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APPLICATION OF SIMILARITY THEORY TO CHEMICAL PROCESSES

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CONTENTS

I. Similarity criteria in chemical processes 297
II. Approximate simulation 300
1. Simulation of processes occurring in the kinetic range 301
2. Simulation of processes occurring in the diffusion range 302
3. Simulation of processes occurring in the diffussion–kinetic range 302
III. Scale equations 303
IV. Some particular cases of the practical use of similarity theory 305

I. SIMILARITY CRITERIA IN CHEMICAL PROCESSES

Design of reaction vessels for chemical processes requires in general the simultaneous examination of the following set of differential equations, for an infinitesimal element of the vessel: (1) equation for mass balance; (2) equation for the energy balance; (3) fundamental equation of hydrodynamics or equation of motion; (4) rate equation for the reaction; and (5) equations defining the conditions for single-valuedness. Since even in the absence of chemical reactions it is impossible to solve this set of equations for the general case, similarity theory is widely used for such problems.

The application of similarity theory to chemical processes requires the simultaneous consideration of all the differential equations enumerated above supplemented by terms taking into account the presence of point sources of energy and mass, which considerably complicate this problem. The complexity lies in the fact that in general it is impossible to observe simultaneously the hydrodynamic, thermal, diffusion, and purely chemical similarity of processes accomplished in apparatus differing in size. It is characteristic of chemical processes that one system cannot be simulated by another, as would be the case with physical processes.

Thus although in the case of hydrodynamic similarity we can maintain the Reynolds number Re constant in the model and in the prototype by changing the system, we cannot do this in the case of chemical similarity since a chemical reaction of a given group of compounds cannot in general be reproduced in compounds of a different group.

As a result of this and other difficulties, similarity theory is comparatively rarely used at present for the simulation of chemical processes. It is quite widely used, however, in the generalisation of experimental results for a great variety of such processes[1].

Transformations of the set of differential equations have yielded the following criteria of chemical similarity:[2-5]

Damköhler's Group I

$$Da_I = \frac{Ul}{cw}, \qquad (1)$$

where U is the reaction velocity in kmole m^{-3} h^{-1}, l a linear dimension in the direction of flow in metres, w the linear rate of flow in metre h^{-1}, and c the concentration of the reactant in kmole m^{-3}.

Since l/w measures the time of flow through the reaction vessel, the ratio c/U will measure the duration of the reaction at constant velocity. Consequently Da_I can be defined as the ratio of the residence time of the flow in the reaction vessel to the duration of the reaction occurring at a constant rate until the reactant is completely exhausted. This dimensionless group can, of course, be treated also as the ratio of the reaction velocity to the rate of flow, both expressed in the same units†, as the ratio of the concentration of substance which has reacted to the concentration introduced by the flow, or finally as the ratio of the actual

† The group $W = w_x/U_k$, deduced by Matz, [6] in which the reaction velocity U_k is expressed in flow-rate units, or for a first-order reaction, as a rate constant; it follows from the definition of Da_I that the Matz number is identical with it.

length of the reaction vessel to the length which would be necessary for completion of the reaction at a constant velocity of the latter.

Damköhler Group II

$$Da_{II} = \frac{Ul^2}{cD}, \quad (2)$$

where D is the coefficient of molecular diffusion in $m^2\ h^{-1}$. Da_{II} gives the ratio of the velocity of a chemical reaction to the rate of molecular diffusion. By analogy with Da_I, this group can also be interpreted in terms of other quantities, as was shown above.

Damköhler Group III

$$Da_{III} = \frac{qUl}{c_p \gamma w \Delta t}, \quad (3)$$

where q is the heat of reaction in kcal $kmole^{-1}$, c_p the specific heat at constant pressure in kcal $kg^{-1}\ deg^{-1}$, γ the density of the medium in kg m^{-3}, and Δt a characteristic temperature difference, which may be, for example, the difference in temperature between the wall of the vessel and the centre of the flow or the change in temperature along the length of the reaction vessel.

It follows from Eqn. (3) that the Damköhler group III expresses the ratio of the quantity of heat evolved in the reaction to the quantity of heat transported by the flow.

Damköhler Group IV

$$Da_{IV} = \frac{qUl^2}{\lambda \Delta t}, \quad (4)$$

where λ is the thermal conductivity of the reaction mixture in kcal $m^{-1}\ h^{-1}\ deg^{-1}$.

The Damköhler group IV represents the ratio of the quantity of heat evolved by the reaction to that transferable by thermal conduction.

Equilibrium or Steady-State Group[3]

$$Eq = \frac{U_r}{U_f} = \frac{k_r c_{B_1}^{\beta_1} c_{B_2}^{\beta_2}}{k_f c_{A_1}^{\alpha_1} c_{A_2}^{\alpha_2}}, \quad (5)$$

where k_f, k_r, are the rate constants for the forward and reverse reactions respectively, and U_f, U_r the corresponding reaction velocities; c_{B_1}, c_{B_2} are the concentrations of the reaction products B_1, $B_2 \ldots$, and c_{A_1}, c_{A_2} the concentrations of the initial components A_1, A_2; β_1, β_2 are the stoichiometric numbers of the reaction products, and α_1, α_2 those of the components A_1, A_2.

The equilibrium group expresses the ratio of the absolute rates of the chemical reaction, *i.e.* of the velocities of forward and reverse reactions.

Contact Group

$$Ko = \frac{U_f}{U} = k_f c^{\Sigma\alpha - 1} \tau, \quad (6)$$

where τ is the residence time of the reaction mixture in the reaction vessels, and $\Sigma\alpha$ the sum of the stoichiometric numbers on the right-hand side of the rate equation. The contact group represents the ratio of one of the individual reaction rates to the overall reaction velocity.

With an irreversible reaction, for which the rate of the reverse reaction is practically zero, the constant group is identical with Da_I, as can be seen on expressing the reaction velocity U in the latter group in terms of the concentrations of the reactants.

It has also been proposed[3,6] that the dimensionless equilibrium constant should be used as a criterion of similarity

Arrhenius Number

$$Ar = \frac{E}{RT}, \quad (7)$$

where E is the activation energy and R the gas constant. Ar represents the ratio of the activation energy to the internal energy of the system.

Radiation Group[7]

$$K_{r_1} = \frac{qcw}{C_0 e T^4}, \quad (8)$$

$$K_{r_2} = \frac{T_1}{T_2}, \quad (9)$$

where C_0 is the constant in the Stefan–Boltzmann radiation equation, e is the emissivity in this equation, and T_1 and T_2 are the temperatures of the more and the less strongly heated surfaces respectively.

Criteria (8) and (9) are obtained not from the main set of differential equations but from the Stefan–Boltzmann equation, and should be used if the reaction temperature is so high that allowance has to be made for the heat transmitted by radiation.

The radiation group (8) represents the ratio of the quantity of heat evolved by the reaction to that transmitted by radiation, while group (9) represents the ratio of the temperatures of the radiating surfaces.

Hydrodynamic-Acceleration Group:[8]

$$K_h = \frac{w}{lU\Delta V}, \quad (10)$$

where ΔV is the increase in volume accompanying the reaction, in $m^3\ kmole^{-1}$.

The hydrodynamic-acceleration group K_h expresses the ratio of the volume of reaction mixture passing through the vessel in unit time to the change in volume due to the occurrence of the chemical reaction. It takes into account the acceleration of the motion of the reaction mixture in the vessel resulting from the chemical reaction. Like the radiation and some other groups, it specifies the conditions under which the process takes place.

Generalised Thermal Group.

$$K_t = \frac{qcw}{q_{st}}, \quad (11)$$

where q_{st} is the heat flow across unit area of the heat--exchange surface in kcal m^{-2} h^{-1}. This group expresses the ratio of the quantity of heat evolved in the reaction to that which is evolved or is supplied through the heat--exchange surface. The usefulness of introducing the group K_t is due to the fact that the flow of heat through unit heat-exchange surface is an independent variable, which the experimenter can change independently of the scale.

In the analysis of chemical processes dimensionless groups are quite often employed which are analogous to those considered above but somewhat modified for application to particular processes. Thus the following criterion has been introduced:[9,10]

$$K_{int} = \int_0^\tau c^{n-1} k_n [T(\tau)]\, d\tau , \qquad (12)$$

where k_n is the rate constant for a reaction of the n-th order, represented as a complicated function of time (it is assumed that the temperature varies with time according to a definite law). The criterion K_{int} is obviously a modified form of Da_I, in which the velocity of the chemical reaction, which varies with time, is taken in integral form. This latter method of representing dimensionless groups is useful in all cases in which the properties of a chemical system change with time (or in space, when integration is carried out with respect to volume).

For the case of a heterogeneous chemical reaction, the following group was introduced:[11]

$$K_{het} = \frac{k_n' \delta}{D} c^{n-1} = \frac{k_n' l}{D} c^{n-1} f(\mathrm{Re}, \mathrm{Pr}), \qquad (13)$$

where k_n' is the rate constant of the heterogeneous chemical reaction per unit area of interface, and $Pr = wl/a\mathrm{Re}$ is the Prandtl number, in which $a = \lambda/c_p\gamma$ is the thermal conductivity. This group uses as linear dimension and thickness of the diffusion layer δ:

$$\delta = l/\mathrm{Nu} = lf(\mathrm{Re}, \mathrm{Pr}).$$

It is readily seen that the group K_{het} is a modified form of Da_{II} in which δ is used as l and the reaction velocity is based on unit surface separating the phases.

The dimensionless multiplier φ used in calculations on absorption processes belongs to the same type of modified groups:[12]

$$\varphi = \frac{x}{\tanh x}, \qquad (14)$$

where

$$x = \delta \sqrt{k_1/D} \qquad (15)$$

Eqn. (14) is obtained by the simultaneous solution of the diffusion and rate equations for a first-order reaction. The dimensionless group (14) is called the Hatta number (Ha). It is readily shown that Ha is a quantity which is functionally related to Da_{II}:

$$\mathrm{Ha} = \frac{x}{\tanh x} = \frac{\delta\sqrt{k_1/D}}{\tanh \delta\sqrt{k_1/D}} = \frac{\sqrt{k_1\delta^2/D}}{\tanh\sqrt{k_1\delta^2/D}} = \frac{\sqrt{\mathrm{Da}_{II}}}{\tanh\sqrt{\mathrm{Da}_{II}}} . \qquad (16)$$

Dimensionless ratios are often used as defining criteria. Among these the following may be mentioned:[3,6,13]

$$X_1 = \frac{c_i}{c_0} \qquad (17)$$

$$X_2 = \frac{c}{c^*}, \qquad (18)$$

where c_1 and c_0 are the concentrations at the inlet and the outlet respectively of the reaction vessel, c is the concentration actually reached in a given reaction vessel, and c^* is the equilibrium concentration. Eqn. (17) represents the ratio of the concentrations at the inlet and the outlet of the reaction vessel, and (18) is a measure of the relative yield of product.

Instead of concentration ratios, use can be made of the ratios of any other physical properties[10] characteristic of the system and linked with the concentration, such as viscosity, density, etc. This method can be employed to specify conditions for the control, regulation, and automation of the process.

Apart from the similarity criteria enumerated above, deriving from the original set of differential equations, the general dimensionless-group equation should include criteria characterising hydrodynamic similarity $Re = wl/\nu$, thermal similarity $Pe = wl/a$, diffusion similarity $Pe_d = wl/D$, etc. In the case of irreversible reactions, the general dimensionless-group equation for a chemical process then has the form.

$$Da_I = f(Da_{II}, Da_{III}, Da_{IV}, Pe, Pe_d, Re, K_i \ldots), \qquad (19)$$

where K_i are groups specifying the conditions under which the process takes place [see Eqns. (8)–(10)]. Instead of Da_I, the dimensionless ratios (17) and (18) can also be used.

In the case of reversible reactions the dimensionless--group equation is of the form

$$Eq = f(Ko, Da_{II}, Da_{III}, Da_{IV}, Pe, Pe_d, Re, K_i). \qquad (20)$$

(The Ar groups should not increase the number of groups in the general dimensionless-group equation, since it characterises the change with temperature of quantities already occurring in groups $Da_I - Da_{IV}$ considered earlier).

Since several of the dimensionless groups in Eqns. (19) and (20) contain the same parameters, the number of groups can be reduced by combining them.

Da_{II}, for example, can be represented as the product $Da_I\, Pe_d$:

$$\mathrm{Da}_{II} = \frac{Ul^2}{cD} = \mathrm{Da}_I\, \mathrm{Pe}_d = \frac{Ul}{cw}\frac{wl}{D} = \frac{Ul^2}{cD},$$

and Da_{III} as the product $Da_I\, qc/c_p\gamma\Delta t$:

$$\mathrm{Da}_{III} = \frac{qUl}{c_p\gamma w\Delta t} = \mathrm{Da}_I \frac{qc}{c_p\gamma\Delta t} = \frac{Ul}{cw}\frac{qc}{c_p\gamma\Delta t} = \frac{qUl}{c_p\gamma w\Delta t}.$$

The expression $qc/c_p\gamma\Delta t$ was defined by D'yakonov[3] as a criterion establishing the proportionality of the temperature and concentration gradients. Let us denote this group as follows‡:

$$K_{tc} = \frac{qc}{c_p\gamma\Delta t} . \qquad (21)$$

Da_{IV} can be represented as the product $Da_I Pr K_{tc}$:

$$\mathrm{Da}_{IV} = \frac{qUl^2}{\lambda\Delta t} = \mathrm{Da}_I \mathrm{PeK}_{tc} = \frac{Ul}{cw}\frac{wl}{a}\frac{qc}{c_p\gamma\Delta t} = \frac{qUl^2}{\lambda\Delta t} .$$

‡ In some papers[14] the group K_{tc} has been termed the Boltzmann number (Bo).

TABLE 1. Scheme for the derivation of the fundamental criteria of chemical similarity. *

Equation for the conservation of mass				
rate of change with time	rate of change due to convection	rate of change due to diffusion	rate of change due to chemical reaction	
$-\partial c/\partial\tau$	$-(w\ \mathrm{grad})\ c$	$+D\ (\mathrm{Div\ grad})\ c$	$+U$	$=0$
c/τ	wc/l	Dc/l^2	U	
	$\longleftarrow$	$\mathrm{Da_I} = \frac{Ul}{cw}$		
		$\mathrm{Da_{II}} = \frac{Ul^2}{cD}$		

Equation for the conservation of energy				
rate of change with time	rate of change due to convection	rate of change due to thermal conduction	rate of change due to chemical reaction	
$-\partial t/\partial\tau$	$-(w\ \mathrm{grad})\ t$	$+a\ (\mathrm{Div\ grad})\ t$	$+qU/c_p\gamma$	$=0$
t/τ	wt/l	at/l^2	$qU/c_p\gamma$	
	$\longleftarrow$	$\mathrm{Da_{III}} = \frac{qUl}{c_p\gamma w\Delta t}$		
		$\mathrm{Da_{IV}} = \frac{qUl^2}{\lambda\Delta t}$		

Rate equation for reaction			
net reaction velocity	rate of forward reaction	rate of reverse reaction	
$-dc/d\tau$	$+k_f\ c_{A_1}^{\alpha_1} c_{A_2}^{\alpha_2}\cdots$	$k_r\ c_{B_1}^{\beta_1} c_{B_2}^{\beta_2}\cdots$	$=0$
c/τ	$k_f\ c^{\Sigma\alpha}$	$k_r\ c^{\Sigma\beta}$	
	$\mathrm{Ko} = k_f c^{\Sigma\alpha-1}\cdot\tau$		
		$\mathrm{Eq} = \frac{k_r\ c^{\Sigma\beta}}{k_f\ c^{\Sigma\alpha}}$	

* A single arrowhead points to the denominator, and a double one to the numerator.

Since Pe and $\mathrm{Pe_d}$ can be represented by the products RePr and $\mathrm{RePr_d}$, division of $\mathrm{Da_{II}}$, $\mathrm{Da_{III}}$, and $\mathrm{Da_{IV}}$ by $\mathrm{Da_I}$, K_{tc}, and Re brings Eqns. (19) and (20) to the form

$$\mathrm{Da_I} = f(K_{tc},\ \mathrm{Pr},\ \mathrm{Pr_d},\ \mathrm{Re},\ K_i), \qquad (22)$$

or

$$X_1 = \frac{c_i}{c_0} = f(\mathrm{Da_I},\ K_{tc},\ \mathrm{Pr},\ \mathrm{Pr_d},\ \mathrm{Re},\ K_i), \qquad (23)$$

and

$$\mathrm{Eq} = f(\mathrm{Ko},\ K_{tc},\ \mathrm{Pr},\ \mathrm{Pr_d},\ \mathrm{Re},\ K_i), \qquad (24)$$

or

$$X_2 = \frac{c}{c^*} = f(\mathrm{Ko},\ K_{tc},\ \mathrm{Pr},\ \mathrm{Pr_d},\ \mathrm{Re},\ K_i). \qquad (25)$$

In the case of heterogeneous chemical processes, some groups (*e.g.* Re, Pr, and $\mathrm{Pr_d}$) can be repeated as many times as there are phases involved in the process. However, the presence of a large number of dimensionless groups, and hence of the relevant physical quantities, in Eqns. (21)–(24), makes it difficult to keep all the criteria constant.

It is impossible, for example, to maintain simultaneous constancy of Re and $\mathrm{Da_I}$ in the model and in the prototype, since the linear velocity which occurs in both these groups varies in different ways with the linear dimension which also is present in both groups. It follows from the condition for the constancy of Re that the linear velocity is inversely proportional to the linear dimension, whereas from the corresponding condition for $\mathrm{Da_I}$ it should be directly proportional to the linear dimension. Thus the direct simulation of chemical processes by obtaining the general dimensionless-group equation proves to be impossible in practice§. This has led to the necessity for approximate simulation. The derivation of the main chemical criteria is shown in the accompanying scheme (Table 1).

II. APPROXIMATE SIMULATION

Approximate simulation is based on the principle of including in the dimensionless-group equation only those groups which relate to the slowest stage of the process. A thermodynamic treatment of this question has been given by D'yakonov[3] showing that these equations need include only those groups related to the non-equilibrium or steady-state stages of the process.

A result of isolating the rate-determining stage in the general dimensionless-group equation is the disappearance of incompatible groups (*e.g.* $\mathrm{Da_I}$ and Re), so that it becomes theoretically possible to find a functional relationship between the groups. The theoretical possibility of isolating the rate-determining stage is based on the fact that in many cases a complex process consists of several successive stages. The slowest of such stages is rate-determining.

In the kinetics of chemical reactions complicated by heat and mass transfer it is usual to distinguish[16] reactions occurring in the kinetic range, where the rate-determining step is the chemical reaction itself, reactions occurring in the diffusion range, in which the rate-determining stage is the diffusion of reactants to the reaction zone, and finally reactions occurring in the diffusion–kinetic range, where the rates of diffusion and of chemical change are comparable in magnitude. The last is the most difficult case to simulate. Heat exchange within the system takes place at the same time as the chemical changes, and therefore cannot be rate-determining. The methods for ascertaining the rate-determining state[17,18] are indicated below.

1. From the temperature coefficient of the overall rate of process. If a 10° change in temperature causes a two- or threefold change in the overall velocity of the process (as follows from the Arrhenius law), the chemical reaction itself is the rate-determining step. If, however, a 10° change in temperature causes an overall change in rate of 30%, material transfer is rate-determining. In intermediate cases the reaction occurs in the diffusion–kinetic range.

§ An artificial decrease in the activity of the catalyst in the simulation of heterogeneous chemical processes[15] is of no practical significance.

2. From the apparent reaction order. If the reaction order differs from unity, the chemical reaction is rate-determining. If, however, the order of reaction is unity, the nature of the rate-determining step remains uncertain since mass transfer also depends on the first power of the concentration.
3. From the dependence of the overall rate of the process on the hydrodynamic conditions under which it is carried out. If the velocity of the process does not depend on the hydrodynamic conditions, the chemical reaction itself is rate-determining; but if there is such a dependence, the rate-determining step involves either mass transfer or both mass transfer and chemical change together (*i.e.* the reaction takes place in the diffusion–kinetic range).

1. Simulation of Processes Occurring in the Kinetic Range

For a process occurring in the kinetic range, the dimensionless-group equation contains only chemical dimensionless groups, and for irreversible chemical reactions Eqns. (22)–(25) become

$$\mathrm{Da_I} = \frac{Ul}{cw} = \text{const}\,, \tag{26}$$

or

$$\mathrm{X_1} = \frac{c_i}{c_o} = f(\mathrm{Da_I})\,. \tag{27}$$

As noted above, the concentration ratio can be replaced by the ratio of a suitable physical property of the system.

For reversible chemical reactions, Eqns. (24) and (25) become

$$\mathrm{Eq} = f(\mathrm{Ko})\,, \tag{28}$$

$$\mathrm{X_1} = f(\mathrm{Ko})\,. \tag{29}$$

Two methods have been suggested[3] for generalising experimental data on chemical reactions whose mechanism is unknown. In the first method the experimental data are used to plot a graph of Eq against τ (the residence time). It is then found that experimental results relating to different temperatures and pressures fall on quite definite curves.

The discovery of a functional relationship (28) is equivalent to combining all the curves into a single curve. Remembering that $\mathrm{Ko} = k\tau c^{\Sigma\beta-1}$ and that $k = f_1(T)$, and assuming that the reaction takes place in the gas phase, *i.e.* that $c = f_2(p)$, we can find the activation energy and the order of the reverse reaction by measuring the distance between these curves. From these values we can find the group Ko and plot the relationship $\mathrm{Eq} = f(\mathrm{Ko})$, *i.e.* combine all the curves into a single curve.

The other method of generalisation consists in finding a functional relationship between the reaction velocity and the thermodynamic potential, used in this method as a driving force: *i.e.* it consists in establishing experimentally a relationship of the form $u = k^* f(G/RT)$, where k^* is a coefficient having the dimensions of reaction velocity, which in many cases can be regarded as constant. The expression G/RT is analogous to the Arrhenius number, G being the thermodynamic potential.

It follows from Eqns. (26)–(29) that, when a process occurs in the purely kinetic range, it is independent of the geometrical shape and size of the system, provided that the time in the reaction vessel remains constant, *i.e.* that l/w = constant. (This conclusion, however, is no longer valid in the case of a chain reaction in which initiation or termination of the chains take place on the walls of the apparatus, or if the chemical reaction is accompanied by considerable evolution of heat.)

The effect of heat exchange on reactions occurring in the kinetic range can be allowed for by introducing the criteria $\mathrm{K_{tc}}$ and $\mathrm{K_t}$, so that the dimensionless-group equation for the kinetic range becomes

$$f(\mathrm{Da_I},\ \mathrm{K_{tc}},\ \mathrm{K_t}) = 0\,. \tag{30}$$

As noted above, heat exchange cannot be isolated as a rate-determining stage. In passing from one scale to another in the case of a strongly exothermic reaction it is desirable to avoid complications due to the formation of a temperature gradient in the reaction vessel. An element of a large reaction vessel is therefore usually taken as the model, with the provision that the large reactor consists of several identical elements (*e.g.* if the latter is a system of tubes filled with catalyst, one of these tubes is used as such an element).

Although there is no need to maintain geometrical similarity in the simulation of chemical processes occurring in the kinetic range, nevertheless, in several cases this is done for purely technical reasons (*e.g.* in the modelling of stirrers[12]).

When reactions accompanied by the evolution or the absorption of a large quantity of heat take place in geometrically similar apparatus, a complication arises from the fact that the ratio of the heat-exchange surface to its volume decreases with increase in size of the vessel, and hence the conditions for the supply and removal of heat are impaired. In order to achieve approximate simulation in such cases, it is recommended[7] that the flow of heat through unit heat-exchange surface of the model reactor should be artificially reduced by making the vessel more adiabatic. This can be achieved either by increasing the thickness of the layer of insulation on the heat-exchange surface of the laboratory vessel or by providing additional heating. In this way it is possible, in spite of the difference in the heat-exchange surface in the model and in the prototype, to ensure that the same quantity of heat is supplied in unit time to unit volume in both.

A further difficulty in the simulation of continuous reaction vessels is that in many forms of continuous apparatus, different portions of the reaction mixture reside for different periods of time, *i.e.* a definite residence-time distribution is established in such apparatus. It has a particularly adverse effect on the course of the process when the main chemical reaction is complicated by subsequent secondary reactions. In the simulation of continuous chemical processes, therefore, it is necessary to keep the residence-time distribution the same in order to obtain the same yield in the model and in the prototype.

In the study of heterogeneous chemical reactions (determination of reaction mechanisms, optimum temperature conditions, etc.) it is important to eliminate or minimise resistance to diffusion in the laboratory apparatus, *i.e.* to ensure that the reaction should take place in the kinetic range. In this case it is very important to be able to estimate how effectively such diffusion resistance has been eliminated, and hence the accuracy of the experimental values for the reaction velocity.

Application of similarity theory enables the following method[20] to be used. The variation of the overall reaction velocity U with the mass flow rate G is determined for a constant residence time in the reaction zone¶. It follows from the above that the kinetic range should correspond to that portion of the curve $U = f(G)$ along which U becomes constant and does not depend, or depends only slightly, on further increase in G. In the latter case the proportion of diffusion resistance can be estimated as follows. On equating U to the quantity of matter transported through the diffusion layer, we obtain

$$U = k_g F_m \Delta p_A , \qquad (31)$$

where U is the reaction velocity expressed as the number of moles of component A which react in unit time per unit mass of catalyst, k_g the coefficient of mass transfer in the gas phase, F_m the surface area per unit mass of the catalyst, and Δp_A the difference in the partial pressures of component A across the diffusion layer.

On the other hand, the mass-transfer coefficient k_g occurs in the generalised equation of Chilton and Colburn[21] as modified by Hougen[20] for application to heterogeneous reactions:

$$j_d = \left(\frac{k_g M_m p}{G}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3} = a_0\left(\frac{\sqrt{F_p}G}{\mu}\right)^{-n} . \qquad (32)$$

On solving Eqns. (31) and (32) simultaneously for $\Delta p_A/p_A$ we obtain

$$\frac{\Delta p_A}{p_A} = \frac{1}{a_0}\left(\frac{\sqrt{F_p}U M_m p}{p_A \mu F_m}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3}\left(\frac{\sqrt{F_p}G}{\mu}\right)^{n-1} . \qquad (33)$$

In the above equations p is the total pressure, p_A the partial pressure of component A, M_m the mean molecular weight of the gas passing through which has a dynamic viscosity μ and density ρ, D_{Am} the mean diffusion coefficient of component A in the gas phase, a_0 a proportionality coefficient, $(F_p G)^{\frac{1}{2}}/\mu$ a modified Re groups, and F_p the surface area of a single catalyst particle.

The first of the groups on the right-hand side of Eqn. (33) is a modified form of Da_I. In fact

$$p_A/p = c' \sqrt{F_p} = l$$

(where c' is the concentration in mole fractions); and $\mu F_m \propto v^*$ m sec^{-1} is some characteristic velocity, since the units of μ are kg sec m^{-2} and those of F_m are m^2(kg$_{mass}$)$^{-1}$ = = m^3(kg$_{force}$)$^{-1}$ sec^{-2}. Thus Eqn. (33) can be reduced to the form

$$\frac{\Delta c'}{c'} = \frac{1}{a_0} Da_I Pr_d^{2/3} Re^{n-1} , \qquad (34)$$

where a and n depend on Re, their values being as follows:

$$\text{for } Re < 620 \quad a_0 = 2.44 \quad n = 0.51 ,$$
$$\text{for } Re > 620 \quad a_0 = 1.25 \quad n = 0.41 .$$

On the basis of Eqns. (33) and (34) $\Delta p_A/p_A$ is plotted against $Da_I Pr^{\frac{2}{3}}/a_0$, the Re numbers being taken as parameter. This yields straight lines passing through the origin and having different slopes for each value of Re.

Having specified the accuracy with which the true rate of the chemical reaction should be determined, and the corresponding pressure difference $\Delta p_A/p_A$ in the diffusion layer, we can find the appropriate rate of flow for the given value of the expression $Da_I Pr^{\frac{2}{3}} a$. Thus, for example, if in a particular investigation the value of the reaction velocity, allowing for the diffusion resistance, should be accurate to within 10%, we take $\Delta p_A/p_A = 0.1$; and if the accuracy is to be within 1%, then correspondingly $\Delta p_A/p_A = 0.01$. The temperature gradients in the boundary layer may be estimated in an analogous fashion.

2. Simulation of Processes Occurring in the Diffusion Range

In this case the dimensionless-group equations (22) and (23) are of the form

$$Da_I = f(Re, Pr) . \qquad (35)$$

Here, too, the ratios X_1 and X_2 can be used as defining criteria.

The simulation of processes occurring in the diffusion range thus reduces to the use of the well-known criteria of physical similarity, [1] and will not be considered here.

3. Simulation of Processes Occurring in the Diffusion–Kinetic Range

These comprise primarily heterogeneous chemical processes — catalysis and absorption accompanied by chemical reaction. Owing to the incompatibility of the groups Da_I and Re occurring in Eqns. (22) and (23), a fundamental difficulty arises here in using such equations for simulation. This is increased by the need to take account of the resistance in each phase by introducing appropriate criteria for each. This difficulty can, however, be eliminated.

Usually the same catalyst (having the same particle-size distribution) or the same packing is employed in the model and in the prototype. The volume elements formed by grains of catalyst or packing in contact therefore remain the same in the model and in the prototype. It must not be forgotten, however, that at low values of the ratio d_a/d_0 (of the diameter of the apparatus d_a to the grain diameter d_0) the effect of the walls must be taken into account. The results obtained in the model may be transferred directly to the prototype if the experimental conditions (charge per unit cross-section of the apparatus, temperature, concentration, etc.) are kept constant and if d_a/d_0 is sufficiently high.

If the reaction is accompanied by the evolution of large quantities of heat, the reaction vessel must be divided into elementary units of small diameter in order to increase the ratio of the external heat-exchange surface of the reaction vessel to its volume, and thus to prevent any possible production within the vessel of inadmissibly high temperatures. In such cases a reaction vessel comprising a system of narrow tubes is normally employed. The diameter is selected by calculating the permissible temperature difference between the centre of flow in the tube and its walls under conditions of a maximum yield[22]. In the simulation, considerations (indicated previously) relating to the use of Eqn. (30) must be taken into account.

At the present time the overall reaction velocity in the diffusion–kinetic range is determined by means of equations analogous to those employed in calculations on processes of simple (physical) mass transfer uncomplicated

¶ Fulfilment of this last condition is equivalent to the assumption that an increase in the mass flow rate is accompanied by a proportionate increase in height of the catalyst layer.

by chemical reaction, *i.e.* the overall rate constant is determined as the reciprocal of the sum of the resistances in each of the stages. The individual mass-transfer coefficients for each phase are determined from the appropriate dimensionless-group equations for the phases.

In the case of a heterogeneous catalytic reaction, the overall reaction velocity can thus be determined from the equation[23]

$$G_a = k_e c_g = \frac{1}{\frac{1}{k_g} + \frac{C}{d_0}\frac{1}{k' F_0 \rho_a \psi}} \times c_g \,, \qquad (36)$$

where k_e is the effective rate constant of the heterogeneous reaction, c_g the concentration of the chemically active component in the gas phase, k_g the mass-transfer coefficient in the gas phase, C/d_0 the ratio of the surface area of a catalyst grain to its volume (for spherical grains $C = 6$), k' the rate constant of the reaction per square centimetre of total surface of the catalyst, F_0 the total surface per gram of catalyst, ρ_a the apparent density of the porous mass of catalyst, and ψ the degree of utilisation of the catalyst surface, which allows for the drop in concentration of a given component within the pores of the catalyst.

A very rapid reaction takes place almost exclusively on the outer surface of the catalyst grains, so that $\psi \to 0$. A very slow reaction involves the whole surface of the catalyst grains, including that within the pores, so that $\psi = 1$. Thus ψ in Eqn. (36) is always less than unity.

The second term in the denominator takes account of the resistance to diffusion within the pores of the catalyst grains in addition to the purely chemical resistance. In some papers[24] these two types of resistance are considered separately, and the denominator then comprises three terms. Such a form of the equation, however, is less convenient for practical use.

Similar equations are used for calculations on absorption processes[25,26] accompanied by chemical reactions, and also for calculations on heterogeneous catalysis in the liquid phase[24].

Thus, in the case of a slow irreversible chemical reaction of the first order occurring in the bulk liquid phase, the following equation was suggested[27]:

$$G_a = k_{og}\left(p - \frac{p_{liq}}{\cosh x}\right) = \frac{1}{\frac{1}{k_g} + \frac{1}{\varphi H k_{liq}}}\left(p - \frac{p_{liq}}{\cosh x}\right), \qquad (37)$$

where H is Henry's constant, k_{og} the overall coefficient of mass transfer for the gaseous phase, p_{liq} the partial pressure of the absorbed material in the bulk of the liquid phase.

In contrast to heterogeneous catalysis, chemical reactions accompanying absorption processes usually occur, not at the interface, but in a zone adjacent to the interface and having a finite thickness. Therefore chemical change and diffusion in the liquid phase do not occur successively but simultaneously. This leads to a continuous diminution in the diffusion flux of the component undergoing absorption as it passes through the diffusion layer in the liquid phase. This factor has led to some complication of the form of Eqn. (37) compared with Eqn. (36).

The use of the groups Ha has been proposed for calculations on absorption processes accompanied by reactions of the second and higher orders.[12,28]

III. SCALE EQUATIONS

The so-called scale equations[2,7,14,29,30] are a consequence of the application of the principles of approximate simulation. Scale equations are obtained by equating in pairs the groups characterising the conditions under which the process occurs in the model and in the prototype, and cancelling out from these groups the physical constants which have the same values in the model and in the prototype.

Let us consider the derivation of the scale equation for a chemical process occurring in the kinetic range and complicated by heat exchange. As was shown above, the general dimensionless-group equation for such a process can be written in the form

$$f(\mathrm{Da_I}, \mathrm{K_{tc}}, \mathrm{K_t}) = 0 \,. \qquad (30)$$

To maintain similarity of the rate-determining stage in the model and in the prototype it is necessary to keep all the groups which characterise it constant. In order to obtain the scale equations, all the groups in Eqn. (30) must be equated in pairs for the model and for the prototype:

$$(\mathrm{Da_I})_m = (\mathrm{Da_I})_p \,, \qquad (38a)$$

$$\frac{U_m l_m}{c_m w_m} = \frac{U_p l_p}{c_p w_p} \,, \qquad (38b)$$

where the subscripts m and p refer to the model and to the prototype respectively.

Cancelling out the physical constants and remembering that the concentration (*e.g.* initial or final) remains unchanged in the model and in the prototype, we obtain for the groups $\mathrm{Da_I}$:

$$\frac{l_m}{w_m} = \frac{l_p}{w_p} \,. \qquad (39)$$

It follows from this equation that the residence time should be identical in the model and the prototype.

For the groups $\mathrm{K_t} = qcw/q_{st}$ we obtain

$$\frac{w_m}{w_p} = \frac{(q_{st})_m}{(q_{st})_p} = \frac{l_m}{l_p} \qquad (40)$$

The groups $\mathrm{K_{tc}} = qc/c_p \gamma \Delta t$ includes only physical constants, and therefore yields no new relationships.

Scale equations can be obtained in an analogous manner for other rate-determining stages. Thus in the case of a heterogeneous chemical reaction occurring in the purely kinetic range, the dimensionless groups of the scale equation contain the activity of the catalyst α and the space velocity s sec^{-1}. In this case we have

$$(\mathrm{Da_I})_m = (\mathrm{Da_I})_p \quad \text{or} \quad \frac{k'_m f(c_m)\alpha_m}{w_m} = \frac{k'_p f(c_p)\alpha_p}{w_p} \,, \qquad (41)$$

where k' is the rate constant for the heterogeneous chemical reaction calculated for unit surface of the catalyst.

On introducing space velocities s sec^{-1}, we obtain

$$\frac{k'_m f(c_m)\alpha_m}{(d_0)_m s_m} = \frac{k'_p f(c_p)\alpha_p}{(d_0)_p s_p} \,, \qquad (42)$$

where d_0 is the grain diameter of the catalyst. With $\alpha_m = \alpha_p$ and $(d_0)_m = (d_0)_p$ (the grain size is assumed to be constant, since a change in it usually alters the activity of the catalyst), we obtain

$$s_m = s_p, \qquad (43)$$

i.e. the space velocity should be the same in the model and in the prototype. It has also been suggested[30] that, in deriving the scale equation for a chemical reaction occurring in the kinetic range, when heat exchange must be taken into account, the Da_{IV} groups could be used in combination with the thermal group Nu. Let us consider the derivation of such an equation applied to a homogeneous chemical reaction carried out in a tubular reaction vessel.

On equating

$$\frac{(Da_{IV})_m}{Nu_m} = \frac{(Da_{IV})_p}{Nu_p},$$

we obtain

$$\frac{q_m U_m d_m^2}{\lambda_m \Delta t_m Nu_m} = \frac{q_p U_p d_p^2}{\lambda_p \Delta t_p Nu_p}, \quad (44)$$

where d_m and d_p are the diameters of the tubular reactors employed as model and as prototype respectively. If the amount of material processed in the prototype is n times greater than in the model, we obtain the following relationship:

$$n d_m^2 w_m = d_p^2 w_p, \quad (45)$$

whence

$$n = \frac{d_p^2 w_p}{d_m^2 w_m}. \quad (46)$$

Since it is necessary to keep the Da_I groups constant in the model and in the prototype, we obtain

$$\frac{U_m l_m}{c_m w_m} = \frac{U_p l_p}{c_p w_p}. \quad (38b)$$

Remembering also that identical yields can be obtained in the model and in the prototype provided that the rise in temperature ΔT is identical in the two systems, and that for a tubular reaction vessel

$$Nu = \text{const.} Re^{0.8}, \quad (47)$$

we obtain from Eqn. (44)

$$\frac{d_m^{1.2}}{w_m^{0.8}} = \frac{d_p^{1.2}}{w_p^{0.8}}. \quad (48)$$

From Eqn. (38b), it follows that

$$\frac{l_m}{w_m} = \frac{l_p}{w_p}. \quad (39)$$

Simultaneous solution of Eqns. (45), (48), and (39) finally yields

$$d_p = d_m n^{0.286}, \quad (49)$$

$$l_p = l_m n^{0.428}, \quad (50)$$

$$w_p = w_m n^{0.428}. \quad (51)$$

In conclusion, let us consider the derivation of scale equations for a homogeneous chemical reaction taking place in the gas phase in a continuously operating tubular reaction vessel. To derive the scale equations, it must be remembered that the pressure drops in the model and in the prototype should be equal, since otherwise the stream of gas would be accelerated in the reaction vessel in which the pressure drop was the greater, and the residence time in this vessel would be reduced. A difference in pressure gradients can be neglected only when the total pressure in the system is high compared with the drop. If the coefficient of drag of the gas is written in the form

$$\Delta p = c_1 \lambda \frac{l}{d} w^2, \quad (52)$$

putting

$$\lambda = c_2 Re^{-m} = c_3 (wd)^{-m}, \quad (53)$$

and remembering that

$$V_{sec} = c_4 d^2 w, \quad (54)$$

where $c_1 - c_4$ are constants, simultaneous solution of Eqns. (52)–(54) yields

$$\frac{l_p}{l_m} = \left(\frac{d_p}{d_m}\right)^{\frac{1+m}{3-m}}, \quad (55)$$

$$\frac{(V_{sec})_p}{(V_{sec})_m} = \left(\frac{d_p}{d_m}\right)^{\frac{7-m}{3-m}}. \quad (56)$$

Under conditions of turbulent flow we can put $m = 0.16$, and substitution of this value in Eqns. (52) and (53) yields

$$\frac{l_p}{l_m} = \left(\frac{d_p}{d_m}\right)^{0.41}, \quad (57)$$

$$\frac{(V_{sec})_p}{(V_{sec})_m} = \left(\frac{d_p}{d_m}\right)^{2.41}. \quad (58)$$

Thus the ratio of the dimensions of the model and of the prototype perpendicular to the direction of flow should be greater than the ratio in the direction of flow. Hence the model tubular reactor should have a greater length: diameter ratio than the prototype. For laminar flow in both reactors, the Poiseuille equation can similarly be used to deduce the following scale equation:

$$\frac{d_p}{d_m} = \left[\frac{(V_{sec})_p}{(V_{sec})_m}\right]^{1/3}. \quad (59)$$

Since the ratio of the lengths of the reaction vessels is equal to the ratio of their diameters, geometrical similarity must be maintained in this case, and since the ratio of the space velocities is equal to the ratio of the cubes of the diameters of the vessels, the space velocity should be proportional to the reactor volume.

An attempt has been made[14] to model reaction vessels with respect to geometrical and regime parameters. The fundamental parameters used were the diameter of the apparatus d_a and the linear rate of flow w. These parameters were used in the form of ratios of corresponding quantities in the model and in the prototype. The space velocity V_{sec}, the geometrical ratio d_a/l, Re, Da_I, the pressure drop Δp, and the thermal flux through the heat-exchange surface $\pi d_a l \alpha$ or jl/d_a, where α is the thermal emission coefficient and j the heat-transfer coefficient, were used as supplementary parameters. The ratio of these in the model and in the prototype was expressed in terms of the ratio of the fundamental parameters. It was assumed that the height of the apparatus varies in direct proportion to the linear rate of flow, *i.e.* that the mean residence time in the apparatus is kept constant.

The following notation is employed in Table 2: ratio of reactor diameters $d_p/d_m = x$, ratio of reactor lengths $l_p/l_m = y$, ratio of linear flow rates $w_p/w_m = z$, and ratio of space velocities $(V_{sec})_p/(V_{sec})_m = \beta$. These ratios have been termed

TABLE 2.

Parameter compared	Scale factor	$x^2z=\beta$ $y/z=1$	$x=1$	$x=\sqrt[3]{\beta}$	$x=\sqrt{\beta}$	$x=\beta$
d, diameter	x	x	1	x	x	x
l, length	y	β/x^2	β	x	1	$1/x$
w, velocity	z	β/x^2	β	x	1	$1/x$
$V_{sec}=\pi d^2w/4$	x^2z	$=\beta$	β	x^3	x^2	x
d/l	x/y	x^3/β	$1/\beta$	1	x	x^2
$Re=\rho wd/\mu$	xz	β/x	β	x^2	x	1
$Da_I=k_1l/w=$	y/z	$=1$	1	1	1	1
$=k_1V/V_{sec}$						
Δp	$yz^2/x\,(xz)^m$	$\beta^3/x^7\,Re^m$	β^{3-m}	x^{+2-2m}	x^{-m-1}	x^{-4}
$\pi dl\alpha$	$y\,(xz)^{1-m}$	$\beta^2/x^3\,Re^m$	β^{2-m}	x^{+3-2m}	x^{-m+1}	x^{-1}
jl/d	$y/x\,(xz)^m$	$\beta/x^3\,Re^m$	β^{1-m}	x^{-3m}	x^{-m-1}	x^{-2}

scale factors (see Table 2). The scale factors giving the ratios between the fundamental parameters are related by the equations

$$x^2z=\beta\,. \tag{60}$$

It was therefore possible to obtain different scales by expressing the ratio of one of the fundamental parameters in the model and in the prototype in terms of the ratio of other parameters. Thus when $z=\beta$, we have $x=1$ (Table 2, column 4). In practice this case corresponds to constancy of diameter in model and in protype.

When $z=x$, we have $x=\beta^{\frac{1}{3}}$ (Table 2, column 5). This corresponds to geometrical similarity of model and prototype, since as a result of the equality $z/y=1$, also $y=x$, *i.e.* the ratio of the lengths of model and prototype is equal to the ratio of their diameters.

Similarly, when $z=1$ (Table 2, column 6), we have $x=\beta^{\frac{1}{2}}$. This means that model and prototype are of equal length, when the ratio of their outputs is equal to the ratio of their cross-sections.

Finally, when $z=x^{-1}$ (Table 2, column 7), we have $x=\beta$. This case corresponds to the maintenance of hydrodynamic similarity in model and in prototype. Actually the condition $zx=1$ means that the ratio of the Re in the model and in the prototype is unity (since physical constants cancel out, the ratio of the groups proves to be equal to the produce zx). Table 2 gives scale relationships showing how the ratio of the supplementary parameters in model and prototype is expressed in terms of the ratios of the fundamental parameters for each of the four examples discussed above. This attempt represents a modified method of using scale equations.

For the particular case of a heterogeneous catalytic reaction occurring in the gas phase over a fixed bed of catalyst, the following rate equation can be obtained[6]:

$$V_{sec}dy=U_k(1-y)\,dF\,. \tag{61}$$

where y is the degree of conversion, dF a surface element of the catalyst, and U_k is the velocity of the chemical reaction expressed in flow-rate units. Eqn. (61) allows the dimensions of the apparatus to be linked with the chemical-reaction velocity and the proportion of material undergoing reaction.

This equation is valid on the following assumptions: the chemical-reaction velocity U_k is constant over the whole length (height) of the apparatus, the quantity of material undergoing change varies along the length of the apparatus in proportion to the difference between the actual composition at a given cross-section of the apparatus and that which is theoretically possible, the reaction is of the first order, and it takes place without change in volume. Integration of Eqn. (61) yields

$$1-y=e^{-U_kF/V_{sec}}\,. \tag{62}$$

Eqn. (62) can be written in the form of the following relationship between three dimensionless groups:

$$A=\Gamma W,\ , \tag{63}$$

where $A=-\epsilon/\ln(1-y)$ gives the degree of conversion expected when a given fraction of the catalyst surface is utilised. The physical significance of this criterion is obviously equivalent to that of the concentration ratio X_1 or the relative yield X_2.

$\Gamma=(l\sigma)^{-1}$ is a criterion of geometrical similarity of the catalyst surface. It is equivalent in physical meaning to the criterion of geometrical similarity.

$W=w/U_k$ is a criterion of kinetic similarity, equivalent in physical significance to Da_I, as already remarked above (see p.297). In the above equations ϵ is the fraction of catalyst surface utilised, σ the specific surface of the catalyst, and w the linear rate of flow.

The applicability of the dimensionless-group equation (63) is subject, however, to the same limitations as those postulated in deriving the original rate equation. Furthermore, it is obviously supposed here that the reaction is occurring in the kinetic range, and consequently that mass transfer has no retarding effect on it. An analogous equation for a first-order homogeneous reaction was suggested by Pozin[31] in deducing an equation for the efficiency of a chemical apparatus (by which he meant the degree of approximation, achievable in the apparatus, to the theoretically possible results). Pozin's equation for this case is

$$\eta=1-e^{-k_1fl/V_{sec}}\,, \tag{64}$$

where η is the efficiency of the chemical apparatus, f the cross-section of the flow (apparatus), and l the length of flow.

Examination of Eqns. (62) and (64) shows their similarity, since, in the case of a first-order reaction, the efficiency of the apparatus is identical with the degree of conversion, as is evident from the definition of the former; the two equations therefore have the same meaning. They relate the dimensions of the apparatus to the rate of flow and the degree of conversion. In using them it must be borne in mind, however, that neither equation takes account either of complications due to heat and mass transfer or of the distribution of residence times within the apparatus.

IV. SOME PARTICULAR CASES OF THE PRACTICAL USE OF SIMILARITY THEORY

Examples of the practical application of similarity theory to chemical processes occurring in the kinetic range are given in D'yakonov's monograph[3]. Thus generalisation of experimental data on the synthesis of ammonia at different temperatures yields the following dimensionless-group equation:

$$X_2=\left(\frac{b\,Ko}{1+b\,Ko}\right)^{1/4}\,, \tag{65}$$

where b is a constant. Generalisation of experimental

results for this synthesis at different temperatures and pressures gave the following equation:

$$Eq = \left(\frac{b\,Ko}{1 + b\,Ko}\right)^2 \qquad (66)$$

Similarly, experimental data on the oxidation of sulphur dioxide at different temperatures yielded the equation

$$X_2 = \frac{Ko}{1 + Ko} \cdot \qquad (67)$$

Using Eqn. (67), the isotherms on a so-called Knitsch diagram could be combined into a single curve represented by this equation.

Generalisation of experimental data on the thermal decomposition of calcium and cadmium salts and oxides[30] showed that all these decomposition processes follow the dimensionless-group equation

$$\frac{1}{Ko} = 1 - Eq. \qquad (68)$$

Generalisation of experimental results for the polymerisation of vegetable oils (in the production of drying oil[10]) gave equations of the form

$$\Phi = f(K_{int}), \qquad (69)$$

where Φ is the ratio of the physical constants used to control the industrial process (viscosities, densities, etc.).

These equations were expressed graphically. Their practical application enabled the control of the process to be considerably improved and production losses to be eliminated. In addition, a scheme was proposed for the automation of this process, based on the use of Eqn. (69).

Analysis of experimental data on flame propagation in a tube filled with a fuel gas mixed with various inert gases having considerably different coefficients of diffusion and of thermal conductivity yielded[32] the following dimensionless-group equation:

$$\left(\frac{w}{\sqrt{ak_2c_2}}\right)\left[\left(\frac{qc_1}{\gamma c_p T}\right)^{3.36}\left(\frac{D}{a}\right)^{0.6}\right] = f\left(\frac{c_1}{c_2}\right), \qquad (70)$$

where w is the velocity of flame propagation, a the temperature conductivity, and c_1 and c_2 are the concentrations of the reactants (methane and oxygen). This equation was also put in a graphical form.

It is easy to show that the group $w(ak_2c_2)^{-\frac{1}{2}}$ represents the ratio $(Pe/Da_I)^{\frac{1}{2}}$:

$$\left(\frac{w}{\sqrt{a_1kc_2}}\right)^2 = \frac{w^2l}{ak_1c_2l} = \frac{wl}{a}\,\frac{w}{k_2c_2l} = \frac{Pe}{Da_I} \cdot \qquad (71)$$

D/a, however, is obviously the ratio of the groups Pe/Pe_d. The remaining groups have already been discussed previously.

Thus the general dimensionless-group equation can be written in the following form:

$$\left(\frac{Pe}{Da_I}\right)^{0.5}\left[(K_{tc})^{3.36}\left(\frac{Pe}{Pe_d}\right)^{0.6}\right] = f(X_3), \qquad (72)$$

where $X_3 = c_1/c_2$, or in a more general form:

$$f = (Da_I,\ Pe,\ Pe_d,\ K_{tc},\ X_3) = 0 \cdot \qquad (73)$$

In the generalisation of experimental data on chemical reactions occurring in the diffusion range, *e.g.* in the absorption of ammonia by sulphuric acid, the processes are described by equations of the form

$$G_a = k_{og}F\Delta p_{av}, \qquad (74)$$

where $k_{og} = k_g$ is the general mass-transfer coefficient for the gas phase, and Δp_{av} is the mean driving force in the apparatus, expressed in partial-pressure units. Here, as always, the mass-transfer coefficient is found from the appropriate dimensionless-group equation for physical absorption.

In a recent paper[33], generalised equations were obtained for physical sorption in packed columns taking account of the hydrodynamic state of the two-phase system.

For readily soluble gases:

$$Nu = A\,Re_g^m Pr_g^n (1 + f). \qquad (75)$$

For sparingly soluble gases:

$$Nu = A_1\,Re_{liq}^{m_1} Pr_{liq}^{n_1} (1 + f), \qquad (76)$$

where f is a factor of the hydrodynamic state of the two-phase system. The values of A, m, n, and f depend on the hydrodynamic regime of the two-phase system.

Normal dimensionless-group equations for mass transfer are used to determine the velocity of chemical processes occurring in a solid–gas system. For example, similarity theory has been used to show[34] that the rate of combustion of carbon is governed by the rate of supply of oxygen through the external diffusion layer in the gas phase.

Dimensionless-group equations for diffusion can be used also for absorption accompanied by a slow chemical reaction, when the absorbed component passes through both diffusion layers (in the gas and the liquid phases) without reacting or almost without reacting, *i.e.* when the reaction takes place mainly in the bulk of the liquid phase. The reaction then affects only the vapour pressure of the component absorbed in the bulk of the liquid phase, without changing the form of the equation. An example of such a process is the absorption of ethyl formate by caustic soda solution[25].

As an example of the use of similarity theory in calculations on chemical processes occurring in the diffusion–kinetic range, we can cite the dimensionless-group equation

$$Nu = C\,Ha\,Re^{3/4}Pr^{1/3}, \qquad (77)$$

obtained in an analysis of experimental data on the absorption of carbon dioxide by solutions of alkalis — sodium carbonate and diethanolamine[12,28]. The design of a catalyst column for the production of phenol by Raschig's method[22] may be cited as an example of the partial application of similarity theory in calculations on heterogeneous catalytic processes. A method which we have already described[20] is suggested here for taking into account the diffusion resistance. A considerable number of examples of the partial use of similarity theory in calculations on chemical processes taking place in the diffusion–kinetic range using a great variety of equipment, can also be found in other papers[35-38].

As an example of the experimental verification of the possibile uses of scale equations, mention may be made of the work of Bretsznajder[30], who confirmed experimentally the possibility of simulating reaction vessels by means of scale equations. Experiments were carried out on a pseudo-homogeneous system, a suspension of zinc dust in a solution of dichromate in sulphuric acid, in two tubular reaction

vessels, the dimensions of which were established in conformity with the requirements of the scale equations. The output of the two reaction vessels differed fivefold. The scale equations (49)–(51) were used as a starting point. These equations are discussed in the present review, and are obtained from the condition for a constant temperature rise in the two vessels. The experiments confirmed that, when the geometrical relationships between the dimensions of model and prototype and the flow rates found from the scale equations were used, the actual increase in temperature in the prototype coincided with the specified value within the limits of experimental error.

Conditions have been formulated for the simulation of packed apparatus for gas–liquid and vapour–liquid systems[39] where diffusion has a decisive effect, *i.e.* for processes occurring in the diffusion range. This becomes possible because the phase-inversion condition in the packing leads to definite values of (1) the velocities at every cross-section of the column, (2) the pressure drop, and (3) the distribution of liquid in the column. Thus every element of a layer of packing reproduces the layer elements arranged on either side of it.

When the same systems are being analysed in the model and in the prototype, the conditions for the simulation of packed columns reduce to the following.

For the heights of the layer of packing:

$$\frac{h_1}{h_2} = \left(\frac{\sigma_2}{\sigma_1}\right)^{1.3} \left(\frac{F_{c_1}}{F_{c_2}}\right)^{1.3} \qquad (78)$$

For the column diameters:

$$\frac{D_1}{D_2} = \left(\frac{\sigma_1}{\sigma_2}\right)^{0.25} \left(\frac{F_{c_2}}{F_{c_1}}\right)^{0.75}. \qquad (79)$$

For the pressure drops:

$$\frac{\Delta p_1}{\Delta p_2} = \left(\frac{\sigma_1}{\sigma_2}\right)^{0.3} \left(\frac{F_{c_2}}{F_{c_1}}\right)^{0.3}, \qquad (80)$$

where σ is the specific surface of the packing (filling) in m^2/m^3, and F_c is the free cross-section or free volume of the packing in m^3/m^3.

In a recent paper[40] conditions have been found for the simulation of chemical processes by the use of Eqns. (75) and (76).

The application of similarity theory to chemical processes opens up opportunities for generalising experimental data on chemical reactions occurring in the kinetic, diffusion, and diffusion–kinetic ranges. In some cases similarity theory makes it possible to simulate chemical processes by the use of scale equations and criteria in integral form.

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