversion degree (ΔX = 48%) and on the volume of the catalyst layer V_{cat} = 0.1 cm^3:

$$r_V = F_{HCOOH} . \Delta X / V_{cat} = [5.10^{-5} (mol/cm^3.min).0,48]/0.1\ cm^3 = 3.10^{-4}\ mol/cm^3.min \qquad (17)$$

Then when k'_V = 300 min^{-1} at diffusion coefficient value De = 6.10^{-2} см^3/min we obtain Thiele modulus $\Phi_{P1} \approx 10$. What is the meaning of this value, what is the information that it is providing to us? In order to interpret this quantity we should first explain what is the meaning of the term ***„effectiveness factor" ε*** and what is its interconnection between the ε and the Thiele modulus. By definition ε, named also ***„utilization factor"***, is the degree of accessibility of the entire surface area of the catalyst:

$$\varepsilon = \frac{\text{Reaction rate in presence of diffusion effect}}{\text{Reaction rate in absence of diffusion effect}} \leq 1 \qquad (18)$$

We can take the ratio between the reaction rate over layer of whole catalyst granules and the reaction rate over layer of crushed catalyst granules [11].

The effectiveness factor $\boldsymbol{\varepsilon}$ is calculated using the Thiele modulus $\boldsymbol{\Phi_{P1}}$:

$$\boldsymbol{\varepsilon = \tanh \Phi_{P1} / \Phi_{P1}} \qquad (19)$$

Then substituting the value $\boldsymbol{\Phi_{P1}}$ = 10, which we determined for this specific case in equation (19) with *tangence hyperbolicus* in the numerator tanh x = $(e^x - e^{-x})/(e^x + e^{-x})$ we obtain that $\boldsymbol{\varepsilon = 0.1}$. This value means that only 10% of the internal surface area of the palladium catalyst is accessible by diffusion of the molecules of HCOOH. In this way we were able to explain the appearance of block oscillations [12-14] in the specific case. As one can see such type of calculations could be very useful for the operator. The so determined value $\boldsymbol{\varepsilon = 0.1}$ can be interpreted in other terms – the depth of the kinetic region ***Dk*** is only 10%, and this factor in its term means, that the catalytic reaction is proceeding in the diffusion region. The saturation of the inner pore surface by HCOOH molecules is a very slow process. At one moment upon reaching saturation degree the oxidation reaction is occurring intensively and the catalyst layer is heated (this is observed by means of a thermocouple, sealed below on the bottom of the plate with catalyst layer on the top of it). At the next moment, however, the entire quantity of HCOOH molecules, which have penetrated into the pores, is exhausted. The diffusion of the molecules of the product CO_2 and H_2O is also slow –the oxidation reaction is extinguished, the reaction rate drops down to zero – this explains the oscillatory regime by diffusion limitations.

Chemical kinetics and thermodynamics

After having already considered in details the interconnection between the chemical kinetics and mass transfer (diffusion and convection) we should consider also in its turn the interconnection between the chemical kinetics and mass transfer phenomena (i.e. thermodynamics). We find here also a complicated mathematical apparatus. Perhaps it is better, in view of training PhD students, instead of excessive burdening them with a multitude of equations (unnecessary for researchers working in neighboring fields of catalysis), which they will probably never use (they will rely in this aspect to scientists kineticians), simply to explain their physical meaning. This is done in the best way by considering a specific example for their visualization.

When a catalytic reaction is proceeding along several routes simultaneously, some of the products could happen to be „products of kinetic control”, while others appear to be „products of thermodynamic control”. The first category – these are products, which are being formed in reaction having lower energy of activation and therefore occurring at higher rate – greater percentage of the collisions between molecules and active sites on the catalyst surface leading to result – chemical transformation. In the second case $\boldsymbol{E_a}$ is high, the rate is low, because a higher energy barrier has to be overcome, but then a product is obtained, which is thermodynamically more favorable, since the decrease in the enthalpy of the reaction system $\Delta\boldsymbol{H}$ has higher value – Fig. 3. The figure illustrates the case of kinetic and thermodynamic control by the example of isomerization of 1-butene (1) into cis-2-butene (C) and trans-2-butene (T) over an industrial Co-Mo catalyst. Our investigation [15] showed that the cis-2-butene (C) is a product of kinetic control, while the trans-2-butene (T) is a product of thermodynamic control:

$$\begin{aligned} &\text{I)} \quad 1\text{-}C_4H_8 \leftrightarrow \text{cis-2-}\ C_4H_8 \\ &\text{II)} \quad 1\text{-}C_4H_8 \leftrightarrow \text{trans-2-}\ C_4H_8 \qquad (20) \\ &\text{III)} \quad \text{cis-2-}\ C_4H_8 \leftrightarrow \text{trans-2-}\ C_4H_8 \end{aligned}$$

The system has 2 linearly independent routes out of a total of 3 occurring reactions. We chose the routes I) and II) as independent routes, because we were feeding 1-butene as a reactant at the inlet of the catalytic reactor (another choice is also possible, but only of 2 routes). It turned out that at the initial stage of the reaction (at small contact times of 1-butene) one obtains mainly cis-2-butene, while at larger contact times the trans-2 butene starts to be the prevailing product. Now we have to seek for an explanation of this experimentally observed fact. For this purpose we applied the **method of Wei-Prater** [15,16]. They elaborated an approach for the analysis of the structure of complex reaction systems. The data, needed for modeling the kinetics, can be evaluated by considering the structure of the reaction system i.e. its qualitative and quantitative characteristics features, which appear to be common for a given class of systems. In our example (20) we have the simplest possible case – the class of „monomolecular reversible reaction systems”. This means that there is „***monomolecularity***” i.e. mutual interconversion between each pair of two reagents, which is a first order reaction and it is reversible – Fig. 4. Then the rate constants $\boldsymbol{k_{ij}}$ are determined based on the initial rates of formation of the three substances A_1, A_2 and A_3. The convenience in this case is that only a small number of experiments are needed, while the data are processed by means of elementary mathematical operations. Wei and Prater introduced the term **“reaction simplex”** – Fig. 4 – it represents an equilateral triangle having peaks (1,0,0), (0,1,0) and (0,0,1), since the sum of the molar fractions in the system is equal to 1. The space pattern of the compositions is three dimensional (3D), but the reaction simplex in this case is two dimensional (triangle in a plane). In the general ***n***-dimensional case the reaction simplex has always one dimension less than the space pattern of the compositions – this is the advantage of the method of Wei-Prate – the simplicity. The reaction pathway represent a bow, starting from a certain initial composition (in our case 100% 1- butene or this is the peak point of the triangle with coordinates (1,0,0)) and moving further upon increasing the contact time towards the equilibrium composition of the tri-component mixture at a fixed catalyst bed temperature – Fig. 4. The tangent line to this bow in the equilibrium point α^* is continued until it intersects with the sides of the triangle. In this way one finds such compositions of bi-component mixture, that the reaction pathway would be a straight line. Moreover there exists a second straight line reaction pathway, which is perpendicular to the tangent line in the point α^*. Taking into account these four initial compositions and the equilibrium composition in point α^* one obtains a matrix, which after transformation gives the values of the the so called relative rate constants. This term is proposed assuming that one of the constants is equal to unity and the values of the other constants are related to this unit value.

There is one basic equation, which should be remembered from thermodynamics – whether one reaction is possible to occur spontaneously:

$$\Delta G = \Delta H - T\,\Delta S \tag{21}$$

The reaction occurs spontaneously only when the change in the ***energy of Gibbs*** ΔG (in the Russian literature the term is „***isobaric-isothermal potential***") has a negative value $\Delta G < 0$ i.e. spontaneously occurring only processes in the direction of decreasing the potential energy. The equation (21) reflects the controversy between two opposite tendency – on one side it is expected that the entropy of the reaction system is tending to increase i.e. ($\Delta S > 0$), while on the other side weak bonds are broken and stronger bonds appear, whereupon the enthalpy of the reaction system is decreasing ($\Delta H < 0$). Depending on the specific case – which one of the two tendencies is prevailing for the considered reaction at a given temperature – we conclude that the reaction is proceeding due to enthalpy factor or due to the entropy factor. There is decrease in the entropy ($\Delta S < 0$) in the case of addition reactions (for example addition of H_2 to a double bond C=C), occurring accompanied by decrease in the number of moles and respectively reduction of the reaction system volume (at constant external pressure), which exerts unfavorable effect. This effect is increase with the increase in the temperature and it could become a dominant factor above certain temperature – the reaction starts to proceed in the opposite direction in case of dominant entropy factor. Useful guidance in such chemical engineering calculations are given in the literature sources [17-19].

Chemical kinetics and statistical analysis

We shall consider in brief two examples of application of statistical analysis to kinetic data from heterogeneous catalytic reactions. The first thing is to check whether we are already having a new steady state after changing the experimental conditions by the statistical method of Wald-Wolfowitz [20-22] for a given set of kinetic data. There is always the probability that the data describe a transition state between two steady states, when we have just changed the composition of the inlet gaseous mixture fed into the reactor or when we have changed the catalyst bed temperature. Especially in the case of continuous flow reactor with external recirculation, when the volume of the gas circulation contour is large, then a certain time interval is needed to establish the new steady state. In some rare cases – mainly in highly exothermal reactions and large contact times at small inlet flow rate and the heat transfer is not fast enough – then oscillations of the temperature of the catalyst bed could appear and respectively of the composition of the converted mixture at the reactor exit i.e. once again there is no steady state available. We should check, if we are having one of these two deviations from steady state and to be sure, that we are really having a steady state. It is logical that the following second step is to verify whether the reaction is proceeding in the kinetic region using the approach of Corrigan [23-24], and not in one of the diffusion regions (internal pore diffusion or external diffusion region), and this can be done only by the respective statistical analysis of the data. Only after these two checks and following verifications we have the right to start with the selection of kinetic model and to draw conclusions about the mechanism of the heterogeneous catalytic reaction.

In order to illustrate the application of the statistical method of Wald-Wolfowitz [20-22] to a given set of kinetic data again we shall use the example of data set for the reaction of butenes isomerization. The analysis is aimed at establishing the time interval for reaching steady state, after which the composition of the reaction mixture at the outlet of the catalytic reactor remains constant (after passing at least five times larger volume of the gaseous mixture in comparison with the total volume of the circulation contour). Thereafter it becomes possible that the system remains unlimited time in this new steady state. During the statistical analysis we count the number of series of the same sign and we determine the number of the inversions. If we have available N=10 number of gas chromatographic analyses of the concentration of 1-butene (%) at the outlet of the catalytic reactor:

38.01(-), 38.83(+), 37.03(-), 40.02(+), 38.19(+),

38.21(+), 40.81(+), 37.20(-), 37.08(-), 36.56(-)

Here we are having 5 series of measurements of the same sign of the measured value – the values higher than that of the so called ***„median”*** value i.e. mean arithmetic value (sign (+)) or lower value (sign (-)), determined in view of the above given data. Out of the above set of ten values there are two middle values 38.01 and 38.19 (we have 4 values higher than them and 4 values lower than them) and then we calculate the mean arithmetic value from them:

Median = 0.5(38.01+38.19) = 38.10

Then we obtain that out of the ten values five are lower than the median and five are higher than the median: N(-) = N(+) = 5. Himmelblau [20] formulated a tabulated criterion – from 2 up to 9 series for 5% deviation (i.e. ά = 0.05) and respectively 95% confidence interval – here we are having 5 series. Therefore we have steady state 30 min after changing the input parameters, when the first value 38.01% was measured. We can reach the same conclusion if we select the other possible approach – the number of the inversions (i.e. reversing the tendency – if there was increase in the value, followed by decrease and vice versa). The tabulated criterion gives us that we can have 11 up to 33 inversions – starting with the first valueиand reaching the tenth value, then we start with the second value i.e. it becomes the first one, while the former first one becomes last and so on. In our case we are having 28 inversions – therefore it is steady state.

The algorithm for checking by the ***statistical method of Corrigan*** [23] whether the heterogeneous catalytic reaction is occurring in the kinetic region:

- Comparing two degrees of conversion $X_1 \leftrightarrow X_2$ at two different quantities of the catalyst in the reactor $W_1 > W_2$ (g-cat)
- Selecting two values of feed flow rates of the reactant $F_1 > F_2$ (mol.hour^{-1}) in such a way that the two contact times are equal $W_1/F_1 = t_1 = t_2 = W_2/F_2$ (hour.g-cat/mol)
- In case $X_2 > X_1$ then we are having diffusion effect at W_1
- If $X_2 = X_1$ – we have kinetic region of operation and absence of diffusion retardation effect

The best approach is to juxtapose the entire kinetic curves for a wide interval of t = W/F of course at the same catalyst bed temperature.

Optimization of reactor input parameters by the method of Taguchi-Grey

Let us suppose that we have 5 input variables i.e. 5 input parameters varied on 5 levels. According to the complete factorial design we should carry out $5^5 = 3125$ experiments. **Kenichi Taguchi** [25] proposed design of experiments (DoE) based on the so called Latin squares and the respective **Orthogonal Array** – in our case we have L32 i.e. only 32 experiments without loss of much accuracy: for some experiments only the middle value of the 5 levels is taken and for other experiment – the highest and the lowest value level.

This approach can be combined with **Grey relational analysis** – which input parameters are significant? What is the percentage of their contribution? Combining the two approaches we can obtain the optimal set of operational input parameters yielding the highest value of the response function F. In our case this was the ethylene conversion degree [26] – $\mathbf{F = f\ (C_e, t_e, I_{il}, RH, N_c)}$ where the variables are the feed concentration of ethylene C_e, the contact time of ethylene t_e, the illumination intensity in the photocatalytic reactor I_{il}, the relative humidity RH of the feed flow also exerts influence, and the number of coatings on the thin layer chromatography TLC flat plate, coated with the photocatalytic material – most often this is TiO_2. Using the F equation as a regression model we can find the residual error and optimize the operation of the reactor.

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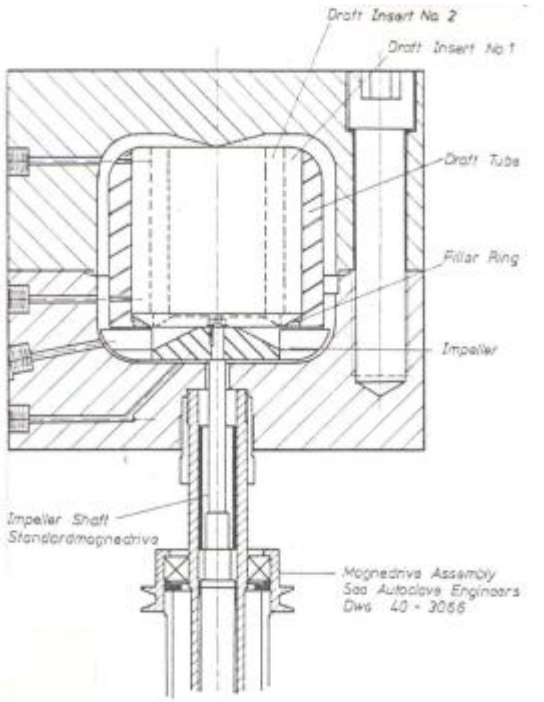


Figure 1. Berty high pressure autoclave reactor with internal circulation and ideal mixing

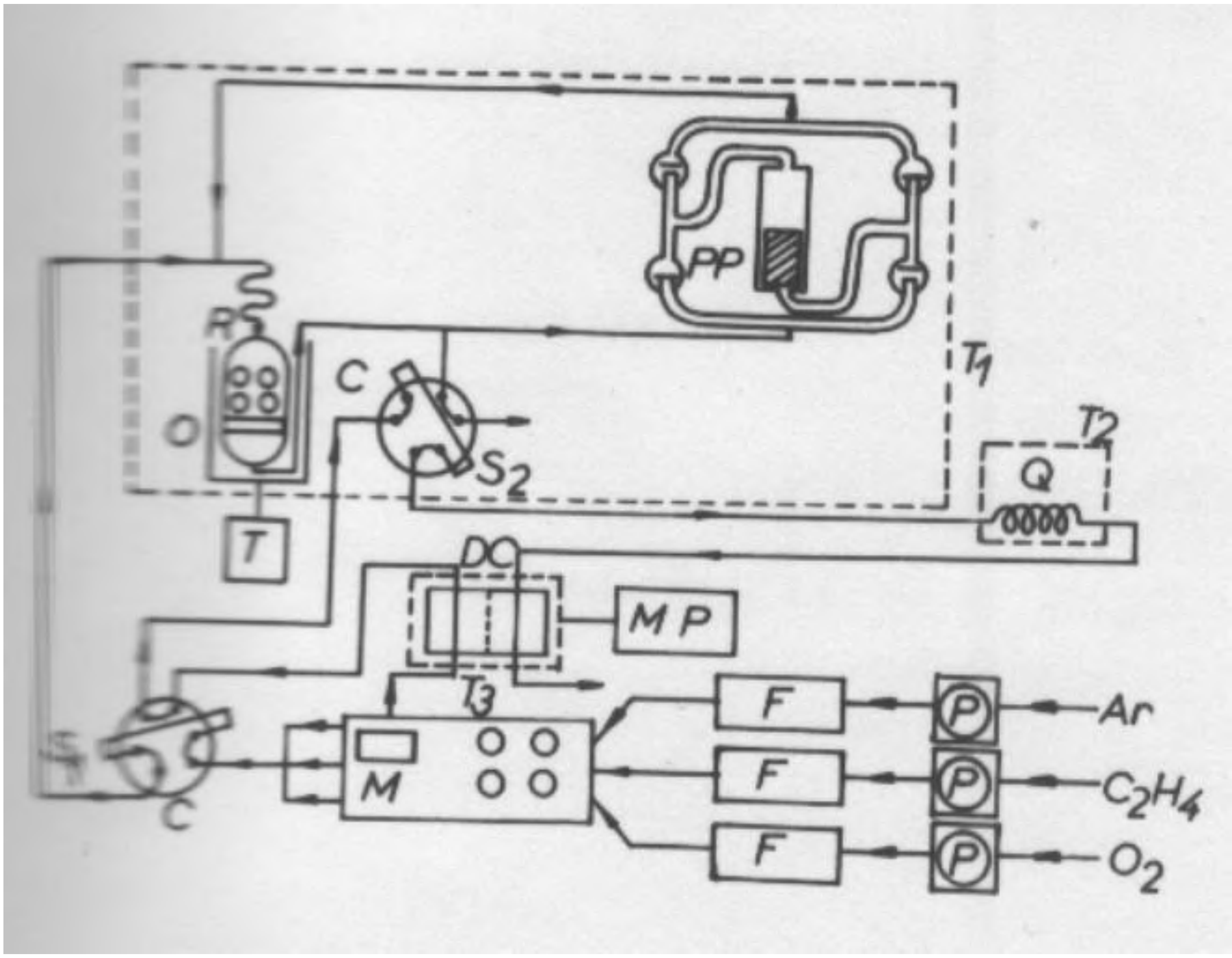


Figure 2. Temkin-Kiperman reactor with external circulation and ideal mixing – reactor R, oven O, thermoregulator T, piston pump P, six way valves S1, S2, detector of conductivity DC, chromatographic column Porapack Q, pressure regulators P, flow controllers F, Matheson mass flow controller M

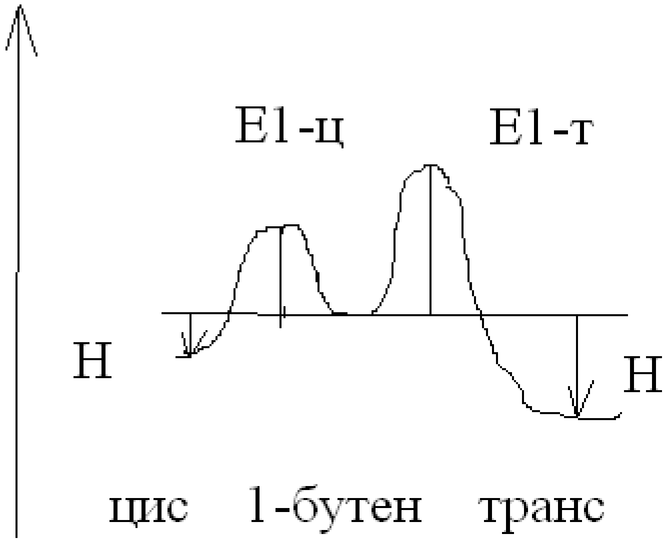
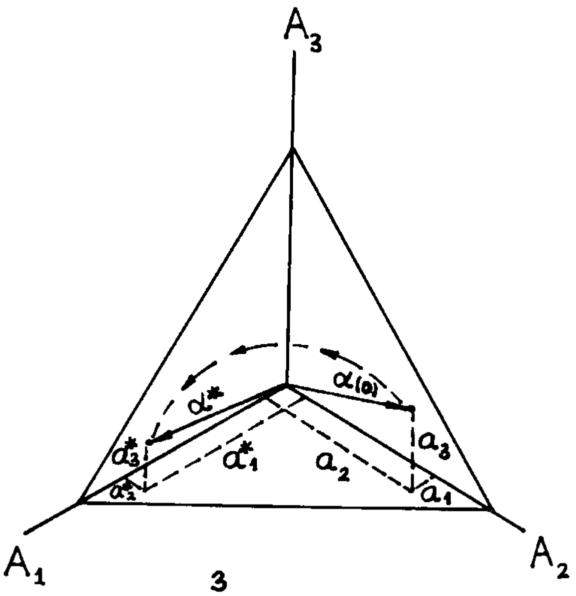


Figure 3. Isomerization of 1-butene into cis -2- butane (low activation energy E1) and trans-2-butene (high activation energy E2 and high thermal effect ΔH)



$$\sum_{\nu=1}^{3} a_\nu = 1$$

$$a_\nu \geqslant 0$$

Figure 4. Reaction simplex of Wei- Prater – 3 dimensional space pattern of compositions and 2 dimensional reaction simplex (100), (010), (001) – reaction pathway.