ONCE MORE ABOUT CRITERIA OF CHEMICAL SIMILARITY

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To evaluate the possibility of results transfer from a model to a real chemical-technological object, it is necessary to establish a similarity of chemical technological processes (CTP) in them, taking into account the geometric and hydrodynamic parameters, the characteristics of mass and heat transfer and chemical reactions.

When investigating equations that should be structurally identical for similar processes, a mathematical modelling results in the construction of generalized variables (similarity criteria) having equal numerical values at similar points of the object and its model.

This allows us to introduce into the model the complexes of the values instead of the original ones. The interaction of different values is reflected in the complex structure [1, p. 27].

Damkehler [2] derived from the differential equations of mass and heat transfer the criteria of "chemical" similarity, considering the rate and the heat of the reaction as internal sources of matter and heat.

At the same time, it is obvious that the "chemical" similarity should be based on the nature of the changes of the quantities of matter and heat in time and space, depending on the process conditions, including the temperature, pressure and composition of the reaction mixture.

In this connection, when deriving the criteria of "chemical" similarity, we use the kinetic equation of the form:

$$r_j = k_1 DC_1 - k_2 DC_2 \tag{1}$$

where k_1 and k_2 – rate constants; DC_1 and DC_2 – the driving forces of direct and reverse reactions (driving forces are determined according to the law of active masses by product of power functions of interacting substances concentrations).

Assuming that the processes of mass transfer in the model and in the object are similar, for their description we use the equations:

$$\frac{\partial r_j'}{\partial t'} + \left[\frac{\partial\left(r_j' \cdot w_x'\right)}{\partial x'} + \frac{\partial\left(r_j' \cdot w_y'\right)}{\partial y'} + \frac{\partial\left(r_j' \cdot w_z'\right)}{\partial z'}\right] = \\ = D\left(\frac{\partial^2 r_j'}{\partial (x')^2} + \frac{\partial^2 r_j'}{\partial (y')^2} + \frac{\partial^2 r_j'}{\partial (z')^2}\right) + k_1' \cdot DC_1' - k_2' \cdot DC_2' \tag{2}$$

$$\frac{\partial r_j''}{\partial t''} + \left[\frac{\partial\left(r_j'' \cdot w_x''\right)}{\partial x''} + \frac{\partial\left(r_j'' \cdot w_y''\right)}{\partial y''} + \frac{\partial\left(r_j'' \cdot w_z''\right)}{\partial z''}\right] = \\ = D\left(\frac{\partial^2 r_j''}{\partial (x'')^2} + \frac{\partial^2 r_j''}{\partial (y'')^2} + \frac{\partial^2 r_j''}{\partial (z'')^2}\right) + k_1'' \cdot DC_1'' - k_2'' \cdot DC_2'' \tag{3}$$

The flow characteristics in the object are expressed through the flow characteristics in the model:

$r_j'' = Q_r \cdot r_j'$; $t'' = Q_t \cdot t'$; $x'' = Q_l \cdot x'$; $y'' = Q_l \cdot y'$; $z'' = Q_l \cdot z'$;

$w_x'' = Q_w \cdot w_x'$; $w_y'' = Q_w \cdot w_y'$; $w_z'' = Q_w \cdot w_z'$;

$r_j'' = Q_r \cdot r_j'$; $\quad D'' = Q_D \cdot D'$; $\quad k_1'' = Q_{k_1} \cdot k_1'$; $\quad DC_1'' = Q_{DC_1} \cdot DC_1'$;
$k_2'' = Q_{k_2} \cdot k_2'$; $\quad DC_2'' = Q_{DC_2} \cdot DC_2'$.

Let us substitute these expressions into (3):

$$\frac{Q_r}{Q_t} \cdot \frac{\partial r_j'}{\partial t'} + \frac{Q_{r_j} \cdot Q_w}{Q_l} \cdot \left[\frac{\partial (r_j' \cdot w_x')}{\partial x'} + \frac{\partial (r_j' \cdot w_y')}{\partial y'} + \frac{\partial (r_j' \cdot w_z')}{\partial z'} \right] =$$
$$= \frac{Q_D \cdot Q_r}{Q_l^2} \cdot \left[\frac{\partial^2 r_j'}{\partial (x')^2} + \frac{\partial^2 r_j'}{\partial (y')^2} + \frac{\partial^2 r_j'}{\partial (z')^2} \right] + Q_{k_1} \cdot Q_{DC_1} \cdot k_1' \cdot DC_1' - Q_{k_2} \cdot Q_{DC_2} \cdot k_2' \cdot DC_2' \tag{4}$$

In order that the equations (2) and (3) be identical (the processes of mass transfer for the model and the object are similar), the ratio of the similarity constants must be equal. We write this equality, numbering its members:

$$\underset{I}{\left(\frac{Q_r}{Q_t}\right)} = \underset{II}{\left(\frac{Q_r \cdot Q_w}{Q_l}\right)} = \underset{III}{\left(\frac{Q_D \cdot Q_r}{Q_l^2}\right)} = \underset{IV}{\left(Q_{k_1} \cdot Q_{DC_1}\right)} = \underset{V}{\left(Q_{k_2} \cdot Q_{DC_2}\right)} \tag{5}$$

We divide in turn the elements of (5) by each other and obtain the following ratios of similarity constants:

by I: $$1 = \frac{Q_w \cdot Q_t}{Q_l} = \frac{Q_D \cdot Q_t}{Q_l^2} = \frac{Q_{k_1} . Q_{DC_1} \cdot Q_t}{Q_r} = \frac{Q_{k_2} . Q_{DC_2} \cdot Q_t}{Q_r}$$

by II: $$\frac{Q_l}{Q_t \cdot Q_w} = 1 = \frac{Q_D}{Q_l \cdot Q_w} = \frac{Q_{k_1} . Q_{DC_1} \cdot Q_l}{Q_r \cdot Q_w} = \frac{Q_{k_2} . Q_{DC_2} \cdot Q_l}{Q_r \cdot Q_w}$$

by III: $$\frac{Q_l^2}{Q_t \cdot Q_D} = \frac{Q_w \cdot Q_l}{Q_D} = 1 = \frac{Q_{k_1} . Q_{DC_1} \cdot Q_l^2}{Q_D \cdot Q_r} = \frac{Q_{k_2} . Q_{DC_2} \cdot Q_l^2}{Q_D \cdot Q_r}$$

by IV: $$\frac{Q_r}{Q_t \cdot Q_r} = \frac{Q_w \cdot Q_r}{Q_l \cdot Q_r} = \frac{Q_D \cdot Q_r}{Q_l^2 \cdot Q_r} = 1 = \frac{Q_{k_2} \cdot Q_{DC_2}}{Q_{k_1} \cdot Q_{DC_2}}$$

by V: $$\frac{Q_r}{Q_{k_2} \cdot Q_{DC_2} \cdot Q_t} = \frac{Q_r \cdot Q_w}{Q_{k_2} \cdot Q_{DC_2} \cdot Q_l} = \frac{Q_D \cdot Q_r}{Q_{k_2} \cdot Q_{DC_2} \cdot Q_l^2} = \frac{Q_{k_1} \cdot Q_{DC_1}}{Q_{k_2} \cdot Q_{DC_2}} = 1$$

Since the ratios of similarity constants located on different sides of the diagonal consisting of ones are always mirror reflections of each other, we consider only ten of twenty complexes. After elimination of interdependent values only independent similarity criteria of mass transfer in the model and in the object remain:

– homochronicity $$\frac{w \cdot t}{l} = Ho$$

– diffusive Fourier $$\frac{D \cdot t}{l^2} = Fo_D$$

– diffusive Peklet $$\frac{w \cdot l}{D} = Pe_D$$

– chemical kinetic $$\frac{\mathrm{k}_1 \cdot \Delta C_1 \cdot l}{w \cdot r} = CK$$

chemical non-equilibrium $$\frac{\mathrm{k}_2 \cdot \Delta C_2}{k_1 \cdot \Delta C_1} = CNE$$

We consider that the thermal processes are similar, if they are described by the same differential equation.

In this connection, the similarity criteria for two thermal processes are derived from the Fourier-Kirchhoff equation, the same as the hydrodynamic similarity criteria are derived from the equations of medium continuity and the Navier-Stokes motion.

After dividing all elements of the heat transfer equation by $rC_p dV$, we receive the equation (7):

$$\frac{\partial T}{\partial t}+\left(w_x\frac{\partial T}{\partial x}+w_y\frac{\partial T}{\partial y}+w_z\frac{\partial T}{\partial z}\right)= \\ =a\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}\right)+\frac{q_1}{r\cdot C_p}\cdot k_1 DC_1-\frac{q_2}{r\cdot C_p}\cdot k_2 DC_2 \quad (7)$$

where q_1 and q_2 – specific heat of direct and reverse reactions, respectively, J/kg.

One can see that all terms of the equation (7) have the same units and reflect the rate of temperature change due to heat transfer in the reaction flow, the interaction of the components of which is accompanied by a reaction heat.

For the flows satisfying the heat similarity condition, the equation (7) can be represented as followings:

$$\frac{\partial T'}{\partial t'}+\left(w_x'\frac{\partial T'}{\partial x'}+w_y'\frac{\partial T'}{\partial y'}+w_z'\frac{\partial T'}{\partial z'}\right)= \\ =a'\left(\frac{\partial^2 T'}{\partial (x')^2}+\frac{\partial^2 T'}{\partial (y')^2}+\frac{\partial^2 T'}{\partial (z')^2}\right)+\frac{q_1'}{r'\cdot C_p'}\cdot k_1' DC_1'-\frac{q_2'}{r'\cdot C_p'}\cdot k_2' DC_2' \quad (8)$$

$$\frac{\partial T''}{\partial t''}+\left(w_x''\frac{\partial T''}{\partial x''}+w_y''\frac{\partial T''}{\partial y''}+w_z'\frac{\partial T''}{\partial z''}\right)= \\ =a''\left(\frac{\partial^2 T''}{\partial (x'')^2}+\frac{\partial^2 T''}{\partial (y'')^2}+\frac{\partial^2 T''}{\partial (z'')^2}\right)+\frac{q_1''}{r''\cdot C_p''}\cdot k_1'' DC_1''-\frac{q_2''}{r''\cdot C_p''}\cdot k_2'' DC_2'' \quad (9)$$

Having determined the similarity constants by expressions:

$$\frac{t''}{t'}=Q_t, \qquad \frac{T''}{T'}=Q_T, \qquad \frac{x''}{x'}=\frac{y''}{y'}=\frac{z''}{z'}=Q_l,$$

$$\frac{w_x''}{w_x'}=\frac{w_y''}{w_y'}=\frac{w_z''}{w_z'}=Q_w, \qquad \frac{a''}{a'}=Q_a, \qquad \frac{q_r''}{q_r'}=Q_q,$$

$$\frac{r''}{r'}=Q_r, \qquad \frac{C_p''}{C_p'}=Q_{C_p}, \qquad \frac{r''}{r'}=Q_r$$

and investigating the differential equation of heat transfer in a moving medium similarly to the previous one, we obtained the following similarity criteria:

– homochronicity $\quad \frac{w\cdot t}{l}=Ho$

– thermal Fourier $\quad \frac{a\cdot t}{l^2}=Fo_T$

– thermal Peklet $\frac{w \cdot l}{a} = Pe_T$

– thermochemical kinetic $\frac{\mathrm{q} \cdot \mathrm{k}_1 \cdot \Delta C_1 \cdot l}{r \cdot C_p \cdot w \cdot T} = TCK$

chemical non-equilibrium $\frac{\mathrm{k}_2 \cdot \Delta C_2}{k_1 \cdot \Delta C_1} = CNE$

The latter two criteria were obtained using the first law of Lavoisier-Laplace and $q_1 = q_2 = |q|$.

In the equilibrium state, when $k_1 DC_1 \approx k_2 DC_2$, $CNE \to 1$.

It can be seen that for a practically irreversible (extremely deviated from equilibrium) process, when $k_1 DC_1 >>> k_2 DC_2$, $CNE \to 0$.

Thus, the domain of the similarity criterion for the chemical technological processes according to the degree of their non-equilibrium is determined by the inequality:

$$0 \leq CNE \leq 1$$

This inequality is common for the transfer of mass and heat as well.

Let us note that only at *CNE* = 0 (irreversible process) the CTP rate is determined by the direct reaction rate and the criterion *CK* coincides with the Damköhler criterion *Da I*, and the criterion *TCK* with *Da III* criterion. In addition, the obtained criteria are in keeping with the criteria assumed by Diakonov [3, p. 49-64].

Thus, to state about the model's traductivity to the real object it is necessary that the CTPs in them be similar in relation to the rate ratio of direct reaction and flow (*CK*), the reaction heat change and change in the flow heat, as well as the process deviation from the equilibrium state.

References:
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