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A New Method for Study of the Adsorption Function of an Adsorbate on an Adsorbent, Applied to the Study of the Adsorption Function of Isopropyl Alcohol on a Zinc Oxide Catalyst

II. Quantitative Treatment of the Data

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Thermodesorption curves of isopropyl alcohol from a zinc oxide catalyst which were given in Part I have been analyzed under the assumption that the Langmuir isotherm for a heterogeneous surface is a valid model. From visual inspection of the desorption curves five sets of adsorption sites were assumed. The number of sites in each set as well as the entropy of adsorption and the enthalpy of adsorption for each set have been determined.

INTRODUCTION

In the previous paper (*1*) the experimental results from thermodesorption of isopropyl alcohol adsorbed on a zinc oxide catalyst were given. It was pointed out that visual inspection of the desorption curves suggested that there might be five sets of adsorbing sites. In this paper it will be shown how the results can be treated quantitatively. The analysis is based on a model assuming Langmuir adsorption on a heterogeneous surface. Fitting such a model to the experimental data, estimate of adsorption enthalpy, adsorption entropy, and number of sites in each set are obtained.

THEORETICAL

The Langmuir adsorption isotherm for a homogeneous surface is usually written

$$\theta = ap/(1 + ap) \qquad (1)$$

where θ is the fraction of surface covered by adsorbate at adsorbate partial pressure p and a is the adsorption constant. The equation may be rewritten slightly

$$W = W_0[ap/(1 + ap)] \qquad (2)$$

with W and W_0 meaning weights of the adsorbate. Langmuir (*2*) showed that if the adsorption takes place on sites of varying activity the adsorption isotherms must take the form

$$W = \sum_i W_i = \sum_i \frac{W_{0i}a_ip}{1 + a_ip} \qquad (3)$$

where the index i indicates that the symbol having this index refers to the ith set of adsorbing sites.

Equation (3) forms the basis of the discussion given here. In the experiments (*1*) carried out in the work reported here a flow system was used and the following mass balance equation is obvious:

(Quantity desorbed from start to time t)
= (quantity adsorbed at high pressure)
− (quantity remaining at time t)
− (quantity desorbed before start of experiment) (4)

From Eqs. (3) and (4) one obtains

$$\int_0^t pvF\,dt = \sum_i W_{0i} - \sum_i \frac{W_{0i}a_ip}{1 + a_ip} - A \qquad (5)$$

where p is pressure, v is carrier gas flow rate, F is a conversion factor converting the pressure–volume product to weight, and A is weight desorbed before start of experiment.

Equation (5) is valid (for the model used) because, as shown in the previous paper (*1*) there is essentially no concentration gradient along the catalyst bed, and the desorption is proceeding under equilibrium conditions.

In principle all information which can be obtained is contained in Eq. (5), but actual trials showed it to be rather difficult to handle in practice. Equation (5) can be differentiated with respect to t. Carrying out this differentiation and making use of the fact that the equilibrium constant of a reaction is given by

$$K = a = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right) \tag{6}$$

the following result is obtained

$$pvF = -\sum_{i=1}^{i=N} \frac{W_{0i}\exp(\Delta S_i/R - \Delta H_i/RT)}{(1 + p\exp(\Delta S_i/R - \Delta H_i/RT))^2} \times \left(\frac{dp}{dt} + p\frac{\Delta H_i}{RT^2}\frac{dT}{dt}\right) \tag{7}$$

It was mentioned in the previous paper that inspection of the desorption curves indicated that there might be five sets of sites contributing to the curves. The final equation to be fitted to the experimental values is thus

$$pvF = -\sum_{i=1}^{i=5} \frac{W_{0i}\exp(\Delta S_i/R - \Delta H_i/RT)}{(1 + p\exp(\Delta S_i/R - \Delta H_i/RT))^2} \times \left(\frac{dp}{dt} + p\frac{\Delta H_i}{RT^2}\frac{dT}{dt}\right) \tag{8}$$

Equation (8) is a differential equation containing 15 unknown parameters. It may be written

$$y = pvF = f(t,\text{par}) \tag{9}$$

where par is written for all unknown parameters. The parameters of Eq. (9) can be estimated by the ordinary least-squares technique [see for instance ref. (*3*)], without actually solving the differential equation, by making the sum of squared deviations between the observed and calculated y values as small as possible. This procedure is possible because dp/dt and dT/dt can be calculated from the experimental results, so all magnitudes in Eq. (8) except the parameters are known. Thus one has

$$\sum_{j=1}^{M} [y_{j,\text{obs}} - f(t_j,\text{par})]^2 = \text{minimum} \tag{10}$$

Equation (9) cannot be transformed into a linear function of the parameters, so an iterative technique had to be used. The technique used was one of cyclic parameter variations with convergence accelerations (*4*). The computations were carried out on a digital computer.

Parameter estimations using an iterative technique require an initial parameter estimate from which better estimates are computed. A useful initial estimate for W_{0i} is to make them all equal and equal to one-fifth of the total quantity adsorbed. For the ΔH_i's an initial estimate of, say, 15 000 cal/mole did not seem implausible. Initial estimates for ΔS_i could then be obtained by taking into account that the product $a_i p$ in each term in the Langmuir isotherm will be of order of magnitude 1 when that term is giving its maximum contribution to the desorption curve. The temperatures where this was (visually) estimated to take place were indicated in Fig. 1 of the preceding article (*1*). The initial estimates for ΔS_i were then obtained from Eq. (6). The computations do not depend critically upon these initial parameter estimates being particularly well chosen. No further use is made of the visually estimated temperatures of maximum contribution to the desorption curve from each set of sites.

An advantage about thermodesorption curves rather than the more common adsorption isotherms is that one can by visual inspection estimate reasonably well how many sites to allow for in the model, and what initial values to give the parameters. Reasonable parameter estimates may be important for obtaining converging iterations, and they will definitely be of importance for the speed of convergence.

Results and Discussion

The least-squares computations were carried out on the data obtained from Experiment I in the preceding paper (*1*). In a curve-fitting problem involving as many as 15 parameters a large degree of coupling between the parameters is to be expected, and a slow convergence results. A fairly long computation time was indeed needed. A satisfactory fit of the computed curve to the observed one was obtained. The observed and calculated results are shown in Fig. 1, which also shows the contributions from each of the five sets of adsorption sites. The estimated parameter values are given in Table 1.

It is clear from Fig. 1 that the fit for the first part of the curve is not perfect. The difference between observed and calculated desorption rates is definitely greater than the experimental uncertainty of the measured desorption rates. This is almost certainly due to the fact that the temperatures have not been measured with sufficient accuracy in the early period of the experiment. The temperature itself is not too critical but its time derivative is. Computations have shown that in the early part of the experiment the contribution from the term containing dT/dt in Eq. (8) is four or five times greater than the calculated desorption rate (pvF). Consequently small errors in the estimate of dT/dt will have a marked influence. The lack of full correspondence between calculated and observed desorption rates does therefore not imply that the model is unsatisfactory.

The parameters which have been determined are all satisfactory in the sense that they are of the order of magnitude one would expect from general chemical knowledge. The estimate of the adsorption enthalpy of the first site (ΔH_1) appears to be somewhat greater (numerically) than one would expect from a site evidently being much weaker

TABLE 1

Parameters of Eq. (8) Determined from the Experimental Points in Fig. 1 by the Least-Squares Procedure of Eq. (10)[a]

	W_{0i} (mg/g catalyst)	ΔS_i (cal/mole degree) (pressure unit torr)	ΔH_i (cal/mole)
1.	4.122	−54.75	−17 580
2.	0.949	−48.03	−17 690
3.	1.702	−43.70	−17 190
4.	0.751	−50.87	−22 100
5.	0.673 (2.553)[b]	−47.50	−22 780

[a] The number of adsorbing sites in each set of sites is obtained by multiplying W_{0i} by 1.0×10^{19}.

[b] 0.673 is the number obtained from Fig. 1, and is known to be too low; 2.553 is a better estimate obtained from Fig. 4.

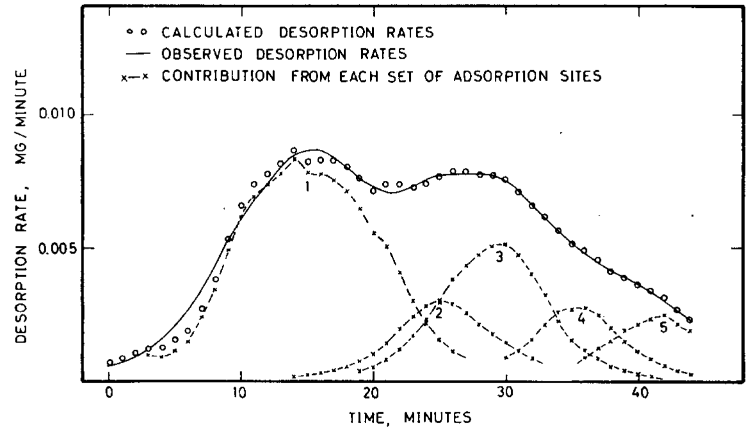

Fig. 1. Experimental and calculated desorption curves plotted against time, Experiment I. The calculated desorption rates have been obtained by fitting Eq. (8) to the experimental curve. The contribution from each set of sites is also shown. Catalyst, 32 mg; predesorption temperature, −20°C.

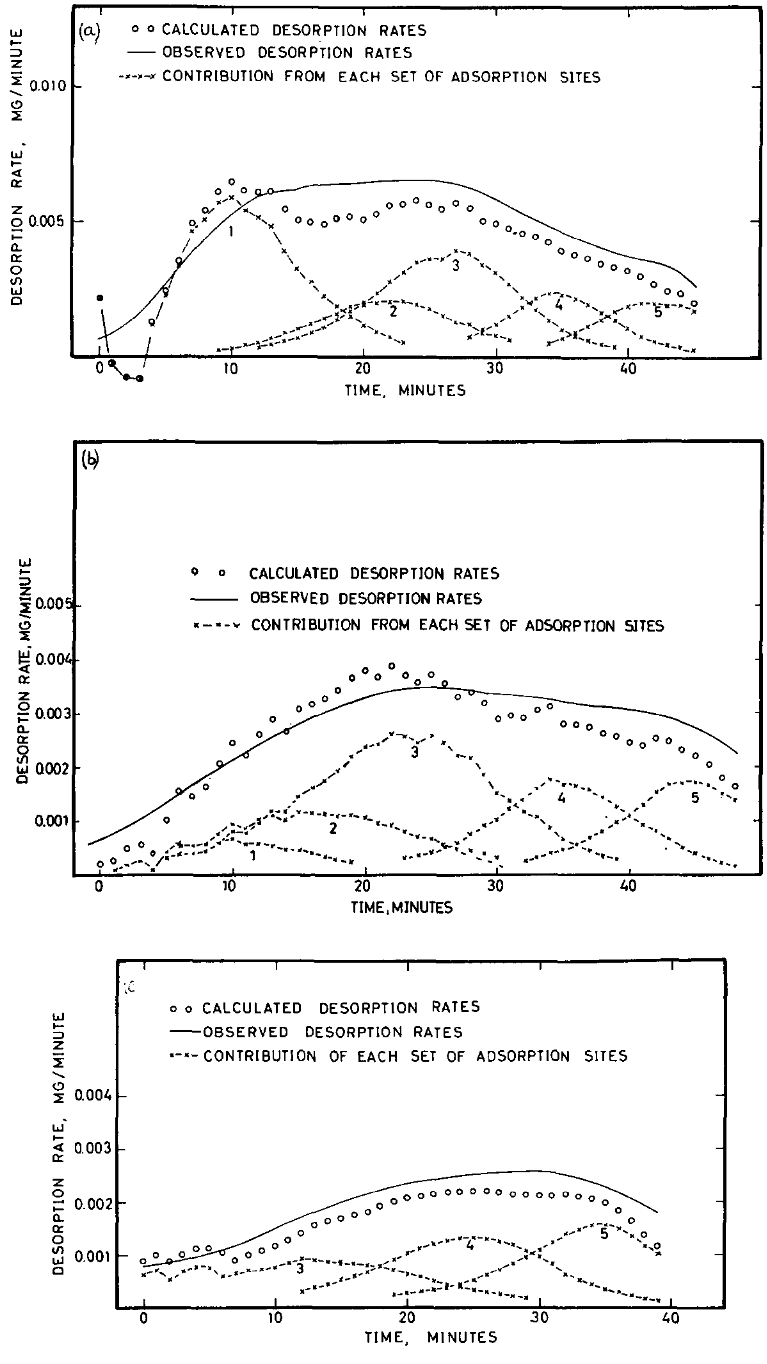

FIG. 2. Experimental and calculated desorption curves from Experiments II, III, and IV. The calculated points have been obtained using the parameter values in Table 1. Calculated contributions from each of the five sets of adsorption sites are also shown. Catalyst, 32 mg; predesorption temperatures: (2a), 5°C; (2b), 20°C; (2c), 60°C.

than the other sites. Due to parameter coupling ΔS_1 is then also out of line. It is believed that this slight irregularity is due to the evidently underestimated temperature increase in the early stages of the experiment. It is easily seen from Eq. (8) that an underestimation of dT/dt leads to an overestimation of ΔH_1. (If an adsorption enthalpy of say $-15\ 500$ cal/mole is assumed ΔS_1 is estimated to be -47.5 cal/mole degree.)

The crucial test of the goodness of a model is its ability to predict. Using a sufficiently flexible model curves may always be fitted to the data, although a bad model will often lead to parameter estimates which are not in accordance with general physical and chemical knowledge. The model used here is satisfactory as far as parameter estimates are concerned, but it was also found of interest to test its predictive properties. Experiments II, III, IV of the preceding paper have been used to this end. In Figs. 2(a), (b), and (c) are shown the observed and calculated desorption rates, using the parameters given in Table 1 and Eq. (8). The contributions from the individual sets of sites are also shown. The agreement between calculated and observed values is not outstanding, but must be considered satisfactory as the very different curve forms have been correctly predicted, and no curve fitting has been involved.

When calculating desorption rates (pvF) according to Eq. (8) the observed pressure is used to calculate the term pvF, i.e., the pressure. The suspicion might therefore arise that because of this the calculated pvF term will always be rather similar to the observed pvF term. A numerical experiment showed that this is not the case, however. If the desorption curve of Experiment II had been obtained in Experiment I, what then would the calculated desorption curve look like? (I.e., the desorption curve of Experiment II and the temperature curve of Experiment I were used for calculating the desorption curve.) The result is shown in Fig. 3, which clearly shows that the input curve is not reproduced. The calculated curve is more similar to the desorption curve of Experiment I than to the input curve, as it should indeed be.

The first part of the curve in Fig. 2(a) merits some further discussion. The calculated points after 2, 3, and 4 min are negative. This is again due to an underestimated temperature increase in the early stages of the experiment. Physically the result is satisfactory, it only means that if the catalyst had been subjected to a pressure and temperature increase as used in the computations, it would adsorb isopropyl alcohol and not desorb it. The fact that the calculated desorption rates around 10 min are higher than the observed desorption rates, is an indication that the number of sites in set 1 is somewhat overestimated.

It was mentioned in the previous paper that the observed desorption rate curves

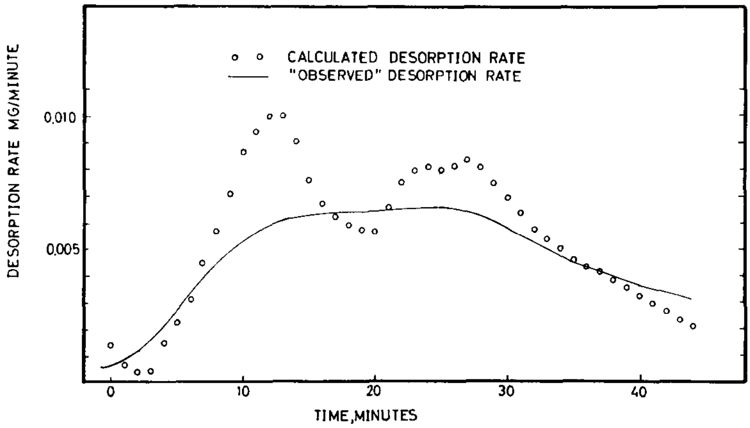

FIG. 3. A simulated experiment. Desorption rates were calculated under the assumption that the desorption curves measured in Experiment II had been obtained in Experiment I. See text.

were too low at the high-temperature ends because a substantial part of the isopropyl alcohol reacted to give acetone and hydrogen at about 170°C. Looking at Figs. 1, and 2(a), (b), and (c), it is apparent that the contribution from site 5 must then be quite strongly underestimated, perhaps by a factor 3 or 4. Using a quite different experimental technique this has indeed been found to be the case. Using a flow vacuum apparatus and a small quartz vessel suspended in a quartz spiral an adsorption isobar of 0.94 g of fresh zinc oxide (heated to 150°C and degassed at 10^{-4} torr before the measurement) was recorded from 15° to 195°C at about 0.4 torr isopropyl alcohol pressure. The isobaric curve to be expected was calculated by means of Eq. (3) using the parameters given in Table 1, apart from W_{05} which was taken to be 4 times greater (2.553). Calculated and observed values are shown in Fig. 4. The predictive properties of the model is seen to be highly satisfactory also in this case. A somewhat steeper slope of the observed curve than the calculated one between 170° and 195°C is to be expected because the dehydrogenation rate is quite high at this temperature, so the isopropyl alcohol pressure inside the catalyst mass will be considerably lower than the bulk pressure of 0.4 torr.

It may be concluded that a satisfactory mathematical description of the adsorption behavior of the system isopropyl alcohol/zinc oxide has been obtained. Experimental results are most often seen displayed as adsorption isotherms, it has therefore been found of interest to calculate some adsorption isotherms for this system. The results of these computations are shown in Figs. 5a, and b. An interesting feature about the adsorption isotherms is apparent from Fig. 5(a) or (b). In spite of the fact that these curves have been calculated from a model which assumed Langmuir adsorption with five distinct sets of adsorption sites no clear sign of fine structure can be seen in the curves. This shows that one cannot expect to see, by visual examination, clear signs of distinct sets of adsorption sites unless the adsorption constants of the various sets of sites are very much different.

No extensive search for other models to explain the observed results has been carried out. The model advanced here has been very successful in explaining and correlating the results. Until more refined experiments are available, where dT/dt is better estimated for the early stages of the experiment, and where the effect of the conversion of isopropyl alcohol to acetone and hydrogen can be corrected for or eliminated, there is probably not much hope that the model can be shown to be insufficient. The fact that the model has been successful is no proof that it reflects the physical reality, however. The model entertained here assumes a discontinuous distribution of adsorption constants.

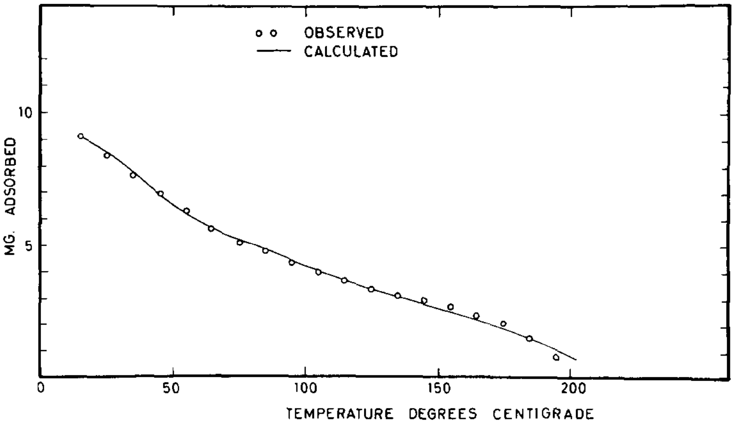

FIG. 4. Comparison of observed and calculated adsorption isobar. The curve was calculated from Eq. (3) using the parameters in Table 1, except W_{05} which is known to be too low, where a value 2.553 was used. Isopropyl alcohol pressure, 0.4 torr; 0.94 g catalyst.

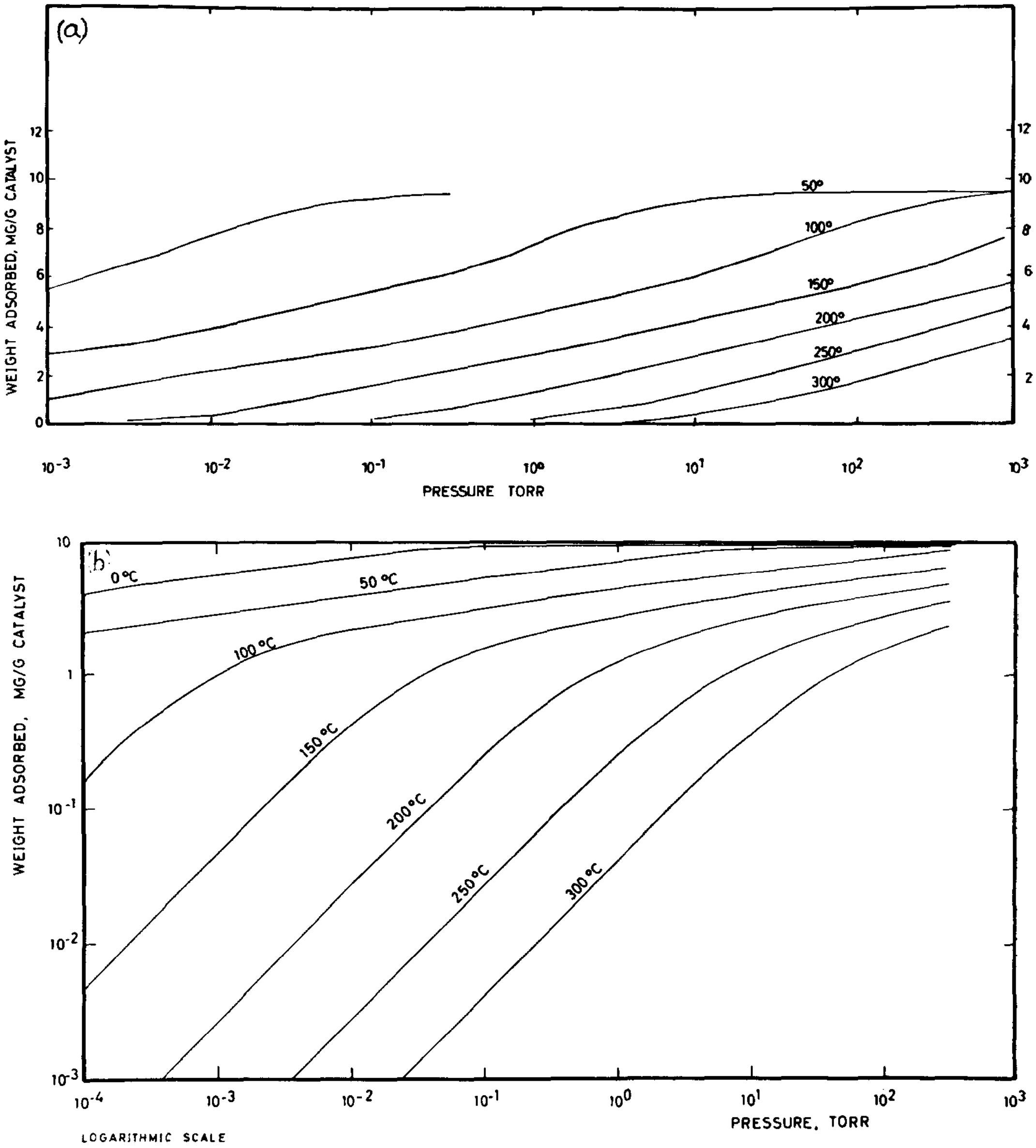

FIG. 5. Adsorption isotherms calculated for a wide range of temperatures and pressures using Eq. (3) and Table 1.

Continuous distribution functions resembling the discontinuous one will then be equally successful, and it is possible that broader continuous distributions may be equally good, although this does not seem probable. (See Appendix.) The Langmuir isotherm is based on the assumption that there is no interaction between the adsorbed molecules and that the surface is not changed by the adsorption taking place on it. These assumptions must clearly be approximations but they may be approximations with a fairly high degree of accuracy. The results obtained here do not give any basis for rejecting these approximations.

The experiments described in this paper and the preceding one (*1*) have all been carried out on zinc oxide samples which have not been aged. Preliminary experiments indicate that aging of the catalyst (prolonged heating of the catalyst to 250–300°C in an isopropyl alcohol stream) does have some influence upon the adsorption constants, in particular the most energetic site appears (from qualitative considerations) to have become even more energetic. Further experiments are planned to clear up these problems.

It should also be pointed out that due to a limitation of the experimental setup the lowest temperature attainable was about −20°C. Adsorption sites weaker than site 1 may then have been depleted completely before the start of the runs. No information is then available on these sites from the experiments carried out here.

CONCLUSION

The procedure outlined in these two papers has allowed a nearly complete analysis of the adsorption behavior of isopropyl alcohol on a zinc oxide catalyst. The procedure will be applicable to a large class of adsorbate–adsorbent systems. The author has recently shown that a model assuming more than one set of active centers on a catalyst may be successful in interpreting rate data for a catalytic reaction (*5*). It is a well-known fact that adsorption constants estimated from adsorption measurements have not generally been in agreement with adsorption constants estimated from kinetic equations of the Langmuir-Hinshelwood-Hougen-Watson type (*6*). The correlations have, however, been attempted under the simplifying assumptions that the adsorption as well as the catalytic reaction proceeded on only one type of adsorption site. Experiments have been carried out to see if more meaningful correlations can be obtained when these simplifying assumptions are discarded (*7*; following paper).

APPENDIX

Remark on the Uniqueness of the Distribution Function

It may be difficult to construct a proof that the distribution function found here is the only possible one, but it may be shown that radically different distribution functions are rather unlikely.

Going back to Fig. 4 we see that the observed adsorption isobar is closely reproduced by the calculated reaction isobar which was computed from Eq. (3) [and (6)] using the parameter values given in Table 1. As was pointed out above the adsorption entropies are rather similar and do not exhibit any trend. The real adsorption entropies may in fact possibly be equal. This possibility has been tested by fitting Eq. (3) [and (6)] to the experimental data in Fig. 4 in the following way. The values of W_{0i} in Table 1 were kept unchanged. The single value $\Delta S = -47.5$ cal/mole degree was chosen and the values of ΔH_i were allowed to take the best possible values. The curve then resulting fitted the observed points somewhat better than shown in Fig. 4.

This means that we have obtained an approximate solution of the integral equation

$$W(T) = \int_{\alpha}^{\beta} \frac{p \exp(\Delta S/R - \Delta H/RT)}{1 + p \exp(\Delta S/R - \Delta H/RT)} \times \phi(-\Delta H)\, d\Delta H \quad (11)$$

where $\phi(-\Delta H)$ is the unknown distribution function. Equation (11) is a Fredholm integral equation of the first kind. The question now is whether there is more than one function $\phi(-\Delta H)$ which is a solution of Eq. (11).

Let the following transformations of the variables be carried out: $\xi = 1/RT$, $q = -\Delta H$, $k = \exp(\Delta S/R)$. Equation (11) then takes the form

$$f(\xi) = \int_{\gamma}^{\delta} \frac{pk \exp(q\xi)}{1 + pk \exp(q\xi)} \phi(q)\, dq \quad (12)$$
$$= \int_{\gamma}^{\delta} \mathrm{K}(q,\xi)\phi(q)\, dq$$

Equation (12), where the kernel $\mathrm{K}(q,\xi)$ is real and symmetric, i.e., hermitian, and furthermore definite, can be shown to have a unique solution (*8*). One may thus rest reasonably assured that when one restricts oneself to a Langmuir model for the adsorption process no radically different site distribution will fit the data. Other adsorption models will of course lead to different site distribution functions.

It may at this point be mentioned that

Eq. (7) has been fitted to the data in Fig 1, assuming $N = 4$. No satisfactory fit was obtained, and the trends of the parameters ΔH_i and ΔS_i were unsatisfactory (e.g., $\Delta S_1 = -50$ cal/mole degree and $\Delta S_4 = -25$ cal/mole degree).

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