

## SOME PROBLEMS OF THE LABORATORY MODELLING OF NON-ISOTHERMAL ADSORPTION IN A FIXED BED OF ADSORBENT

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The course of non-isothermal adsorption of carbon dioxide from a nitrogen stream in laboratory glass adsorbers with a polyurethane insulation, without insulation, with a vacuum silvered jacket and with a vacuum jacket with radiation curtain of aluminium sheet was investigated from the point of view of the possibility to employ a one-dimensional model to describe the adsorption course. The assumptions of the one-dimensional model are fulfilled, from the adsorbers investigated, by the adsorber with vacuum silvered jacket and the adsorber with vacuum jacket with radiation curtain.

The non-isothermal adsorption of one or more components from a stream of inert in the adsorbent fixed bed is characterized by an unsteady mass and heat transfer. In industrial conditions, the adsorbers working non-isothermally are, as a rule, insulated and have a great ratio of the adsorbent volume to the heat exchanging adsorber surface, which ensures low heat losses per the adsorbent volume unit and makes it possible to consider them, in a good approximation, as adiabatic or damped adiabatic. The course of adsorption and desorption in such adsorbers is described by the one-dimensional model comprising the respective resistances to mass and heat transfer. Low, and from the technical point of view negligible radial gradients of concentration and temperature give evidence of suitability of using the one-dimensional model to describe the non-isothermal sorption in the industrial adsorbers. The experimental modelling of such a system requires a suitable design of the laboratory, bench-scale or pilot-plant model of adsorber. The adsorbers employed in laboratory conditions have, in comparison with the industrial ones, the ratio of heat exchanging surface to the adsorbent volume more than one order higher. Therefore it is difficult to ensure in the laboratory conditions such an adsorber construction in which the radial gradients of temperature and concentration are negligible.

### *Laboratory Investigation of Course of Non-Isothermal Adsorption*

The course of non-isothermal adsorption in a fixed bed of adsorbent was investigated

by us previously in a laboratory glass apparatus described in paper<sup>1</sup>. Carbon dioxide was adsorbed from a stream of nitrogen in a bed of molecular sieve Calsit 5. Glass adsorbers illustrated schematically in Fig. 1 were used in the measurements. Adsorber *a* with six hollows for thermocouples was used with a polyurethane insulation or without insulation. The insulation of 4.5 cm width was prepared by foaming polyurethane into a cylindrical container in which the adsorber was placed centrally. After curing, the insulation was cut lengthwise to enable us to set it after the adsorbent activation again on the adsorber. Adsorber *b* has a silvered jacket. Adsorber *c* is an improved version of adsorber *b*. It is equipped with hollows for thermocouples and with silvered jacket. Adsorber *d* is equipped with a jacket in which the radiation curtain from aluminium sheet of width 0.05 mm is located. The jackets of adsorbers *b*, *c*, and *d* were evacuated to a pressure of 2–3 Pa during the measurement. In the course of adsorbent activation, the adsorber jackets were aerated. The measuring conditions are listed in Table I. To judge the suitability of the adsorbers with insulation, without insulation, and with silvered vacuum jacket as laboratory models, the comparison was used of results of measurements of the carbon dioxide adsorption from a stream of nitrogen with the results of calculations in terms of the one-dimensional model involving the resistance to the mass transfer in the solid phase. For comparing the adsorbers with vacuum silvered jacket with the adsorber with aluminium radiation curtain in vacuum jacket, the approximate calculated heat losses into surroundings were used.

### *One-Dimensional Model of Sorption*

The course of non-isothermal adsorption of one component from a stream of inert in a fixed bed of adsorbent can be described by the following dimensionless equations<sup>2</sup>:

Material balance:

$$\left(\frac{\partial Y}{\partial Z}\right)_\theta + \varepsilon R_2 \left(\frac{\partial Y}{\partial \theta}\right)_Z + \left(\frac{\partial X}{\partial \theta}\right)_Z = 0. \quad (1)$$

Heat balance:

$$MC_P \left[ (1 + Y) \left(\frac{\partial Y}{\partial Z}\right)_\theta + T \left(\frac{\partial Y}{\partial Z}\right)_\theta \right] + \left\{ 1 + \varepsilon R_0 C_P + R_A C_{PA} \left[ \left(\frac{D_{22}}{D_{11}}\right)^2 - 1 \right] \right\} \cdot \left(\frac{\partial T}{\partial \theta}\right)_Z - H \left(\frac{\partial X}{\partial \theta}\right)_Z + \frac{4K_T}{D_{11}} (T - T_F) = 0. \quad (2)$$

Equilibrium relation:

$$X^* = A \exp(-BT) \frac{\exp(R/T) Y}{D \sqrt{T + [D \sqrt{T + \exp(R/T)}] Y}}. \quad (3)$$

TABLE I

Conditions of measurements  $Y_{go} = 0.25 \text{ kmol kmol}^{-1}$ 

Measur- ement No.	Densities of flow $\text{kmol m}^{-2} \text{ h}^{-1}$		Temperatures K		Pressure in adsorber kPa		Adsor- ber	Pressure in jacket Pa
	$\text{N}_2$	$\text{CO}_2$	$T_{g2}$	$T_{go}$	max.	min.		
A1	22.24	5.56	303.0	303.0	128.0	126.1	$a^a$	—
A2	40.91	10.23	303.0	303.0	126.5	126.1	$a$	—
A3	48.24	12.10	303.0	303.0	149.3	138.9	$b$	2.4
A4	35.50	8.89	303.2	303.2	110.2	110.0	$c$	2.1
A5	36.23	9.07	303.2	303.2	112.5	112.4	$d$	2.0

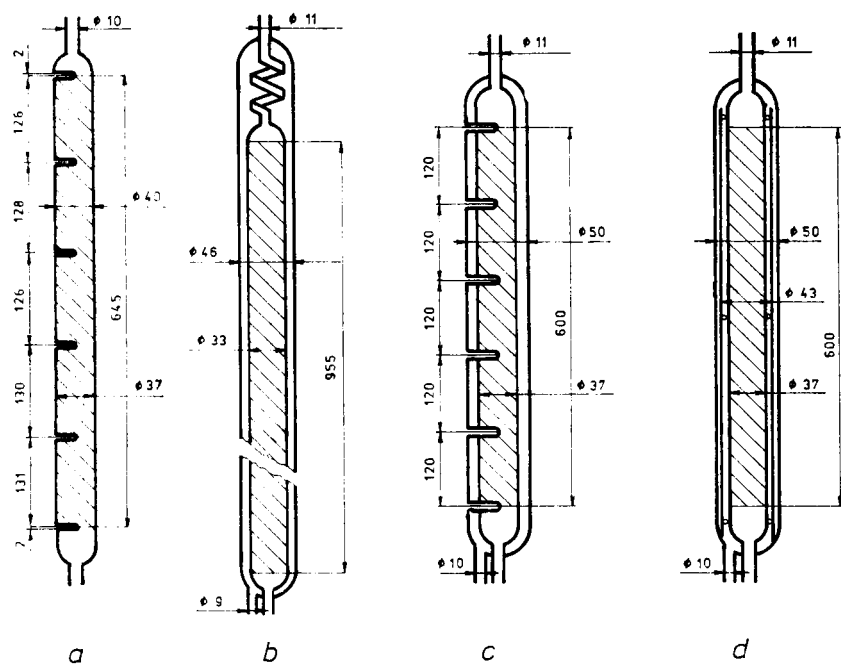
<sup>a</sup> Adsorber with insulation.

FIG. 1

Schemes of adsorbers

Rate relation:

$$\left(\frac{\partial X}{\partial \theta}\right)_Z = K_{sc}(X^* - X). \quad (4)$$

Initial and boundary conditions:

$$\begin{aligned} Y(0, Z) &= Y_Z, \quad T(0, Z) = T_Z, \quad X(0, Z) = X_Z \\ Y(\theta, 0) &= Y_0, \quad T(\theta, 0) = T_0, \quad \text{for } \theta > 0. \end{aligned} \quad (5)$$

Relations (1)–(5) hold also for the desorption of adsorbate from a fixed bed of adsorbent by a stream of inert gas. For the desorption,  $Y_0 < Y_Z$ .

The given model of non-isothermal sorption, as a one-dimensional model, considers the changes of investigated variables only in the axial direction of adsorber. The unfamiliarity of actual temperatures in the adsorber wall and in insulation does not make it possible to calculate correctly the heat accumulation in insulation and the heat losses into surroundings. It follows from the fact that the one-dimensional model in the given place in the chosen time makes it possible to use only the temperature of system and the temperature of surroundings. At the same time it is assumed that the resistance to the heat transfer in a particle and from the adsorbent particle into gas is negligible. With the aim of including the heat capacity of insulation into heat balance in the framework of one-dimensional model, we introduced a hypothetical insulation whose temperature is equal to the system temperature. The heat capacity of insulation can then be expressed as the  $k$  multiple of heat capacity of the adsorber wall. The temperature of the adsorber wall is equal to the temperature of adsorption system. The factor occurring in the expression characterizing the heat accumulation in Eq. (2) has then the form

$$Z_C = 1 + \varepsilon R_0 C_P + k R_A C_{PA} [(D_{22}/D_{11})^2 - 1]. \quad (6)$$

The application of coefficient  $k$  stemmed from the knowledge obtained in the experimental investigation of the temperature course in different places of polyurethane insulation, on the surface of adsorber and insulation during the laboratory measurements of the course of adsorption and desorption and from ensuing heat balances.

#### *Evaluation of Results of Measurements*

The results of measurements A1 to A3 are given in Figs 2–6 along with the curves according to the model. In the calculations, the dependence of change of mean molar mass of mixture on the relative fraction of adsorptive was taken into account by the relation

$$\bar{M} = \frac{M_1 Y + M_2}{(1 + Y) M_2}. \quad (7)$$

Dimensionless parameter  $K_{SC}$  was expressed by the relation

$$K_{SC} = \frac{15D_{eo}z_oQ_s \exp[-E/(RT_{go}T)]}{r_p^2 \dot{n}_2 M_2} = P_K \exp(-E_K/T). \quad (8)$$

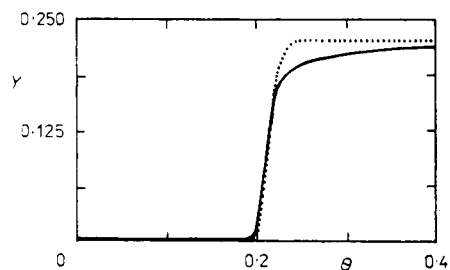


FIG. 2

Breakthrough curves: — experiment A1 with insulated adsorber, ····· model

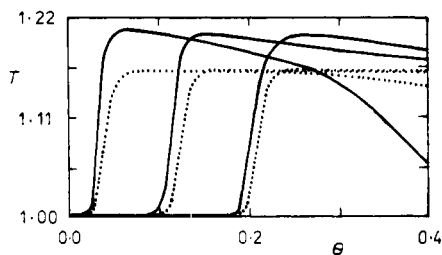


FIG. 3

Temperature courses in 1/5, 3/5, and 5/5 of height of adsorbent bed: — experiment A1 in axis of adsorber, ····· model

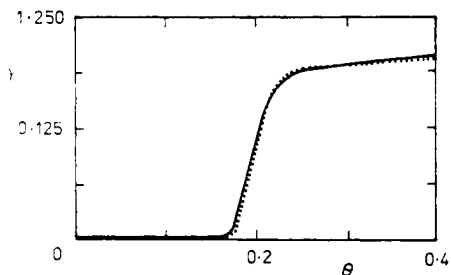


FIG. 4

Breakthrough curves: — experiment A2 with non-insulated adsorber, ····· model

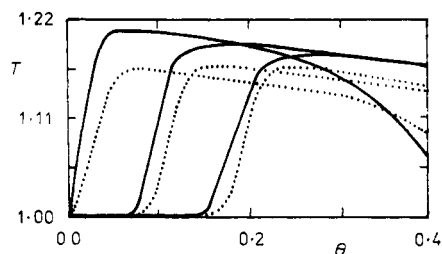


FIG. 5

Temperature courses in 1/5, 3/5, and 5/5 of height of adsorbent bed: — experiment A2, ····· model

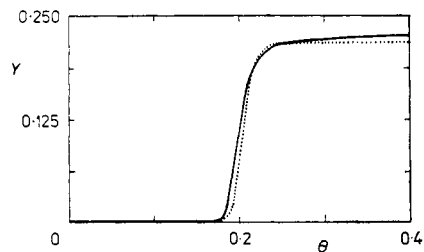


FIG. 6

Breakthrough curves: — experiment A3, adsorber *b* with vacuum silvered jacket, ····· model

Parameter  $k$  was chosen so that the total adsorbed amount obtained from the experimental breakthrough curve and the breakthrough curve according to model should not differ more than 5%. The values of the other dimensionless parameters used in calculating are given in Table II. The values of diffusion coefficients taken from paper<sup>3</sup> were used for calculating parameters  $P_K$  and  $E_K$  defined by Eq. (8). The parameters of equilibrium dependences were calculated from published data<sup>4</sup>.

The breakthrough curve and the courses of temperatures in the adsorbent bed as obtained on using the insulation are plotted in Figs 2 and 3 along with the curves corresponding to the model. The experimental breakthrough curve and the curve according to model agree well in the region of breakthrough point. However, they do not agree in the plateau region where the curve according to the model corresponds to a higher adsorbent saturation. The higher degree of saturation is conditioned by a lower adsorbent temperature in model in comparison with the experiment as it can be seen also in Fig. 3. Differences between the experimental breakthrough curve and the curve according to the model in the region of plateau are probably connected with the complexity of heat and mass transfer when saturating up the adsorbent bed. In the measurements during saturating up the adsorbent bed in the adsorber section where the gas temperature is lower than that of inner insulation surface, the heat flow from the insulation to the adsorber takes place, which influences the course of saturating up the adsorbent. It is evident that this effect will be the greater the higher the temperature and the heat capacity of adsorber insulation will be. This effect is not included in the model.

The experimental breakthrough curve of the measurement in non-insulated adsorber and the breakthrough curve according to the model are given in Fig. 4. The very good agreement of the experimental breakthrough curve with the model curve is, however, reached only with  $k = 1.4$ . The application of other  $k$  values did not lead to a better agreement of the experimental breakthrough curve with the model one. The correct value for non-insulated adsorber is  $k = 1$ . The fact that the agreement occurred of the experimental breakthrough curve with the model curve only when considering a hypothetical insulation shows that in the non-insulated adsorber,

TABLE II  
Values of dimensionless parameters

Fig. No.	$R_2 \cdot 10^4$	$H$	$Z_C$	$k$	$K_T$	$P_K \cdot 10^{-6}$	$E_K$
2, 3	7.363	5.382	2.250	2.04	0.538	2.5	11.5
4, 5	7.363	5.382	1.810	1.40	3.270	1.3	11.5
6	8.740	5.382	1.900	1.30	1.000	1.4	11.5

a more complex mechanisms takes place of mass and heat transfer than it is assumed in the model. Owing to greater losses of heat into surroundings in comparison with insulated adsorber, it is possible to expect the radial temperature gradients in the adsorber and a lower temperature of adsorbent. It is also proved by the courses of temperatures in chosen places of adsorber depicted in Fig. 5. The courses of

TABLE III  
Results of calculations

Experiment A4					Experiment A5			
Time min	$n_A$ mol	$Q_A$ mol	$Q_S$ kJ	$\frac{Q_S}{Q_A} \cdot 100$	$n_A$ mol	$Q_A$ kJ	$Q_S$ kJ	$\frac{Q_S}{Q_A} \cdot 100$
10	0.85	35.59	0.22	0.6	0.74	30.98	0.19	0.6
20	1.05	43.96	1.32	3.0	1.08	45.22	0.74	1.6
30	1.22	51.08	2.05	4.0	1.24	51.92	1.22	2.3
40	1.36	56.94	2.49	4.4	1.36	56.94	1.56	2.7
50	1.49	62.39	2.83	4.5	1.47	61.55	1.83	3.0
60	1.59	66.57	2.96	4.4	1.57	65.74	2.06	3.1
70	1.68	70.34	3.10	4.4	1.65	69.09	2.11	3.1
80	1.72	72.05	3.12	4.3	1.68	70.34	2.15	3.0
90	1.75	73.27	3.12	4.3	1.70	71.18	2.16	3.0

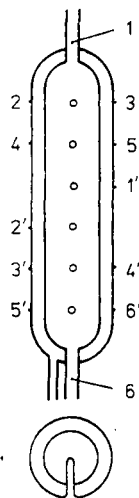


FIG. 7  
Scheme of location of thermocouples

temperatures according to the model are lower than the experimentally found ones in the axis of adsorber and apparently correspond to the mean temperature over the adsorber cross section.

The breakthrough curve of measurement in the adsorber with vacuum jacket and the model curve are illustrated in Fig. 6. The value of  $k = 1.3$  corresponds to the design of adsorber used. The relatively good agreement of the experimental breakthrough curve with the curve according to the model on using the physical parameters characterizing the system shows the possibility to employ the one-dimensional model for describing the course of non-isothermal adsorption in the laboratory adsorber

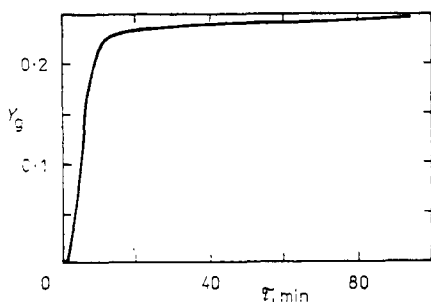


FIG. 8  
Breakthrough curve of experiment A4

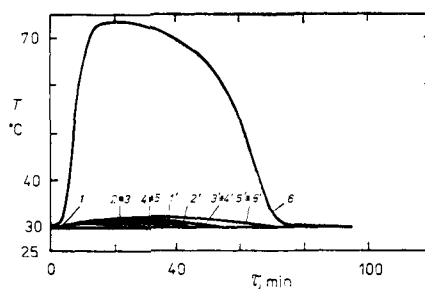


FIG. 9  
Temperature courses of gas at the inlet and outlet of adsorber and of chosen places of the adsorber surface during measurement A4. Location of thermocouples is in Fig. 7

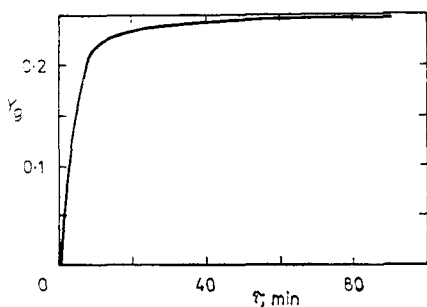


FIG. 10  
Breakthrough curve of experiment A5

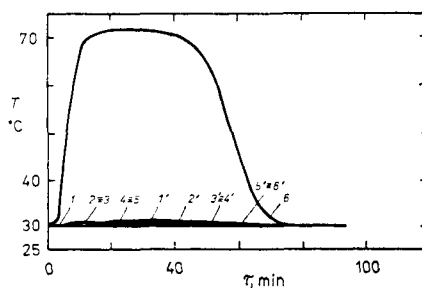


FIG. 11  
Temperature courses of entering and leaving gas and of chosen places of adsorber surface during measurement A5. Location of thermocouples is in Fig. 7



with vacuum silvered jacket. Low heat losses into surroundings and low heat capacity of insulation make it possible to realize the laboratory investigation of the course of adsorption under the conditions near adiabatic.

For the comparison of heat losses from vacuum-jacket adsorbers *c* and *d*, temperatures were investigated during adsorption at the inlet and outlet of adsorber and on the chosen places of surface. The location of thermocouples is depicted in Fig. 7. The results of measurements with the adsorber with silvered jacket and with the adsorber with radiation curtain are represented in Figs 8–11. Some results of calculations of approximate heat balances are given in Table III. The heat liberated during adsorption was calculated from the relation

$$Q_A = (-\Delta H) \cdot n_A, \quad (9)$$

where  $(-\Delta H) = 41.87 \text{ kJ mol}^{-1}$ . Heat losses into surroundings through the adsorber vacuum jacket were calculated from the relation

$$Q_S = \sum_{j=1}^m \sum_{i=1}^n \alpha_s S_i (t_{w_{ij}} - t_r) (\tau_{j+1} - \tau_j), \quad (10)$$

where the combined coefficient of heat transfer by radiation and convection  $\alpha_s = 35.15 + 0.251 (t_{w_{ij}} - t_r)$  in  $\text{kJ m}^{-2} \text{ h}^{-1} \text{ K}^{-1}$  (ref.<sup>5</sup>),  $S_i$  is the outer surface area of jacket of the part of adsorber on which there is mean temperature  $t_{w_{ij}}$  in time interval  $\tau_{j+1} - \tau_j$ ,  $t_r$  is the temperature of surroundings.

It can be seen in Table III that the heat losses into surroundings in the course of adsorption of the adsorbers investigated do not reach 5% of heat liberated by adsorption. Simultaneously, the differences between both the adsorbers are lower than 2%. Thus, it is possible to say that the one-dimensional model can be exploited when investigating the non-isothermal adsorption in laboratory glass adsorbers with vacuum silvered jacket or with vacuum jacket with radiation curtain.

## SYMBOLS

$a_p$	specific surface area of adsorbent particle, $\text{m}^2 \text{ m}^{-3}$
$A$	$= A_1 M_2$ dimensionless parameter in equilibrium relation
$A_1$	parameter in equilibrium relation, $\text{kmol kg}^{-1}$
$B$	$= B_1 T_{g0}$ dimensionless parameter in equilibrium relation
$B_1$	parameter in equilibrium relation, $\text{K}^{-1}$
$c_p$	specific heat capacity in fluid phase, $\text{J kg}^{-1} \text{ K}^{-1}$
$c_{pa}$	specific heat capacity of adsorber wall, $\text{J kg}^{-1} \text{ K}^{-1}$
$c_{ps}$	specific heat capacity of solid phase, $\text{J kg}^{-1} \text{ K}^{-1}$
$C_p$	$= c_p/c_{ps}$ dimensionless specific heat capacity of fluid phase
$C_{PA}$	$= c_{pa}/c_{ps}$ dimensionless specific heat capacity of adsorber wall
$d_1$	adsorber inside diameter, m
$d_2$	adsorber outside diameter, m

$D$	$\equiv D_1 \sqrt{T_{go}/P}$ dimensionless parameter in equilibrium relation
$D_e$	$\equiv D_{eo} \exp(-E/RT_g)$ effective diffusion coefficient, $m^2 s^{-1}$
$D_1$	parameter in equilibrium relation, $Pa K^{-1/2}$
$D_{11}$	$\equiv d_1/z_o$ dimensionless inside diameter of adsorber
$D_{22}$	$\equiv d_2/z_o$ dimensionless outside diameter of adsorber
$E$	activation energy of diffusion, $J mol^{-1}$
$E_K$	dimensionless activation energy of diffusion defined by Eq. (8)
$H$	$\equiv (-\Delta H)/(T_{go}c_{ps}M_2)$ dimensionless adsorption heat
$(-\Delta H)$	adsorption heat, $J kmol^{-1}$
$k$	correction factor
$k_{sc}$	$\equiv 15D_e/(a_p r_p^2)$ partial mass transfer coefficient of substance in solid phase, $m s^{-1}$
$k_{11}$	heat transfer coefficient related to surface of inside wall of adsorber, $W m^{-2} K^{-1}$
$K_{SC}$	$\equiv k_{sc} \rho_s z_o a_p / (\dot{n}_2 M_2)$ dimensionless mass transfer coefficient in solid phase
$K_T$	$\equiv k_{11} / (\dot{n}_2 M_2 c_{ps})$ dimensionless heat transfer coefficient
$m$	number of time increments
$M$	$\equiv \bar{M}/M_2$ dimensionless mean molar mass of fluid phase
$M_2$	molar mass of indifferent gas, $kg kmol^{-1}$
$\bar{M}$	mean molar mass of fluid phase, $kg kmol^{-1}$
$n$	number of increments into which was outside adsorber surface lengthwise divided
$n_A$	adsorbed amount of $CO_2$ , mol
$\dot{n}_2$	flow density of indifferent component, $kmol m^{-2} s^{-1}$
$P$	pressure in system, Pa
$P_K$	dimensionless parameter
$R$	gas constant, $J mol^{-1} K^{-1}$
$R$	$\equiv R_1/T_{go}$ dimensionless parameter in equilibrium relation
$R_A$	$\equiv \rho_o/\rho_s$ dimensionless density of adsorber wall
$R_o$	$\equiv \rho/\rho_s$ dimensionless gas density
$R_1$	parameter of equilibrium relation, K
$R_2$	$\equiv \rho_2/\rho_s$ dimensionless density of indifferent component
$T$	$\equiv T_g/T_{go}$ dimensionless temperature
$T_f$	temperature of surroundings, K
$T_g$	temperature of fluid phase, K
$T_{go}$	temperature of fluid phase at adsorber inlet, K
$T_{g2}$	temperature in adsorber before starting adsorption, K
$T_F$	$\equiv T_f/T_{go}$ dimensionless temperature of surroundings
$x$	concentration of adsorbate, $kmol kg^{-1}$
$X$	$\equiv xM_2$ dimensionless concentration of adsorbate
$Y$	$\equiv Y_g/Y_{go}$ dimensionless concentration of adsorptive
$Y_g$	relative mole fraction of adsorptive in gas phase, $kmol kmol^{-1}$
$z$	axial coordinate, m
$z_o$	height of adsorbent bed, m
$Z$	$\equiv z/z_o$ dimensionless axial coordinate
$\epsilon$	porosity of adsorbent bed
$\theta$	$\equiv \dot{n}_2 M_2 \tau / (\rho_s z_o)$ dimensionless time
$\rho$	density of fluid phase, $kg m^{-3}$
$\rho_a$	density of adsorber wall, $kg m^{-3}$
$\rho_s$	bulk density of adsorbent, $kg m^{-3}$
$\rho_2$	density of indifferent component in gas phase, $kg m^{-3}$
$\tau$	time, s

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