Pergamon

0017–9310(94)00112–X

Evolution of a particulate system governed by exchange with its environment

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Abstract—Evolutionary processes of a polydisperse assemblage of particles in metastable or reactive surroundings are studied with allowance for the back influence of the assemblage upon the transient properties of the surroundings. Each particle either grows or reduces in size due to mass and heat exchange with the ambient medium in which it is immersed, the growth or reduction rate being given in a sufficiently general form as a function of both the particle size and the state of the medium. However, there is no generation of nuclei that give rise to new particles and the external supply to, or the forced withdrawal of particles from, the system are left out of the account. A mathematical model to deal with such processes is put forward, which is based on the kinetic equation for the particle population density and on mass and heat conservation equations for the system as a whole. The model can be generalized to situations when the particles are not distributed over their radius but over another relevant physical character. Examples of the application of the model to assemblages involved in evolution processes of different physical origin lead to very simple final formulae which agree well with experimental findings.

1. INTRODUCTION

A great number of processes occurring in both nature and industry are based on a particulate system interacting with its environment. A prominent place is taken by the formation and subsequent development of a system of discrete elements of a new phase in a metastable medium. Good examples are offered by the condensation and evaporation of droplets in super- or undersaturated gas–vapour mixtures [1, 2], of extreme importance in power engineering, as well as by crystallization [3, 4] and dissolution [5] of polydisperse solids in a metastable liquid or gaseous phase—the processes forming a background for a wide variety of batch crystallizers, granulators and other devices in chemical engineering.

A significant feature of such processes the existence of non-linear feedbacks between the evolution of a particulate assemblage and an ensuing change in the state of the metastable surroundings. So far as the emergence of a dispersed phase is concerned, the degree of metastability is gradually reduced as the assemblage evolves, with evident consequences for both the growth rate of individual particles and the

generation of initial critical nuclei [6] that give rise to new particles.

Apart from the growth and reduction of the dispersed phase, many processes of the same type are encountered while manufacturing and handling diverse dispersed solid materials as well as in the course of their thermochemical processing. Among these, one may mention the processes of drying [7] and chemical conversion [8] of powders and granulated solids, including widespread technologies of either oxidation or reduction under flow conditions. A particular case is also provided by the combustion of liquid dropwise and powdered solid fuels in different circumstances [9]. The kinetics of all these processes is governed by the rate of exchange of heat and mass of various relevant reagents between the particulate assemblage under question and the ambient medium which may be either gaseous or condensed.

The obvious need for the proper design of the above-mentioned processes in practice, as well as the selection of optimal performance conditions, naturally necessitates the development and careful elaboration of corresponding models and calculation schemes. A review of the suggestions advanced so far can be found in the references cited above and also in ref. [10]. The models and schemes are usually based on the study of the solutions to the kinetic equation of the particle population density for the particle size

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NOMENCLATURE

A	kernel in equations (23) and (24)		β	coefficients in equations (31), (48) and (58)
B	quantity in equation (74)			
a, b	coefficients in equations of type (16)		γ	coefficient in equation (58)
c	concentration, also specific heat capacity		η	constant coefficient
D	diffusivity		ϑ	temperature difference
E	activation energy		κ	heat capacity ratio in equation (52)
F	function introduced by equation (5)		λ	heat conductivity, also coefficients in equations (32), (34), (38) and (77)
f	distribution density			
G	mass flow rate			
K, K_r	empirical coefficients		μ	ratio of initial mass of droplets to that of gas
k	mass transfer coefficient, also parameter in equation (48) and kinetic constant in equation (58)		ξ	variable of particle distribution
			ρ	density
L	latent heat of evaporation		τ	characteristic time defined in equations (66) and (68), also dimensionless time in Fig. 3
M, N	functions introduced in equation (2)			
n	number concentration of particles		φ	degree of reduction.
Nu	Nusselt number			
Q, q	effective heats introduced in equation (48)			
q_R	reaction heat			

Subscripts

R	function introduced by equation (5)
r	particle radius
s	parameter in equation (5) and in other relations of the same kind
T	temperature
t	time
v	velocity
w	transformation rate, dr/dt or $d\xi/dt$
x	coordinate vector
y	degree of transformation.

Subscripts

b	boiling
f	reaction front
g	gas
h	hydrogen
o	initial
p	particles, also constant pressure
s	saturation, also solid
v	vapour.

Greek symbols

α	function in equation (26), also parameter in equation (32) and heat transfer constant in equation (58)

Superscript

*	equilibrium temperature or concentration.

or another significant parameter, with allowance for spontaneous origination of new critical nuclei and external supply or withdrawal of particles, as well as on a set of pertinent mass and heat conservation equations. All the equations are strongly non-linear, partly due to the dependence of the transient state of the ambient medium on the rate of assemblage evolution. Sometimes this causes unsurmountable difficulties in solving them.

Without going into particulars, we will enumerate three basic methods conventionally used to overcome these difficulties. The first consists of the reduction of the kinetic equation to an integro-differential one and the subsequent investigation of the latter equation. The second method involves replacing the kinetic equation by a few equations for the main moments of the particle distribution over the indicated parameter. The third method involves dividing an actual poly-

disperse system into a set of interacting fractions consisting of approximately uniform particles, and bringing into effect separate kinetic equations for all the fractions—the operation lacking both principles and ideas. The listed approaches commonly lead to rather tedious and cumbersome calculations. The intended purpose of this paper is to suggest a very simple alternative method which seems to be quite sufficient for the majority of applications.

2. BASIC EQUATIONS AND A GENERAL METHOD

We consider a polydisperse particulate assemblage involved in mass and heat exchange with an ambient medium. The exchange results in either changes in the particle size, as in the case of evaporation, condensation, crystallization, granulation, dissolution and

combustion processes, or changes in some other pertinent character that can be assigned to define the transient state of a particle. Representative examples are provided by drying processes, when the moisture content of any particle plays the role of such a charac-·ter, and also by chemical transformation processes, such as oxidation or reduction of a powdered material, when the amount of conversion attributed to a single particle is significant. Although there may be several relevant parameters characterizing the particles which must be taken into account simultaneously while studying the assemblage evolution, we confine ourselves below to treating situations in which only one parameter, henceforth denoted as ξ, is essential.

The particles are assumed to be continuously distributed over the parameter ξ, so that the assemblage is to be described with the help of the particle population density, $f(t, \mathbf{x}; \xi)$, which is regarded as normalized to the number concentration $n(t, \mathbf{x})$ of the particles. If possible, the fluctuations in the rate $d\xi/dt$ of change of ξ are ignored; this quantity has to be looked upon as a deterministic one, and there is no need to allow for particle diffusion along the ξ-axis. We also suppose that there are no external sources or sinks of particles, and the origination of new particles from initial parent nuclei may be neglected. The particle concentration is then constant or decreases with time, and the evolution of $f(t, \mathbf{x}; \xi)$ is governed by a first-order kinetic equation:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\mathbf{v}f) + \frac{\partial}{\partial \xi}(wf) = 0 \quad w = \frac{d\xi}{dt} \quad (1)$$

which is the simplest version of the Fokker–Plank equation.

The quantity w has to be regarded as a function of t, $\mathbf{x}$ and ξ. In what follows, we give attention to the cases in which w is expressed as a product of separate functions of t and $\mathbf{x}$, and of ξ, and which covers the great majority of possible applications. Thus:

$$w = M(t, \mathbf{x})N(\xi). \quad (2)$$

Exact forms of the functions in equation (2) are dictated by the very nature of the process under study and by the kinetic peculiarities of the transformation of a single particle. The function $M(t, \mathbf{x})$ usually depends implicitly on its arguments, through some variables which are employed to describe the instantaneous state of the ambient medium, such as the medium temperature T and concentrations c_i of various admixtures and reagents. Equation (1) must be supplemented with equations for the variables stemming from the mass and energy conservation laws. A representative of such equations can be written in symbolic form as

$$\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\mathbf{v}c_i) = \eta_i \int f(t, \mathbf{x}; \xi)w(t, \mathbf{x}; \xi)\phi_i(\xi)\,d\xi \quad (3)$$

where integration is performed over the whole range of allowable ξ, and η_i and $\phi_i(\xi)$ are a coefficient and a

function determined by the physical essence of the process being investigated. The term on the right-hand side of equation (3) presents an effective source of quantity c_i per unit volume caused by the particle transformation.

Imposing the initial conditions

$$f(0, \mathbf{x}; \xi) = f_o(\mathbf{x}; \xi) \quad \int f_o(\mathbf{x}; \xi)\,d\xi = n_o(\mathbf{x})$$

$$c_i(0, \mathbf{x}) = c_{io}(\mathbf{x}) \quad (4)$$

limits the problem of solving equations (1)–(3). It is worth noting that the conditions may be imposed not at the initial instant $t = 0$, but at some fixed $\mathbf{x}$ or even at a certain surface $\mathbf{x} = \mathbf{x}_o(t)$.

The essence of the method suggested is really very simple. By making use of the fact that w is expressed in the form of equation (2), we look for elementary solutions of equation (1) in a familiar form and construct a complete solution by means of summing the elementary ones. This gives

$$f(t, \mathbf{x}; \xi) = S\{F(t, \mathbf{x}; s)R(\xi, s)\} \quad (5)$$

where s is the free parameter and the symbol $S\{\ldots\}$ indicates summation or integration over different s. Equation (1) then splits into two equations:

$$\frac{\partial F}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\mathbf{v}F) + 2sMF = 0 \quad \frac{d}{d\xi}(NR) - 2sR = 0 \quad (6)$$

and equation (3) reduces to

$$\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\mathbf{v}c_i) = \eta_i S\left\{F(t, \mathbf{x}; s)\right.$$

$$\left. \times M(t, \mathbf{x})\int R(\xi; s)\,N(\xi)\phi_i(\xi)\,d\xi\right\}. \quad (7)$$

Let us solve the equation for $R(\xi; s)$ in the set of equations (6) at a given s accurate to an arbitrary constant multiplier and then accept $f_o(\mathbf{x}; \xi)$ as successfully approximated in a form similar to that of equation (5):

$$f_o(\mathbf{x}; \xi) = S\{F_o(\mathbf{x}; s)R(\xi; s)\}. \quad (8)$$

The first equation in set (6) and equations (7) for all $c_i(t, \mathbf{x})$ together with the last conditions in (4) and the initial condition $F(0, \mathbf{x}; s) = F_o(\mathbf{x}; s)$ present a correct problem to determine both $F(t, \mathbf{x}; s)$ and $c_i(t, \mathbf{x})$.

Thus, the crux of the matter lies in approximating the initial population density in compliance with equation (8). Usually this can be done in a reasonable way by using a few terms in equation (8) that correspond to different s and suitable functions $F_o(\mathbf{x}; s)$.

To simplify the matter, we consider the system under conditions of ideal mixing, when all the variables are only time-dependent. By way of an example, we concentrate on a detailed discussion of a mist evaporation problem. Let us presume for the sake of definiteness that the reduction of liquid droplets suspended in a gaseous mixture is limited by the rate of diffusional transport of the vapour away from a drop-

let and the thermal effect of evaporation may be ignored. These conditions are actually met if the mixture temperature is well below the liquid boiling point and the vapour concentration is low enough. In this case, there is only the parameter—the droplet radius r—that determines the state of the droplets and the only relevant mixture characteristic is the mean vapour concentration $c(t)$. Moreover, if the droplet radius is much larger than the mean free path length of molecules in the gas,

$$w = \frac{dr}{dt} = \frac{D}{r\rho}[c(t) - c^*(t)]$$

$$M = \frac{D}{\rho}[c(t) - c^*(t)] \quad N = \frac{1}{r} \tag{9}$$

and equation (3) can be integrated to yield

$$c(t) = c_o + \frac{4\pi}{3}\rho n_o \langle r_o^3 \rangle - \rho \int f(t;r) r^3 \, dr. \tag{10}$$

By applying the well-known method of characteristics to the problem under study, one gets from equations (1) and (9)

$$f(t;r) = \frac{r}{(r^2 + \theta(t))^{1/2}} f_o[(r^2 + \theta(t))^{1/2}]$$

$$\theta(t) = \frac{2D}{\rho} \int_0^t [c^*(t) - c(t)] \, dt \tag{11}$$

for any functions $f_o(r)$ and $\theta(t)$. Next, substituting equations (11) into equation (10) one obtains an integral equation for $\theta(t)$, the solution of which is not a simple task. The last function determines the vapour concentration in an explicit form:

$$c(t) = c^*(t) - \frac{\rho}{2D}\frac{d\theta}{dt} \tag{12}$$

and, further, $f(t;r)$ in accordance with the relation in the set of equations (11).

Now we are going to apply the proposed method to the same problem. The desired solution of the second equation in set (6) is

$$R(r;s) = 2Csr \exp(-sr^2) \tag{13}$$

C being a constant. The simplest case is that in which the initial population density can be approximated with sufficient accuracy by function (13) with a certain s. It is then convenient to choose $C = n_o$ from the very beginning and, consequently, to demand that $F_o = 1$.

The first equation in set (6) can now be represented in the form

$$\frac{dF}{dt} + \frac{2D}{\rho}s[c^*(t) - c(t)]F = 0 \quad F(0) = 1 \tag{14}$$

and equation (10) yields

$$c(t) = c_o - (4\pi/3)\rho n_o \langle r_o^3 \rangle [1 - F(t)]. \tag{15}$$

The use of the last formula in set (14) results in

$$\frac{dF}{dt} + a(t)F + bF^2 = 0 \quad b = \frac{8\pi}{3}Dn_o\langle r_o^3 \rangle s$$

$$a(t) = \frac{2D}{\rho}\left[c^*(t) - c_o - \frac{4\pi}{3}\rho n_o\langle r_o^3 \rangle\right]s$$

$$\langle r_o^3 \rangle = \frac{3\sqrt{\pi}}{4s^{3/2}}. \tag{16}$$

It is not difficult to solve the equation in set (16) at an arbitrary dependence of c^* on t that might be dictated by the thermal regime of evaporation. If isothermal conditions are maintained, both c^* and a are independent of time, and

$$F(t) = [(1 + b/a) \exp(at) - b/a]^{-1}$$

$$\approx (1 + b/a)^{-1}\exp(-at) \tag{17}$$

the approximate equality being valid at $at \gg 1$. In view of equations (5) and (13), the size distribution density and the particle number concentration are expressed as

$$f(t;r) = 2sn_o F(t)r \exp(-sr^2)$$

$$n(t) = n_o F(t) \quad s = \left(\frac{4}{3\sqrt{\pi}}\langle r_o^3 \rangle\right)^{2/3} \tag{18}$$

with $F(t)$ being defined in equation (17). It is worthwhile to point out that the particle population density (18) is self-similar in the sense that the assemblage evolution affects merely the total number of droplets which eventually vanish during the process and not the distribution moments $\langle r_o^m \rangle$ at any m.

In a more general case, the initial population density cannot be represented according to equation (13). However, it can sometimes be given as a sum of a few elementary self-similar functions of the type of equation (13):

$$f_o(r) = 2\sum_{i-1}^{I} C_i s_i r \exp(-s_i r^2) \quad \sum_{i-1}^{I} C_i = n_o. \tag{19}$$

In order to obtain $f(t;r)$, each elementary function $R(r;s_i)$ must be multiplied by a certain $F(t;s_i)$, and then the products have to be summed similarly to equation (19). The problem of finding $F(t;s_i)$ is essentially the same as before, with s being replaced by s_i. Hence, equations similar to that in set (14) follow. They lead at once to the following relations:

$$s_i \ln F_j = s_j \ln F_i, \quad F_j^{s_i} = F_i^{s_j} \quad F_i = F(t;s_i) \tag{20}$$

for any numbers i and j smaller that I in equation (19).

Because of the obvious inequality $F(t;s_i) < 1$ at $t > 0$, it can be seen that the maxima of the population density attained at small values of r degenerate faster than those reached at larger ones. This means that any moment $\langle r^m \rangle$ must increase with time due to the assemblage evaporation. Moreover, relations (20) prove that only a single function among $F(t;s_i)$ must be found to determine all of them. For definiteness,

we arrange s_i in such a way that $s_j > s_i$ at $j > i$ and choose $F(t; s_1) = F_1(t)$ to be determined first. After a simple manipulation, we arrive at a problem

$$\frac{dF_1}{dt} + \left(a_1 + \sum_{i=1}^{I} b_i F_1^{s_i/s_1} \right) F_1 = 0 \quad F_1(0) = 1$$

$$a_1 = \frac{2D}{\rho} \left[c^*(t) - c_0 - \pi^{3/2} \rho \sum_{i=1}^{I} \frac{c_i}{s_i^{3/2}} \right] s_1$$

$$b_i = \frac{2\pi^{3/2} D s_1}{s_i^{3/2}} C_i. \tag{21}$$

This equation can be integrated numerically. Besides, if c^* is constant and $s_i = k_i s_1$ and k_i are integral numbers, the right-hand side of the equation represents a polynomial. After expanding the polynomial into elementary multipliers, the equation can be integrated to yield an algebraic transcendental equation relating F_1 to t in implicit form.

The size distribution density is expressed in this case as

$$f(t; r) = 2 \sum_{i=1}^{I} C_i s_i F_1^{s_i/s_1}(t) r \exp(-s_i r^2). \tag{22}$$

At last, we turn to the case when the initial distribution is described by an arbitrary continuous function $f_0(r)$ with a finite number of discontinuities of the first kind. The very form of equation (13) suggests looking for $f(t; r)$ as an integral transformation of a certain function $F(t; s)$, with a kernel belonging to the same class as function (13). It means that [11]

$$f(t; r) = r \int_0^\infty A(s) F(t; s) \exp(-sr^2) \, ds \tag{23}$$

and, after accepting that $F(O; s) = 1$,

$$f_0(r) = r \int_0^\infty A(s) \exp(-sr^2) \, ds. \tag{24}$$

With the introduction of a new independent variable $\rho = r^2$ we are able to rewrite equation (24) as a Laplace transformation:

$$\left. \frac{f_0(r)}{r} \right|_{r=\sqrt{\rho}} = \int_0^\infty A(s) \exp(-s\rho) \, ds \tag{25}$$

which enables us to regard the unknown function $A(s)$ as the inverse Laplace transformation of the known function, that is, of the one on the left-hand side of the equation (25).

It is natural, by analogy with equation (20), to take $F(t; s) = F^s(t)$, in which case we obtain from equations (1), (9), (10) and (23)

$$\frac{dF}{dt} + \left(\alpha(t) + \pi^{3/2} D \int_0^\infty \right.$$

$$\left. \times \exp(-sr^2) F^s s^{-5/2} \, ds \right) F = 0$$

$$F(0) = 1 \quad s\alpha(t) = a(t). \tag{26}$$

The function $\alpha(t)$ is expressed in terms of $a(t)$ from equation (16) and is independent of s. This equation is integro-differential as well as that resulting from equations (10) and (11). However, it seems to be somewhat simpler and more apt to be investigated numerically than the latter equation. Solving equation (26) brings to an end the matter of finding the population density in the form of equation (23).

Thus, we are now capable of envisaging the consequences of the assemblage evolution in full detail under sufficiently general initial conditions. The developed calculation scheme possesses an evident advantage over conventional ones based on either dividing the assemblage into separate fractions or considering changes in moments of the particle size distribution. Even so, it can be greatly simplified further when evaluating the majority of processes of practical interest.

Irrespective of its initial form, the population density commonly tends to a self-similar function of type (18) as time grows. Such a conclusion can be immediately drawn from equation (22) since $s_i/s_1 > 1$ for all $i > 1$ and $F_1(t)$ is smaller than unity and monotonously decreases with time. With this provision, the first term in the series in equation (22) inevitably becomes dominant at large t, no matter what coefficients C_i are assigned to determine the initial distribution in accordance with equation (19). Thus, after an interval of time, the system forgets particulars of its initial state and, consequently, a final self-similar stage of the assemblage evolution ultimately takes place, during which that part of the initial distribution that corresponds to the largest droplets remains essential.

The self-similar stage often happens to be much longer than the initial one, and it is only the former stage that usually governs evolution processes at large. This is a rather fortunate occurrence, because the population distribution density and other pertinent assemblage and ambient medium characteristics are then advantageously described by equations (17) and (18), and by simple formulae which result from these equations. Among those characteristics, the degree of transformation

$$y(t) = n(t) \langle r^3(t) \rangle / n_0 \langle r_0^3 \rangle \tag{27}$$

is commonly of especial use. The quantity $\langle r^3(t) \rangle$ remains unchanged and $y(t) = n(t)/n_0 = F(t)$ during the self-similar stage.

An important point is that the above inference is of general character and, for example, is not affected by either neglect of the thermal effect of evaporation or use of the simplest formula (9) for the evaporation rate. Both of the last assumptions are, in principle, unnecessary and have been successfully avoided in ref. [11].

3. EXAMPLES OF APPLICATION

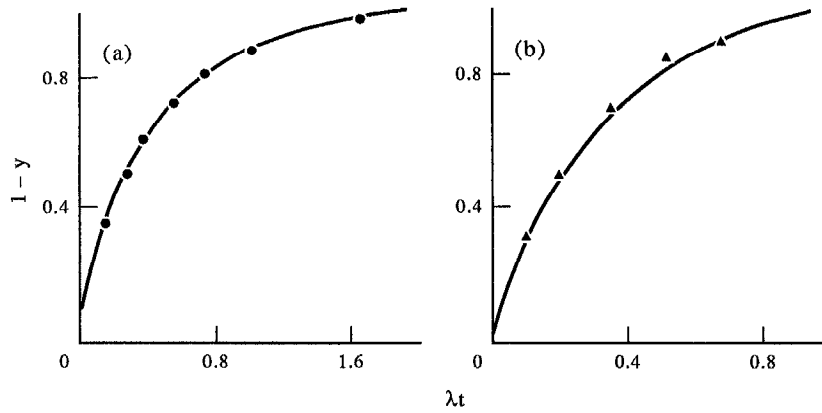In the remainder of this paper we turn to a brief account of a few concrete problems concerning diverse

Fig. 1. Kinetics of dissolution of $CaSO_4 \cdot 2H_2O$ crystals in water in mixer-type devices (a) and of KCl crystals in water in a counter-flow apparatus (b); curves, equation (32), dots; experiments in ref. [5].

physical situations. Each of them appears to be of independent interest in the corresponding field of applied science. At the same time, when taken together, these problems convincingly demonstrate the great capability of the method developed above for treating assemblage evolution in different circumstances.

3.1. Dissolution of dispersed solids

A review of numerous technological processes which involve dissolution of a polydisperse system of solids particles in a liquid mixture can be found in ref. [5]. If particles dissolve in a device with intense mixing, the dissolution rate of a single particle happens to be approximately independent of its size and can be described by a formula

$$\frac{dr}{dt} = w = -\frac{k}{\rho}(c^* - c) \qquad (28)$$

where k is a constant mass transfer coefficient. This formula holds true in a mixer-type apparatus, in which there is a periodic external supply of solids and withdrawal of solution, as well as under the conditions of co-current two-phase mixture flow. In both cases the mass balance equation can be written as [5]

$$c(t) = c_0 + \beta[1 - y(t)] \qquad (29)$$

where the degree of transformation $y(t)$ has to be defined in accordance with equation (27) and β stands for the mass of solids per unit volume of the mixture.

By using the kinetic equation with w identified in (28) we get a self-similar solution:

$$f(t;r) = F(t) R(t) \quad R(r) = n_0 s \exp(-sr)$$

$$F(t) = y(t) \quad s = \langle r_0 \rangle^{-1} \qquad (30)$$

which substitutes for that defined by equations (5) and (13). An equation governing the degree of transformation is derived with the help of equation (29) in the same manner as before. It coincides with equation (16) where, now [12],

$$a = (ks/\rho)(c^* - c_0 - \beta) \quad b = \beta ks/\rho. \qquad (31)$$

The relevant solution is given by equation (17) with the above coefficients a and b. It can be conveniently rewritten in the form

$$y(t) = [(1 - \alpha)^{-1} \exp(\lambda t) + \alpha^{-1}]^{-1}$$

$$\alpha = (c^* - c_0)/\beta \quad \lambda = (ks/\rho)(1 - \alpha). \qquad (32)$$

Under the conditions of counter-current flow, equations (28) and (29) must be replaced by [5]

$$w(t) = -(k/\rho)[c^* - c_0 - \beta y(t)] \quad c(t) = c_0 + \beta(t). \qquad (33)$$

In this case, equation (32) is valid as before but [12]

$$\lambda = (ks/\rho)\alpha. \qquad (34)$$

Comparison of theoretical results from equations (32) with experiments of refs. [5, 13] is illustrated in Figs. 1 and 2. The agreement seems to be quite
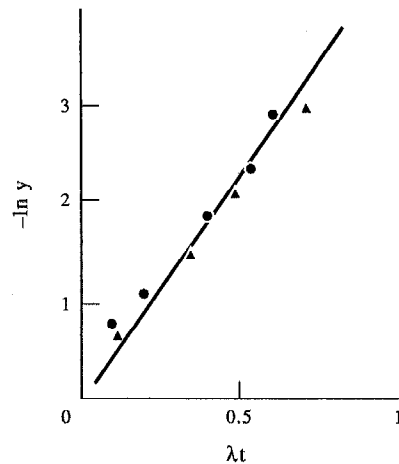

Fig. 2. Kinetics of dissolution of NaCl crystals in mixer-type apparatuses according to equation (32); dots, data of ref. [13].

satisfactory in spite of the fact that the simplest possible solution of the problem has been actually used to correlate the experimental findings. It is worth noting that achieving the same purpose of making the theory agree with experiments required a tremendous volume of numerical calculations in ref. [5] and, especially, in ref. [13], where the system was subdivided into separate particulate fractions.

3.2. Evaporation of a polydisperse mist

We consider, next, liquid droplets suspended in an ambient gas–vapour mixture whose temperature is sufficiently close to or even considerably exceeds the liquid boiling point. The kinetics of evaporation is dictated by the rate of heat transport to the droplets, in contrast with the evaporation in a relatively cool gaseous medium, which was studied at the end of the preceding section, when the kinetics was governed by the rate of vapour removal away from the surface of a droplet. Such a process constitutes in essence the evaporative cooling of gases and is rather popular in power engineering.

An empirical expression of the rate of evaporation of a single droplet results in [14]

$$\frac{\mathrm{d}r}{\mathrm{d}t} = w = -\left(\frac{\langle r_0 \rangle}{r}\right)^m \frac{k}{\rho L}(T - T_s) \qquad (35)$$

where k now plays the role of a constant heat exchange coefficient and m is a constant factor. The mass balance equation of the type of either equation (29) or (33) has to be replaced by that for the heat balance:

$$c_p \frac{\mathrm{d}T}{\mathrm{d}t} = \mu L \frac{\mathrm{d}y}{\mathrm{d}t} \quad c_p = c_g + \mu(1-y)c_v \qquad (36)$$

where μ is the ratio of an initial mass of the droplets to the mass of gas, c_p is the isobaric heat capacity of the gas–vapour mixture expressed in terms of the specific heat capacities c_g and c_v of the gas and vapour, respectively, and y is understood to be the degree of evaporation in compliance with equation (27). Equation (36) establishes the fact that heat delivered to the droplets from the mixture is spent entirely on evaporation. The saturation temperature T_s is assumed constant under the condition of constant pressure.

Now, the self-similar distribution density is of the form

$$f(t;r) = F(t)R(r) \quad F(t) = y(t)$$

$$R(r) = n_0(m+1)sr^m \exp(-sr^{m+1})$$

$$s = \left[\Gamma\left(\frac{m+2}{m+1}\right)\right]^{m+1} (\langle r_0 \rangle)^{-(m+1)} \qquad (37)$$

where $\Gamma(x)$ denotes the Eulerian gamma-function, and $F(t)$ satisfies the equation

$$\frac{\mathrm{d}F}{\mathrm{d}t} + \lambda \vartheta F = 0 \quad \vartheta = T - T_s \lambda = \frac{(m+1)(\langle r_0 \rangle)^m k}{\rho L} s. \qquad (38)$$

In the particular cases when $m = 1$ and $m = 0$, we get, from equation (37), formulae (18) and (30).

Equation (36) yields

$$\vartheta(y) = \vartheta_0 - \frac{L}{c_v} \ln \frac{c_p(y)}{c_g} \quad \vartheta_0 = T_0 - T_s \qquad (39)$$

and, next, it follows from equations (38) and (39) that

$$\frac{\mathrm{d}y}{\mathrm{d}t} + \lambda \left[\vartheta_0 - \frac{L}{c_v} \ln \frac{c_p(y)}{c_g}\right] y = 0. \qquad (40)$$

By expanding the second term in this equation into the Taylor series and by retaining only the terms up to the second order inclusive, we derive a new equation instead of equation (40):

$$\frac{\mathrm{d}y}{\mathrm{d}t} + ay + by^2 = 0 \quad a = \lambda(\vartheta_0 - \vartheta^*)$$

$$b = \lambda \vartheta^* \quad \vartheta^* = \frac{\mu L}{c_g}. \qquad (41)$$

The solution of equation (41) under the initial condition $y(0) = 1$ is written in the form of equation (17). When a and b are identified by equations (41),

$$y = \frac{\vartheta_0 - \vartheta^*}{\vartheta_0 \exp[\lambda(\vartheta_0 - \vartheta^*)t] - \vartheta^*}. \qquad (42)$$

Hence, for $t \gg [\lambda(\vartheta_0 - \vartheta^*)]^{-1}$, $\vartheta_0 > \vartheta^*$, we get

$$y = (1 - \vartheta^*/\vartheta_0) \exp[-\lambda(\vartheta_0 - \vartheta^*)t]. \qquad (43)$$

When $\vartheta_0 < \vartheta^*$, some droplets remain intact after the equilibrium state of the mixture is reached. That is determined as

$$y_\infty = 1 - \vartheta_0/\vartheta^*. \qquad (44)$$

In the special case when $\vartheta_0 = \vartheta^*$ this state is attained in an asymptotic way, and formula (43) must be replaced by

$$y = (1 + \lambda \vartheta_0 t)^{-1}. \qquad (45)$$

The use of $y(t)$ from equation (42) in equation (36) leads to the equation

$$\vartheta \frac{\mathrm{d}^2 \vartheta}{\mathrm{d}t^2} - \left(\frac{\mathrm{d}\vartheta}{\mathrm{d}t}\right)^2 + \lambda \vartheta^2 \frac{\mathrm{d}\vartheta}{\mathrm{d}t} = 0 \quad \vartheta(0) = \vartheta_0 \qquad (46)$$

the relevant solution of which to describe the temperature evolution during the processes of evaporative cooling is expressed as [14]

$$\vartheta(t) = \vartheta_0(1 - \vartheta^*/\vartheta_0) \{1 - (\vartheta^*/\vartheta_0)$$

$$\times \exp[-\lambda(\vartheta_0 - \vartheta^*)t]\}^{-1}. \qquad (47)$$

Figure 3 shows a rather good agreement of the above theoretical results with the experimental data of Dean et al. [15].

3.3. Combustion of a liquid dispersed fuel

The combustion processes of polydisperse propellants rather predominate in various furnaces and other devices of different origin and design. The kinetics of these processes is governed by the rate of
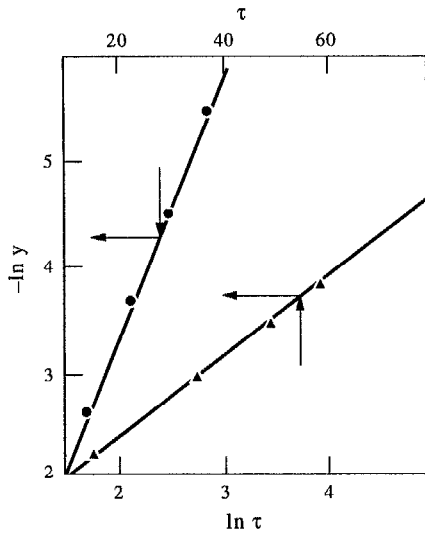
Fig. 3. Kinetics of evaporation of water droplets in hot air in accordance with equation (43) and experimental data of ref. [15] (dots); $\tau = \lambda(\vartheta_o - \vartheta^*)t$.

burning of a single particle, which happens to be strongly dependent on the very nature of the actual combustion regime. The most common type of such regimes includes, as far as the droplets of a liquid fuel are concerned, preliminary evaporation of the liquid from the droplet surfaces and a subsequent exothermal reaction between the vapour and an oxidant in the gaseous phase. The combustion kinetics is usually diffusionally controlled by transport of one of the reagents. Below we consider the evolution of the droplet system by following the model of ref. [16], under the conditions that the consumption of the reagents strictly correspond to the reaction stoichiometry, that there is neither coagulation nor disintegration of droplets, which are maintained at the liquid boiling point temperature, and the mass concentration of the dispersed phase is low. These assumptions are often met in practice. The combustion rate of a single droplet in the diffusional type of regime is given by the relation [16]

$$\frac{dr}{dt} = -M(t)N(r) \quad M(t) = k + \beta \ln \frac{Q}{q}$$

$$N(r) = \frac{1}{r} \quad Q = q + (c_{vf} - c_g)\Delta$$

$$q = q_R - L - c_v(T_f - T_b)$$

$$\Delta = \vartheta_o - \vartheta \quad \vartheta = T_f - T_g$$

$$k = \frac{\lambda}{c_{vf} - c_g} \ln\left[1 + \frac{c_v}{L}(T_f - T_g)\right]$$

$$\beta = \frac{\lambda_f}{\rho(c_{vf} - c_g)}. \tag{48}$$

Here λ and λ_f are the gas heat conductivities in front of and behind the reaction front, respectively, c_v, c_{vf} and c_g denote the heat capacities of the vapor ahead

of and beyond the front, and of an inert component of the gaseous mixture, and T_f, T_g and T_b are the front temperature, the gas mixture temperature beyond the combustion zone, and the liquid fuel boiling point.

The equation of the heat balance law per unit gas mass is

$$c_P \frac{d\vartheta}{dt} = \mu Q \frac{dy}{dt} \quad y(0) = 1$$

$$\vartheta(0) = \vartheta_o \quad c_p = c_g + \mu(1 - y)c_{pf} \tag{49}$$

where c_g and c_{pf} are the specific heat capacities of the gas and the reaction products, respectively, and both y and μ have their former meaning.

The population density is now expressible in a form similar to equation (18), that is,

$$f(t; r) = F(t) R(r) \quad F(t) = y(t)$$

$$R(r) = 2n_o sr \exp(-sr^2) \quad s = \pi/4\langle r_o \rangle^2 \tag{50}$$

and the equation for $F(t)$ reads

$$\frac{dF}{dt} + 2sM(t)F = 0 \tag{51}$$

$M(t)$ being identified as in equation (48). If T_f and T_b are supposed to be constant, then, by accounting for the above expressions of Q and c_p, we obtain from equation (49)

$$\frac{Q}{q} = \left(\frac{c_p}{c_g}\right)^\kappa \quad \kappa = \frac{c_{vf} - c_g}{c_{pf}}. \tag{52}$$

Therefore equation (51) becomes

$$\frac{dy}{dt} + 2sky + 2s\beta\kappa\left(\ln\frac{c_p}{c_g}\right)y = 0. \tag{53}$$

Equation (53) is strongly non-linear because of the dependence of c_p on y. A considerable simplification can be gained by treating the linear version of the heat balance equation instead of equation (49). This amounts to dropping the term with y from the definition of c_p in equation (49) and substituting q for Q, which means ignoring the heating of the gas at the reaction front compared to the thermal effect of the reaction. Equation (49) then reduces to

$$c_P \frac{d\vartheta}{dt} = q\frac{dy}{dt} \quad y(0) + 1 \quad \vartheta(0) = \vartheta_o \quad c_p = \text{constant} \tag{54}$$

so that

$$\vartheta_o - \vartheta = \vartheta^*(1 - y) \quad \vartheta^* = \mu q/c_p. \tag{55}$$

The final equation to be obtained for y takes the same form as that in equation (16). Its solution is

$$y = \frac{a}{k\exp(at) + b} \quad a = 2sk - b \quad b = -2s\frac{\mu\lambda_f}{\rho c_p}. \tag{56}$$

This has to be supplemented with an expression for the transient gas temperature:
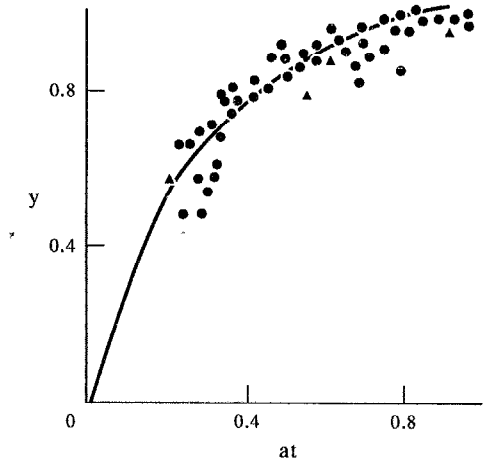
Fig. 4. Kinetics of combustion of a spray of liquid fuel according to equation (56); dots, experiments of ref. [17].

$$T_g \doteq T_{go} + \vartheta^*\{1 - a[k \exp{(at)} + b]^{-1}\}. \tag{57}$$

Comparison of the theoretical prediction with experiments in ref. [17] is demonstrated in Fig. 4. In view of natural difficulties encountered when measuring the properties of burning liquid droplets, the agreement seems satisfactory.

3.4. Combustion of a solid dispersed fuel

Combustion of solid particles usually differs from that of droplets by a more complex mechanism of single-particle conversion. An attempt to address the problem for a carbon-bearing breeze on the basis of the above reasoning has been undertaken in ref. [18]. The combustion rate for one particle is determined by [19]

$$\frac{dr}{dt} = -\frac{\gamma c}{\rho} \frac{1}{k^{-1} + \alpha^{-1}}$$

$$k = k_o \exp\left(-\frac{E}{RT_s}\right) \quad \alpha = \frac{D}{2r} Nu. \tag{58}$$

Here γ is the ratio of the mass of gasified carbon to that of spent oxygen, ρ is the particle density, and the carbon concentration and diffusivity in the gaseous phase are described by

$$D = D_o\left(\frac{T_g}{273}\right)^2 \quad c = c_o\left(\frac{273}{T_g}\right) \tag{59}$$

T_s and T_g standing for the absolute particle and gas temperatures, respectively.

Diffusionally and kinetically controlled combustion regimes must be distinguished, depending on which term in the denominator of the first expression in set (58) dominates. In both cases, this expression corresponds to the concept of combustion proceeding to completion through one primary reaction which transforms carbon directly to carbon dioxide. This is well confirmed by experiments [19].

If the diffusional regime is affected, which is commonly the case for large coal particles, k^{-1} in equation (58) may be ignored and the Nusselt number

$$Nu = 2 + Kr^m \approx Kr^m. \tag{60}$$

The functions involved in the general representation (2) of $w = dr/dt$ are then as follows:

$$M(t) = \frac{\gamma c}{\rho} \frac{KD}{2} \quad N(r) = \frac{1}{r^{1-m}}. \tag{61}$$

As before, the heat balance equation is given by equation (49), save for the fact that now c_{pf} means the specific heat capacity of the reaction products mixed with the remaining oxygen. A linear equation of type (55) can again be obtained. It reads

$$\vartheta = T_g - T_{go} = \vartheta^*(1-y) \quad \vartheta^* = \mu q_R/c_g \tag{62}$$

y being defined by equation (27).

In this case,

$$f(t;r) = F(t) R(r) \quad F(t) = y(t)$$

$$R(r) = (2-m)sr^{1-m} \exp{(-sr^{2-m})}$$

$$s = \left[\Gamma\left(\frac{3-m}{2-m}\right)\right]^{2-m} \langle r_o \rangle^{-(m-2)} \tag{63}$$

and $F(t)$ satisfies the equation

$$\frac{dF}{dt} + (2-m)sMF = 0. \tag{64}$$

By using equation (62) and the oxygen mass balance equation which can be presented as

$$\gamma c_o = y c_{so} \tag{65}$$

where c_o is the oxygen concentration at $T_g = 273$ K and c_{so} is the initial fuel concentration, we are able to transform $M(t)$ in equation (61) and also get an equation for $y(t)$. It would be of the form of equation (16) except for both coefficients, a and b, being linearly dependent on y. Thus, the equation is

$$\frac{dy}{dt} + \frac{T_{go} + \vartheta^*}{273\tau} y^2 - \frac{\vartheta^*}{273\tau} y^3 = 0$$

$$\frac{1}{\tau} = \frac{(2-m)sKc_{so}D_o}{2\rho} \quad y(0) = 1. \tag{66}$$

Its solution can be written in an implicit form as

$$t = \frac{273\tau}{T_{go} + \vartheta^*}\left[\frac{\vartheta^*}{T_{go} + \vartheta^*}\ln\left(\frac{T_{go} + \vartheta^*}{T_{go}}\frac{1-y}{y}\right) - \frac{1-y}{y}\right]. \tag{67}$$

The results of the correlation of the experimental data in refs. [20, 21] by formula (67) are presented in Fig. 5. Again, the correspondence between the theory and experiments appears to be not bad.

A special case is provided by diffusionally controlled combustion at a small Peclet number for one particle. Equation (60) must then be replaced by $Nu \approx 2$ and equations (66) and (67) can both be
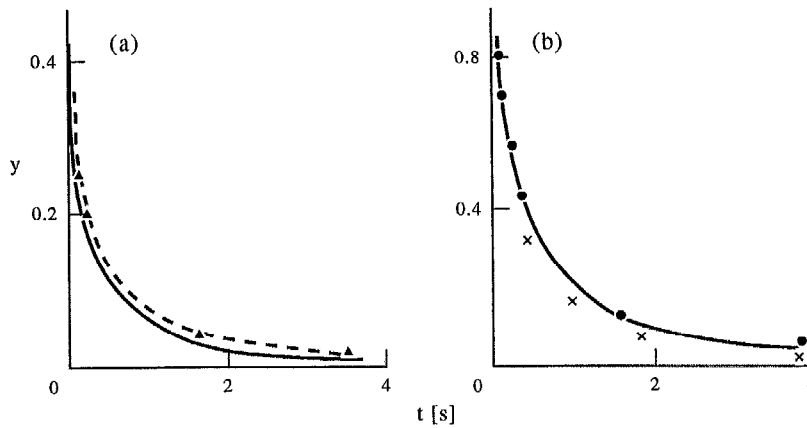
Fig. 5. Kinetics of anthracite breeze combustion in accordance with equation (67) and experimental data of refs. [20] (a) and [21] (b); different dots correspond to experiments with different values of the air excess coefficients; dashed line, numerical calculation by means of dividing the breeze into several separate fractions.

shown to hold true if the expression of τ^{-1} in equation (66) is changed to

$$\frac{1}{\tau} = \frac{2sc_{so}D_o}{\rho}.\tag{68}$$

If the kinetic regime is established, we get $M(t) = \gamma ck/\rho$ and $N(r) = 1$ instead of equation (61). The population density is again given by the simplest expression (30) and the equation for $F(t)$ becomes $dF/dt + sMF = 0$. However, M happens to depend on y in a strongly non-linear manner, and a numerical solution is needed in a general case. Without going into particulars, we point out that the kinetic regime has also been studied advantageously in ref. [18] and an agreement with the experiments of ref. [20] has been found.

3.5 Other problems

In the remainder of this paper we address ourselves to the evolution processes in which the particle population distribution over a certain parameter other than the particle radius is relevant.

Among such processes, the first and most evident one concerns the drying of an almost monodisperse system of particulate solids, the particles being distinguished by their content ξ. The density $f(t;\xi)$ of the distribution over ξ is again governed by equation (1), and the rate (2) of changing ξ under invariable conditions is commonly independent of time, $M(t) = 1$. A general expression

$$f(t;\xi) = S\{\exp(-st) R(\xi;s)\}\tag{69}$$

of the type of equation (5) happens to be valid, and the function $R(\xi;s)$ is determined by the form of $N(\xi)$ in equation (2).

A simple power law may often be used to describe empirically the drying of a single particle [7]:

$$d\xi/dt = w = -\eta\xi^m\tag{70}$$

m and η being constant parameters. Then,

$$R(\xi;s) = \frac{C_s}{\eta\xi^m}\exp\left[-\frac{s}{\eta(1-m)}\xi^{1-m}\right].\tag{71}$$

Another representation for the drying rate follows from the model of ref. [22], according to which a particle is divided into two regions: a central core is fully saturated with water, whereas a peripheral region is completely dry. In this case,

$$\frac{d\xi}{dt} = w = -\frac{\eta\xi^{1/3}}{\xi_m^{1/3} - \xi^{1/3}}\tag{72}$$

where ξ_m is the maximal moisture content when a particle is saturated entirely. Then,

$$R(\xi;s) = C_s\left(\frac{1-\xi_m^{1/3}}{\xi_m^{1/3}}\right)$$

$$\times \exp\left\{-\frac{s\xi_m}{\eta}\left[\frac{3}{2}\left(\frac{\xi_m}{\xi}\right)^{1/3} - 1\right]\right\}.\tag{73}$$

The relative mass of remaining moisture is to be found from the relations

$$y(t) = \left[\int_0^{\xi_m}\xi f_o(\xi)\,d\xi\right]^{-1}\int_0^{\xi_m}\xi f(t;\xi)\,d\xi$$

$$= S\{\exp(-st) B(s)\}$$

$$B(s) = \left[S\left\{\int_0^{\xi_m}\xi R(\xi;s)\,d\xi\right\}\right]^{-1}\int_0^{\xi_m}\xi R(\xi;s)\,d\xi.\tag{74}$$

The number of particles that become dry at a certain moment can be determined in a similar way. A calculation along the above scheme can be carried out in a quite straightforward manner, but the real problem is merely to approximate the initial distribution density with the help of a series or integral in equality (69) at $t = 0$, that is, to find proper coefficients C_s at $R(\xi;s)$ from either equation (71) or (73). This scheme can be shown to describe drying processes with a

sufficient accuracy without the necessity of making use of complicated numerical methods of calculation.

The second example discussed pertains to the process of the reduction of particles of dispersed oxide suspended in a flow of hydrogen, carbon monoxide or another reducing gas. This problem has been treated in ref. [23]. Transformation of a single particle can be characterized with the help of the empirical relation

$$\frac{d\xi}{dt} = w = -\frac{K_r}{\varphi}\frac{G_h}{G_p} \tag{75}$$

where G_h and G_p are the flow rates of hydrogen and the particles at the input of a co-current gas reactor, respectively, and K_r is a specific constant reduction factor. The distribution parameter $\xi = r$ is now the radius of the particle core that remains unreduced at moment t and $\varphi = 1 - y$ plays the role of the overall degree of reduction, y being formally defined by equation (27).

It is easy to derive an equation that governs φ in the form

$$d\varphi/dt - sw(1 - \varphi) = 0 \quad \varphi(0) = 1. \tag{76}$$

This equation yields a very simple solution:

$$\varphi + \ln(1 - \varphi) = -\lambda t \quad \lambda = K_r s(G_h/G_p). \tag{77}$$

A significant feature of this formula, which defines φ as an implicit function of time, is that it does not involve a value of s chosen to characterize the initial population density. This means that equations (77) can be applied to describe the final stage of the reduction process under quite a variety of conditions and practically irrespective of the original properties of the population.

The validity of equations (77) has been confirmed by a great deal of both laboratory and industrial experiments. By way of example, in Fig. 6 theoretical curves of t are presented as functions of G_h/G_p at different φ for iron oxides of two iron ore deposits [23]. The agreement of the developed theory with these

experiments seems to be satisfactory enough to recommend equations (77) for practical usage.

4. DISCUSSION

The primary general conclusion that follows from the presented treatment of diverse processes of time evolution of various particulate assemblages under different circumstances is the assertion that commonly there is no need to turn to difficult refined methods of theoretical and numerical study in order to foresee changes in the pertinent properties of the assemblages and processes with a lapse of time. Such properties can be well predicted by comparatively simple analytical means without recourse to tedious numerical calculation. Moreover, a self-similar approximation of the particle distribution density works well during the final stage of the assemblage evolution whether or not the initial density is self-similar from the very beginning. A wide variety of examples show that the last stage constitutes the main part of the total evolution period. A serious advantage of the proposed approach lies in the straightforward possibility of getting corrections to results of the self-similar analysis by way of introducing a few self-similar terms instead of one when correlating the initial distribution.

In conclusion, let us enumerate the limitations inherent in the developed calculation scheme. The most prominent consequences are the assumptions concerning the absence of both external and internal sources and sinks of particles, and the insignificance of an intrinsic scatter of the transformation rate for identical particles caused by random reasons, thus permitting the diffusional term to be dropped from the kinetic equation (1). It would certainly seem promising to try to extend the scheme in such a way as to allow for all of the mentioned effects. This is not a simple matter to do, but some progress can be attained by supplementing the above method with new recently suggested ideas which are relevant when taking into
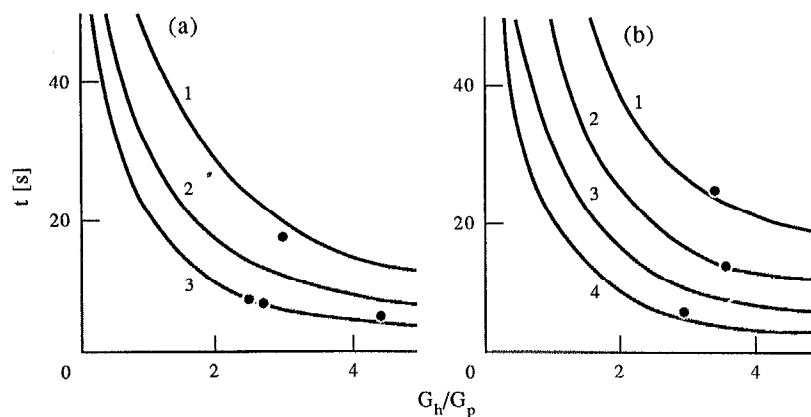

Fig. 6. Correlations between reduction time and ratio of hydrogen flow rate to that of particles at various φ for iron ore particles from deposit in Kachkanar at $T = 880°C$ (a) and from deposit in Kremenchug at $T = 680°C$ (b); 1–4, $\varphi = 0.8, 0.7, 0.6$ and 0.5, respectively; dots, data of ref. [23].

account the natural origination of particle nuclei in metastable surroundings [24], with a due regard for the existence of an external supply, and the effect of the withdrawal of the transformation of a single particle upon the particle distribution over size or another parameter [25, 26].

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