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CHEMISTRY

INVESTIGATION OF CHEMICAL PROCESSES USING CONCEPTION OF STOICHIOMETRIC REACTION MIXTURE

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Abstract. *A new approach of investigation of chemical interactions based on logical separation of stoichiometric stream from feed mixture is proposed. Principles of method result from the fundamental kinetic laws and thermodynamic theory. Applying of the method considerably simplifies the study of unknown chemical processes and leads to increase of efficiency of its mathematical simula-tion. The applications to three well-known industrial processes are given. Obtained dependences based only on theoretical data (thermodynamic equilibrium constant) for methanol and carbamide synthesis, catalytic oxidation of NO shown good agreement with experimental data for industrial processes. Dependencies of stoichiometric yield under various conditions or even for different pro-cesses have similar form of mathematical expressions, they have explicit form, simple to calculation, control and optimization of industrial chemical processes.*

Keywords*: chemical processes, stoichiometric, concentrations, yield, calculation.*

It is commonly accepted that the investigation and description of chemical processes practically are based on the use of relative values which reflect the composition of feed and output mixture. There are some criteria traditionally accepted in chemical kinetics and thermodynamics for registration of amount of substances, such as, (a) concentration (molar and volume) of reagents or products and (b) their ratios.

These factors are sufficient for investigation of simple chemical processes but analysis of more complicated interactions reveals that their flaws. Mutual influence of concentration of reagents by common denominator makes this criterion inadequate for investigation of more than 2-component reaction mixture. The ratios are free of this negative feature and more prospective, but great number of possible ratios (6 - for 3-component, 12 for 4-component mixture ...) leads to the problem of the subjective choice of the “best” ratios.

The main cause of this problem is the absence of direct physical association between these criteria and the reaction of process being studied. We can show that there is a new criterion which are free of the above-mentioned disadvantages.

If ratios between reagents are strictly stoichiometric (stoichiometric stream, SS) and reaction carries out entirely and without formation of by-products it can be easily proved that the output mixture of products of synthesis will have also strictly stoichiometric composition. Amounts of products are defined only by SS and addition of any substance which does not affect SS (it may be even not reagent) will not result in change of maximum amount of products. Therefore feed mixture can be divided into SS which determines yield and resting overstoichiometric stream (OSS) which does not take part in reaction. Theoretically this part of stream is constant for all time while reaction proceeds but in practice ratio of amount of component in the OSS to amount of the SS is important relative value (stoichiometric excess, SE) which shows how real composition differs from theoretical one.

Ratio of real quantity of product to its theoretical possible amount gives a new criterion – stoichiometric yield (α_s). Contrary to yield of any component which shows degree of **utilization** of only this component, a_s is unified parameter for the whole process and expresses the degree of **completeness** of chemical reaction.

Theoretical value of stoichiometric yield can be calculated through thermodynamic equilibrium constant for equilibrium state. In practice these conditions usually do not hold and α_s has different value. Comparison of theoretical and practical α_s easily allows to take into account by-product reaction with participation of reagents and their products, influence of diffusion resistance and

other peculiarities of the proceeding process. Expressions of α_s from SE nearly always have explicit form and great reliability. It considerably simplifies the following technological calculation and therefore it is especially important for new unexplored reactions.

Consider the generalize method of the proposed approach that can be applied to any chemical reaction of the form:

$$a_1A_1 + a_2A_2 + \cdots + a_nA_n \Leftrightarrow b_1B_1 + b_2B_2 + \cdots + b_mB_m .$$

The amount of stoichiometric stream is determined by the quantity of the component without stoichiometric excess – known as limiting reagent (in the stoichiometric stream stoichiometric excesses of any component always equal zero). In this case the C_S value (concentration of stoichiometric stream unit) can be calculated as

$$C_S = \min\left(\frac{C_1^0}{a_1}, \frac{C_2^0}{a_2}, \ldots, \frac{C_n^0}{a_n}\right).$$

C_S -concentration of stoichiometric stream unit in input mixture

C^0_j -concentration of the j-component in input reaction mixture

a_j -stoichiometric coefficient of the j-reagent

b_j -stoichiometric coefficient of the j-product of reaction

According to equation of reaction $C_S \cdot a_j$ parts of any reagents restricts an amount of matter involved in the reaction. The rest of reagent is the stoichiometric excess of corresponding component of reaction

$$E_j = \frac{C_j^0 - a_j \cdot C_S}{C_S}.$$

E_j -stoichiometric excess of the j- component in output reaction mixture

E_i -stoichiometric excess of inerts

C_j -concentration of the j-component in equilibrium reaction mixture

Proceeding of the reaction can cause change of the volume of reaction mixtureand in this case the concentration or partial pressure of components in output mixture must be correct. So expression of stoichiometric yield can be rewritten as

$$\alpha_S = \frac{C_j}{b_J \cdot C_S} \cdot K_V$$

C_S -stoichiometric yield

Approach considered enables to pass easily to traditional values, like concentration of component, degree of conversion of any component, partial pressure and so on. So initial concentration of any component may be written as relation of stoichiometric excess of j-component and concentration of unit of SS

$$C_j^0 = C_S \cdot \left(a_j + E_j\right).$$

and conversion degree by j-component is expressed by formula

$$\alpha_j = \frac{\alpha_S}{1 + E_j / a_j}.$$

Proposed approach was examined on well-known and already described process with the great number of empirical data. In order to make the clear conclusion about the proposed approach, three wide-spread industrial processes which are not complicated by proceeding co-product reaction and have enough experimental material were selected.

The methanol synthesis is described by the equation

$$CO + 2H_2 = CH_3OH$$

For industrial process pressure of the reaction mixture (P) is equal 20 MPa and temperature of the output mixture (T) — 630 'C [1, p.211]. Evidently that there is only one reagent with non-zero stoichiometric excess in the input mixture. Stoichiometric excess other reagent always will be zero and its degree of conversion into products will coincide with the stoichiometric yield. Curves calculated by means of thermodinamic equilibrium constant and maximum possible concentration of product in the output mixture (to irreversible reaction) are shown on the Fig.1. Experimental data [1] are given as points which are always less than the values obtained through equilibrium constant. This deviation have regular nature (insufficient contact time), it does not change a form of dependency and it can be taken into account if needed.

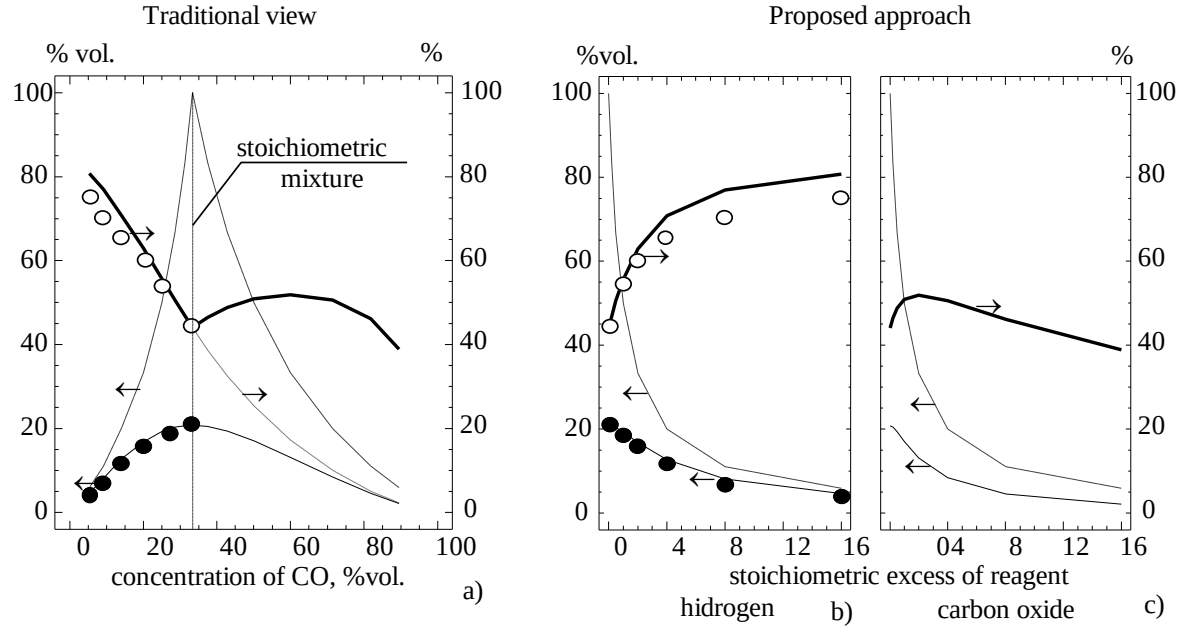

Fig.1. Characteristics of methanol synthesis

- experimental value of concentration of methanol, %vol;
- theoretical equilibrium concentration of methanol after reaction, %vol;
- experimental value of degree of CO conversion, %;
- traditional degree of CO conversion, %;
- theoretical equilibrium stoichiometric yiel of product, %;
- concentration of methanol for irreversible process, %vol.

Treatment of as under equilibrium steady state conditions gives an equation of stoichiometric yield which depends only on stoichiometric excesses of H_2 and CO

$$\alpha_S = 0.178 - \frac{1.08}{2.5 + E_{H_2}} + 47.4\frac{E_{CO} + 0.5}{(E_{CO} + 0.6)\cdot(E_{CO} + 57)}. \quad (1)$$

Good agreement of the calculated and empirical data allow us to make important conclusions about the described process even without performance of the experiments. So, synthesis of methanol with CO-enriched mixture as well as with more that 4-multiply excess of H_2 is hopeless. Earlier, these conclusions were received through analysis of empirical data; the offered approach allows to get it from the well-known theoretical regularities.

Since in industry only mixture with excess of H_2 is used, the latter member of equation (1) can be transformed to the constant and stoichiometric yield will be congruent with degree of CO conversion.

$$\alpha_S = \alpha_{CO} = 0.871 - \frac{1.08}{2.5 + E_{H_2}} \quad (2)$$

Use of empirical data of this process gives the possibility to transform equation (2) in new dependence with participation of pressure, temperature of reaction and excess of inerts (E_i).

$$\alpha_S = \alpha_{CO} = 6.16 + \frac{0.0039}{E_i + 0.009} - \frac{0.0449 \cdot T}{P + 19} - \frac{1052}{1800 - T} \cdot \left(\frac{1}{2.5 + E_{H_2}} + 5.51 \right)$$

Analysis of this equation shows that the dependence is true in wide range of varying parameters and it gives a perceptible error only at a_S less than 0.05 and more than 0.95. So offered equation have a considerable advantage over traditional unexplicit dependencies used to perform optimization and design calculations.

Synthesis of carbamide is described by the equation

$$CO_2 + 2NH_3 = CO(NH_2)_2 + H_2O$$

The standart conditions of comercial process assume pressure of the reaction mixture (P) equal 25 MPa, temperature of the output mixture (T) equal 630 'C [2, p.211].

Treatment of data of stoichiometric yield calculated using thermodynamic theoretical data gives the equation

$$\alpha_S = 1.27 - \frac{1.48}{2.7 + E_{NH_3}} - \frac{0.229}{1.1 + E_{CO_2}}. \quad (3)$$

It shows that performance of process is less effective for the excess of CO_2 than for the excess of NH_3 (Fig. 2). Maximum yield for excess of carbon monoxide is no more 0.76, whereas the unrestricted excess of ammonia enables to reach stoichiometric yield closely approached to 1. Thus, using only theoretical assumptions we came to conclusions which was earlier obtained by means of the experimental methods.

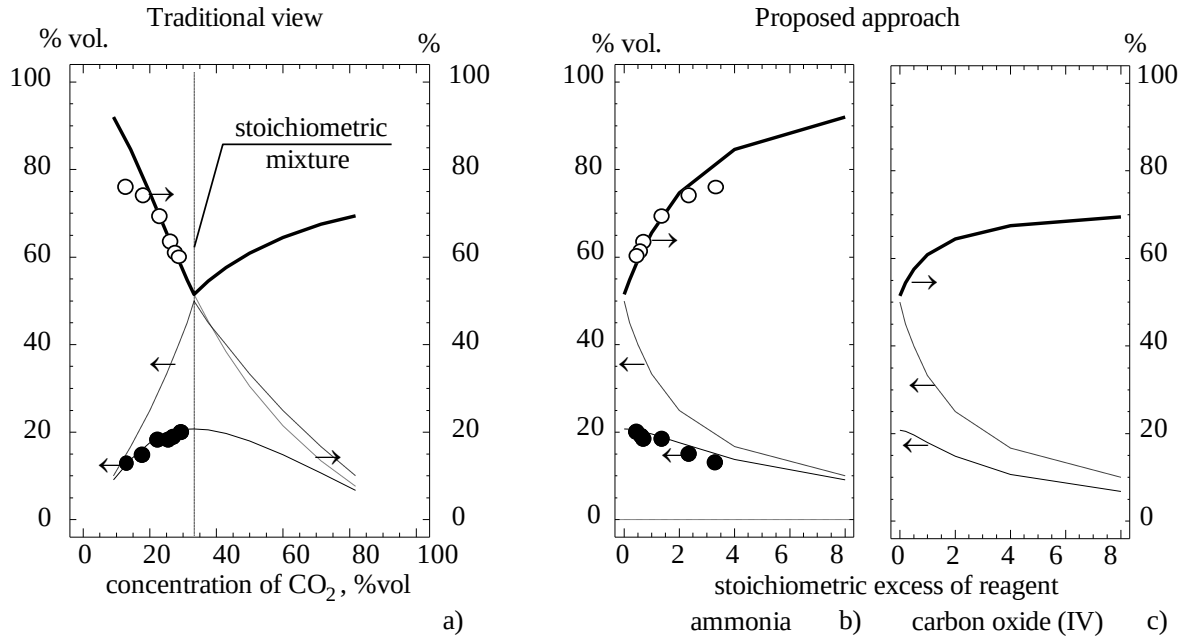

Fig.2. Characteristics of synthesis of carbamid

- experimental value of concentration of carbamid, %vol;
- theoretical equilibrium concentration of carbamid after reaction, % vol;
- experimental value of degree of CO_2 conversion, %;
- traditional degree of CO_2 conversion, %;
- theoretical equilibrium stoichiometric yiel of product, %;
- concentration of carbamid for irreversible reaction, %vol.

In practice this synthesis is carried out under excess of ammonia, therefore equation (3) can be simplified and stoichiometric yield will be congruent with conversion degree of reagent which have zeroth stoichiometric excess (CO_2).

$$\alpha_S = \alpha_{CO_2} = 1.06 - \frac{1.48}{2.7 + E_{NH_3}} \quad (4)$$

This expression is in complete agreement with empirical data. Its varying interval is 22-26 MPa for pressure and 620-650'C for temperature. Use of more complicated data allows to make more accurate equation, and to introduce new factors which affect process. But even in such form, relation (4) enables to conduct fast optimization and design calculation, and to forecast easily composition of the output mixture.

Catalytic oxidation of NO is described by equation

$$2NO + O_2 = 2NO_2$$

Main conditions of this process are [2, p.69]: 1) pressure of the reaction mixture P=0.1 MPa; 2) concentration of NO in the reaction mixture - C_{NO}=1% vol.; 3) concentration of O_2 in the reaction mixture - C_{O_2}=0.1-5.4% vol.; 4) temperature of the output mixture - 623 K; 5) cobalt-zirconium catalyst.

For simplicity one can assume that total volume of the reaction mixture is changed insignificantly (for high concentration this factor can be taken into account). Calculation stoichiometric yield using of theoretical data give us the equation that is in complete agreement with experimental data for small concentration of nitrogen oxide (II) and oxygen (total less than 10% vol.)

$$\alpha_S = 1.39 - \frac{2.21}{3.5 + E_{NO}} - \frac{1.51}{3.5 + E_{O_2}}. \quad (5)$$

The catalyst operation enables to reach maximum possible efficiency of process. This is evident from the entirely full coincidence of empirical data with theoretical curve. Without catalyst stoichiometric yield would be less than theoretically calculated as it was shown in previous examples (Fig.1, 2).

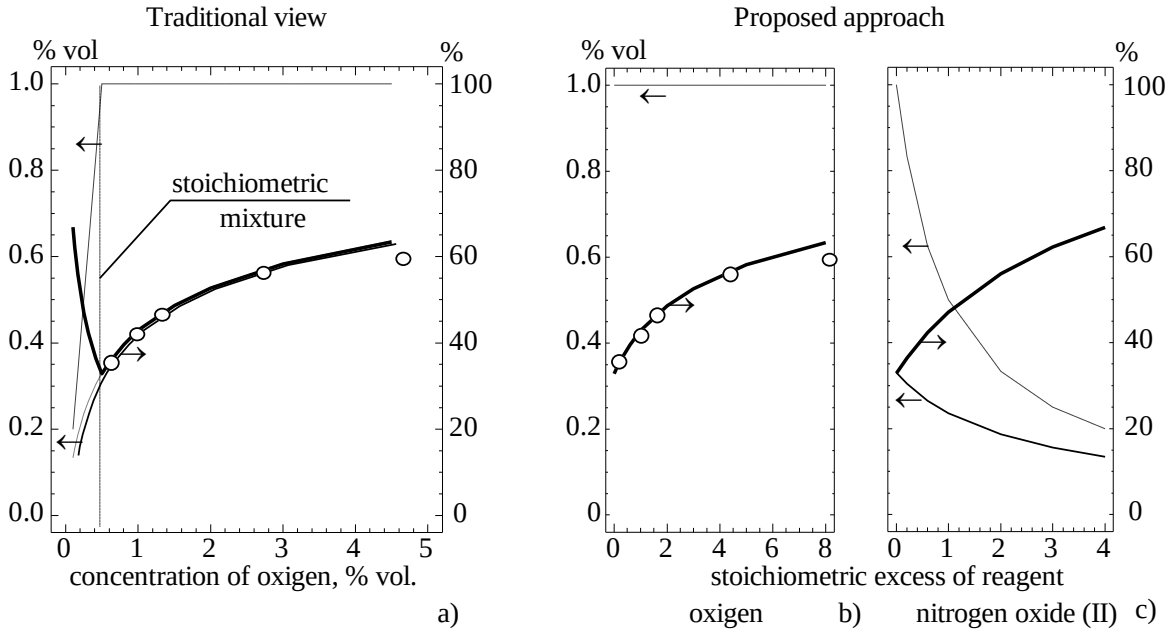

Fig.3. Characteristics of process of NO oxidation

- theoretical equilibrium concentration of nitrogen oxide (IV), %vol;
- experimental value of oxidation degree of NO, %;
- oxidation degree of NO, %;
- theoretical equilibrium stoichiometric yiel of product, %;
- concentration of nitrogen oxide (IV) for irreversible process, %vol;

Analysis of the equation (5) shows that the maximum degree of utilization of stoichiometric stream under these conditions is less than 0.62 in the case of O_2 excess and less than 0.66 in case of NO. Therefore in practice increasing stoichiometric excess of O_2 more than 4 is inexpedient since it leads to unproductive loss of O_2 so equation (5) can be transformed to relation

$$\alpha_S = \alpha_{NO} = 0.759 - \frac{1.51}{3.5 + E_{O_2}}.$$

This expression is fitted to optimization and technological calculation and allows to predict easily behavior of process for certain initial parameters of the reaction mixture.

So, essential advantage of proposed approach is introducing objective, united criterion with explicit physical meaning reflecting the efficiency of process (stoichiometric yield) instead of number of degrees of conversion of several components that are used now.

Obtained dependencies of stoichiometric yield under various conditions or even for different processes have similar form of curve and mathematical expression. It considerably simplifies building of the mathematical model of unknown or still not clearly understood chemical processes.

Explicit form of mathematical dependence, simplicity of calculation and use of this creation allow to take a fresh look at the problem of control and optimization of industrial chemical processes, to simplify considerably forecasting of many technological decisions.

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