

Gas and vapour sorption in a gradientless reactor

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This paper is concerned with an apparatus which enables to measure kinetic and equilibrium sorption data of gases and vapours (one- or multicomponent mixtures) on solid substances — adsorbents by using the stream of an inert carrier gas. The design respects the demands on gradientless reactor in which the concentration and temperature on the surface of adsorbent and in the whole volume of gaseous phase is equal. The measuring procedure and evaluation of results are illustrated by an example comprising the sorption of *n*-heptane from a stream of nitrogen serving as a carrier gas.

В работе предложена аппаратура для измерения кинетических и равновесных сорпционных характеристик газов и паров (одно- и многокомпонентных смесей) из тока инертного газа-носителя на твердых веществах — адсорбентах. Конструкционное оформление учитывает требования предъявляемые к безградиентным реакторам, в которых концентрация и температура на поверхности адсорбента одинакова как во всем объеме газовой фазы. Методика измерений и их обработка иллюстрируется для случая сорпции *n*-гептана из азота как газа-носителя.

For the study of gas and vapour sorption (one component being adsorbate) on solid substances several devices have been developed. These devices differ from one another mainly in the method and accuracy of determining the sorbed amount of substances under given conditions. A survey and appreciation of the methods as well as of the proper sorption apparatuses is presented in [1]. In most of these apparatuses, either the kinetics and sorption equilibrium of multicomponent mixtures cannot be investigated at all or the measurement is burdened with the errors due to temperature and concentration gradients between the surface of solid substance and the main flow of gaseous mixture. These errors increase with increasing adsorption heat and the rate of gas sorption. Equal problems also appear in laboratory study of the kinetics of heterogeneous catalytic reactions for which the flow circulation reactors with differential layer of catalyst [2—4] and certain modifications of the Carberry type reactors [5, 6] proved to be the best.

The apparatus described in this paper was developed for measuring the kinetics and equilibrium of sorption of one- or multicomponent gaseous mixtures in the temperature interval 40—400°C and at pressures of 0.1—0.3 MPa, but it may be

also successfully used for the study of the kinetics and equilibrium of heterogeneous catalytic reactions under the above conditions. The apparatus consists of these principal parts (Fig. 1):

- stirred flow reactor with accessories,
- set of equipment for the preparation of sorption gas,
- analyzer of gaseous flow with accessories,
- set of equipment for measuring and controlling important operational variables.

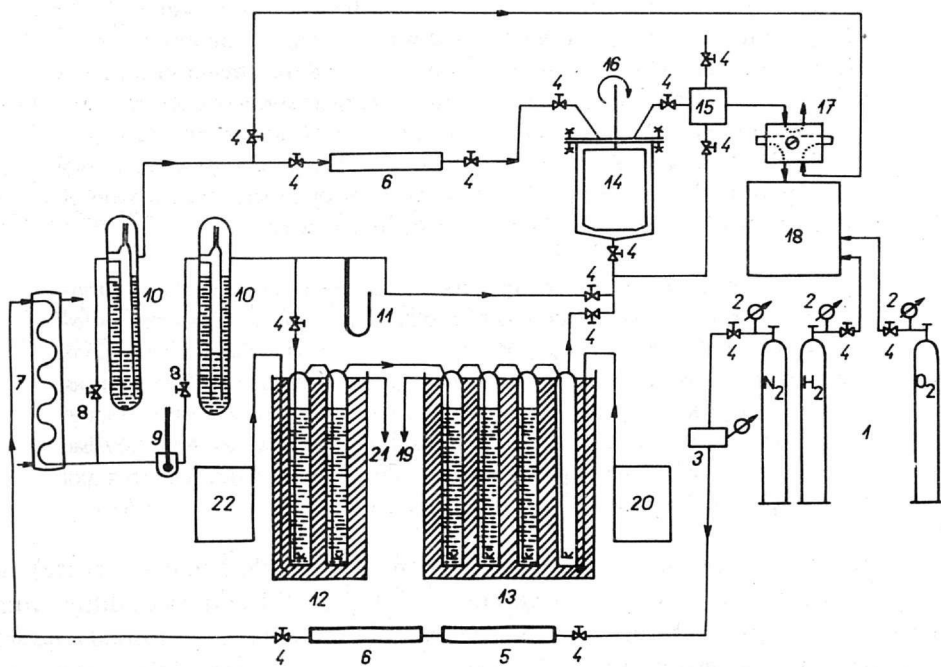


Fig. 1. Diagram of apparatus.

1. Gas reservoirs; 2. reduction valve; 3. membrane manostat; 4. needle valve; 5. catalyst tower; 6. drying tower; 7. thermostat; 8. fine dosing needle valve; 9. thermometer; 10. capillary flow meter; 11. differential mercury manometer; 12. saturator (1st step); 13. saturator (2nd step); 14. reactor; 15. capillary gas distributor; 16. electric motor; 17. dosing tap; 18. analyzer; 19., 20. cryostat; 21., 22. thermostat.

Components of the apparatus

The most important part of the apparatus is a stirred flow reactor which is schematically represented in axial section in Fig. 2. A control circuit maintains isothermal working conditions in the reactor by means of a heater (2—7) built in

the reactor jacket. The temperature may be controlled within the range 40–400°C, the accuracy being better than 0.5%. The major component of the circuit is a controller TRS-1 connected with a resistance temperature sensor Pt 100 which is put into a hole (2–13) of the reactor body. The controller processes the signal sent by the resistance sensor which is represented by a deviation from demanded value. After amplification and modification this signal serves for controlling a relay connected with the outlet. A line recorder ZEPk is used for recording the temperature.

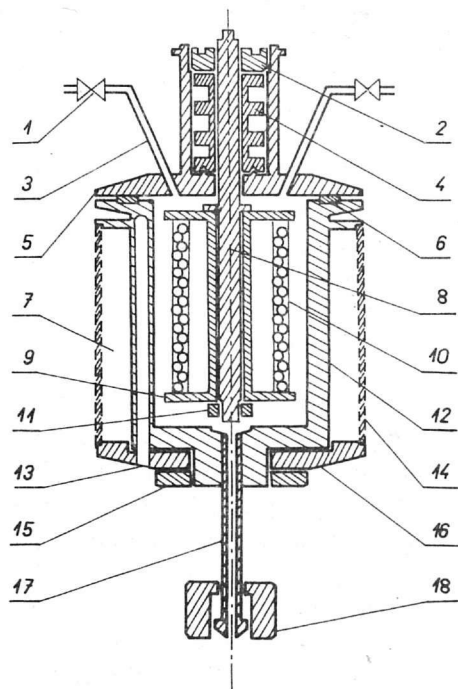


Fig. 2. Section through reactor.

1. Needle shutoff valve; 2. packing spring; 3. capillary; 4. packing; 5. reactor lid; 6. packing ring; 7. heater; 8. axis of reactor rotor; 9. supporter of sample; 10. bed of sample; 11. fastening spring; 12. reactor body; 13. hole of controlling sensing element; 14. perforated steel jacket; 15. fastening spring; 16. reactor lid; 17. input capillary; 18. cap nut.

Inside the reactor there is an exchangeable rotor (2–9) with the sample of adsorbent put on six beds. This rotor is in a vertical axis of rotation (2–8) driven by an electric motor. Each bed is made of cantal wire wound into the form of coil the diameter and lead of which is chosen according to the size of sorbent particles. A detail of bed and deposition of sample particles is schematically represented in Fig. 3.

A change in hydrodynamic regime of reactor may be simulated by a suited choice of rotor revolutions. The revolutions are measured with a tachodynamo K4A2 which produces d.c. voltage linearly dependent on revolutions accurate to 1%.

The upper lid (2–5) is joined to the body of reactor (2–12) with semicircular jaw clamps and the joint is packed with a sealing ring (2–6) which is put into

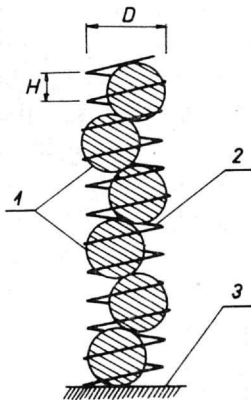


Fig. 3. Detail of the sample bed.

1. Particles of sample; 2. bed spiral; 3. supporter lid.

D — bed diameter;

H — spiral pitch.

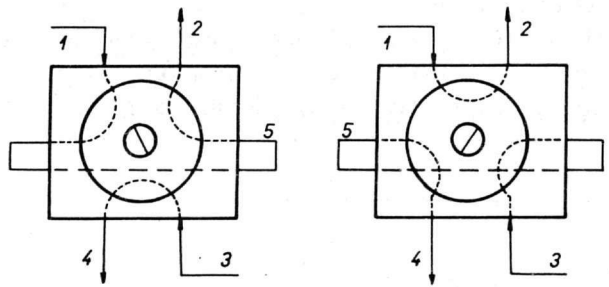


Fig. 4. Diagram of the function of the tap for sample dosing.

1. Supply of the gas stream from reactor; 2. waste gas in atmosphere; 3. carrier gas supply into analyzer; 4. inlet into analyzer; 5. calibrated vessel for the dosed sample.

a groove of ring form milled out in the head of reactor body. The tightness near the axis of rotation in the upper lid of reactor is secured by a specially formed teflon packing (2—4). The axial pressure produced by the torsion spring of packing results in a regulated strain of the packing in the places of weakened wall by means of which a multiple sealing ring is formed on the perimeter of the axis of rotation.

The demanded concentration of sorbate in gas flow is secured by saturating the stream of carrier gas in saturators where the carrier gas bubbles through a layer of liquid sorbate. The temperature of bath in the saturators is held at constant value by means of an ultrathermostat or ultracryostat. The carrier gas (nitrogen) is purified (deprived of oxygen) on porous Ronge copper and deprived of humidity on a layer of activated molecular sieve (Fig. 1.5, 1.6).

The steady flow of carrier gas is kept by a measuring and controlling system comprising a reduction valve (2—2), membrane manostat (1—3), fine dosing needle valve (1—8), and capillary flow meter (1—10). The flow of carrier gas may be controlled and measured in the range $10\text{--}60\text{ ml min}^{-1}$ within accuracy better than 0.5%.

The concentration of sorbate in gas flow at the entrance and exit from reactor is analyzed by means of a flame ionization detector. The dosing of a sample of gas stream from calibrated vessel into analyzer is rendered possible by a 6-way two-position dosing tap (1—17). Its function and connection with the calibrated vessel is evident from Fig. 4. The analysis of gas stream may be thus repeated in one minute or shorter time intervals.

Experimental

Materials

1. Adsorbent — spherical particles (2.8—3.0 mm) of the molecular sieve Calsit 5A produced in the Research Institute of Petroleum and Hydrocarbon Gases, Bratislava. The physical surface parameters determined by the sorption method [7] with an instrument Gravimat are as follows: specific surface $578 \text{ m}^2 \text{ g}^{-1}$, specific pore volume $0.247 \text{ cm}^3 \text{ g}^{-1}$, porosity 22.1%, mean pore diameter 0.85 nm.

2. Adsorbate — hydrocarbon *n*-heptane with following properties: density (20°C) 684 kg m^{-3} , refractive index (20°C) 1.3876, content of *n*-C₇H₁₆ at least 99.5%, content of water 0.01% at the most, the rest after evaporation 0.001% at the most.

3. Carrier gas — nitrogen of electric bulb industry deprived of oxygen and water vapour.

Sorption measurements and processing of experimental values

Before sorption measurements, the weight of the activated sample is determined. The weighed amount of adsorbent is activated for 6 h at 420°C in a thin-walled glass tube held in a thermostated block. Then the tube is sealed and on cooling to room temperature the loss of weight during activation as well as the weight of the activated sample is determined. The sample is transported from the tube into the reactor, the reactor is closed and the test of tightness is carried out. Undesirable impurities which could be adsorbed on the molecular sieve during the sample preparation in reactor are removed by desorption in a stream of purified nitrogen at 420°C. The time of desorption is 5 h.

After desorption (activation) the temperature of activation is reduced to the working temperature and the reactor is closed. The carrier gas is led through the saturators where it is saturated with the vapours of sorbate. When the composition gets settled, the gas stream is turned over and led through the reactor and the exit gas stream is analyzed in convenient time intervals. During adsorption, the adsorbate concentration in the exit stream successively increases with the saturation of adsorbent surface till it reaches the value to be found at the entrance into the reactor. Then the first step of adsorption is achieved and the surface of sample is saturated. Afterwards the reactor is closed, the partial pressure of sorbate in the gas stream is raised and the gas stream is led again into the reactor. Simultaneously, the analyzer records the change in the composition of the gas stream during the second step of adsorption. Similarly, the course of adsorption is recorded in subsequent steps when the partial pressure of sorbate in the carrier gas stream is successively increased.

The measurement of desorption is an immediate continuation of the measurement of adsorption. The measured stream of carrier gas is directly led through the reactor and the analyzer records the gradual decrease in the partial pressure of sorbate in the gas stream behind the reactor.

The sorption measurements provide a differential record of the deflections of recorder pen Δs as a function of time t registered by a line recorder

$$\Delta s = f(t) \quad (1)$$

The corresponding values of partial pressure of sorbate p may be assigned to instantaneous deflections Δs according to the calibration curve of the analyzer. Thus, a set of experimental values of the partial pressure of sorbate in gas stream p is to be obtained as a function of time t

$$p = f(t) \quad (2)$$

The adsorbed amount of sorbate $a(t)$ at the time moment t is to be determined from the measured data on the basis of material balance according to the algorithm resulting from the subsequent procedure.

The density of nitrogen serving as a carrier gas ρ_{N_2} may be calculated from the known (measured) value T_{N_2} and the pressure of nitrogen p_{N_2} in a flow meter

$$\rho_{N_2} = \frac{M_{N_2}}{RT_{N_2}} p_{N_2} \quad (3)$$

The mass flow of nitrogen \dot{Q} can be determined on the basis of the measured volume flow \dot{V} in a flow meter from the product

$$\dot{Q} = \dot{V} \rho_{N_2} \quad (4)$$

The relative mass fraction of sorbate in gas stream as a function of time $\bar{Y}(t)$ corresponding to the experimental value of partial pressure $p(t)$ is given by the ratio

$$\bar{Y}(t) = \frac{M p(t)}{[\pi - p(t)] M_{N_2}} \quad (5)$$

where π is the total working pressure in the reactor.

The mass flow of sorbate in gas stream at the exit from reactor as a function of time $\dot{G}(t)$ may be expressed as follows

$$\dot{G}(t) = \dot{Q} \bar{Y}(t) \quad (6)$$

The adsorbed amount $a(t)$ of adsorbate on adsorbent at the time moment t ensues from the equation

$$a(t) = \int_{t=0}^t [\dot{G}_z(t) - \dot{G}(t)] dt \quad (7)$$

where $\dot{G}_z(t)$ is the mass flow of sorbate in the gas stream at the exit from reactor at the time moment t provided no adsorption takes place. It may be determined by using the measured residence time distribution function in the system $F(t)$ [8]. Thus the values of $\dot{G}_z(t)$ are found from the product

$$\dot{G}_z(t) = \dot{G}_0 F(t) \quad (8)$$

where \dot{G}_0 is the mass flow of sorbate in gas stream at the entrance into the reactor.

The residence time distribution function $F(t)$ as an important hydrodynamic characteristic of reactor was experimentally found by the method of stimulus and response using the jump change in the input signal. Its course for the system reactor—joining branch—analyzer is shown in Fig. 5.

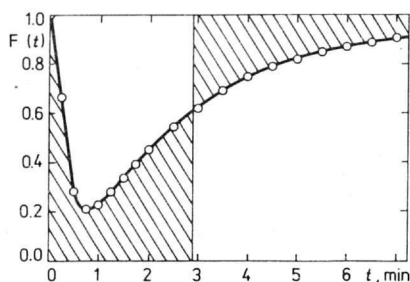


Fig. 5. Residence time distribution function in apparatus $F(t)$, for the system: reactor—joining branch—analyzer.

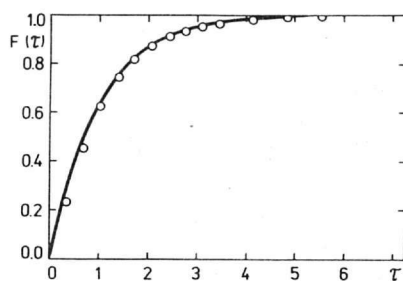


Fig. 6. Dimensionless residence time distribution function in reactor $F(\tau)$.
— Ideally stirred reactor; \circ experimental reactor.

For the evaluation of the efficiency of mixing in the reactor, Fig. 6 shows the course of the function of dimensionless residence time $F(\tau)$ for the proper experimental reactor as well as the ideally stirred reactor. As obvious a regime close to that of the ideally stirred reactor may be stabilized in the experimental apparatus.

In the region of diffusion at constant temperature, the value of the adsorbed amount $a(t)$ depends on the flow of gas stream through reactor and on the number of revolutions of the rotor in which the adsorbent is deposited. For the delimitation of this region a series of kinetic measurements was carried out and processed in the form of the functional relationship

$$c(t) = f(t_b) \quad (9)$$

where $c(t)$ is the dimensionless (relative) concentration of sorbate in the exit gas stream defined by the expression

$$c(t) = \frac{C(t) - C_{p0}}{C_0 - C_{p0}} \quad (10)$$

and t_b is the dimensionless time of sorption expressed as the ratio

$$t_b = \frac{t}{t_k} \quad (11)$$

In eqn (11), the quantity t_k represents the shortest possible time in which the adsorbate may be transported in the necessary amount into reactor in one adsorption step at a given flow of the gas stream. It may be determined from the equation

$$t_k = \frac{(m - m_{p0}) + (C_m - C_{p0}) V}{\dot{G}_0} \quad (12)$$

For illustration, we present the results of the kinetic sorption measurements of *n*-heptane on a molecular sieve under the following conditions: temperature 98°C, pressure in reactor 100.3 kPa, flow of carrier gas through reactor 0.025 g min⁻¹, number of rotor revolutions 0 min⁻¹, 50 min⁻¹, 165 min⁻¹, and 420 min⁻¹. The results are summarized in Fig. 7.

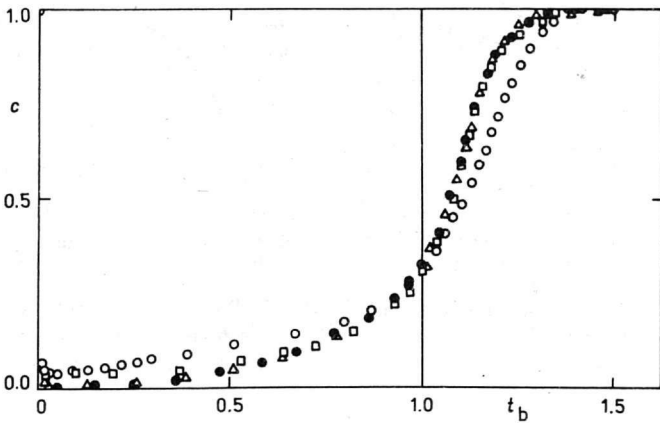


Fig. 7. Adsorption wave at different numbers of rotor revolutions.

○ 0 min⁻¹; □ 50 min⁻¹; △ 165 min⁻¹; ● 420 min⁻¹.

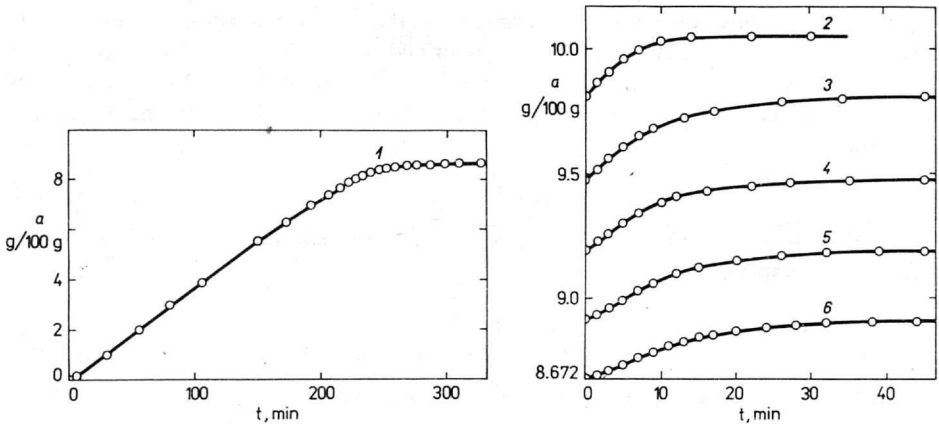


Fig. 8. Kinetic curves of the amount adsorbed at 420 revolutions per minute $a(t)$.

First step of adsorption — left part of diagram; further steps of adsorption — right part of diagram.

1. $p = 557$ Pa; 2. $p = 4.72$ kPa;
 3. $p = 3.44$ kPa; 4. $p = 2.33$ kPa;
 5. $p = 1.52$ kPa; 6. $p = 0.927$ kPa.

The kinetic data of the adsorbed amount $a(t)$, numerically calculated on a digital computer according to eqn (7) are presented in Fig. 8.

It is obvious from Fig. 7 that the results of the measurements at higher numbers of revolutions (above 165 min⁻¹) are only little different. It ensues from this fact that a change in hydrodynamic conditions does not significantly influence the sorption kinetics in this region which may be regarded as a kinetic region where the concentration and temperature gradients between the sorbent surface and the main gas stream are negligible.

Discussion

The experimental results have confirmed that the proposed reactor is suited for measuring the kinetics and equilibrium of gas and vapour sorption of pure components and their mixtures as well as for studying the kinetics and equilibrium of heterogeneous catalytic reactions especially for these reasons:

- Under certain hydrodynamic conditions which may be simulated by rotor revolutions in a wide range, the concentration and temperature gradients between the sorbent surface and the main gas stream may be eliminated.
- Possibility of using low flow of inert gas and sorbate through reactor.
- Possibility of relatively rapid achieving a hydrodynamically steady state in reactor. This piece of knowledge is to be confirmed by measuring the residence time distribution function in reactor.
- Reliable control of the isothermal regime in reactor.
- Relatively simple evaluation of the measured kinetic data.
- Rapid and direct analysis of the exit gas stream leaving the reactor.

Symbols

- $a(t)$ adsorbed amount of adsorbate on adsorbent
 C_0 mass concentration of sorbate in gas stream at the entrance into reactor
 C_m mass concentration of sorbate in gas stream corresponding to the mass of sorbate on sorbent m
 C_{p0} mass concentration of sorbate in gas stream after saturation in the preceding step of sorption
 $C(t)$ mass concentration of sorbate in gas stream at the exit from reactor
 $c(t)$ dimensionless concentration of sorbate in gas stream
 $F(t)$ residence time distribution function
 $F(\tau)$ dimensionless residence time distribution function
 \dot{G}_0 mass flow of sorbate in gas stream at the entrance into reactor
 $\dot{G}(t)$ mass flow of sorbate in gas stream at the exit from reactor
 $\hat{G}_z(t)$ mass flow of sorbate in gas stream at the exit from reactor provided no adsorption takes place
 M molecular weight of sorbate
 M_{N_2} molecular weight of carrier gas
 m weight of sorbate on a sample of sorbent
 m_{p0} weight of sorbate on a sample of sorbent after saturation in the preceding step of sorption
 p_{N_2} partial pressure of carrier gas
 $p(t)$ partial pressure of sorbate in gas flow
 \dot{Q} mass flow of carrier gas
 Δs deflection of recorder pen

t	time
T	temperature of reactor
T_{N_2}	temperature of carrier gas in flow meter
V	free volume of reactor
\dot{V}	volume flow of carrier gas in flow meter
$\bar{Y}(t)$	relative mass fraction of sorbate in gas stream
π	total working pressure in reactor
ρ_{N_2}	density of carrier gas

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