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HETEROGENEITY EFFECTS IN ADSORPTION KINETICS OF GAS MIXTURES

By

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Abstract

The fundamental differential equation of kinetics of gas adsorption has been formulated for adsorption of multicomponent gas mixtures on energetically heterogeneous solid surfaces. This approach leads to a simple dependence for two arbitrary adsorbing components; namely, the ratio of surface coverages is a simple power function of the ratio of partial pressures. Many experimental data available from the literature fit very well this relationship.

Introduction

The kinetics of adsorption process is determined by rates of adsorption, desorption and diffusion. In the case of adsorption from gaseous phase the diffusion is generally sufficiently fast that it plays no role in the determination of the kinetics. Thus the diffusion effects may be neglected.

Many attempts have been made to describe the adsorption kinetics of single gases on homogeneous surfaces.¹⁻⁶⁾ Only a few of them consider the adsorption kinetics of gas mixtures.^{3,7)} However, for the case of a heterogeneous surface, the kinetics of monolayer adsorption is usually discussed at low surface coverages or at surface coverages close to unity.^{2,3,8)} In the other cases, the adsorption kinetics is modelled by the empirical equations. The recent studies of Wojciechowski *et al.*^{9,10)} lead to the expressions describing kinetics of monolayer adsorption of single gases on heterogeneous surfaces in the whole region of the surface coverages.

In this paper we propose an approach to the kinetics of monolayer mixed-gas adsorption on heterogeneous solid surfaces, basing on the theory of mixed-gas adsorption¹¹⁻²¹⁾ and partially applying the results obtained by Wojciechowski *et al.*^{9,10)} for adsorption kinetics of single gases.

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Equation of sorption rate

Let us consider a n -component gas mixture on a heterogeneous surface by neglecting the lateral interactions and assuming identical molecular area for all components. Such assumptions occur frequently in the theory of gas adsorption.¹⁻¹³⁾ The fundamental equation of kinetics of gas adsorption may be formulated as follows:

$$\frac{dN_{i(n),l}}{dt} = k_{il}^a p_i (M_l - \sum_{i=1}^n N_{i(n),l}) - k_{il}^d N_{i(n),l} \quad (1)$$

where the subscripts i and l concern the i -th component and l -th surface patch, respectively; M_l is the number of adsorption sites on the l -th surface patch; $N_{i(n),l}$ is the number of adsorbed molecules of the i -th component on the l -th surface patch; p_i is the partial pressure of the i -th component; k_{il}^a and k_{il}^d are adsorption and desorption constants for the i -th component and l -th surface patch. According to the treatment¹¹⁻¹⁴⁾ each adsorption site is characterized by vector of activation energies of all components. Then, the total number of adsorbed molecules of the i -th component on the whole surface is equal to

$$N_{i(n)} = \sum_{l=1}^L N_{i(n),l} \quad (2)$$

where L is the number of surface patches. However, the rate equation for the whole surface is

$$\frac{dN_{i(n)}}{dt} = p_i \sum_{l=1}^L k_{il}^a (M_l - \sum_{i=1}^n N_{i(n),l}) - \sum_{l=1}^L k_{il}^d N_{i(n),l} \quad (3)$$

Replacing in Eq. (3) the symbols $N_{i(n),l}$ and $N_{i(n)}$ by the relative surface coverages, we obtain:

$$\frac{dV_{i(n)}}{dt} = p_i \sum_{l=1}^L k_{il}^a h_l (1 - \theta_{(n)}) - \sum_{l=1}^L k_{il}^d h_l \theta_{i(n)} \quad (4)$$

where $\theta_{i(n)} = N_{i(n),l}/M_l$ and $V_{i(n)} = N_{i(n)}/M$ are monolayer surface coverages of the i -th component from n -component gas mixture on homogeneous and heterogeneous surfaces, respectively; $M = \sum_{l=1}^L M_l$ is the total number of adsorption sites; $h_l = M_l/M$; and $\theta_{(n)} = \sum_{i=1}^n \theta_{i(n)}$. Now we apply in Eq. (4) a similar approximation to that, which has been introduced by Wojciechowski *et al.*^{9,10)} In the case of adsorption kinetics of n -component gas mixtures this approximation may be expressed by means of two equations:

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$$\sum_{i=1}^L k_{il}^a h_i (1 - \theta_{i(n)}) = \bar{k}_i^a (1 - V_{(n)}) \cdot X(1 - V_{(n)}) \quad (5)$$

and

$$\sum_{i=1}^L k_{il}^d h_i \theta_{i(n)} = \bar{k}_i^d V_{i(n)} \cdot Y(V_{i(n)}) \quad (6)$$

Simulations for adsorption kinetics of single gases⁹⁾ have shown that in practice X and Y are well represented by simple power functions. Thus, in the case of mixed-gas adsorption the functions X and Y may be expressed by:

$$X(1 - V_{(n)}) = (1 - V_{(n)})^\omega; \quad \omega > 0 \quad (7)$$

and

$$Y(V_{i(n)}) = (V_{i(n)})^{m_i}; \quad m_i > 0 \quad (8)$$

Applying Eqs. (5)-(8) in Eq. (4) we get

$$\frac{dV_{i(n)}}{dt} = \bar{k}_i^a p_i (1 - V_{(n)})^{\omega+1} - \bar{k}_i^d (V_{i(n)})^{m_i+1} \quad (9)$$

At the equilibrium Eq. (9) generates the following adsorption isotherm:

$$(V_{i(n)})^{m_i+1} / (1 - V_{(n)})^{\omega+1} = (\bar{k}_i^a / \bar{k}_i^d) p_i \quad (10)$$

The constants ω and m_i may be treated as heterogeneity parameters. For many adsorption systems these parameters are approximately identical, *i. e.*, $\omega = m_i$, and then we get

$$\frac{dV_{i(n)}}{dt} = \bar{k}_i^a p_i (1 - V_{(n)})^{\omega+1} - \bar{k}_i^d (V_{i(n)})^{\omega+1} \quad (11)$$

and

$$V_{i(n)} = \frac{c_i (p_i)^r}{1 + \sum_{j=1}^n c_j (p_j)^r} \quad (12)$$

where

$$r = (\omega + 1)^{-1} \quad \text{and} \quad c_i = (\bar{k}_i^a / \bar{k}_i^d)^r \quad (13)$$

The adsorption isotherm (12) is very similar to the equation of adsorption isotherm of single gases, which has been obtained by Sips.²²⁾

The presence of a precursor state

The generalization of the results of Crickmore and Wojciechowski¹⁰⁾, concerning the presence of a precursor state, to the mixed-gas adsorption gives the following rate equation:

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$$\frac{dV_{i(n)}}{dt} = \frac{\bar{k}_i^a M_p}{M} [V_{i(n)}^0(p_1, p_2, \dots, p_n)]^{w^0} - \bar{k}_i^d (V_{i(n)})^{m_i+1} \quad (14)$$

where M_p is the initial number of adsorption sites in the preadsorbed state, M is the total number of adsorption sites, and $V_{i(n)}^0$ is the adsorption isotherm for the precursor. Let us consider two equations for $V_{i(n)}^0$; Henry's and Langmuir's isotherms. In the first case we get

$$\frac{dV_{i(n)}}{dt} = \frac{\bar{k}_i^a M_p}{M} (K_i^H p_i)^{w^0} - \bar{k}_i^d (V_{i(n)})^{m_i+1}; \quad w^0 > 0 \quad (15)$$

At the equilibrium Eq. (15) generates the classical Freundlich isotherm at low adsorbate pressures:

$$V_{i(n)} = \left[\frac{\bar{k}_i^a M_p}{\bar{k}_i^d M} (K_i^H)^{w^0} \right]^{1/(m_i+1)} p_i^{w^0/(m_i+1)} \quad (16)$$

where K_i^H is the Henry's constant for i -th component. The application of the Langmuir isotherm in Eq. (14) leads to the following rate equation:

$$\frac{dV_{i(n)}}{dt} = \frac{\bar{k}_i^a M_p}{M} \left[\frac{a_i p_i}{1 + \sum_{j=1}^n a_j p_j} \right]^{w^0} - \bar{k}_i^d (V_{i(n)})^{m_i+1} \quad (17)$$

which generates the following mixed-gas adsorption isotherm:

$$V_{i(n)} = \left[\frac{\bar{k}_i^a M_p}{\bar{k}_i^d M} \right]^{1/(m_i+1)} \cdot \left[\frac{a_i p_i}{1 + \sum_{j=1}^n a_j p_j} \right]^{w^0/(m_i+1)} \quad (18)$$

If $(\bar{k}_i^a M_p)/(\bar{k}_i^d M) = 1$ we get from Eq. (18) the generalized Freundlich adsorption isotherm for gas mixtures,

$$V_{i(n)} = \left[\frac{a_i p_i}{1 + \sum_{j=1}^n a_j p_j} \right]^{r_0}; \quad r_0 = w^0/(m_i+1) \quad (19)$$

which has been earlier obtained by Jaroniec.²³⁾

Analysis of adsorption isotherm (12)

The most interesting equation of adsorption isotherm for gas mixtures is Eq. (12). The ratio of two partial isotherms $V_{i(n)}$ and $V_{j(n)}$ for $i \neq j$, given by Eq. (12), is equal to:

$$V_{i(n)}/V_{j(n)} = (c_i/c_j) \cdot (p_i/p_j)^r \quad (20)$$

Eq. (20) may be rewritten in this simpler form:

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$$V_{ij(n)} = c_{ij} \cdot p_{ij}^r \quad (21)$$

or

$$\ln V_{ij(n)} = \ln c_{ij} + r \ln p_{ij} \quad (22)$$

where $V_{ij(n)} = V_{i(n)}/V_{j(n)}$, $c_{ij} = c_i/c_j$ and $p_{ij} = p_i/p_j$.

Now let us discuss the constant c_{ij} more exactly. According to the papers^{9,10} the constants \bar{k}_i^a and \bar{k}_i^d may be expressed in the form:

$$\bar{k}_i^a = K_i^a \exp(-\bar{E}_i^a/RT) \quad (23 a)$$

and

$$\bar{k}_i^d = K_i^d \exp(-\bar{E}_i^d/RT) \quad (23 b)$$

where \bar{E}_i^a and \bar{E}_i^d are average activation energies for adsorption and desorption, respectively, whereas, K_i^a and K_i^d are pre-exponential factors. Using the definition of c_{ij} and Eqs. (23 a) and (23 b), we obtain:

$$c_{ij} = \left[\frac{K_i^a K_j^d}{K_j^a K_i^d} \right]^r \exp \left[\frac{r(\bar{E}_i^d - \bar{E}_i^a) - r(\bar{E}_j^d - \bar{E}_j^a)}{RT} \right] \quad (24)$$

As it is known, that the difference between \bar{E}_i^d and \bar{E}_i^a is equal to the adsorption energy E ; thus

$$(\bar{E}_i^d - \bar{E}_i^a) - (\bar{E}_j^d - \bar{E}_j^a) = E_i - E_j = E_{ij} \quad (25)$$

and

$$c_{ij} = (K_{ij}^a K_{ji}^d)^r \exp(rE_{ij}/RT) = (c_{ij}^0)^r \quad (26)$$

From Eq. (22) the difference of the isosteric heats of adsorption, $Q_{i(n)}$ and $Q_{j(n)}$, may be evaluated, it is

$$Q_{ij(n)} = Q_{i(n)} - Q_{j(n)} = RT^2 (\ln p_{ij}/dT)_{V_{i(n)}, V_{j(n)}} = -RT^2 (\ln c_{ij}^0/dT) \text{ for } r(T) = \text{const} \quad (27 a)$$

and

$$Q_{ij(n)} = -RT^2 (\ln c_{ij}^0/dT) + RT^2 [d(1/r)/dT] \ln V_{ij(n)} \text{ for } r(T) \neq \text{const} \quad (27 b)$$

After a few simple manipulations in Eqs. (27 a) and (27 b) we get

$$Q_{ij(n)} = -RT^2 [d \ln(K_{ij}^a K_{ji}^d)/dT] + E_{ij} \text{ for } r(T) = \text{const} \quad (28 a)$$

and

$$Q_{ij(n)} = -RT^2 [d \ln(K_{ij}^a K_{ji}^d)/dT] + E_{ij} + RT^2 [d(1/r)/dT] \ln V_{ij(n)} \text{ for } r(T) \neq \text{const} \quad (28 b)$$

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For chemically similar components i and j , the product $K_{ij}^a K_{ji}^d$ is practically temperature independent, *i. e.*,

$$K_{ij}^a(T) \cdot K_{ji}^d(T) = \text{const} \quad (29)$$

Then

$$Q_{ij(n)} = E_{ij} \text{ for } r(T) = \text{const} \quad (30)$$

The exact analysis of the function $r(T)$ leads to the following expression²⁴⁾:

$$r(T) = \hat{r} RT \quad \text{where } \hat{r} = \text{const} \quad (31)$$

Using in Eq. (28 b) the assumptions (29) and (31) we obtain

$$Q_{ij(n)} = E_{ij} = (1/\hat{r}) \ln V_{ij(n)} \quad (32)$$

The selectivity coefficient s_{ij} , defined by the equation²⁵⁾

$$s_{ij} = p_{ji} V_{ij(n)}, \quad (33)$$

for adsorption isotherm (12) is equal to:

$$s_{ij} = V_{ij(n)}^{(r-1)/r} \cdot c_{ij}^0 \quad (34)$$

Taking into account the relationships (27 a) and (27 b) we have

$$d \ln s_{ij} / dT = -(1/RT^2) Q_{ij(n)} \text{ for } r(T) = \text{const} \quad (35 \text{ a})$$

and

$$d \ln s_{ij} / dT = -(1/RT^2) Q_{ij(n)} + (1/\hat{r} RT^2) \ln V_{ij(n)} \quad (35 \text{ b})$$

The last equations after integration give:

$$\ln s_{ij} = Q_{ij(n)} / RT + \text{const} \quad (36 \text{ a})$$

and

$$\ln s_{ij} = Q_{ij(n)} / RT - \ln V_{ij(n)} / (RT \hat{r}) + \text{const} \quad (36 \text{ b})$$

Applications

To demonstrate the well applicability of the adsorption isotherm (12), the experimental data available from the literature,²⁶⁻³⁰⁾ concerning the mixed-gas adsorption, have been taken to compute the best-fit straight lines according to Eq. (22). These data have been measured for adsorption of simple hydrocarbons on different carbon adsorbents, silica gel and adsorption of nitrogen on cesium iodide (Table 1 contains some informations about the adsorbent samples). However, in Table 2 the parameters of Eq. (22), *i. e.*, r , c_{12} and the standard deviation

$$SD = \left\{ \sum_{\beta=1}^M \left[\ln V_{12(2),\beta}^{\text{exp}} - \ln V_{12(2),\beta}^{\text{cal}} \right]^2 / (M-2) \right\}^{1/2} \quad (37)$$

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TABLE 1. Informations concerning the adsorbent samples

Adsorbent	Abbreviation of the adsorbent sample	Reference	Specific surface area (m ² g ⁻¹)
Charcoal "Nuxit-AL"	NA	26	1200
activated carbon	AC 1	30	—
activated carbon	AC 2	27, 28	705
silica gel	SG	27, 28	751
cesium iodide	CsJ	29	—

TABLE 2. Parameters of Eq. (22) characterizing the mixed-gas adsorption systems

No.	Adsorbent	Gas mixture		Temp. (K)	Ref. ^a	r	c_{12}	SD·10 ²	E_{12}	E_{12}^b	Ref. ^b
		gas 1	gas 2								
1	NA	CH ₄	C ₂ H ₄	293	18	0.956	0.779	7.59	-150	—	—
2	NA	CH ₄	C ₂ H ₆	293	18	0.904	0.598	6.58	-330	—	—
3	NA	C ₂ H ₄	C ₃ H ₆	293	18	0.996	0.083	8.06	-1460	—	—
4	AC 1	C ₂ H ₄	C ₃ H ₆	280	22	0.959	0.070	13.9	-1550	-1600	31
5	AC 1	C ₂ H ₄	C ₃ H ₆	298	22	0.893	0.083	11.7	-1660	-1670	31
6	SG	C ₂ H ₄	C ₃ H ₆	273	20	0.958	0.132	19.3	-1150	-1140	25
7	SG	C ₂ H ₄	C ₃ H ₈	273	20	0.935	0.525	10.2	-380	—	—
8	SG	C ₂ H ₄	C ₃ H ₈	298	20	0.982	0.548	5.98	-360	-190	25
9	SG	C ₂ H ₄	C ₃ H ₈	313	20	0.984	0.551	6.43	-380	—	—
10	NA	C ₂ H ₆	C ₃ H ₈	333	18	0.879	0.174	3.47	-1320	-1080	25
11	NA	C ₃ H ₈	C ₄ H ₁₀	293	18	0.954	0.321	15.0	-690	-630	25
12	AC 2	C ₃ H ₆	C ₃ H ₈	298	19	1.000	1.107	22.7	-60	140	25
13	NA	CO ₂	C ₂ H ₄	293	18	0.940	0.373	4.34	-620	-990	25
14	CsJ	N ₂	CO	83.6	21	0.772	0.059	12.9	-610	—	—

^a Reference concerning the given adsorption system.

^b Reference from which the value of E_{12}^b was taken.

are summarized. The symbols $V_{12(2),\beta}^{\text{exp}}$ and $V_{12(2),\beta}^{\text{cal}}$ denote the experimental and calculated relative surface coverages $V_{1(2)}/V_{2(2)}$ for the β -th point, respectively, whereas, M is the number of experimental points. The subscripts 1(2) and 2(2) refer to the relative surface coverages of the 1-st and 2-nd component adsorbing from binary gas mixture. In Table 2 the values of E_{12} are also summarized; they have been calculated according to Eq. (26) by assuming $K_{ij}^a K_{ji}^d = 1$. These values have been compared to the literature data (next column in Table 2). Fig. 1 presents the linear dependences (22) for five chosen adsorption systems. It follows from Table 2 and Fig. 1 that Eq. (22) is a good equation for characterizing the adsorption systems.

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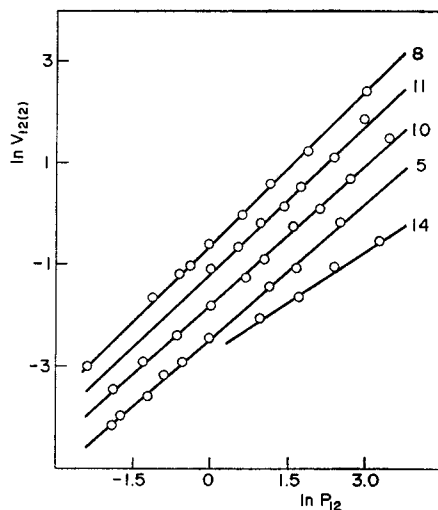


Fig. 1. Linear dependences $\ln V_{12(2)}$ vs. $\ln p_{12}$ calculated according to Eq. (22) for five chosen adsorption systems. The integers at straight lines denote No. of adsorption system summarized in Table 2.

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