THEORETICAL TREATMENT OF RAPID SORPTION KINETICS MEASURED IN BATCH ARRANGEMENT

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Universal solution of a family of sorption kinetic models which are based on superposition principle has been developed to describe sorption experiments in a closed system. The models account for the interactions of a sorbate–sorbent system with the apparatus which arise (i) from the mass balance condition in a closed system and (ii) from a finite rate of sorbate supply to the sorbent, the latter effect being of importance particularly in rapid nonstationary kinetic processes. Theoretical uptake curves for the intracrystalline sorption kinetics in zeolite crystals are exemplified using numerical solution of the corresponding Volterra integral equations which represent kinetic models of the overall transient sorption process in the apparatus. The approach appears to be promising for treatment of sorption kinetics in multicomponent systems.

The Volterra Integral Equation (VIE) approach has recently been proposed to solve mathematical models of sorption kinetics from the gas phase measured under constant volume/variable pressure conditions[1]. For fast sorption kinetics with characteristic times amounting to about one second, one arrives at the limits of the experimental method and thus, the valve used to start the experiment may distort the uptake curves considerably.

In a previous publication[2], the valve effect was analyzed thoroughly for a special type of sorption kinetics. The use of the VIE approach[1,3,4], offers a general way to compute sorption uptake curves affected by the limited rate of sorbate supply through valves and tubings of the experimental apparatus. In such a manner the limits of the experimental methods can in principle be displaced about one order of magnitude to lower intrinsic time constants of sorption kinetics whatever type of valve may be used.

DESCRIPTION OF THE EXPERIMENT

The principal scheme of the experimental piezometric apparatus is given in Fig. 1. The apparatus consists of a dosing vessel of the volume V_d, with the pressure $p_d(t)$ of sorbing species kept at the temperature T_d and of a sample vessel of the volume V_v with the pressure $p_v(t)$ of sorbing species kept at the temperature T_v. The sample volume contains sorbent particles of the total volume V_s. Both vessels are separated from each other by a valve with the conductivity κ defined for small pressure differences $p_d - p_v$ as

$$\kappa = \frac{\dot{n}}{p_d - p_v} , \qquad (1)$$

where $\dot{n}$ denotes the amount of sorbing species passing through the valve per unit time. The apparatus is operated stepwise increasing the pressure of sorbing species by a small increment to the initial value

$$p_d(0) = p_d^0 \qquad (2)$$

at the beginning of each experimental run.

The conductivity κ is assumed to be a function of an average pressure in the apparatus. For small pressure differences one takes

$$\bar{p} = \frac{p_d^0 + p_v^0}{2} , \qquad (3)$$

where p_v^0 and p_d^0 are the equilibrium pressures in the apparatus prior to starting subsequent experimental runs. The averaged pressure $\bar{p}$ is considered to be constant for a given experimental run, but the conductivity κ is assumed to be externally controlled according to a known time programme, i.e.

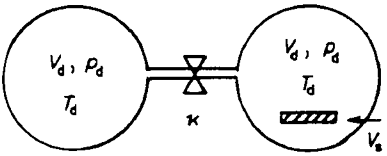

Fig. 1
Schematic diagram of the piezometric apparatus

$$\kappa = \kappa(\bar{p},t) = \kappa(p_d,p_v,t) \ . \tag{4}$$

It is supposed that κ increases monotonically from $\kappa = 0$ at $t = 0$ to a limiting value $\kappa = \kappa_\infty$ for $t > t_0$ where t_0 is a time interval necessary to adjust the valve to be entirely open. The functions in Eq. (*4*) are estimated on the basis of blank experiments.

In the present model, all heat transport phenomena are neglected which accompany the mass transport from the dosing vessel into the sorption vessel. Usually, the sorption kinetics is observed by measuring the pressure p_d by means of a membrane manometer included into the volume V_d so that one determines the pressure p_d^0 and the function $p_d(t)$ until the corresponding equilibrium pressure p_∞ is established in the apparatus.

THEORETICAL

Overall Mass Balance in the Apparatus

The mass balance at time t is expressed by the equation

$$K_d[p(t) - p_d^0] + K_v[p_v(t) - p_v^0] + V_s[\bar{a}(t) - \bar{a}_0] = 0 \tag{5}$$

which can be written for $t \rightarrow \infty$ as

$$1 - \frac{K_d}{K_v}\ \frac{p_d^0 - p_\infty}{p_\infty - p_v^0} + \frac{V_s}{K_v}\ \frac{[f(p_\infty) - f(p_v^0)]}{p_\infty - p_v^0} = 0 \ , \tag{6}$$

where f denotes the sorption isotherm (see Eq. (*16*)). Using Eq. (*6*), the equilibrium pressure p_∞ can be calculated uniquely by numerical methods. In these equations K_d and K_v are the capacities of the respective volumes given as

$$K_d = V_d\ /RT_d \tag{7}$$

$$K_v = V_v\ /RT_v \ , \tag{8}$$

$\bar{a}(t)$, $\bar{a}(\infty) = f(p_\infty)$ and $\bar{a}_0 = f(p_v^0)$ are the sorbed amounts of the sorbing species at respective times averaged over the volume of sorbent particles, i.e.

$$\bar{a}(t) = \frac{1}{V_\Delta} \int_{V_\Delta} a(t,\boldsymbol{x})\mathrm{d}\boldsymbol{x} \tag{9}$$

with $a(t,\mathbf{x})$ expressing the amount sorbed per unit volume of the sorbent. Furthermore, one introduces

$$\nu \equiv K_\mathrm{d}/K_\mathrm{v} \tag{10}$$

$$\lambda \equiv \frac{V_\mathrm{s}}{K_\mathrm{v}} \frac{[\bar{a}(\infty) - \bar{a}_0]}{p_\infty - p_\mathrm{v}^0} \; . \tag{11}$$

Thus it follows from Eq. (*6*) that

$$\frac{p_\mathrm{d}^0 - p_\infty}{p_\infty - p_\mathrm{v}^0} = \frac{1 + \lambda}{\nu} \; . \tag{12}$$

The sorption equilibrium is characterized by the isotherm

$$a_\mathrm{s} = f(p) \; . \tag{13}$$

Besides, it is assumed that at any instant t sorption equilibrium is established between the gaseous phase and the surface of sorbent particles, i.e.

$$\bar{a}(\infty) = a_\mathrm{s}(\infty) = f(p_\infty) \tag{14}$$

$$\bar{a}(0) = \bar{a}_0 = a_\mathrm{s}(0) = a_\mathrm{s}^0 = f(p_\mathrm{v}^0) \tag{15}$$

and

$$a_\mathrm{s}(t) = f[p_\mathrm{v}(t)] \; , \tag{16}$$

where a_s denotes the adsorbed amount sorbed at the surface of sorbent particles. Introducing the dimensionless quantities

$$\gamma_{\mathrm{d}}(t) = \frac{p_{\mathrm{d}}(t) - p_\infty}{p_{\mathrm{d}}^0 - p_\infty} \tag{17}$$

and

$$\gamma_{\mathrm{v}} = \frac{p_{\mathrm{v}}(t) - p_{\mathrm{v}}^0}{p_\infty - p_{\mathrm{v}}^0} \ , \tag{18}$$

$$\gamma_{\mathrm{v}}(t) + (1+\lambda)\gamma_{\mathrm{d}} + \lambda \ \frac{[a(t) - a_0]}{f(p_\infty) - f(p_{\mathrm{v}}^0)} = 1 + \lambda \ . \tag{19}$$

Equation (*16*) can be rewritten as

$$a_{\mathrm{s}}(t) = f\{(p_\infty - p_{\mathrm{v}}^0)\gamma_{\mathrm{v}}(t) + p_{\mathrm{v}}^0\} \ . \tag{20}$$

Kinetic Equations

Any information on the intrinsic sorption kinetics is given by the function $H(t)$ which represents the molecular uptake by the sorbent particles for the unit step change in surface concentration a_{s}. Using the superposition principle[5], one can write

$$\bar{a}(t) - \bar{a}_0 = \int_0^t H'(t-s)\ [a_{\mathrm{s}}(s) - a_s^0]\ \mathrm{d}s \tag{21}$$

and, therefore, one obtains

$$\frac{\bar{a}(t) - \bar{a}_0}{f(p_\infty) - f(p_{\mathrm{v}}^0)} = \int_0^t H'(t-s)\ F[\gamma_{\mathrm{v}}(s)]\ \mathrm{d}s \tag{22}$$

with

$$F(x) = \frac{f\{x(p_\infty - p_{\mathrm{v}}^0) + p_{\mathrm{v}}^0\} - f(p_{\mathrm{v}}^0)}{f(p_\infty) - f(p_{\mathrm{v}}^0)} \ . \tag{23}$$

The rate of depletion of the substance in the volume V_{d} is expressed as

$$-\frac{\mathrm{d}p_\mathrm{d}(t)}{\mathrm{d}t} = \beta(t)\,[p_\mathrm{d}(t) - p_\mathrm{v}(t)]\ , \qquad \beta(t) = \frac{\kappa(t)}{K_\mathrm{d}} \tag{24}$$

or as

$$\frac{\mathrm{d}\gamma_\mathrm{d}}{\mathrm{d}t} + \beta(t)\gamma(t) = \beta(t)\,\frac{\nu}{1+\lambda}\,[\gamma_\mathrm{v}(t) - 1]\ . \tag{25}$$

Solution of the Mathematical Model

Integrating Eq. (*25*) with the initial condition $\gamma_\mathrm{d}(0) = 1$ yields

$$\gamma_\mathrm{d}(t) = \mathrm{e}^{-z(t)} + \frac{\nu}{1+\lambda}\int_0^t \beta(s)[\gamma_\mathrm{v}(s) - 1]\mathrm{e}^{-[z(t)-z(s)]}\,\mathrm{d}s\ , \tag{26}$$

where

$$z(t) = \int_0^t \beta(s)\,\mathrm{d}s\ . \tag{27}$$

Inserting for γ_d from Eqs (*22*) and (*26*) into Eq. (*19*) and rearranging, one obtains

$$\gamma_\mathrm{v}(t) + \nu\int_0^t \beta(s)\gamma_\mathrm{v}(s)\mathrm{e}^{-[z(t)-z(s)]}\,\mathrm{d}s + \lambda\int_0^t H'(t-s)F[\gamma_\mathrm{v}(s)]\,\mathrm{d}s = (1+\lambda+\nu)\,(1 - \mathrm{e}^{-z(t)})\ . \tag{28}$$

Solving the non-linear VIE (*28*) for selected functions $H(t)$, $\beta(t)$ and values of the parameters λ and ν, one computes the function $\gamma_\mathrm{v}(t)$. This function can in principle be compared with experimental data, provided it is possible to monitor the pressure in both vessels.

Usually, however, the pressure is measured only in the dosing volume, and the function $\gamma_\mathrm{d}(t)$ is the observable quantity. Thus the solution of the problem proceeds in two steps: (i) solving Eq. (*28*) to compute $\gamma_\mathrm{v}(t)$ and (ii) computing the function $\gamma_\mathrm{d}(t)$ according to Eq. (*22*).

It is of interest to discuss two particular cases of the valve behaviour (see Fig. 2)

$$\kappa(t) = \begin{cases} 0 & \text{for } t \le 0 \\ \kappa_\infty & \text{for } t > 0 \end{cases} \tag{29}$$

$$\kappa(t) = \begin{cases} 0 & \text{for } t \le 0 \\ \dfrac{\kappa_\infty}{t_0} t & \text{for } 0 < t \le t_0 \\ \kappa_\infty & \text{for } t > t_0 \end{cases} . \qquad (30)$$

In the case described by Eq. (*29*), one inserts into Eqs (*26*) and (*28*)

$$\beta(t) = \beta = \kappa_\infty / K_\mathrm{d} \quad \text{for } t > 0 \qquad (31)$$

and

$$\gamma_\mathrm{d}(t) = \mathrm{e}^{-\beta t} + \beta \frac{\nu}{1+\lambda} \int_0^t \mathrm{e}^{-\beta(t-s)} \, [\gamma_\mathrm{v}(s) - 1] \, \mathrm{d}s \, . \qquad (32)$$

For γ_v one obtains the equation

$$\gamma_\mathrm{v}(t) + \nu\beta \int_0^t \gamma_\mathrm{v}(s) \mathrm{e}^{-\beta(t-s)} \, \mathrm{d}s + \lambda \int_0^t H'(t-s) F[\gamma_\mathrm{v}(s)] \, \mathrm{d}s = (1 + \lambda + \nu) \ (1 - \mathrm{e}^{-\beta t}) \, . \qquad (33)$$

In the case described by Eq. (*30*) it holds

$$\beta(t) = \begin{cases} \dfrac{\kappa_\infty t}{K_\mathrm{d} t_0} = \alpha t & \text{for } 0 < t \le t_0 \\ \dfrac{\kappa_\infty}{K_\mathrm{d}} = \alpha t_0 & \text{for } t > t_0 \end{cases} , \qquad (34)$$

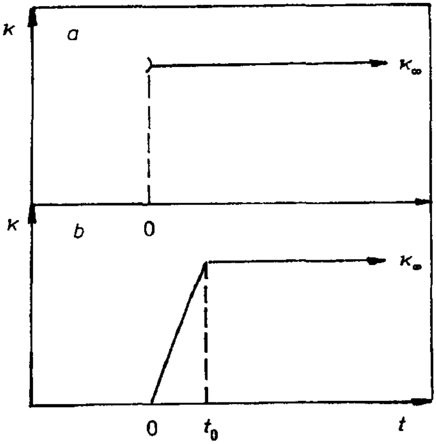

FIG. 2
Behaviour of the valve conductivity κ of the model *a* described by Eq. (*29*) and model *b* described by Eq. (*30*); κ and *t* are plotted in arbitrary units

where

$$\alpha = \frac{\kappa_\infty}{K_d t_0} \tag{35}$$

and the function $z(t)$ in Eq. (*28*) acquires the form

$$z(t) = \begin{cases} \frac{\alpha}{2} t^2 & \text{for } 0 < t \leq t_0 \\ \alpha t_0 t - \frac{\alpha}{2} t_0^2 & \text{for } t > t_0 \ . \end{cases} \tag{36}$$

RESULTS AND DISCUSSION

To examine the effect of the valve (with the characteristics expressed by Eqs (*29*) and (*30*)) on the form of uptake curves, the uptake curves were simulated for situations at which the contribution of the valve to the total time constant of the transient response was estimated to be about 50% based on the calculation of statistical moments of the uptake curves.

For these calculations, experiments with a linearized sorption isotherm, i.e.

$$F\,[\gamma_v(t)] = \gamma_v(t) \ , \tag{37}$$

were selected and the sorption kinetics was considered to be limited by the diffusion into spherical particles of uniform size, i.e. we have[6]

$$H(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\frac{n^2 \pi^2 D t}{R^2}} \tag{38}$$

with R and D being the radius of the spherical particles and the diffusion coefficient, respectively.

All examples of simulation were calculated by means of the programme package ZEUS for sorption kinetics on porous adsorbents. The algorithm for the solution of the Volterra Integral Equations is based on adapted quadrature formulas described elsewhere[7 - 11].

The results of this simulation are exemplified in Fig. 3. Therein, curve *1* represents the case of intrinsic sorption kinetics not distorted by the valve effect. In contrast to this case, the curves *2* and *3* represent cases of instantaneous sorption equilibrium hindered by a valve effect of type (*29*) for different conductivity parameters κ_∞ (such curves are called relaxation curves). One yields the model without valve effect if κ_∞ goes to infinity. In this case, the curve γ_v approximates more and more a pressure jump from p_v^0 to p_d^0 at the time t = 0. For small values of κ_∞, the valve effect dominates the behaviour of γ_v. The curves γ_d from Fig. 3 are shown in Fig. 4. Curve *1* represents again the case without valve effect being identical with curve *1* from Fig. 3 but now with the normalization of γ_d (see Eq. (*17*)). In both figures the normalization of all curves is the same because of the equilibrium pressure p_∞ being independent of the kind of valve.

Both Figs 5 and 6 illustrate the behaviour of the model in the case of the simultaneous effect of diffusion and valve, where a valve model characterized by Eq. (*30*) is used. The curves were calculated for different t_0 at fixed κ_∞ = 1 000. The time t_0 is a measure for speed of opening the valve. Large values of t_0 show the same effect as small values of κ_∞ within the valve model of Eq. (*29*).

It should be noted that one can estimate a relative importance of the valve effect combining the time constant of sorption uptake curve with the parameters obtained from blank experiments into the following relation (cf. treatment in ref.[2])

$$\chi = \frac{K_v(1+\lambda)}{K_d + K_v(1+\lambda)} \frac{K_d}{\kappa} \frac{1}{\tau} , \qquad (39)$$

where

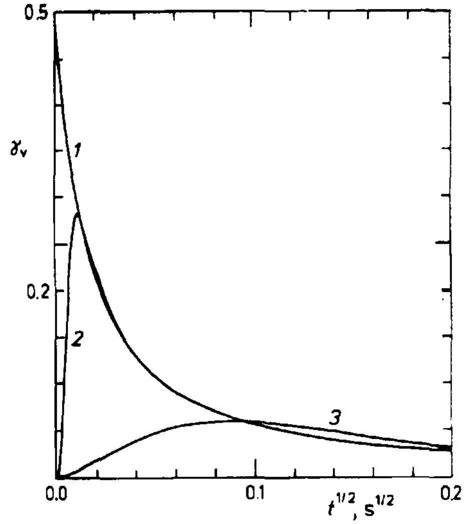

FIG. 3

Simulated curves γ_v for p_d^0 = 11 Pa, p_v^0 = 10 Pa, *R T* V_s/V_v = 50 J mol^{-1} K^{-1}: *1* $\kappa_\infty = \infty$, *2* κ_∞ = 1 000, *3* κ_∞ = 10 mol s^{-1} Pa^{-1}

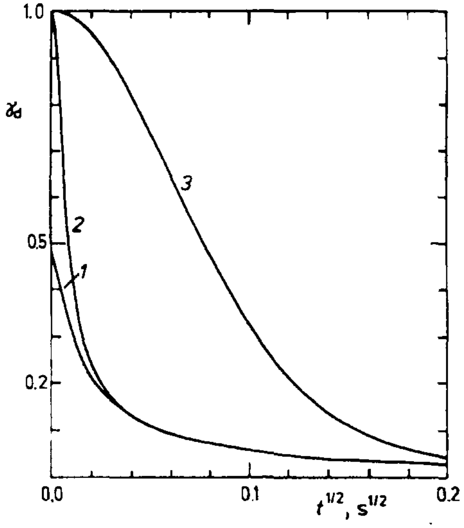

FIG. 4

The curves γ_d corresponding to the situations given in Fig. 3

$$\tau = \int_0^\infty \gamma_d(t)\,dt \tag{40}$$

represents the time constant of the kinetic run considered which is obtained from the corresponding experimental uptake curve. As to our experience, the valve effect should be taken into account provided $\chi > 0.01$ otherwise the curve fitting fails at least in the initial part of the uptake curves.

CONCLUSIONS

The VIE model presented allows one to decide in which way a measured sorption curve is influenced by a valve of the apparatus. By means of this model, the apparatus configuration can be optimized for certain sorption kinetics and the valve effect on sorption kinetics can be eliminated numerically. In contrast to the method of statistical moment, the new approach can be extended to the case of sorption uptake of multicomponent mixtures[12].

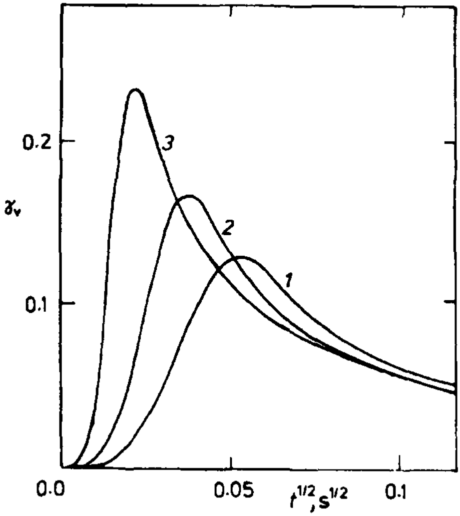

FIG. 5

Simulated curves γ_v for $p_d^0 = 11$ Pa, $p_v^0 = 10$ Pa, $R\ T\ V_s/V_v = 50$ J mol^{-1} K^{-1}: *1* $t_0 = 2.0$, *2* $t_0 = 0.5$, *3* $t_0 = 0.05$ s

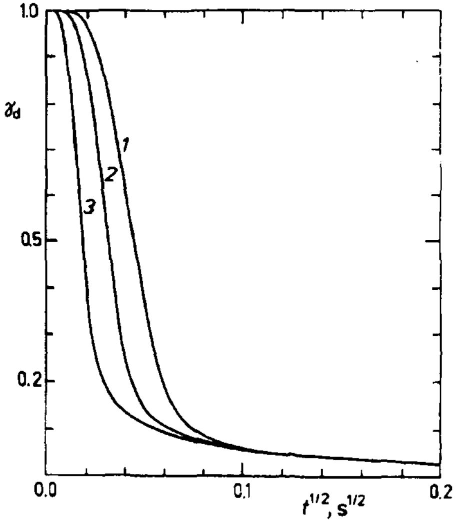

FIG. 6

The curves γ_d corresponding to the situations given in Fig. 5

SYMBOLS

$\underline{a}$	adsorbed amount, mol m^{-3}
$\bar{a}$	adsorbed amount averaged over the volume of the sorbent particle, mol m^{-3}
a_s	adsorbed amount at particle surface, mol m^{-3}
D	coefficient of intraparticle diffusion, $m^2\,s^{-1}$
f	function which expresses the adsorption isotherm
F	function defined by Eq. (*23*)
$H(t)$	molecular uptake by sorbent particle for the unit step change in its surface concentration
$\boldsymbol{K}$	capacity of respective volume of the apparatus for sorbing species accumulation, mol Pa^{-1}
$\dot{n}$	molar flow of sorbing species through the valve, mol s^{-1}
p	pressure of sorbing species, Pa
$\bar{p}$	average pressure of sorbing species in the apparatus, Pa
$\boldsymbol{R}$	gas constant, J $mol^{-1}\,K^{-1}$
R	radius of sorbent particle, m
s	integration variable, s
T	temperature, K
t	time variable, s
t_0	valve opening parameter, s
V	volume, m^3
$\boldsymbol{x}$	positional vector within the sorbent particle
z	function defined by the relation $z(t) = \int_0^t \beta(s)\,ds$
α	valve opening parameter, s^{-2}
β	function defined by Eq. (*24*)
γ	relative molecular uptake defined by Eqs (*17*) and (*18*)
κ	valve conductivity, mol $s^{-1}\,Pa^{-1}$
λ	parameter defined by Eq. (*11*)
ν	parameter defined by Eq. (*10*)
τ	time constant of the sorption uptake experiment defined by Eq. (*40*)
χ	criterion of relative importance of valve effect defined by Eq. (*38*)

Superscripts

0	refers to initial value of a variable
$'$	refers to the operator d/dt

Subscripts

d	refers to the dosing volume
s	refers to the sorbent
v	refers to the sorption volume
∞	refers to the value of a variable at $t \to \infty$

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REFERENCES

1. Kočiřík M., Tschirch G., Struve P., Bülow M.: J. Chem. Soc., Faraday Trans. 1 *84*, 2247 (1988).
2. Struve P., Kočiřík M., Bülow M., Zikánová A., Bezus A. G.: Z. Phys. Chem. (Leipzig) *264*, 49 (1983).
3. Kočiřík M., Tschirch G., Struve P., Bülow M., Zikánová A.: J. Chem. Soc., Faraday Trans. 1 *86*, 3087 (1990).
4. Tschirch G., Wisotzki C.: *Scientific Report 1988, Lösung linearer volterrascher Integralgleichungen zur Modelllierung von Adsorptionsprocessen in Zeolithen.* Institute of Informatics and Computing Techniques, Berlin 1988.
5. Courant R., Hilbert D.: *Methoden der matematischen Physik*, Vol. II, p. 180. Springer, Berlin 1937.
6. Crank J.: *The Mathematics of Diffusion*. Clarendon Press, Oxford 1964.
7. Micke A., Wisotzki C.: Z. Angew. Math. Mech. *68*, 601 (1988).
8. Micke A.: Z. Angew. Math. Mech. *67*, 37 (1987).
9. Micke A.: Computing *42*, 203 (1981).
10. Micke A.: Z. Angew. Math. Mech. *70*, 49 (1990).
11. Micke A.: Z. Angew. Math. Mech. *71*, 81 (1991).
12. Micke A., Bülow M.: Gas Separ. Purif. *4*, 165 (1990).

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