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CHROMATOGRAPHIC INVESTIGATIONS OF MIXED CATALYSTS

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SUMMARY

Studies on the energetic heterogeneity of the surfaces of SiO_2 and Co_3O_4 catalysts and their mechanical mixtures are described. The additivity of retention data and thermodynamic values resulting from them for mixed adsorbents and catalysts is discussed.

INTRODUCTION

Cobalt oxide (Co_3O_4) is an important component of active catalysts for the oxidation¹⁻³, hydrogenation⁴, polymerization⁵ and disproportionation^{6,7} of olefins, and also for the oxidation of some inorganic compounds^{8,9} (such as ammonia and carbon monoxide). In catalytic reactions, in addition to impregnated catalysts, mechanical mixtures of Co_3O_4 with inactive carriers are also used. In some reactions, e.g., oxidation of hydrocarbons and carbon monoxide, such mixtures have a higher catalytic activity than catalysts obtained by impregnation methods^{10,11}.

The surface properties of Co_3O_4 and its mixtures with other oxides have been studied by many workers¹²⁻¹⁶, and much interesting information in studies on catalysts was obtained from methods of determining the energetic heterogeneity of their surfaces^{16,17}. This heterogeneity can determine the rate of chemical reactions¹⁸ and many other properties of catalysts¹⁹.

In this paper, studies on the energetic heterogeneity of the surfaces of SiO_2 and Co_3O_4 and their mechanical mixtures are described. We were interested in correlations between the course of the energy distribution function energies and the composition of complex catalysts. The possibility of the practical utilization of such studies is also considered. Chromatographic methods for the determination of the energetic heterogeneity of the surface adsorbents were used, as described earlier²⁰⁻²⁴.

CALCULATIONS OF THE ENERGY DISTRIBUTION FUNCTION

In previous papers²⁰⁻²⁴, we proposed the following expression for the retention volume, $V_{N,t}$, on heterogeneous adsorbents:

$$V_{N,t}(p) = \exp \left(\sum_{i=0}^N B_i p^i \right) \quad (1)$$

where p is the adsorbate pressure, coefficients B_i are suitable parameters and the subscript i denotes the retention volume for a heterogeneous surface.

Eqn. 1 appeared to be very useful for determining the energy distribution function, $\chi(\varepsilon)$, directly from chromatographic data. As we showed previously, the following energy distribution function corresponds with eqn. 1:

$$\chi(\varepsilon) = -\frac{y^2}{F(RT)^2} \sum_{i=1}^N i B_i y^{i-1} \exp \left(\sum_{i=0}^N B_i y^i \right) \quad (2)$$

where

$$y = \frac{1}{K} \exp \left(-\frac{\varepsilon}{RT} \right) \quad (3)$$

In the above equation, K is a pre-exponential factor of Henry's constant and can be easily calculated from chromatographic measurements²⁰⁻²⁴; F is the James-Martin compressibility factor, T is the absolute adsorption temperature and R is the universal gas constant.

EXPERIMENTAL

Preparation of oxides

SiO₂. Wide-pore silica gel, produced by POCh, Gliwice, Poland, of grain fraction 0.15–0.25 mm was purified from surface impurities of bi- and trivalent metal ions by treatment with hydrochloric acid. The silica gel was then modified with steam in an autoclave for 5 h at 423 °K. After drying, the silica gel was roasted at 773 °K for 5 h. The surface area of the silica gel, determined by thermal desorption of argon, was 99 m²/g.

Co₃O₄. Cobalt nitrate [Co(NO₃)₂·6H₂O] produced by POCh, Gliwice, was roasted at 400 °C for 6 h. The Co₃O₄ obtained was tabletted and, after grinding, the 0.15–0.25 mm fraction was sifted for use in the chromatographic measurements. The surface area of this oxide was 8 m²/g.

Mixed catalysts

SiO₂ and Co₃O₄ oxides prepared as described above were carefully mixed mechanically to give catalysts containing 63, 50.11 and 30.28% (w/w) of SiO₂.

Chromatographic experiments

Chromatographic measurements of the dependence of the volume retentions of the tested substances on their vapour pressures were performed on a Giede 18.3

chromatograph equipped with stainless-steel columns (0.5 m \times 0.2 mm I.D.) and a thermal conductivity detector. Argon was used as the carrier gas, from which moisture was removed on a pre-column filled with molecular sieve 5A and oxygen admixtures were removed on Cu-Al₂O₃ and MnO-Al₂O₃ catalysts. After purifying the carrier gas, its oxygen content was less than 1 part per 10^{9.5} parts of argon^{25,26}. The flow-rate of the carrier gas was 20 ml/min.

Carbon tetrachloride and chloroform were used as test adsorbates. From the point of view of catalytic reactions, the use of hydrocarbons would be more suitable, but they are oxidized in the presence of Co₃O₄. Moro-oka¹² poisoned the oxide surface with *cis*-butene in order to determine the heats of adsorption of hydrocarbons on Co₃O₄ before chromatographic measurements.

The constant K in eqn. 3 was determined from the temperature dependences of retention volumes extrapolated to zero values [$V_{N,t}(O)$] of the density of the adsorbates in the gaseous phase^{23,24}. For this purpose, test adsorbates were applied to the columns in amounts from 0.1 to 1 μ l. The temperatures at which these measurements were made and the values of $V_{N,t}(O)$ obtained are given in Table I. Figs. 1 and 2 show graphs of $\ln V_{N,t}(O) = f(1/T)$ for carbon tetrachloride and chloroform, respectively.

Energy distribution functions, $\chi(\epsilon)$, of both test adsorbates were determined at 353 $^{\circ}$ K. A detailed description of the method of measurement and the relevant calculations was given in earlier papers.

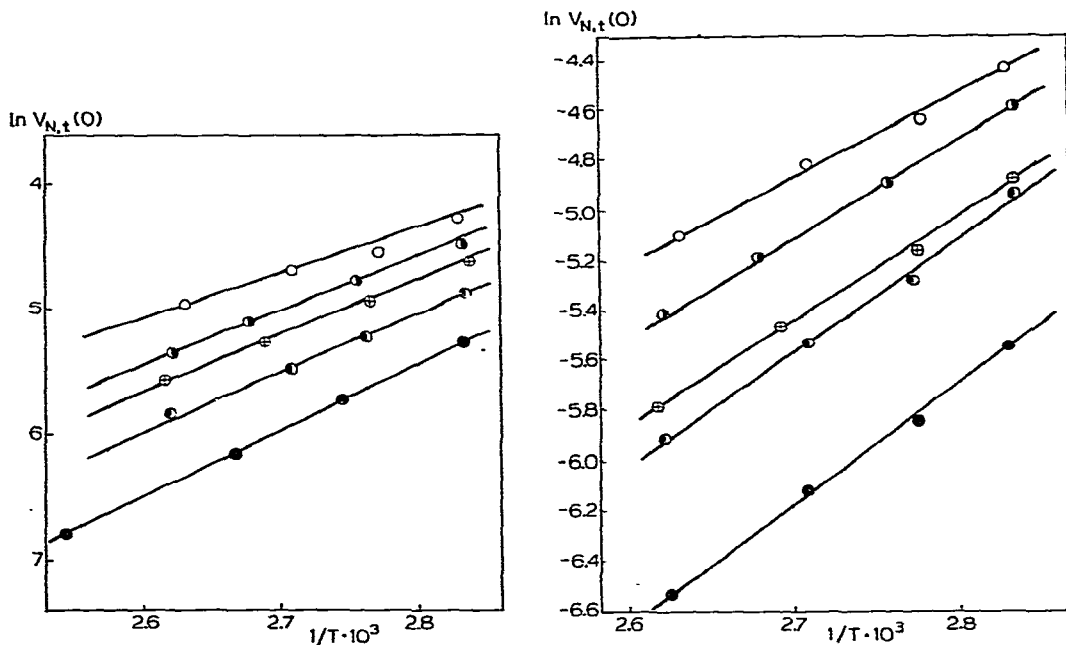


Fig. 1. $\ln V_{N,t}(O)$ versus $1/T$ for carbon tetrachloride on different mixed catalysts. Composition of catalyst: \circ , 100% SiO₂; \bullet , 100% Co₃O₄; \bullet , 63% SiO₂ + 37% Co₃O₄; \oplus , 50.11% SiO₂ + 49.89% Co₃O₄; \bullet , 30.28% SiO₂ + 69.72% Co₃O₄.

Fig. 2. $\ln V_{N,t}(O)$ versus $1/T$ for chloroform on different mixed catalysts. Compositions of catalysts as in Fig. 1.

TABLE I
 ADSORPTION PROPERTIES OF CARBON TETRACHLORIDE-MIXED CATALYST AND CHLOROFORM-MIXED CATALYST SYSTEMS
 AT DIFFERENT TEMPERATURES

Composition	Carbon tetrachloride			Chloroform		
	Temperature (°K)	$L_{11} V_{N,1} (O)$ ($l/g \cdot 10^{-3}$)	$q_{st}^0 \approx \bar{\epsilon}$ (cal/mole)	Temperature (°K)	$L_{11} V_{N,1} (O)$ ($l/g \cdot 10^{-3}$)	$q_{st}^0 \approx \bar{\epsilon}$ (cal/mole)
100% SiO ₂	353.7	-4.276	7200	353.7	-4.42	7000
	360.8	-4.54		360.8	-4.68	
	369.3	-4.69		369.3	-4.82	
	380.1	-4.95		380.1	-5.10	
100% Co ₃ O ₄	352.9	-5.28	10,500	353.0	-5.55	9800
	364.4	-5.73		361.6	-5.85	
	374.8	-6.15		369.2	-6.12	
	393.1	-6.79		381.1	-6.54	
63% SiO ₂ + 37% Co ₃ O ₄	353.0	-4.48	8700	353.0	-4.58	7800
	362.6	-4.77		362.6	-4.89	
	373.6	-5.11		373.6	-5.17	
	381.6	-5.36		381.6	-5.42	
50.11% SiO ₂ + 49.89% Co ₃ O ₄	352.3	-4.61	9400	353.0	-4.87	8400
	361.6	-4.93		361.6	-5.16	
	372.3	-5.27		372.3	-5.47	
	382.3	-5.58		382.3	-5.79	
30.28% SiO ₂ + 69.72% Co ₃ O ₄	352.9	-4.90	9850	352.9	-4.93	9000
	362.1	-5.23		362.1	-5.28	
	369.2	-5.49		369.2	-5.54	
	381.5	-5.81		381.5	-5.92	

RESULTS AND DISCUSSION

In previous papers^{17,27}, the nature of the adsorption centres on the surface of the oxides studied was discussed. According to the results obtained on the surface of Co_3O_4 , the adsorption centres were constituted mainly by Co^{2+} , Co^{3+} and O^{2-} ions. Chloroform molecules may have interacted with these ions with various forces, and three maxima were obtained on the curve of $\chi(\epsilon)$ versus ϵ for this substance adsorbed on Co_3O_4 (Fig. 3, I). Molecules of carbon tetrachloride have a high polarizability and possess a dipole moment²⁸ and they may have interacted with the Co^{2+} and Co^{3+} ions. On the curve of $\chi(\epsilon)$ versus ϵ for this substance two maxima were obtained (Fig. 4, I).

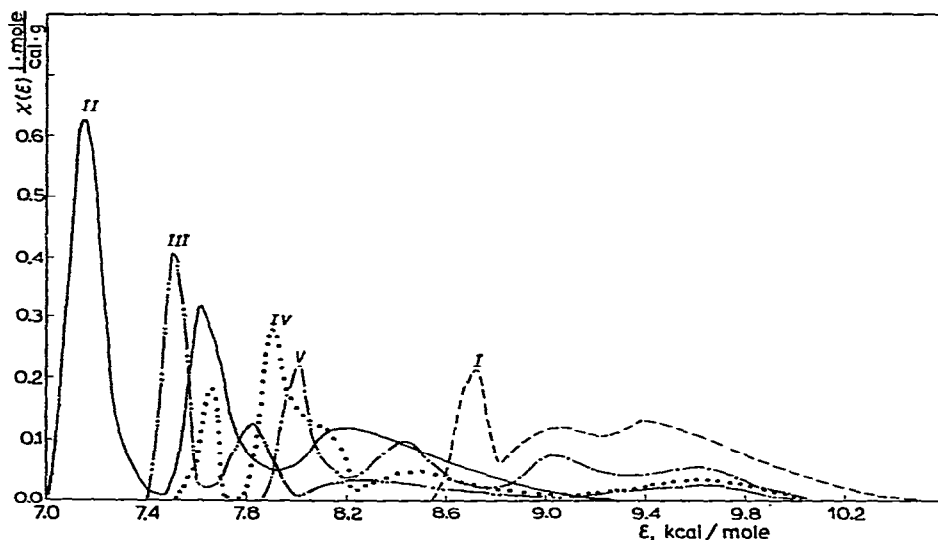


Fig. 3. Energy distribution functions for chloroform adsorbed on: I, Co_3O_4 ; II, SiO_2 ; III, 63% SiO_2 + 37% Co_3O_4 ; IV, 50.11% SiO_2 + 49.89% Co_3O_4 ; V, 30.28% SiO_2 + 69.72% Co_3O_4 .

Three maxima were obtained for each of the two test substances adsorbed on silica gel (Figs. 3, II and 4, II). For chloroform and carbon tetrachloride the adsorption centres on this adsorbent were constituted by free and partially bound surface hydroxyl groups and Si^{4+} ions. Molecules of these substances together with hydroxyl groups may have formed hydrogen bonds^{28,29}. Moreover, such bonds may have been formed by chloroform with strained siloxane bridges present on the surface of the silica. Because of the chemical structure of the chloroform molecule, there was a greater possibility of "indication" on the curve of $\chi(\epsilon)$ versus ϵ of adsorption centres present on the silica surface. Therefore, the peaks on the $\chi(\epsilon)$ versus ϵ curve for this substance were less symmetrical than those on such curves for carbon tetrachloride (Figs. 3, II and 4, II) and less well separated (broaden).

In Figs. 3 and 4 the energy distributions, $\chi(\epsilon)$, for test adsorbates on mixtures of the two oxides are also presented. From a comparison of the courses of the $\chi(\epsilon)$ versus ϵ curves it can be seen that close correlations exist between the shape of the energy distribution function and the distribution of a complex catalyst. The shape of

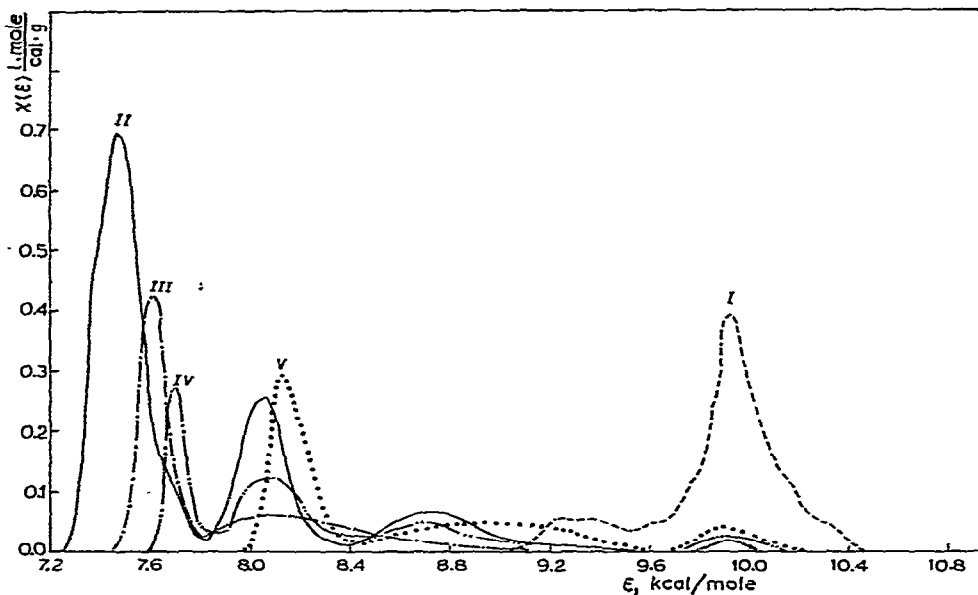


Fig. 4. Energy distribution functions for carbon tetrachloride adsorbed on: I, Co_3O_4 ; II, SiO_2 ; III, 63% SiO_2 + 37% Co_3O_4 ; IV, 50.11% SiO_2 + 49.89% Co_3O_4 ; V, 30.28% SiO_2 + 69.72% Co_3O_4 .

the $\chi(\varepsilon)$ function for a complex catalyst is, in general, the resultant of its composition. The curves of $\chi(\varepsilon)$ versus ε for the mixed catalysts lie between those for pure SiO_2 and Co_3O_4 , although there is a greater shift of the function $\chi(\varepsilon)$ on the axis ε for mixtures of the oxides for peaks representing energy centres with lower energy. In the case of the strongest adsorption centres the peak maxima coincide in general. The average adsorption energy, $\bar{\varepsilon}$, on the surface of heterogeneous adsorbents is

$$\bar{\varepsilon} = \sum S_n \varepsilon_n \quad (4)$$

where S_n denotes the fraction of the adsorbent surface occupied by the n th type of adsorption centres, having an average adsorption energy ε_n . From a comparison of the $\chi(\varepsilon)$ versus ε curves for test substances adsorbed on pure SiO_2 and Co_3O_4 (Figs. 3, I and II and Figs. 4, I and II), it can be seen that much greater differences exist between minimum than between maximum adsorption energies. A similar situation applies to the differences between the average adsorption energies of the weakest adsorption centres with regard to energy or energies characteristic of the maximum of the peaks on the $\chi(\varepsilon)$ versus ε curves for these centres on SiO_2 and Co_3O_4 as well as to the differences between the strongest adsorption centres. Further, with Co_3O_4 most of the adsorption centres are constituted by the strongest adsorption centres. Therefore, in accordance with eqn. 4, for mixtures of the oxides a greater shift (to the right) of the peaks on the $\chi(\varepsilon)$ versus ε curves representing weaker adsorption centres is observed than the shift to the left of the peaks representing the strongest adsorption centres. The above problem is dealt with in more detail below.

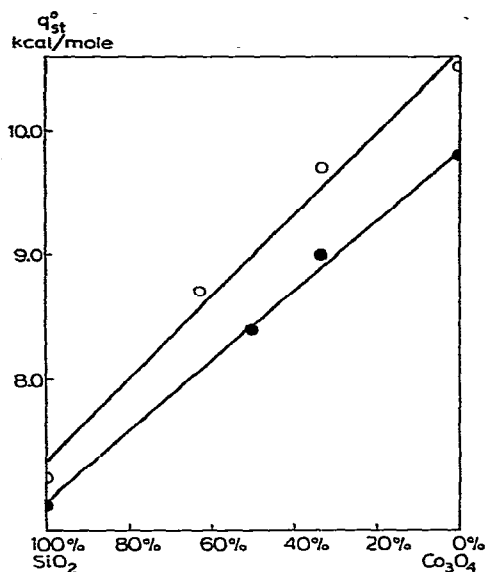


Fig. 5. Dependence of q° on composition of mixed catalyst. ○, Carbon tetrachloride; ●, chloroform.

Fig. 5 shows the dependence of average the adsorption energies of chloroform and carbon tetrachloride on the mixed composition of the catalyst. These energies were calculated from the temperature dependences of $\ln V_{N,t}(O)$:

$$q_{st}^{\circ} = R \cdot \frac{d \ln V_{N,t}(O)}{d \left(\frac{1}{T} \right)} \quad (5)$$

In a previous paper¹⁷ we also studied the dependences of $\bar{\varepsilon} = f$ (complex composition of a catalyst), using the average adsorption energies calculated from the energy distribution function:

$$\bar{\varepsilon} = \int \varepsilon \chi(\varepsilon) d\varepsilon / \int \chi(\varepsilon) d\varepsilon \approx q_{st}^{\circ} \quad (6)$$

From Fig. 5, it can be seen that the dependences of q_{st}° on the complex composition of the catalyst are linear for both test adsorbates. Dependences of this type can be utilized for the determination of the composition x_1 and x_2 of a mixture of catalysts or any solid bodies, the average adsorption energy of the components of mixture ($\varepsilon_1, \varepsilon_2, \varepsilon_m$) or the surface area of one or both components in a mixture (S_1, S_2, S_m). These determinations are possible, of course, only when neither component changes its properties during mixing. Moreover, the sites of contact of the grains being mixed should be as small as possible. The calculations of the above parameters can be made graphically by using diagrams as shown in Fig. 5 and by solving a simple system of equations:

$$\left. \begin{aligned} X_m &= x_1 \cdot X_1 + x_2 \cdot X_2 \\ 1 &= x_1 + x_2 \end{aligned} \right\} \quad (7)$$

where X_m denotes the value of ε_m and $S_m \cdot X_1$ and X_2 denotes ε_1 and S_1 and ε_2 and S_2 respectively, whereas x_1 and x_2 denote the weight fractions of the first (1) and second (2) catalyst (or adsorbent).

For example, the average adsorption energy of carbon tetrachloride on the mixed catalyst containing 63% of SiO_2 calculated from the temperature dependences of $\ln V_{N,i}(\text{O})$ is 8.7 kcal/mole (Table I), whereas that calculated from eqn. 7 is 8.5 kcal/mole. Considering the fact that the error of chromatographic measurement is, in general, ± 0.2 kcal/mole, it can be assumed that these data are in good agreement. In the above calculations the following values were used: $x_1 = 0.63$, $x_2 = 0.37$, $\varepsilon_1 = 7.2$ kcal/mole and $\varepsilon_2 = 10.5$ kcal/mole (Table I).

Taking into account the error of chromatographic measurement of ± 0.2 kcal/mole, the values of x_1 and x_2 are read from Fig. 5 with an accuracy of $\pm 7\%$. This error can be considerably decreased by choosing suitable test adsorbates, so that possibly the highest energy values on one of the adsorbents and possibly the lowest ε values on the other adsorbent would be obtained, in which event graphs of the type shown in Fig. 5 will be steeper. Average adsorption energies calculated both from the temperature dependences of $\ln V_{N,i}(\text{O})$ and the energy distribution function $\chi(\varepsilon)$ can be utilized for calculations of X_m . From the practical point of view, measurements of $V_{N,i}(\text{O})$ are more convenient. However, it appears from the discussion of these results and from the data published earlier¹⁷ that it is useful to study energy distribution functions with a view to testing adsorbents and catalysts. This is supported by correlations between the composition of a complex catalyst and the shape of the function $\chi(\varepsilon)$.

We were interested in the additivity of retention data and the thermodynamic values resulting from them for adsorbents and complex catalysts³⁰. We shall confine ourselves to a theoretical discussion of the problem of additivity of retention volumes for zero density of the adsorbate in the gaseous phase, $V_{N,i}(\text{O})$, and average adsorption energies and distribution functions, $\chi(\varepsilon)$, for mixtures of catalysts (adsorbents).

In a previous paper³¹, it was shown that the retention volume in adsorption gas chromatography can be presented in the form of the following virial equation:

$$V_N = W'_1 \varrho + \left[\sum_{m=2} m^2 W_m \varrho^{m-1} + \sum_{m=2} \sum_{k=1} mk W_m \beta_k (k-m) \varrho^{m+k-1} \right] \times \left(1 + \sum_{k=1} k \beta_k \varrho^k \right)^{-2} \quad (8)$$

where ϱ is the density of the adsorbate, β_k are the irreducible Mayer integrals and W_m are cluster integrals defined as follows: $m!W_m =$ the sum of the contributions of all connected graphs of m distinct square vertices so that the basic part of these graphs consists of white squares and their terminal sub-parts of black squares, the remaining squares being white. The contributions to W_m associated with a given graph are calculated as follows:

(a) to each line corresponds a factor $f_{ij} = \exp(-u_{ij}/kT) - 1$, where u_{ij} denotes the energy of interaction of two adsorbate molecules localized at r_i and r_j ;

(b) to each white vertex corresponds the factor

$$g_i = \begin{cases} \exp[-v(r_i)/kT] & r_i \notin V \\ 0 & r_i \in V \end{cases} \quad (9)$$

where $v = v(r_i)$ is the external potential field at r_i , due to the adsorbent surface, and V is the volume of adsorption space;

(c) to each terminal part of λ black vertices factor $-1 + \prod_{i=1}^{\lambda} g_i$ is associated;

(d) the integration is made all over configurational space which, according to (b), in the case of white squares is reduced to integration after V .

In eqn. 8, W'_1 is identical with the retention volumes $V_{N,t}(O)$ used so far. Let us consider for example:

$$\left. \begin{aligned} 1!W'_1 &= \int_V [g(r_1) - 1] dr_1 \\ 2!W'_2 &= \iint_{V \infty} \{g(r_1) [g(r_2) - 1] f_{12}\} dr_1 dr_2 \\ 3!W'_3 &= \iiint_{V \infty} \{3 g(r_1) [g(r_2) - 1] [g(r_3) - 1] f_{12} f_{13}\} dr_1 dr_2 dr_3 + \\ &\quad + \iiint_{V \infty} \{g(r_1) [g(r_2) g(r_3) - 1] f_{12} f_{13} f_{23}\} dr_1 dr_2 dr_3 \end{aligned} \right\} (10)$$

etc. Let us first consider the simplest case of the dependence of $V_{N,t}(O)$ on the composition of a complex catalyst adsorbent. The adsorption system will consist of two adsorbents with a homogeneous surface with the energy interactions $v_1(r_1)$ and $v_2(r_i)$. The surface area, S_m , of such a system will be

$$S_m = x_1 S_1 + x_2 S_2 \quad (11)$$

Then, because

$$V_{N,t}(O) = W'_1 \quad (12)$$

we obtain

$$\begin{aligned} W'_1 &= \int_{S_m} dS_m \int_0^{\infty} dz_1 [g_1(\tau, z_1) - 1] = \int_{\{x_1 S_1\} \cup \{x_2 S_2\}} dS' \int_0^{\infty} dz_1 [g(\tau, z_1) - 1] = \\ &= x_1 W'_{1(c1)} + x_2 W'_{1(c2)} = x_1 V_{N1t}(O) + x_2 V_{N2t}(O) \end{aligned} \quad (13)$$

where

$$v(\tau, z_1) = \begin{cases} v_1(\tau, z_1) & \tau \notin \{x_1 S_1\} \\ v_2(\tau, z_2) & \tau \notin \{x_2 S_2\} \end{cases} \quad r = (\tau, z)$$

where τ is a two-dimensional vector. It appears from the last equation that in the case discussed the additivity of zero retention volumes, $V_{N,t}(O)$, is preserved. By analogy, the additive value should be the average adsorption energy

$$\epsilon_m = x_1 \epsilon_1 + x_2 \epsilon_2 \quad (14)$$

and the isosteric heat of adsorption, q_{st}^o , within the zero limit of adsorption is

$$q_{st,m}^o = x_1 q_{st,1}^o + x_2 q_{st,2}^o \tag{15}$$

It can be proved that for a heterogeneous surface the integral W'_1 is defined by the following equation:

$$W'_1 = \int_{\Omega} d\varepsilon \int_V [g(r_1; \varepsilon) - 1] dr_1 = \int_{\Omega} W_1^{hom}(\varepsilon) \chi(\varepsilon) d\varepsilon \tag{16}$$

where $W_1^{hom}(\varepsilon)$ is the value of W'_1 for an energetically homogeneous surface with parameter ε and Ω is the range of possible variations of the adsorption energy, ε .

The distribution function $\chi_i(\varepsilon)$ for the i th adsorbent is defined as

$$\chi_i(\varepsilon) = \frac{\partial S_i}{\partial \varepsilon} \tag{17}$$

If we consider a two-component complex catalyst (adsorbent), then because $S_m = x_1 S_1 + x_2 S_2$, we obtain

$$\chi_m(\varepsilon) = x_1 \chi_1(\varepsilon) + x_2 \chi_2(\varepsilon) \tag{18}$$

Therefore, from eqns 16, 17 and 18 we obtain

$$\left. \begin{aligned} W'_{1,m} &= x_1 W'_1 + x_2 W'_1 \\ V_{N,m}(O) &= x_1 V_{N,1t}(O) + x_2 V_{N,2t}(O) \end{aligned} \right\} \tag{19}$$

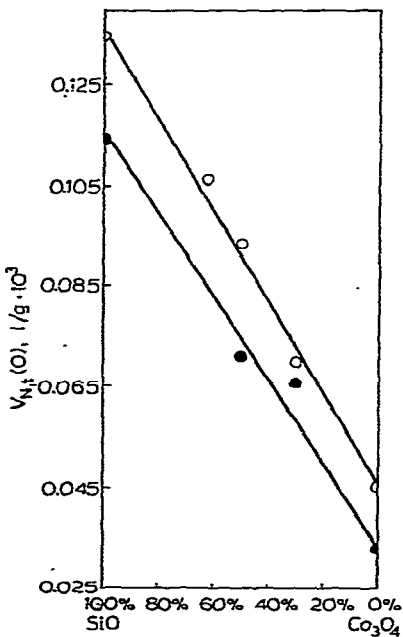


Fig. 6. Dependence of $V_{N,t}(O)$ on composition of mixed catalyst. ○, Carbon tetrachloride; ●, chloroform.

From the last equations, it appears that for energetically heterogeneous adsorbents (catalysts), the additivity of such values as $V_{N,r}(O)$, q_{st}^o , S and $\bar{\epsilon}$ is preserved for the components of the mixture. The additivity of $V_{N,r}(O)$ values simplifies, in an experimental sense, studies of the composition or surfaces of complex adsorbents (catalysts) or their components (in the catalysis of a selective surface). It should be stressed that the above considerations are valid for mixtures of adsorbents or catalysts the contact surface of which is very small and, as mentioned earlier, for solid bodies that do not change their properties on mixing. These assumptions are not difficult to satisfy in chromatographic systems, as many of the adsorbents used have spherical particles. Fig. 6 presents plots of $V_{N,r}(O)$ against the composition of a mixed catalyst.

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