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## Experimental adsorption isotherms based on inverse gas chromatography

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### Abstract

A new chromatographic perturbation method is used for studying the adsorption–desorption equilibrium in various gas–solid heterogeneous systems. It is the reversed-flow method giving accurate and precise values of many physico-chemical constants including the basic and necessary adsorption isotherm values. For four inorganic oxides, namely,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{PbO}$ , and two aromatic hydrocarbons (benzene, toluene) these adsorption isotherms have been determined through a non-linear model.

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### 1. Introduction

Progress in many areas of material science and engineering requires the development of new advanced methods for studying processes occurring at phase boundaries. Reversed-flow gas chromatography (RF-GC) [1] is used to study gas–solid interfaces [2,3].

The RF-GC method differs from the classical chromatographic methods in that the stationary phase properties rather than the solute properties are of interest. Thus, it provides information about the nature and behavior of the material surface in various environments, including individual material prop-

erties and the influence of air pollution on these properties. In addition, traditional inverse gas–solid chromatography [4] has roughly the same aims, but as it is a classical chromatographic elution method, it has several weak points: it does not take into account the sorption effect, it neglects the mass-transfer phenomena taking place, and is also influenced by the carrier gas flow.

With the use of suitable personal computer programs [3,5], the study of the absorption–desorption phenomena of many solutes on many solids becomes possible, without specifying a priori an absorption isotherm equation. Two significant advantages of this method are simplicity and low cost in relation to the time required.

In contrast to the work accomplished with the same RF-GC method based on a linear model [6], this study is based on a non-linear–adsorption isotherm model [2] which is appropriate for studying

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oxides and non-metals in general. The failure of a linear model in this case is attributed to surface heterogeneity of these substances [7].

This work focuses on the experimental examination of some powders which are used in processing in the paint and ceramic industries as well as in catalyst preparation and utilization, namely  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{PbO}$ .

## 2. Experimental

The RF-GC technique involves perturbation of the flow-rate of the carrier gas, simply achieved experimentally by using a four- or six-port gas sampling valve and reversing the direction of flow of the carrier gas, usually for a short time interval. If pure carrier gas passes through the sampling column, nothing happens on reversing the flow. If a solute comes out of the diffusion column at  $z=0$  (Fig. 1) as a result of its diffusion into the carrier gas, filling the column  $z$  and also running along the sampling column, the flow reversal records the concentration of the solute at the junction of the sampling and diffusion columns at the moment of reversal. This recording of concentration has the form of extra chromatographic peaks superimposed on the otherwise continuous detector signal (Fig. 2). The moment of injection is time 0 and some flow reversals

and flow restorations are indicated on the chart recorder strip (Fig. 2).

The chromatograph used was a Shimadzu 8A, slightly modified, with a flame ionization detection (FID) system. The experimental arrangement was analogous to that used in catalytic studies [8], and is very different from those used in the past [3]. Here the  $L_1$  section (20.5–23.4 cm) did not contain any solid material, while the  $L_2$  (4.0–5.0 cm) section contained the solid bed. Both sections,  $L_1$  and  $L_2$ , were made of Pyrex glass with I.D. 3.5 mm. The sampling column  $l'+l$  (40 cm+40 cm) was a stainless steel chromatographic tube of 4.0 mm I.D.

A small quantity of liquid benzene (4.0  $\mu\text{l}$ ) or toluene (4.7  $\mu\text{l}$ ) was injected into the end of column containing the solid bed ( $\text{PbO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ). After the appearance of the continuously rising concentration–time curve, the reversing procedure for the nitrogen carrier gas flow started, each reversal lasting 10 s. The narrow fairly symmetrical sample peaks created by the flow reversals were recorded and their height was printed as a function of time  $t$ .

Conditioning in situ at 473.2 K, under a continuous flow of nitrogen, for 24 h, is necessary, followed each time by adjustment of the working temperature (363.2 K for benzene and 393.2 K for toluene).

Toluene was a Mallinckrodt analytical reagent and benzene a special laboratory reagent for chromatography from BDH (UK). The inorganic oxides ( $\text{PbO}$ ,

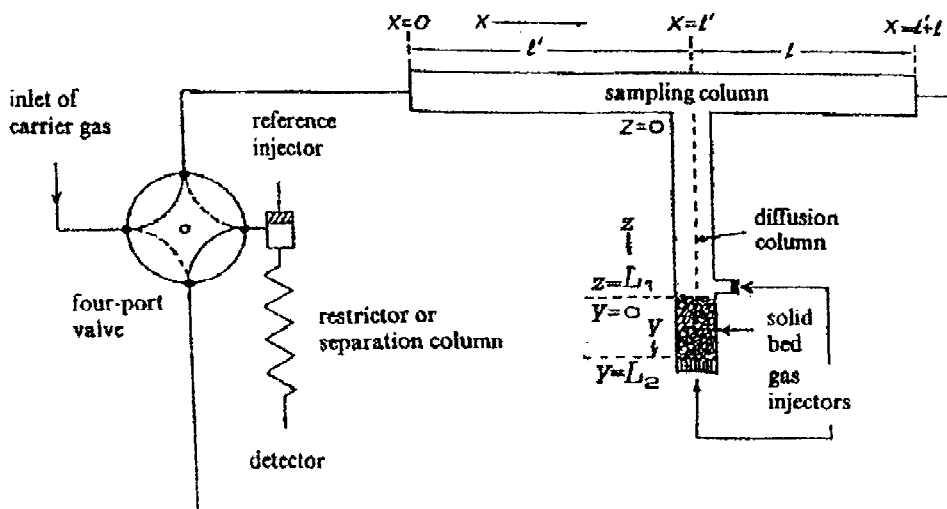


Fig. 1. Outline for the experimental arrangement for the study of adsorption isotherms.

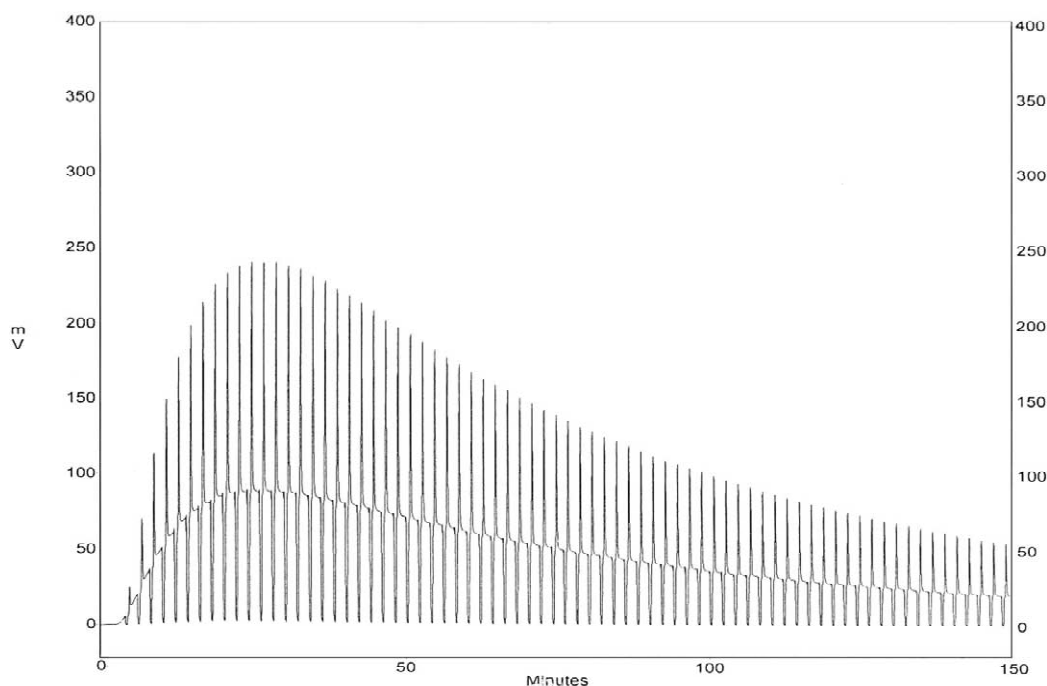


Fig. 2. Sample peaks from the chromatograph Shimadzu 8A with FID.

$\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ) were Merck analytical reagents, and were used as such. The external porosity and the specific surface of the solids are shown in Table 1. The volumetric flow rate of the nitrogen carrier gas was equal to  $26.0 \text{ cm}^3 \text{ min}^{-1}$ .

### 3. Calculations

The theoretical analysis relevant to the present work, dealing with physicochemical parameter determination under non-steady-state conditions, has been published elsewhere [9,10]. All the calculations have been made with a GW-Basic personal computer program using the experimental data (heights of

chromatographic peaks in relation to time). Only the absolutely necessary mathematical equations are quoted here to help the reader understand how the parameters in the tables and figures were extracted from the experimental data.

Four basic equations are mentioned.

First, the local adsorption isotherm of the solute studied is:

$$c_s^* = \frac{m_s}{a_s} \cdot \delta(y - L_2) + \frac{a_y}{a_s} \cdot k_1 \int_0^t c_y(\tau) d\tau \quad (1)$$

where  $c_s^*$  is equilibrium adsorbed concentration of the solute at time  $t$ ,  $\text{mol g}^{-1}$ ;  $m_s$  is initially adsorbed amount of this solute,  $\text{mol}$ ;  $a_s$  is amount of solid material per unit length of column bed,  $\text{g cm}^{-1}$ ;  $\delta(y - L_2)$  is Dirac's delta function for the initial condition of the bed, when the solute is introduced as an instantaneous pulse at point  $y = L_2$ ,  $\text{cm}^{-1}$ ;  $y$  is length coordinate along section  $L_2$ ,  $\text{cm}$ ;  $a_y$  is cross-sectional area of the void space in region  $y$ ,  $\text{cm}^2$ ;  $k_1$  is local adsorption parameter,  $\text{s}^{-1}$ ;  $c_y$  is gaseous concentration of the solute as a function of time  $t$  and coordinate  $y$  along the column,  $\text{mol cm}^{-3}$ ; and  $\tau$  is dummy variable for time.

Table 1

External porosity ( $\epsilon$ ) and specific surface area (SSA) of the four solids used

Solid	$\epsilon$	SSA ( $\text{cm}^2 \text{ g}^{-1}$ )
$\text{Cr}_2\text{O}_3$	0.7252	33400
$\text{Fe}_2\text{O}_3$	0.7988	23400
$\text{PbO}$	0.5551	300
$\text{TiO}_2$	0.5459	31100

Secondly, the mass balance equation for the solute in the gaseous region  $z$  of the diffusion column is:

$$\frac{\partial c_z}{\partial t} = D_1 \cdot \frac{\partial^2 c_z}{\partial z^2} = k_{\text{app}} c_z \quad (2)$$

where  $c_z$  is gaseous concentration of the solute as a function of time  $t$  and length coordinate  $z$  along the column,  $\text{mol cm}^{-3}$ ;  $D_1$  is diffusion coefficient of this solute into the carrier gas (nitrogen),  $\text{cm}^2 \text{s}^{-1}$ ; and  $k_{\text{app}}$  is apparent rate constant of a first-order or pseudofirst-order reaction of the solute in the gas phase,  $\text{s}^{-1}$ .

Next, the mass balance equation of the same solute in the region  $y$  of the diffusion column, filled with the solid material under study is:

$$\frac{\partial c_y}{\partial t} = D_2 \cdot \frac{\partial^2 c_y}{\partial y^2} - k_{-1} \cdot \frac{a_s}{a_y} \cdot (c_s^* - c_s) - k_{\text{app}} c_y \quad (3)$$

where  $D_2$  is diffusion coefficient of this solute into the gas phase in section  $y$ ,  $\text{cm}^2 \text{s}^{-1}$ ;  $k_{-1}$  is rate constant for desorption of the solute from the solid bulk,  $\text{s}^{-1}$ ; and  $c_s$  is concentration of the solute adsorbed on the solid at time  $t$ ,  $\text{mol g}^{-1}$ .

Finally, the rate of change of the adsorbed concentration is given by the equation:

$$\frac{\partial c_s}{\partial t} = k_{-1}(c_s^* - c_s) - k_2 c_s \quad (4)$$

where  $k_2$  ( $\text{s}^{-1}$ ) is the rate constant of a possible first-order or pseudofirst-order surface reaction of the adsorbed solute.

With the initial conditions

$$c_y(0, y) = \frac{m}{a_y} \cdot \delta(y - L_2),$$

and  $c_s(0, y) = 0$ ,  $m$  being the amount (mol) of the solute introduced as a pulse at  $y = L_2$ , the solution of the system of differential Eqs. (1)–(4) leads to the function [9]:

$$H^{1/M} = gc(l', t) = \sum_{i=1}^4 A_i \exp(B_i t) \quad (5)$$

where  $H$  is height of sample peaks resulting from the flow reversal,  $\text{cm}$ ;  $M$  is response factor of the detector, dimensionless;  $g$  is calibration factor of the detector,  $\text{cm per mol/cm}^3$ ; and  $c(l', t)$  is measured sampling concentration of the solute,  $\text{mol cm}^{-3}$ .

The explicit calculation of the isotherm can be carried out as described elsewhere [2]. However, the following equations are improved [11], as they are based on Eq. (5), rather than Eq. (6), as done originally [2]:

$$H^{1/M} = gc(l', t) = \sum_{i=1}^3 A_i \exp(B_i t) \quad (6)$$

$$\frac{\partial c_s^*}{\partial c_G} = k_1 \cdot \frac{a_y \sum_{i=1}^4 A_i \exp(B_i t)}{a_s \sum_{i=1}^4 A_i B_i \exp(B_i t)} \quad (7)$$

$$c_s^* = \frac{k_1 a_y}{g a_s} \cdot \sum_{i=1}^4 A_i [\exp(B_i t) - 1] / B_i \quad (8)$$

$$c_G = \frac{1}{g} \cdot \sum_{i=1}^4 A_i \exp(B_i t) \quad (9)$$

where  $c_G$  is the gaseous concentration of the probe solute ( $\text{mol/cm}^3$ ), and  $A_i$  and  $B_i$  are the pre-exponential factors and the exponential coefficients of Eq. (5). One can consider  $\tau$  in the above equations as a dummy independent variable and calculate, for chosen arbitrary values of  $\tau$ , both the differential isotherm  $\partial c_s^* / \partial c_G$  and  $c_s^*$ , together with the corresponding values of  $c_G$ . Plotting  $\partial c_s^* / \partial c_G$  or  $c_s^*$  against  $c_G$  for each chosen  $\tau$ , independent experimental isotherms are obtained.

#### 4. Results and discussion

The differential isotherms for the four oxides and the two aromatic hydrocarbons are shown in Tables 2 and 3, while the integrated isotherms are plotted and shown in Figs. 3 and 4.

From Figs. 3 and 4, it is obvious that characterization of the adsorptive properties of the different solids is possible. It is shown for example that PbO behaves very differently from the other oxides used. That is, among  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and PbO studied with benzene or toluene, the isotherms of the last oxide have the lowest  $c_s^*$  values. The shapes of all isotherms remain unchanged.

As a result, safe and accurate conclusions about chemical reactivity and kinetics can be made to-

Table 2  
The differential isotherms for the adsorption of benzene on four oxides at 363.2 K

Dummy variable (min)	$(\partial c_s^*/\partial c_G) (\text{cm}^3 \text{g}^{-1})$			
	PbO	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
25	0.3086	3.086	4.473	171.7
30	0.2359	2.442	2.538	5.501
35	0.2159	2.411	2.213	3.974
40	0.2151	2.570	2.207	3.687
45	0.2261	2.823	2.351	3.769
50	0.2474	3.136	2.602	4.049
55	0.2792	3.487	2.944	4.473
60	0.3225	3.860	3.371	5.017
65	0.3781	4.241	3.873	5.660
70	0.4463	4.617	4.435	6.381
75	0.5258	4.977	5.036	7.154
80	0.6136	5.310	5.649	7.948
85	0.7051	5.611	6.248	8.731
90	0.7948	5.877	6.807	9.474
95	0.8775	6.106	7.310	10.15

gether with correct explanations about the studied systems based on these experimentally obtained isotherms, since the kinetic parameters are closely related to the existing adsorption isotherm, depending strongly on the adsorption–desorption phenomena. Many other systems can be examined with the same method.

We believe that this method is to be preferred to the classical inverse gas chromatographic methods,

Table 3  
The differential isotherms for the adsorption of toluene on four oxides at 393.2 K

Dummy variable (min)	$(\partial c_s^*/\partial c_G) (\text{cm}^3 \text{g}^{-1})$			
	PbO	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
25	0.3660	1.750	−30.21	−3.702
30	0.1899	0.9990	2.147	9.302
35	0.1484	0.8467	1.327	3.326
40	0.1322	0.7984	1.082	2.501
45	0.1257	0.7994	0.9804	2.252
50	0.1248	0.8350	0.9378	2.205
55	0.1278	0.9024	0.9286	2.272
60	0.1344	1.003	0.9423	2.425
65	0.1448	1.140	0.9739	2.653
70	0.1594	1.315	1.021	2.951
75	0.1786	1.530	1.082	3.314
80	0.2030	1.778	1.158	3.731
85	0.2331	2.049	1.246	4.185
90	0.2687	2.329	1.345	4.655
95	0.3094	2.599	1.453	5.116

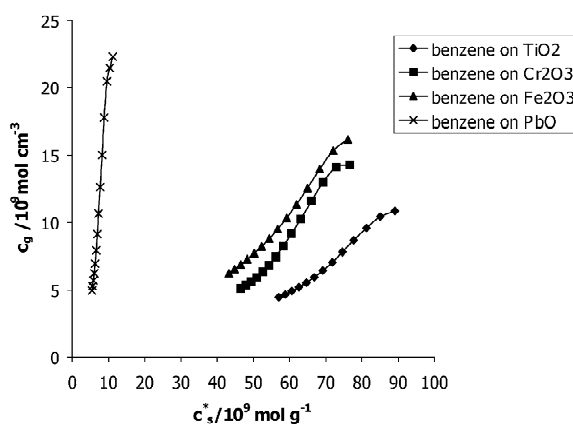


Fig. 3. Adsorption isotherms for PbO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and Cr<sub>2</sub>O<sub>3</sub> with benzene.

which are elution techniques. This method has the following advantages [2]: (a) it does not need an a priori isotherm equation; (b) it accounts for the mass transfer phenomena; (c) it takes desorption into account; (d) a sorption effect is absent; and (e) it produces isotherms in the presence of a possible heterogeneous and also an homogeneous reaction in the gas-phase.

In addition further advances have been achieved: (a) explicit calculation of the isotherms was not carried out as described in Ref. [2] but was based on further improved equations; (b) the adsorption and kinetic measurements were rendered independent of the diffusion coefficient of the gas injected, which until now was determined independently, found in

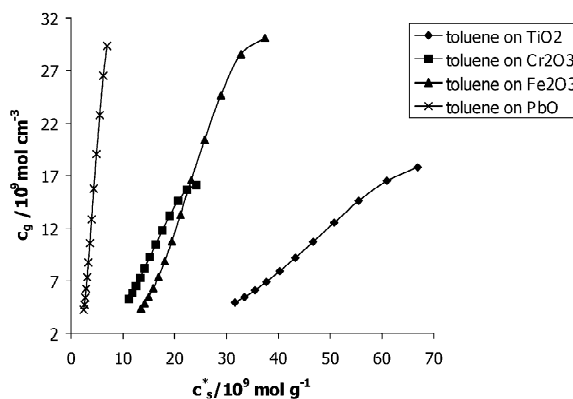


Fig. 4. Adsorption isotherms for PbO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and Cr<sub>2</sub>O<sub>3</sub> with toluene.

the literature or calculated theoretically, under different conditions, and used for the kinetic calculations; (c) the experimental set-up does not include a denuder tube as in Ref. [2], but a diffusion column containing the solid adsorbent or an ordinary catalytic bed. This arrangement was first used in Ref. [5] but the results were based on linear isotherms.

For all these reasons, the results based on this new arrangement and the improved mathematical model of a non-linear adsorption isotherm are accurate. The present method gives accurate values of the kinetic constants studied [10] because of the non-linear model isotherm calculation, helped by the use of a suitable personal computer program, as the non-homogeneity of the surface of the oxides studied here does not permit a linear adsorption isotherm model [8]. A point worth mentioning is that comparison of these isotherms with others measured by established methods is impossible, since in the present case we are dealing with local isotherms, with each value referring to a particular adsorption energy changing with time, whilst those based on traditional methods are global overall isotherms.

## References

- [1] N.A. Katsanos, *Flow Perturbation Gas Chromatography*, Marcel Dekker, New York, 1988.
- [2] V. Sotiropoulou, G.P. Vasilev, N.A. Katsanos, H. Metaxa, F. Roubani-Kalantzopoulou, *J. Chem. Soc., Faraday Trans. 91* (1995) 485.
- [3] G. Karagéorgos, F. Roubani-Kalantzopoulou, *Z. Phys. Chem.* 203 (1998) 231.
- [4] J. Roles, G. Guiochon, *J. Phys. Chem.* 95 (1991) 4098.
- [5] I. Topalova, A. Niotis, N.A. Katsanos, V. Sotiropoulou, *Chromatographia* 41 (1995) 227.
- [6] N.A. Katsanos, F. Roubani-Kalantzopoulou, *J. Chromatogr. A* 710 (1995) 191.
- [7] B. Gates, in: *Catalytic Chemistry*, Wiley, New York, 1992, p. 326.
- [8] X. Yun, Z. Long, D. Kou, X. Lu, H. Li, *J. Chromatogr. A* 736 (1996) 151.
- [9] Ch. Abatzoglou, E. Iliopoulou, N.A. Katsanos, F. Roubani-Kalantzopoulou, A. Kalantzopoulos, *J. Chromatogr. A* 775 (1997) 211.
- [10] A. Kalantzopoulos, S. Birbatakou, F. Roubani-Kalantzopoulou, *Atmos. Environ.* 32 (1998) 1811.
- [11] N.A. Katsanos, R. Thede, F. Roubani-Kalantzopoulou, *J. Chromatogr. A* 795 (1998) 133.