DETERMINATION OF NORMALIZED CHARACTERISTIC CURVES OF POLYDISPERSED SOLIDS FROM KINETIC DATA ON THEIR DISSOLUTION

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Kinetic data on the dissolution of polydisperse solids can be used for estimating the granulometric state of a dissolved polydisperse material. From the point of view of the dissolution process, each disperse solid is characterized by its normalized — characteristic equation, which is fully specific for the given type of the granulometric spectrum. If the linear rate of dissolution is constant and independent of the particle size during the dissolution, the normalized — characteristic curve can be determined by finding the corresponding values of the dimensionless decrease in the particle size from the total dissolution time of the polydisperse material.

Values of the total dissolution time cannot be found from experiment; due to this reason, for the total dissolved fraction of 0·9995 they were determined by using a substitutive function of a preliminarily selected shape. The function $1 - F(t) = t \exp[-P(t)]$ was found to approximate best the time course of the dissolution. The course of these normalized — characteristic curves was compared with those obtained from the knowledge of the original granulometric composition and good agreement between the two sets of curves was found.

Investigated normalized — characteristic curves of uranium oxides lie close to each other, which corresponds well with their almost identical granulometric state. The normalized characteristic curves obtained from experimental data on dissolution point to a decrease in the degree of dispersion of the dissolved polydisperse material due to a deagglomeration of the secondary dispersion during the dissolution.

The granulometric analysis is based on the fact that a given granulometric state of a polydispersion can be quite unambiguously assigned to a definite shape of the so called normalized — characteristic curve or equation which describes the relation between the relative decrease in the characteristic size of particles of the polydispersion and the corresponding relative decrease in mass of the dissolved polydispersion.

Proposed methods make it possible to determine the granulometric spectrum in terms of relative sizes of particles of the polydispersion; if the size of the largest particle in the polydispersion or that close to it is known, these methods enable to find the granulometric composition of the polydispersion in terms of the absolute sizes of the particles.

The granulometric analysis was verified on powdered uranium dioxides and kieserite. Chemical nonstoichiometricity of uranium dioxides did not present any difficulties for these methods.

THEORETICAL

The mutual relation between the process of dissolution of a polydisperse material and its granulometric state follows from the fact that the rate of mass decrease of the dissolved solid, $-dm/dt$, is proportional to the magnitude of the liquid — solid interface. On the other hand, the magnitude of the interface is related directly to the granulometric state of the disperse solid.

The basic equation of the heterogeneous kinetics of dissolution assumes in this case the following form[1]:

$$-dm/dt = S(m) \cdot F(\text{sol}) . \qquad (1)$$

The magnitude of the active surface of the solid, $S(m)$, depends generally on its dissolved mass fraction. The function of the composition of the solution, $F(\text{sol})$, may be interpreted as the amount of the solid m, which will be dissolved on unit surface of the solid per unit time t.

An exact solution of the dissolution kinetics of polypisperse solids must be therefore based on their granulometric state. This requires the introduction of a mass distribution function into relations describing the dissolution kinetics. Most often, however, model representations of the dissolution of solids are employed in which a system containing an infinite number of particles of a polydispersion is replaced by a finite number of particles representing in a definite manner the entire polydispersed system of particles[2-4].

In this respect, an idea emerged to perform the complete analysis of the dissolution process in the reverse direction, namely, to try to determine the granulometric state of the dissolved dispersion from the experimental dissolution process and from preliminarily selected assumptions on the dissolution kinetics and geometric shape of dissolved particles. Similarly as in all other methods of granulometric analysis, a definite shape of dissolved particles is assumed also here.

Supposing that: *1*) isometric particles are being dissolved whose initial characteristic dimension is $x(0)$ and whose shape does not change during the dissolution, *2*) the content of the dissolved material in particles is constant, homogeneous and independent of their dimension $x(0)$ and the dissolved mass fraction and *3*) the linear rate of dissolution, v, is identical at all points of the particle surface, we may define a normalized — characteristic equation which relates two dimensionless quantities to one another — the dissolved mass fraction of the polydispersion, $F(\tau)$, and the relative decrease in the characteristic particle size. Parameters in this equation

and/or the shape of this curve are fully defined by the granulometric state, namely by the mass distribution curve of polydispersed particles $m[x(0)]$.

If the linear rate of dissolution is constant during the dissolution and the dissolved mass fraction is expressed as a function of time t, the normalized − characteristic equation assumes the form of[4]

$$F(t) = 1 - \int_{2vt}^{\infty} \left(1 - \frac{2vt}{x(0)}\right)^3 m[x(0)] \, \mathrm{d}x(0) \qquad (2)$$

or, if the linear rate of dissolution is not constant,

$$F(t) = 1 - \int_{(x)t}^{\infty} \left(1 - \frac{x(t)}{x(0)}\right)^3 m[x(0)] \, \mathrm{d}x(0) \qquad (3)$$

with

$$x(t) = \int_0^t 2v(t) \, \mathrm{d}t \ .$$

Both these equations may be expressed[5] through the dimensionless particle age τ defined as the relative change in the characteristic particle size $x(t)$ (dimension in which the particle disappears earliest) with respect to the initial particle size $x(0)$

$$\tau = [x(0) - x(t)]/x(0)$$

Eqs (2) and (3) can be then rewritten as

$$F(\tau) = 1 - \int_{\tau x_{m}(0)}^{x_{m}(0)} \left(1 - \frac{x_{m}(0)}{x(0)} \tau\right)^3 m[x(0)] \, \mathrm{d}x(0) \qquad (4)$$

and

$$F(\tau) = 1 - \int_{\tau(t)x_{m}(0)}^{x_{m}(0)} \left(1 - \frac{x_{m}(0)}{x(0)} \tau(t)\right)^3 m[x(0)] \, \mathrm{d}x(0) , \qquad (5)$$

where x_m is the characteristic size of the largest particle in the polydispersion.

The equations may be applied to dispersions composed of isometric particles. This conditions is satisfied by most finely dispersed powdered materials. If the shape of dispersed particles cannot be approximated by an isometric particle, analogous relations may be derived *e.g.* for laminar or fibrilar dispersed particles.

The derivation of these relations is based on the fact that relative changes of one (fibrilar dispersed particles) or two (laminar dispersed particles) dimensions of such particles are negligible during dissolution (the dimension is taken to be constant

during dissolution)[5]. The normalized-characteristic dissolution curve of particles for which relative changes in one dimension are negligible, possesses then the form of

$$F(\tau) = 1 - \int_{\tau x_m(0)}^{x_m(0)} \left(1 - \frac{x_m(0)}{x(0)} \tau \right)^2 m[x(0)] \, dx(0) \tag{6}$$

or, in the case of particles for which relative changes of two dimensions are negligible

$$F(\tau) = 1 - \int_{\tau x_m(0)}^{x_m(0)} \left(1 - \frac{x_m(0)}{x(0)} \tau \right) m[x(0)] \, dx(0) \tag{7}$$

The choice of the form of the normalized-characteristic equation, *i.e.* the determination of the shape of dissolved particles and an appropriate approximation of their shape by a corresponding particle may be performed best by microscopic analysis on an optical or electron microscope. If the mass distribution functions of particles and of the dissolved component are not identical, the former must be replaced in the above equations by the distribution function of the dissolved component $m_A[x(0)]$. According to the definition, all these equations contain implicitly the mass distribution function $m[x(0)]$ of particles with respect to their characteristic size (it is the dimension in which the particle disappears earliest during the dissolution). This normalized − characteristic curve may be then employed for determining the granulometric state of the dispersion provided that it can be found experimentally from the dissolution process.

Thus, Akselrud[3] differentiated the shape of normalized − characteristic curves of dissolved dispersions with respect to a quantity α which, to the detriment of generality, was introduced only for a logarithmic − normal distribution of particle occurrences through the equation

$$\alpha = \bar{x}_v / \sigma , \tag{8}$$

where $\bar{x}_v$ is the weighted mean of particle sizes, σ is the mean degree of dispersity defined by the equation

$$\sigma = \left(\sum_{i=1}^{i=p} n_i (x_i - \bar{x}_v)^2 \right)^{1/2} \cdot \left(\sum_{i=1}^{i=p} n_i \right)^{-1/2} \tag{9}$$

and n_i is the number of dispersed particles with the characteristic size x_i.

Thus, for a monodisperse material we obtain $\alpha = \infty$. Shapes of normalized − characteristic curves for different values of α are given in the cited literature[3]. However, equations similar to (8) and (9) may also be used for determining normalized − characteristic curves of granulometric spectra described by other probability functions (*e.g.* normal distribution, χ-squared, Student's distribution, binomial distribution, *etc*).

F.MELICHAR and L.NEUMANN

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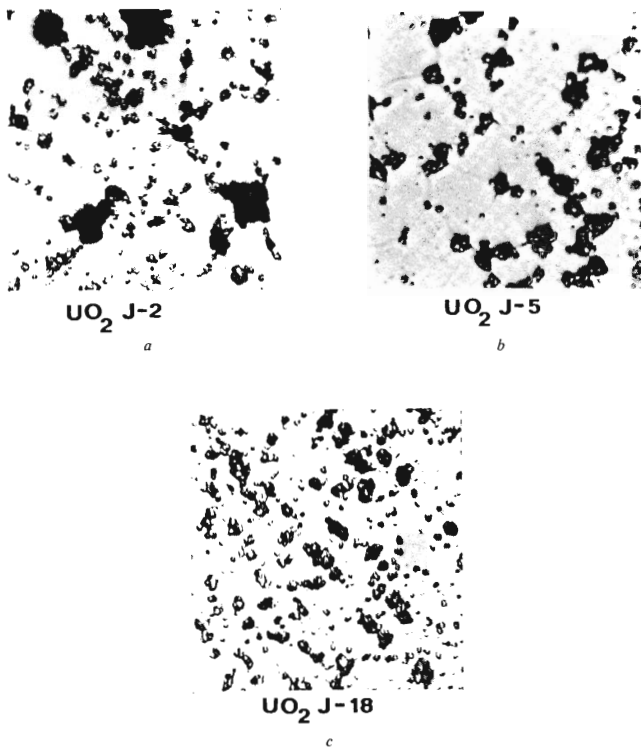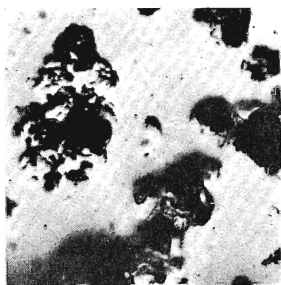

UO$_2$ J-2

a

UO$_2$ J-5

b

UO$_2$ J-18

c

FIG. 1

Microscopical Photographs of Uranium Dioxides from an Optical Microscope, Magnification 800× *a* J-2; *b* J-5; *c* J-18 and from an Electron Microscope; *d* J-2 4500×; *e* J-5 4500×; *f* J-18 1200×

U O₂ J - 2

d

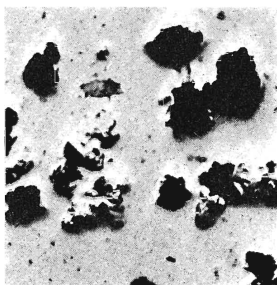**U O₂ J - 5**

e

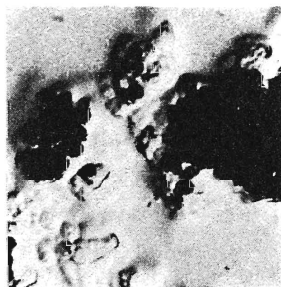**U O₂ J - 18**

f

FIG. 1
(*Continued*)

The determination of the time dependence of the dissolved fraction of the dispersion from the solution of normalized — characteristic equations is extremely difficult. Even the distribution function itself can be expressed only with limited accuracy *e.g.* through the Rosin–Rammler–Sperlinger substitutive function[6]. However, the solution of such an equation presents difficulties as well and according to available literature sources it has been performed only by Steidl[7,8] and several other authors[9]. Except the work by Steidl, these solutions have not been verified experimentally.

In the solution of the dissolution kinetics, the granulometric state of the dispersion is usually expressed in the form of a table or graphically. In this case, a graphical or a numerical solution of the normalized — characteristic equation is employed, which considers the dissolution of a polydispersion composed of a finite number of monodispersions.

Some of the outlined principles were therefore used in our search for the granulometric composition of a dispersion which would be based on kinetic data on its dissolution.

EXPERIMENTAL

Apparatus

The dissolution of uranium dioxide was performed in a 500 ml four-neck flask with rounded bottom. An electrically driven agitating propeller with constant revolutions of 1 300 min^{-1} passed through the middle neck. For measuring the redox potential of the solution, other necks contained a platinum indicating electrode and a conductivity bridge (saturated ammonium sulphate) which connected the system with the reference calomel electrode. The third side neck served for addition of a concentrated solution of potassium permanganate and for withdrawing samples of the dispersion.

In first experiments, the redox potential of the solution was measured by a Wheatstone bridge in the compensating Poggendorf arrangement. In further experiments it was determined by an automatic Radelkis titrator (accuracy $\pm 1\cdot 0$ mV) provided with an automatic sampling of the concentrated potassium permanganate solution for maintaining a fixed value of the redox potential.

The temperature of the leaching flask, in which the dissolution proceeded, was maintained constant by an U 10 thermostat with a $\pm 0\cdot 1°C$ accuracy.

Uranium Dioxide

The dissolution method proposed for determination of the granulometric composition was verified on uranium dioxides which had been prepared preliminarily in a Yugoslavian laboratory from ammonium polyuranate[10] and marked as UO_2 J-2, J-5, J-18. Other three oxides were prepared from uranium dioxide J-2 by oxidation in air at a temperature[4] of 200°C. This thermal treatment was followed by annealing in vacuum (10^{-3} Torr, quartz tube) for 14 days at 390°C to achieve a perfect homogenization from the point of view of the stoichiometric content of oxygen and the formation of the equilibrium lattice, *i.e.* of the one-phase oxide. The stoichiometric composition of dissolved uranium oxides expressed as the ratio O/U, was 2·10 for J-2, 2·08 for J-5, 2·22 for J-18.

Granulometric Analysis

To verify the proposed methods, a granulometric analysis of prepared uranium dioxides was performed by two different methods — microscopically and by sedimentation analysis. The microscopically determined (on a Quantimet apparatus)[11] distribution function of particle occurences in dependence on their size, $n_0(x)$, was recalculated to a cumulative mass distribution function of particles, $M(x)$, according to the relation

$$M(x) = \sum_{i=1}^{i=p} x^3 \, n_0(x) \Big/ \sum_{i=1}^{i=j} x^3 \, n_0(x) , \qquad (10)$$

where $p \in \langle 1, j \rangle$ and j is the total number of granulometric classes.

The granulometric spectrum determined in this manner was described by the Rosin–Rammler– –Sperlinger equation as

$$1 - M(x) = \exp\left[-(x/x')^w\right] , \qquad (11)$$

where x' and w are constants of this equation. The value of the constant x' — the characteristic dimension — is defined by $M(x') = 0.6321$. The main criterion for the choice of this substitutive function was the accuracy of the description of the granulometric composition through the function $M(x)$ in a linear form and an easy determination of constants in this equation.

The sedimentation analysis was performed on a Sartorius sedimentation balance. The cumulative mass distribution function was obtained by the Oden tangent method[12].

Results of both methods of granulometric analysis are given in Table I. Values of constants in the Rosin–Rammler–Sperlinger equation (determined only by the microscopic analysis) are: sample J-2, $x' = 13.2\,\mu m$, $w = 2.9$; J-5, $x' = 12.0\,\mu m$, $w = 2.35$; J-18, $x' = 14.5\,\mu m$, $w = 2.04$. These results confirm the expected high degree of agglomeration of smallest particles in the primary powder. Constants in this equation could not be determined in the case of the sedimentation analysis (nonlinear course)[4]. Resulting agglomerates stick together above all by electrostatic forces. These agglomerates disintegrate considerably in a 1% aqueous solution of the wetting agent (commercial product "JAR"). The size of the largest polydispersion particle found by the microscopic analysis was approximately 17.5 μm. However, the sizes of largest polydispersion particles found by the sedimentation analysis were in the range 12—14 μm.

The granulometric composition of prepared uranium dioxides was identical with that of the basic dioxide because at the given experimental preparation conditions of these dioxides neither sintering of particles nor a casual deagglomeration was observed.

The granulometric analysis of uranium dioxides was supplemented by the determination of the specific surface of dissolved polydispersions by the Nelsen–Eggertsen method[13]. The values of the specific surface are: sample J-2, 1.72 m²/g; J-5, 2.05 m²/g; J-18, 6.52 m²/g. Photographs from optical and electron microscopes (Fig.1*) show that the polydispersed oxides are formed above all by secondary particles — agglomerates or, occasionally, by aggregates of an irregular and articulate shape which, however, may be approximated by regular particles of spherical shape.

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*   See insert facing p. 204.

Methods

Uranium dioxides were dissolved in an aqueous solution of 0·152M sulphuric acid of pH 1·5. Trivalent iron in the form of ammonium iron sulphate was used as oxidant. To obtain the required redox potential, bivalent iron in the form of ammonium iron sulphate was added into the solution in an amount which would make the total concentration of iron(III) and iron(II) constant and equal to 0·0116M in all experiments. The total concentration of sulphate ions was therefore also constant and equal to 0·1752M in all experiments.

To maintain a defined value of the redox potential in the solution during the dissolution, a concentrated solution of potassium permanganate was added into the leaching solution so that changes in the total volume of the liquid phase may not exceed 1·5%. The total volume of the liquid phase at the beginning of the dissolution was 200 ml.

The dissolved amount of uranium dioxide was constant in all experiments and corresponded to 0·5 g of uranium at the oxygen index of 2·000. The range of the redox potential in which the dissolution was being performed was $400-510$ mV and the temperature range was $0-15°C$. Sludge samples, which were being withdrawn during the dissolution at appropriate time intervals,

TABLE I

Results of the Microscopical and Sedimentation Granulometric Analyses of Uranium Dioxide[a]

J-2		J-5		J-18	
Microscopical	sedimentation	microscopical	sedimentation	microscopical	sedimentation
1·3/0·0010	1·9/0·039	1·1/0·0023	1·5/0·0088	0·9/0·0009	1·5/0·0375
1·4/0·0024	2·0/0·0744	1·2/0·0054	1·6/0·0880	1·0/0·0026	1·7/0·1147
1·6/0·0031	2·1/0·1241	1·3/0·0079	1·7/0·1424	1·1/0·0044	1·9/0·1940
2·1/0·0044	2·2/0·2163	1·4/0·0083	1·8/0·1880	1·2/0·0048	2·1/0·2721
2·9/0·0161	2·3/0·2767	1·8/0·0116	2·8/0·2650	1·6/0·0069	2·2/0·3006
2·7/0·0311	2·7/0·4039	2·6/0·0357	2·2/0·2910	2·4/0·0233	3·1/0·3750
4·5/0·0518	2·8/0·4529	3·5/0·0737	2·5/0·3430	3·3/0·0478	3·5/0·3913
5·4/0·0806	3·1/0·4611	4·3/0·1161	3·1/0·3650	4·1/0·0838	3·7/0·4076
6·2/0·1152	3·5/0·4612	5·1/0·1551	3·3/0·3790	4·9/11770·	4·4/0·4239
7·0/0·1704	3·8/0·4965	6·0/0·2010	3·7/0·3930	5·7/0·1610	4·9/0·4266
7·8/0·2199	4·2/0·5210	6·8/0·2593	4·4/0·4430	6·6/0·2052	5·2/0·4484
8·6/0·2741	4·7/0·5781	7·6/0·3331	5·4/0·4760	7·4/0·2622	5·5/0·4565
9·5/0·3281	5·2/0·5917	8·4/0·3914	6·3/0·4895	8·2/0·3065	5·9/0·4674
11·1/0·4276	6·0/0·6081	9·3/0·4568	6·6/0·4920	9·0/0·3600	6·3/0·4837
12·8/0·5965	6·6/0·6135	10·9/0·5976	7·4/0·5030	10·7/0·4743	6·9/0·5027
14·4/0·7188	8·5/0·6516	12·6/0·7072	7·9/0·5140	12·3/0·5739	7·3/0·5109
16·1/0·8761	10·4/0·7033	14·3/0·8039	8·5/0·5250	14·0/0·6094	8·3/0·5299
17·8/0·9999	14·7/0·8950	16·0/0·9124	10·4/0·5364	15·7/0·7899	9·8/0·6685
		17·6/0·9999	12·3/0·5475	17·3/0·9999	12·6/0·9728
			14·7/0·8800		

[a] The figures in the numerator and denominator refer to x (μm) and $M(x)$, respectively.

were centrifuged, filtered, and analyzed for the uranium content in the liquid phase by the Sacharov method[14]. Only AR grade chemicals were used for the preparation of the leaching solution and for the analytical determinations. The reproducibility of our experimental results was verified in early stages of the dissolution experiments on J-2 and J-18 uranium dioxides.

RESULTS AND DISCUSSION

Determination of the Normalized Dissolution Curve

The determination of the normalized-characteristic equation from kinetic data on the dissolution of uranium dioxides is based on the determination of values of the dimensionless age of particles corresponding to dissolved fractions of the polydispersion, *i.e.* on the determination of the functional relation $F(\tau)$.

From an obtained time course of the dissolution, $F(t)$, values of the particle age τ_j may be assigned to corresponding given dissolved fractions $F(t_j)$ in the two following ways:

a) If the linear rate of dissolution is constant during the dissolution and independent of the particle size, then

$$\tau_j = t_j/t_{total}, \qquad (12)$$

where $t_{total} = x_m(0)/2v$ is the total time of dissolution which must be determined either experimentally or by calculation from the course of the dissolution.

b) The linear rate of dissolution is not constant during the dissolution and it is a general function of the particle size. At limited conditions, *e.g.* on the assumption that the diffusional layer on dissolved particles grows linearly with the particle age, the relation derived from the Jandera equation[15] may be employed

$$\tau_j^2 = J \cdot t_j, \qquad (13)$$

where J is a constant whose value must be found experimentally or estimated.

In our experimental conditions, where the linear rate of dissolution was constant in all cases, the particle age could be determined from relation (12).

However, an experimental determination of the total dissolution time is practically hardly realizable and a graphical interpolation in a finite interval of the dissolution, where the dissolution curve approaches asymptotically the value $F(t) = 1$, is very inaccurate. Similarly, the values of $dF(t)/dt$ approach asymptotically zero. The total dissolution time was therefore determined from a substitutive function describing the time dependence of the dissolved mass fraction, $F(t)$. This substitutive function of a preliminarily selected shape was used for expressing the time course of the dissolution and for finding the value of t_{total} for a preliminarily determined total dissolved fraction of the polydispersion.

A determination of the theoretical total dissolution time from an exact solution of the following expression

$$t_{total} = \lim_{F(t) \to 1} t = \infty \qquad (14)$$

was, after replacing the dissolution curve by the substitutive function and transformation into the inverse form, consequently impossible.

The following functions were tested as substitutive equations describing the mass transfer from the solid to the liquid phase

$$1 - F(t) = \sum_{i=1}^{i=u} K_i \exp\left[-k_i t\right], \qquad (15)$$

$$1 - F(t) = \sum_{i=1}^{i=u} K_i^2 \exp\left[-k_i^2 t\right], \qquad (16)$$

$$1 - F(t) = \exp \sum_{i=1}^{i=u} K_i t^i. \qquad (17)$$

A comparison of these substitutive functions on several experimental data sets showed that functions (17) describes best the time course of the dissolution. It was therefore employed for calculation[16] of the total dissolution time and further for description and analysis of the normalized-characteristic dissolution curve. The value of the total dissolution time of the polydispersion was determined with a definite error which is due to the total experimental error in the measured data $(t; F(t))$ at the end of the dissolution and to a limited accuracy with which the selected substitutive function describes the dissolution kinetics in this finite interval of values $(t; F(t))$; this is in agreement with literature data[17-19].

The value of the dissolved fraction $F(t) = 0.9995$ was chosen for calculation of the total dissolution time and the calculation was performed with those experimental data where the dissolved fraction of the polydispersion was minimally $F(t) = 0.80$. Simultaneously, boundary values of the total dissolution time were found which correspond to estimates of the standard deviations of coefficients k_i in the substitutive function (17).

Mean values of the total dissolution time, t_{total}, and boundary values $t_{total}(-\delta k_i)$ and $t_{total}(+\delta k_i)$ are given in Table II for several dissolution experiments. The highest degree of the polynomial in the substitutive function was $u = 3$, because an estimate of the standard deviation of coefficients k_i for a higher-order polynomial was of the same order as absolute values of coefficients k_i. In some cases, the functional dependence $F(t)$ might be expressed with sufficient accuracy even by a first-order polynomial due to the fact the values of $\bar{G}_{exp}$ introduced through the relation

$$\bar{G}_{exp} = p^{-1} \sum_{j=1}^{j=p} [F(t_j) \cdot \vartheta_U]^2, \qquad (18)$$

TABLE II

Values Calculated from the Substitutive Function (17) (UO_2 J-5; 5°C)

Quantity		420	450	470	490	510
				$u = 1$		
$k_i \cdot 10^2$		0.8867 ± 0.0187	0.8821 ± 0.0321	0.9739 ± 0.1904	1.1189 ± 0.0164	1.1959 ± 0.0229
$t_{total} \cdot 10^{-2}$	(0.995)	351.21 358.52 366.24	372.14 386.68 402.40	320.17 326.42 332.93	280.03 284.11 376.04	406.99 411.42 415.93
	(0.999)	457.78 467.43 477.49	485.19 504.14 524.33	417.43 425.58 434.06	365.06 371.23 382.30	427.27 433.05 438.93
	(0.9995)	503.72 514.33 525.41	533.87 554.73 577.28	459.31 768.23 468.29	388.95 395.75 402.64	445.17 451.53 458.00
$\bar{c} \cdot 10^7$	(0.995)	2.406	2.236	2.642	3.035	3.245
	(0.999)	1.845	1.711	2.027	2.328	2.489
	(0.9995)	1.677	1.555	1.842	2.116	2.263
$\bar{\Omega} \cdot 10^4$		4.692	11.357	4.302	2.709	3.971
				$u = 2$		
$k_1 \cdot 10^2$		0.9517 ± 0.0441	0.8824 ± 0.0819	0.9481 ± 0.0542	1.0774 ± 0.0067	1.1662 ± 0.0551
$k_2 \cdot 10^6$		-5.1148 ± 3.1857	-5.6290 ± 0.9973	2.0780 ± 3.2885	3.9659 ± 3.1587	3.0038 ± 5.0209
$t_{total} \cdot 10^{-2}$	(0.995)	464.12 487.19 493.91	377.66 406.98 441.23	298.56 315.46 334.38	259.48 270.19 281.83	240.71 256.11 273.61
	(0.999)	472.05 502.23 510.99	492.38 530.60 575.26	389.25 411.28 255.95	338.30 352.27 367.43	313.84 333.91 356.72
	(0.9995)	480.80 520.16 529.79	541.79 538.85 632.98	428.30 452.55 479.70	374.64 387.61 404.30	345.32 367.41 392.51
$\bar{v} \cdot 10^7$	(0.995)	2.249	2.119	2.734	3.192	3.368
	(0.999)	1.725	1.625	2.097	2.448	2.583
	(0.9995)	1.725	1.477	1.906	2.225	2.348
$\bar{\Omega}_2 \cdot 10^4$		3.556	10.317	3.766	1.891	3.389

$u = 3$

$k_1 . 10^2$	$1{\cdot}1172 \pm 0{\cdot}0646$	$1{\cdot}1112 \pm 0{\cdot}1429$	$1{\cdot}1443 \pm 0{\cdot}0495$	$1{\cdot}2359 \pm 0{\cdot}0313$	$1{\cdot}3953 \pm 0{\cdot}0524$
$k_2 . 10^5$	$-3{\cdot}4731 \pm 1{\cdot}0283$	$-5{\cdot}8309 \pm 2{\cdot}9245$	$-3{\cdot}3247 \pm 0{\cdot}7772$	$-2{\cdot}8743 \pm 0{\cdot}5656$	$-4{\cdot}6399 \pm 0{\cdot}9885$
$k_3 . 10^7$	$1{\cdot}1029 \pm 0{\cdot}3729$	$2{\cdot}4532 \pm 1{\cdot}3326$	$1{\cdot}2792 \pm 0{\cdot}2767$	$1{\cdot}3622 \pm 0{\cdot}2279$	$2{\cdot}1616 \pm 0{\cdot}4173$
$t_{total} . 10^{-2}$ (0·995)	210·75 345·94 362·60	344·44 371·17 402·39	243·74 255·58 268·63	225·82 232·22 239·06	191·01 200·40 210·76
(0·999)	431·21 451·63 472·75	449·08 483·92 524·63	317·78 333·22 350·23	294·42 302·80 311·68	249·03 261·27 274·78
(0·9995)	474·49 496·28 520·18	494·14 532·48 577·27	349·67 366·66 385·37	323·96 333·19 342·95	274·02 287·49 302·35
$\bar{v} . 10^7$ (0·995)	2·493	2·324	3·374	3·714	4·304
(0·999)	1·912	1·782	2·588	2·848	3·301
(0·9995)	1·738	1·620	2·352	2·584	3·000
$\bar{\sigma}_3 . 10^4$	1·635	6·443	1·071	2·595	6·298
$\bar{\sigma}_{exp} . 10^4$	3·524	2·691	4·617	4·805	4·860

where ϑ_U is the relative error of the analytical determination of the uranium concentration in the solution — are of the same order or higher than values of $\bar{G}$.

Generally it may be said that with increasing the oxygen index of dissolved uranium dioxide and temperature, a polynomial of the degree $u \leqq 3$ will be sufficient for expressing the dissolution kinetics from the point of view of the considered criteria $\bar{G}_{exp} < \bar{G}_U$, $\bar{G}_{u=3} < \bar{G}_{u=2} < \bar{G}_{u=1}$, $(\delta k_i) < (k_i)$, where $\bar{G}_u$ is the mean value of the sum of squared deviations for the corresponding n-th-order polynomial in the substitutive function.

The accuracy of the approximation of the total dissolution time by the substitutive function was also verified by comparing the linear rate of dissolution $\bar{v}$ determined from this total dissolution time with the value v determined experimentally by the method of geometrical model. The ratio $p = v/\bar{v}$ for several experimental points is in Table III.

Disregarding the inaccuracy which follows from the use of the substitutive function for calculation of $\bar{v}$, the difference between the values of v and $\bar{v}$ is also brought about by the fact that the particle with the size of $x_n(0)$ does not represent the largest particle of the polydispersion. Most probably, however, actual sizes of dissolved polydispersion particles are smaller than those determined originally by microscopic analysis due to a deagglomeration of the secondary dispersion in the solution during the dissolution.

TABLE III

Linear Dissolution Rates Calculated from the Substitutive Function for the J-5 Uranium Dioxide at $u = 3$

mV	$\bar{v} \cdot 10^7$ mm s^{-1}	$\pm \Delta \bar{v} \cdot 10^8$ mm s^{-1}	γ	mV	$\bar{v} \cdot 10^7$ mm s^{-1}	$\pm \Delta \bar{v} \cdot 10^8$ mm s^{-1}	γ
		5°C				10°C	
400	0·931	0·17	1·196	375	1·561	0·24	1·074
420	0·978	0·12	1·183	400	1·680	0·49	1·102
450^a	1·149	0·49	1·227	420	2·001	0·44	1·120
470	1·373	0·18	1·129	450	2·069	1·08	1·209
490	1·560	0·23	1·073	470	2·748	1·27	1·050
510	1·774	1·53	0·893	490	2·967	1·47	1·046
				510	3·241	1·36	1·046

^{a} $u = 1$.

The Evaluation of the Normalized-Characteristic Equation
through the Substitutive Function

The normalized-characteristic equation was derived from the substitutive function *(17)*, which describes the course of the dissolution, by substituting the total dissolution time for t in the form of

$$1 - F(\tau) = e^{-p(\tau)} \tau . \qquad (19)$$

Introducing a new constant $q_i = k_i t_{total}^i \, (0.9995)$, the normalized − characteristic equation takes the form of

$$1 - F(\tau) = \exp\left(-\sum_{i=1}^{i=u} q_i \tau^i\right) . \qquad (20)$$

If the substitutive function *(17)* contains the first order polynomial, the constant q_i is entirely independent of the total dissolution time. If, therefore, the normalized-characteristic equation may be approximated with sufficient accuracy by the first-order polynomial, almost identical relative granulometric compositions of corresponding polydispersions might be expected. Generally, however, shapes of the normalized − characteristic equations expressed through second and third-order polynomials can be compared only with difficulties. As a criterion of "close similarity" of individual functions, the value P of the following integral was proposed

$$\int_0^T \sum_{i=1}^{i=u} k_i t^{i-1} \, dt \approx P , \qquad (21)$$

where $T = \bar{t}_{total} \, (0.9995)$, and which itself represents the area under the curve with coordinates $(t; P(t))$. Quantity T may be defined as the mean value of the total dissolution time until the disappearance of the last particle of the polydispersion.

In the further analysis of the normalized curves, the real solution was accomplished mainly with first or second, rarely with third-order polynomials in the substitutive function, even though constants in the third-order polynominal were determined with sufficient accuracy. Table IV then contains a comparison between values calculated from these normalized-characteristic equations at different experimental conditions and those determined from the original granulometric state.

The graphical comparison on Fig. 2 between normalized − characteristic curves obtained experimentally from our dissolution data and original curves determined from the granulometric state points to good agreement between both kinds of curves. In the case of normalized − characteristic curves determined from the original granulometric state, the region above $\tau = 0.7$, where − according to the original model $-F(\tau)$ reaches values of 0.995, appears to be of limited reliability. For nor-

Table IV

Comparison of Values Calculated from Normalized-characteristic Curves Obtained from the Dissolution Data ($u = 2$) or on the Basis of the Granulometric Analysis (J-5 uranium dioxide)

$F(\tau)$	τ (granul.)	τ (dissoln.), 5°C			τ (dissoln.), 10°C			
		450 mV	490 mV	470 mV	375 mV	420 mV	450 mV	490 mV
0·2000	0·033	0·0204	0·0237	0·0194	0·0273	0·0264	0·0227	0·0275
0·3000	0·053	0·0395	0·0384	0·0316	0·0439	0·0420	0·0367	0·0420
0·4000	0·075	0·0497	0·0557	0·0464	0·0631	0·0611	0·0531	0·0632
0·5000	0·103	0·0708	0·0768	0·0650	0·0872	0·0835	0·0732	0·0861
0·6000	0·138	0·1006	0·1037	0·0899	0·1147	0·1113	0·0987	0·1143
0·7000	0·183	0·1514	0·1404	0·1267	0·1522	0·1480	0·1332	0·1511
0·7500	0·211	0·1824	0·1651	0·1543	0·1743	0·1717	0·1562	0·1746
0·8000	0·244	0·2117	0·1970	0·1965	0·2063	0·2013	0·1858	0·2036
0·8500	0·318	0·2789	0·2789	0·2789	0·2768	0·2714	0·2612	0·2712
0·9200	0·376	0·3323	0·3323	0·3323	0·3323	0·3296	0·3316	0·3260

malized − characteristic dissolution curves obtained from dissolution data, the value of $F(\tau) = 1$ is not reached before $\tau = 1$.

These findings are in accordance with the theoretical assumptions and prove that the relative granulometric composition of a polydispersion may be predicted already from the course of the normalized − characteristic curve. At the given conditions, the stoichiometric composition of uranium dioxide polydispersions and experimental effects do not affect the determination of normalized − characteristic curves.
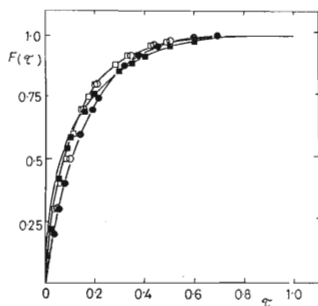

Fig. 2

Normalized-Characteristic Curves of the J-5 Uranium Dioxide Determined by the Microscopical Analysis (●), from the Dissolution Kinetics (□ 430 V, 5°C, ○ 375 V, 10°C) and from the Sedimentation Analysis (■)

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