

## EFFECT OF PARTICLE SIZE DISTRIBUTION ON THE KINETICS OF SOLID PHASE-GAS REACTIONS

J. SKŘIVÁNEK and J. ŠUBRT

*Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, 250 68 Prague - Řež*

Received March 20th, 1974

The effect of the particle size distribution in a polydisperse system on the kinetics of the solid phase reactions, in which the course of reaction of single particles may be described by the Jander or Ginstling-Broinštejn equation, was solved numerically. The distribution of particle size influences the course of reaction of the polydisperse system so that this course crosses the curve of reaction course of the monodisperse system and consequently it is not possible to find any average particle diameter whose use would enable one to describe the behaviour of the polydisperse system by using the equations valid for the monodisperse one.

The reaction of a gaseous component with a solid phase in a porous spherical particle is described by the partial differential equation (1) with corresponding initial and boundary conditions:

$$\frac{\partial c}{\partial t} = \frac{1}{R^2} \cdot \frac{\partial}{\partial R} \left( DR^2 \frac{\partial c}{\partial R} \right) + \varphi(c). \quad (1)$$

In general it is necessary to solve this equation numerically. Therefore simplified equations are used for the description of heterogeneous reactions which are derived by solving this equation under simplifying conditions, as for instance the Jander<sup>1</sup> equation (Eq. (2)), the Ginstling-Broinštejn<sup>2</sup> equation (Eq. (3)), and others like those:

$$1 - 2/3x - (1 - x)^{2/3} = (k/r^2) t, \quad (2)$$

$$[1 - (1 - x)^{1/3}]^2 = (k/r^2) t. \quad (3)$$

The equations were derived to describe the reactions of spherical particles of diameter  $r$  in which a change of particle density does not occur in the course of reaction. In practice, however, these and similar equations are often used successfully even for the description of reactions of real polydisperse systems.

Assuming the validity of some of these equations for the description of reaction course of one particle, Eq. (4) holds for the real polydisperse system at any moment

of reaction:

$$\bar{x}_t = \int_0^\infty x_t f(r) dr / \int_0^\infty f(r) dr, \quad (4)$$

where  $f(r)$  is the probability density of the occurrence of particles with diameter  $r$  in the given polydisperse system and  $\bar{x}_t$  is conversion of the polydisperse system at a time  $t$ .

Considering that it is possible to calculate from Eqs (2) or (3) the conversion of particles with given  $r$  for each moment of reaction and a certain particle diameter then, if we know the distribution curve of particle diameters in the given system, it is also possible to calculate from Eq. (4) the conversion of the system ( $\bar{x}_t$ ) at each moment of reaction on the assumption that the particle size does not change in the course of reaction.

It is evident from the said that the shape of distribution curve will influence the value of  $\bar{x}_t$ .

The distribution curve of polydisperse systems can be very often approximated by a function of the type

$$f(r) = (r^n/n!) \exp(-r). \quad (5)$$

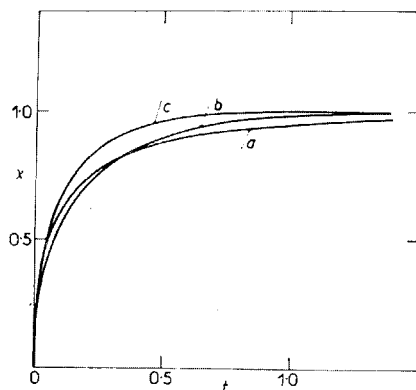


FIG. 1

Comparison of the Course of Reaction Solid Phase-Gas in Polydisperse and Monodisperse System Whose Single Particles React according to Eq. (2)

**a** Reaction course in polydisperse system with distribution parameter  $n = 3$ ; **b** reaction course in monodisperse system plotted through the curve **a** so that the quantity  $\beta$  should be minimum in the range of  $x$  (0–1); **c** reaction course in monodisperse system plotted through the curve **a** so that the quantity  $\beta$  should be minimum in the range of  $x$  (0–0.5).

This function conforms to the conditions of probability density, *i.e.*

$$\int_0^{\infty} f(r) dr = 1; \quad r \rightarrow 0, \quad f(r) \rightarrow 0; \quad r \rightarrow \infty, \quad f(r) \rightarrow 0. \quad (6)-(8)$$

The calculation can be further simplified by introducing a new variable  $\xi$  defined by the equation

$$r = n\xi. \quad (9)$$

The distribution curve of particle diameters takes then the form of Eq. (10):

$$f(\xi) = [(n\xi)^n/n!] \exp(-n\xi). \quad (10)$$

The average particle diameter  $\bar{r}$  and the standard deviation  $\sigma$  of this distribution are defined by Eqs (11)–(13):

$$\bar{r} = \left( \int_0^{\infty} rf(\xi) d\xi \right) / \int_0^{\infty} f(\xi) d\xi, \quad (11)$$

$$\bar{r} = [1 + (1/n)] r_{\max}, \quad (12)$$

$$\sigma = (1/n)^{1/2}. \quad (13)$$

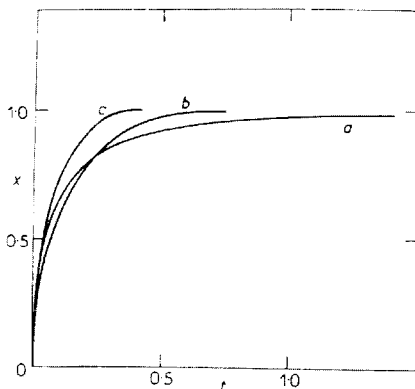


FIG. 2

Comparison of the Course of Reaction Solid Phase-Gas in Polydisperse and Monodisperse System Whose Single Particles React according to Eq. (3)

**a** Reaction course in polydisperse system with distribution parameter  $n = 3$ ; **b** reaction course in monodisperse system plotted through the curve **a** so that the quantity  $\beta$  should be minimum in the range of  $x$  (0–1); **c** reaction course in monodisperse system plotted through the curve **a** so that the quantity  $\beta$  should be minimum in the range of  $x$  (0–0.5).

To evaluate quantitatively the difference of reaction course in various systems we use the quantity  $\beta$  defined by the integral

$$\beta = \int_0^{\infty} (x_a - x_b)^2 dt . \quad (14)$$

In Figs 1 and 2 the courses of time dependence of conversion, as obtained by numerical integration of Eq. (4) on a computer Gier, in the polydisperse system (the curve *a*)

TABLE I  
Differences in Conversion of Monodisperse and Polydisperse System  
Kinetics of Reaction Is Controlled by Eq. (3).

Parameter <i>n</i> of Eq. (10)	$\sigma$	Conversion of system	
		polydisperse	monodisperse
2	0.7071	0.40	0.422
		0.80	0.914
3	0.5770	0.40	0.420
		0.80	0.898
4	0.5000	0.40	0.408
		0.80	0.884
25	0.2000	0.40	0.403
		0.80	0.812
36	0.1670	0.40	0.401
		0.80	0.808

TABLE II  
Comparison of Reaction Course in Monodisperse and Polydisperse Systems

Parameter <i>n</i> of Eq. (10)	Controlling Eq. of system		Value of quantity $\beta$	Radius of monodisperse system
	monodisperse	polydisperse		
3	(2)	(2)	$1.6020 \cdot 10^{-3}$	1.329
3	(3)	(3)	$1.3179 \cdot 10^{-3}$	1.307
3	(3)	(2)	$4.1928 \cdot 10^{-4}$	1.126
36	(3)	(3)	$2.0973 \cdot 10^{-5}$	1.027

are plotted in which single particles react according to Eq. (2) or (3). As the distribution function of particle size we used the dependence defined by Eq. (10) with parameter  $n = 3$ . When comparing this course with that of the monodisperse system reaction (the curves *b* and *c* in Figs 1 and 2) which conforms to the same equations, we see that if we had the possibility to observe the reaction course in the entire range of  $x$  (0–1), then it would not be possible to find any value of particle size  $\bar{r}$  of the monodisperse system for which the reaction course of polydisperse system would be represented with a sufficient accuracy. We can see in these figures that the curve expressing the dependence of the reaction of polydisperse system intersects the courses of curves which describe the reaction of monodisperse system. With monodisperse systems the conversion  $x = 1$  is reached in a finite time whereas in polydisperse system where the size particle distribution complies with Eq. (10), this conversion cannot be reached in a finite time because the probability of occurrence of however large particle is always larger than 0. It is also obvious from the figures that if we investigate the reaction only in a limited range of  $x$ , as it is often done in practice, then in this limited interval it is possible to find such a diameter of particles of monodisperse system that the deviations of these courses are smaller than the experimental error (curves *a* and *c* in Figs 1 and 2). For instance, when investigating the reaction course of the monodisperse and the polydisperse systems within the range of conversion 0–0.5, the mean deviations of the course of polydisperse and monodisperse system which conform to the same kinetic equation are lower than 1%.

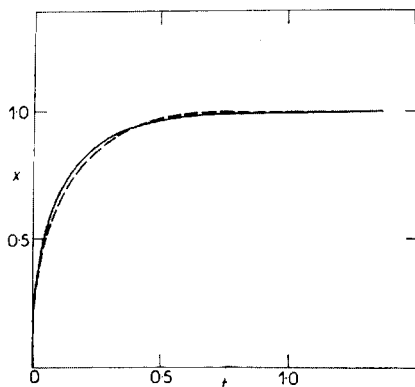


FIG. 3

Comparison of the Course of Reaction Solid Phase-Gas in Polydisperse and Monodisperse System Whose Single Particles React according to Eq. (3)

----- Course of reaction in monodisperse system compared with that in polydisperse system so that the quantity  $\beta$  should be minimum in the range of  $x$  (0–1); ——— course of reaction in polydisperse system with distribution parameter  $n = 36$ .

The differences in the reaction course of the solid phase in the polydisperse and monodisperse systems decrease of course with decreasing standard deviation of distribution function. It is evident from Fig. 3 that for the value of distribution parameter  $n = 36$  ( $\sigma = 1/6$ ) these courses practically coincide.

The differences in the reached conversion as a function of the distribution parameter  $n$  at conversions of polydisperse system 0.4 and 0.8 are presented in Table I. The course for the monodisperse system is obtained so that the value  $\beta$  should be minimum in the range of conversion 0–0.5. For the kinetics of single particles the controlling equation is Eq. (3).

The investigation of the value of quantity  $\beta$ , which characterizes the degree of deviation of courses of reactions studied, leads as well to interesting conclusions. The curve  $b$  in Fig. 1 expresses the course of reaction in monodisperse system which conforms to Eq. (2) and in addition the particle size is chosen so that the value of  $\beta$  should be minimum when comparing this curve with the reaction course in the polydisperse system in which the course of reaction of single particles conforms to the same equation (the curve  $a$ ). By using the same method, the curve  $b$  in Fig. 2 was also calculated, where the Jander equation is the controlling kinetic equation. The values are given in Table II.

In this table the value of the quantity  $\beta$  is given, too, obtained so that the curve representing the reaction course in the monodisperse system, which conforms to Eq. (2), was plotted through the curve of reaction course of polydisperse system which conforms to Eq. (1). In this case the radius of particles in this system was chosen so that the value of  $\beta$  should be minimum. It is interesting to note that the quantity  $\beta$  has in this case substantially lower value than when comparing in this way the reaction courses of the polydisperse and monodisperse systems which conform to the same fundamental kinetic equations. A decrease of this quantity is also evident from that table with increasing value of  $n$  (*i.e.* with a decrease in standard deviation of distribution function of particle size).

Accordingly it is evident that it is necessary to consider the distribution of particle size of reacting substance when correlating, by means of Eqs (2) and (3), the experimental data on kinetics of the solid phase heterogeneous reactions in which diffusion is assumed to be the process influencing reaction rate. Neglecting this factor can lead to incorrect results even in the case that we interpret accurate experimental data obtained in a wide range of conversion of solid phase. It is not possible as well to find any average particle diameter of polydisperse system whose use would make it possible to describe the reaction in the system in terms of equations valid for the monodisperse system.

## LIST OF SYMBOLS

$r$	particle diameter of solid phase
$t$	time
$f(r)$	distribution function of particle size of solid phase
$x$	conversion of solid phase
$x_t$	conversion of solid phase at a time $t$
$\bar{x}_t$	conversion of polydisperse system
$n$	parameter of distribution function
$\bar{r}$	average particle diameter
$x_a, x_b$	conversion of compared systems of solid phase
$k$	reaction rate constant
$c$	concentration of reacting component in heterogeneous system
$r_{\max}$	particle radius of maximum rate
$\beta$	integral defined by Eq. (14)
$\varphi(c)$	function describing the chemical reaction rate in system
$\sigma$	standard deviation of distribution
$\zeta$	parameter defined by Eq. (9)

## REFERENCES

1. Ginstling A. M., Broinštejn B. I.: *Ž. Prikl. Chim.* 23, 1942 (1950).
2. Jander W.: *Z. Anorg. Allgem. Chem.* 163, 1 (1937).
3. Sharp J. H., Brindley G. W., Nazahar Achar B. N.: *J. Am. Ceram. Soc.* 49, 379 (1966).

Translated by J. Linek.