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MATHEMATICAL ANALYSIS OF THE EFFECTS OF SURFACE HETEROGENEITY IN CHEMISORPTION: A NEW/OLD MODEL

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ABSTRACT

Two models of chemisorption, based on the conventional notion of 'mechanism,' are postulated to explain differential rate and heat data observed in true differential calorimeters. In one mechanism, the kinetic mechanism, it is assumed adsorption occurs in parallel to several different types of surface sites, and that the rate of adsorption to each type of site is controlled by the site activation energy and concentration of the sites. There is no assumed correlation between activation energy and heat of adsorption of the sites. Moreover, it is assumed that equilibrium between adsorbed species essentially never occurs. The second mechanism, the equilibrium mechanism, is similar except that it is assumed that equilibration among adsorbed species occurs rapidly. The adsorption mechanisms are described by a set of coupled differential equations which are solved numerically to give differential heats of adsorption and the kinetics of adsorption for quasi-differential gas doses. In systems in which kinetics and not equilibrium essentially controls the adsorption process it is shown that observed differential heats of adsorption will not necessarily be monotonically decreasing. The rate of adsorption in such systems; however, will steadily decline. In the event that equilibrium does exist within the adsorbed phase, differential heats of adsorption will decline monotonically. The kinetic behavior in such systems will vary as a function of adsorption site parameter values. These results are shown to be consistent with observations.

INTRODUCTION

Batch-type differential calorimetry provides both kinetic and thermodynamic information regarding the chemisorption process. Data can be readily interpreted to yield nearly-differential rates and heats of adsorption, and amount adsorbed vs. equilibrium vapor pressure (equilibrium adsorption isotherms). A full explanation of the data requires a model of both the heat and the rate of adsorption in a batch system. Yet, most models have been developed to explain either rate (1-7) or equilibrium (8-11) phenomena, and only a few qualitative attempts have been made (12-20) to develop models that predict behavior of all aspects of the chemisorption process.

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Below a mathematical model of chemisorption, based on earlier qualitative models in which kinetics determine the nature of the adsorption process (12,16-18), is presented. It is shown that this model qualitatively explains all prior heat and kinetic data obtained using true differential calorimeters. Models, which is essence are based on equilibrium considerations and not kinetics fail to explain cases in which heats of adsorption are found to increase or fluctuate with increasing surface coverage.

METHOD

This study focuses on a mathematical analysis of the adsorption process taking place in a true differential calorimeter. No real data is presented and success is judged on the basis of a qualitative comparison between the model data and previously published studies.

Calorimeter- The model calorimeter is assumed to be for the measurement of the heat released when quasi-differential doses of gas are adsorbed on a solid. For purposes of modelling it is assumed to be an ideal batch, heat-flow type which operates essentially isothermally. The system is assumed 'ideal' in several respects. It is assumed (i) that diffusion has no effect on the observed behavior, (ii) that physical adsorption releases an insignificant amount of heat and is unactivated, (iii) that the heat of expansion is unimportant, and (iv) that the entropy of adsorption on all sites is the same. Several calorimeters which very nearly meet these 'ideal' standards are described in the literature (12,21). A schematic is shown in Figure 1.

Model- Two simple models of chemisorption are presented below which are based on the general concept of mechanism so often used to explain homogeneous chemical reactions. Two broad classes of adsorption are modelled; (i) kinetically controlled adsorption, and (ii) equilibrium adsorption. It is shown that on a qualitative level these models explain frequently observed phenomena well.

For kinetically controlled adsorption of gas phase species (oxygen in this case) onto a material with only five site types (A,B,C,D,E) the mechanism is given below:

$$A+O_2 \Rightarrow AO_2$$

$$B+O_2 \Rightarrow BO_2$$

$$C+O_2 \Rightarrow CO_2$$

$$D+O_2 \Rightarrow DO_2$$

$$E+O_2 \Rightarrow EO_2$$

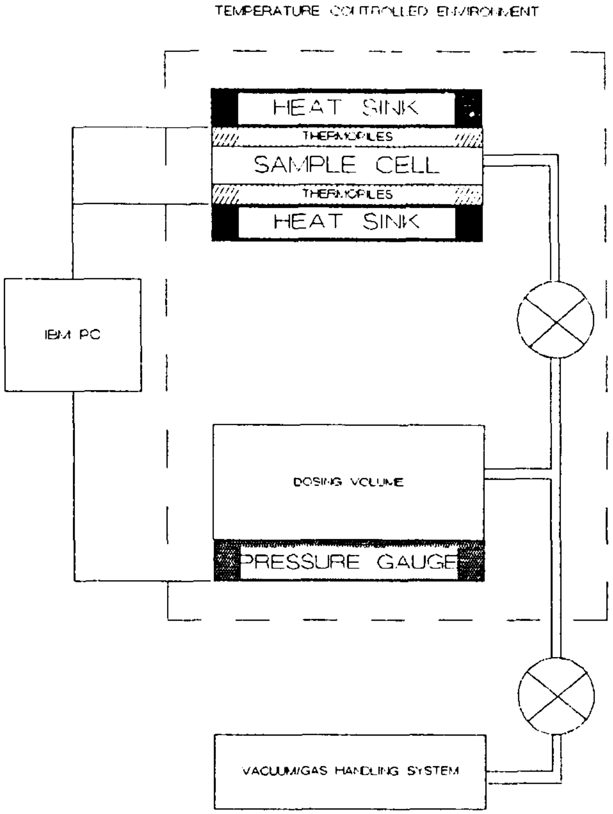
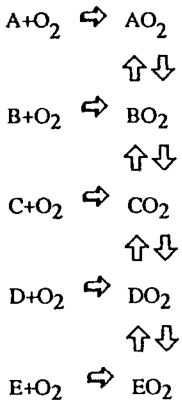


Figure 1. Model Batch, Heat-Flow Type Differential Calorimeter. The model calorimeter measures the heat released when quasi-differential doses of gas are adsorbed on a solid. Operation of the calorimeter is essentially isothermal due to the small quantities of heat released.

The adsorption process is irreversible. Given the values of the enthalpy of adsorption frequently observed this is reasonable. No physical significance is attached to the choice of five sites. Five sites were chosen because that number could qualitatively represent all real observations without the needless assumption of more site types. Although, qualitatively this model is similar to several earlier ones (12,14,16-20), a thorough mathematical analysis has never been performed.

An equilibrium mechanism, that is one which allows the adsorbed species to re-arrange such that the lowest energy configuration is realized, is shown below:



In this case the 'vertical' reactions are reversible, and the relative rates for the vertical reactions are determined by equilibrium considerations.

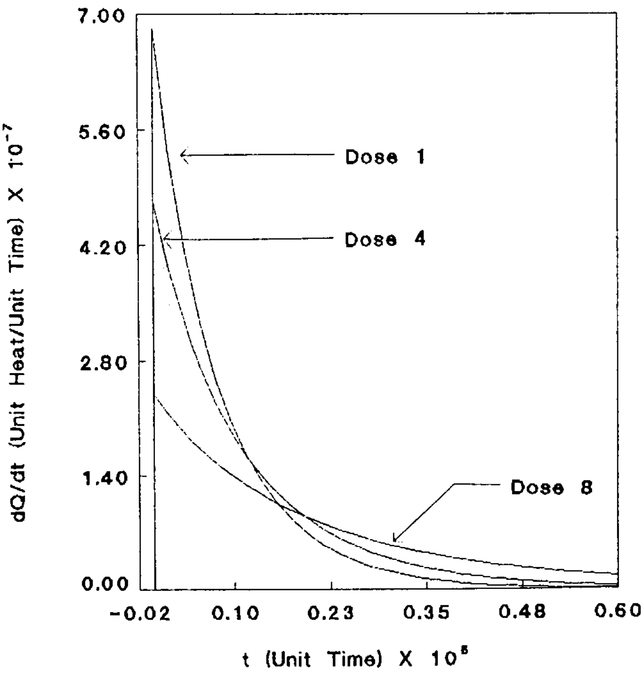


Figure 2. Representative Ballistic Curves for Run 1.
These curves are used to determine the quasi-differential heats of adsorption (area under the curve divided by the quantity of gas adsorbed) and the NCWHM (dimensionless time to half the maximum value of heat output normalized to the first dose).

For both mechanisms a set of second order rate expressions, and a set of differential mass balances on all the species are set up and solved using a standard differential equation solver, Continuous System Modelling Program (CSMP) run on an IBM 6180 mainframe computer. In each case the 'dose size' is quasi-differential, such that the program, with reset site concentrations and gas concentration, has to be run over and over.

RESULTS/DISCUSSION

Typical computer generated ballistic curves are shown in Figure 2. These ballistic curves are used to derive two pieces of data for each point; quasi-differential heat of adsorption, and the normalized cooling width, which is the time from maximum heat output to the half-max point, normalized to the first data point in any run. The quasi-differential heats and the normalized cooling widths are plotted as a function of surface coverage to demonstrate how the heat and kinetics (qualitative) change as a function of surface coverage.

The results of running a five site kinetically controlled model are shown in Figures 3 and 4, and the parameter values used in each case are given in

TABLE 1. MODEL PARAMETERS AND INITIAC INPUT VALUES

CHEMISORPTION OR ADSPECIES MIGRATION $i + O_2 \xrightarrow{ki} i \cdot O_2$ OR $i \cdot O_2 + j \underset{kji}{\overset{kij}{\rightleftarrows}} j \cdot O_2 + i$	FORWARD RATE CONSTANT ki or kij (unit pressure x unit time)$^{-1}$ OR (volume/mol time)	HEAT OF ADSORPTION OR FORWARD (ij) MIGRATION ΔHi or ΔHij (unit heat/mol gas ads)	INITIAL SITE CONCENTRATION io (mol/unit vol solid)
$A + O_2 \xrightarrow{kA} A \cdot O_2$	0.70	-20	4.5
$B + O_2 \xrightarrow{kB} B \cdot O_2$	1.60	-125 (- 45)*	3.0
$C + O_2 \xrightarrow{kC} C \cdot O_2$	7.50	- 65	1.8
$D + O_2 \xrightarrow{kD} D \cdot O_2$	3.80	- 10	4.0
$E + O_2 \xrightarrow{kE} E \cdot O_2$	9.45	- 90	2.8
$A \cdot O_2 + B \underset{kBA}{\overset{kAB}{\rightleftarrows}} B \cdot O_2 + A$	7.00×10^{4}	-150	ALL INITIAL i and j FOR DOSE 1 GIVEN ABOVE.
$B \cdot O_2 + C \underset{kCB}{\overset{kBC}{\rightleftarrows}} C \cdot O_2 + B$	5.4×10^{-40}	+ 60	
$C \cdot O_2 + D \underset{kDC}{\overset{kCD}{\rightleftarrows}} D \cdot O_2 + C$	4.11×10^{-36}	+ 55	INITIAL i, j, $i \cdot O_2$ and $j \cdot O_2$ FOR SUBSEQUENT DOSES ARE THE FINAL VALUES FROM THE PREVIOUS DOSE AS DETERMINED FROM SOLUTION OF THE MATERIAL BALANCE EQUATIONS.
$D \cdot O_2 + E \underset{kED}{\overset{kDE}{\rightleftarrows}} E \cdot O_2 + D$	4.50×10^{4}	- 80	
$A \cdot O_2 + E \underset{kEA}{\overset{kAE}{\rightleftarrows}} E \cdot O_2 + A$	1.00×10^{4}	- 70	
$A \cdot O_2 + D \underset{kDA}{\overset{kAD}{\rightleftarrows}} D \cdot O_2 + A$	9.26×10^{-4}	+ 10	
$E \cdot O_2 + B \underset{kBE}{\overset{kEB}{\rightleftarrows}} B \cdot O_2 + E$	7.50×10^{4}	- 35	
$A \cdot O_2 + C \underset{kCA}{\overset{kAC}{\rightleftarrows}} C \cdot O_2 + A$	3.50×10^{4}	- 45	
$E \cdot O_2 + C \underset{kCE}{\overset{kEC}{\rightleftarrows}} C \cdot O_2 + E$	6.92×10^{-15}	+ 25	
$B \cdot O_2 + D \underset{kDB}{\overset{kBD}{\rightleftarrows}} D \cdot O_2 + B$	1.80×10^{-80}	+115	

- ALL TABLE VALUES USED FOR RUN 3
- STEPS 6 - 15 APPLY TO RUN 3

* - HEAT OF ADSORPTION FOR RUN 2

- INITIAL DOSE PRESSURE Po = 16765 FOR ALL RUNS
- ΔS = 0 FOR ALL STEPS
- ALL EXOTHERIC MIGRATION STEPS ARE UNACTIVATED

Table 1. Figure 3 shows that the heat of adsorption can actually increase with coverage when kinetics control the adsorption process. Figure 4 shows that the values can also fall in this case. It is interesting that the clear difference in behavior between the two runs results from changing only one of fifteen parameters (see Table 1). Other examples, not shown, worked out with

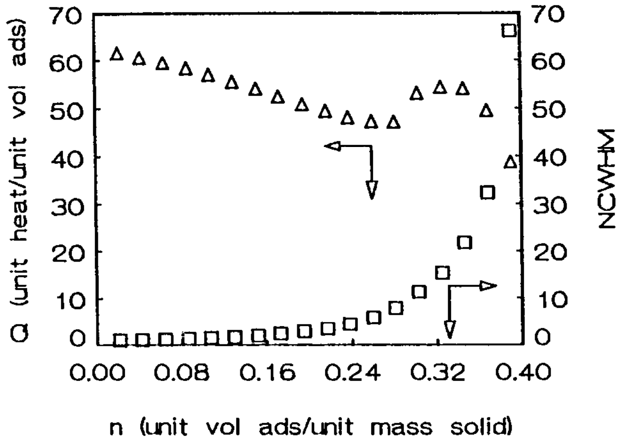


Figure 3. Differential Heat of Adsorption Δ and NCWHM □ versus the quantity of gas adsorbed for Run 1 (kinetically controlled adsorption - see Table 1).

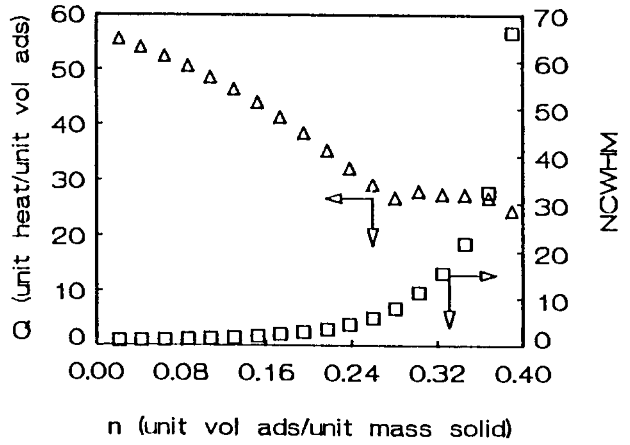


Figure 4. Differential Heat of Adsorption Δ and NCWHM □ versus the quantity of gas adsorbed for Run 2 (kinetically controlled adsorption - see Table 1).
All parameters identical for Runs 1 and 2 except the differential heat of adsorption for site-type B.

different parameter sets for the five site model show that the heat of adsorption values can fluctuate dramatically from point to point. One aspect of the results which is unchanging is the finding that the kinetics of adsorption slow with each additional step.

The results of one run with the equilibrium model are shown in Figure 5. In this case it was assumed that the 'vertical' processes, that is the processes which allow the gas to re-arrange after initial adsorption, were unactivated. Relative reaction rates for these processes were determined on the basis of equilibrium. For this equilibrium study the site parameters were chosen to have the same values as those of one of the kinetics cases (Figure 3, Table 1), yet the outcome is entirely different. For example, the initial sites fill with a heat value almost double that in the equivalent kinetically controlled run, and the range of observed differential heats is much broader. Also, the maximum value of the cooling widths is significantly less than that observed in the kinetically controlled cases. Another feature noted in this and other equilibrium controlled models tested (results not shown) is that the kinetics tend to fluctuate to a small extent and the rate of adsorption does not monotonically decrease as it does in the kinetically controlled cases.

There are examples in the literature of adsorption behavior which matches that of each of the cases discussed above; although, a search of the literature does reveal that in most cases for gas adsorption onto metal that the heat of adsorption declines monotonically with coverage suggesting equilibrium adsorption. There are some cases with metal films and supported

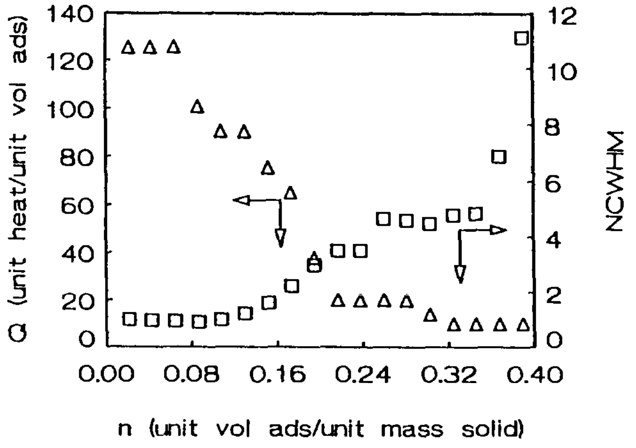


Figure 5. Differential Heat of Adsorption Δ and NCWHM □ versus the quantity of gas adsorbed for Run 3 (equilibrium controlled adsorption - see Table 1).
All parameters for adsorption onto sites are the same as in Run 1 except for equilibrium adsorption the adspecies may re-arrange to the lowest energy configuration.

particles which suggest kinetic processes. Among the possible equilibrium examples are oxygen (22,23), hydrogen (24,25), and CO (16) adsorption onto a variety of metal films and oxygen (26), hydrogen (27,28), CO (28), and ammonia (29) adsorption onto supported metal particles. Kinetically controlled cases also seem to exist. For example, several workers have observed 'fluctuating' or increasing heats of adsorption (16,23-25) (30,32) onto metal films.

Adsorption of gases on microporous materials often appears to be a kinetically controlled process. Increases in differential heat are reported in the early calorimetric studies of oxygen adsorption on activated carbon by Bull et al. (33) and oxygen adsorption on charcoal by Marshall and MacInnes (34), and on microporous carbon by O'Neil and Phillips (12).

Gas-zeolite systems present an interesting contrast in mechanistic behavior. Heats of adsorption that fall in steps with intermittent plateaus have often been reported (35,36), yet in numerous other cases (37-39) heats smoothly increase before dropping off; still another study (40) reveals heat vs. coverage profiles with multiple maximas and minimas. Auroux and coworkers (38,39) suggest the combined effect of three independent phenomena are responsible for the increase in heats: (i) adspecies are immobile on these zeolites (ii) there is a significant intraparticle diffusion limitation and (iii) the highest heat sites are located in the internal pores. Augul et al. (40) found heats for adsorption of water and n-alcohols on alkali metal X-type zeolites that generally fluctuated over a wide range. They acknowledged this behavior as a reality but offered no plausible explanation.

Chemisorption on metal oxides frequently appears to be a kinetically controlled process. The early work of Garner and Veal (41) and the more recent work of Gravelle and his co-workers (28,42-44) and Bolis et al. (45) indicates that there are often fluctuations in the differential heat of adsorption on metal oxides. Moreover, particularly in the studies of Gravelle's group, there are reports that the rate of adsorption slows drastically at high coverages.

In several of the previous studies discussed a precise determination of which type of mechanism is operative is not possible. This is because these studies give only fragmentary data; all studies report differential heat vs. coverage behavior, but few studies list data concerning the kinetics of the process (e.g., NCWHM vs. coverage) and no study of diffusion in the samples is available.

SUMMARY

A model of chemisorption as a competitive adsorption process, with equilibrium re-arrangement possible in some cases, was shown to qualitatively explain all previous differential calorimetric data. The results of the modelling also suggest calorimetric data should not be overinterpreted to yield information regarding type and number of surface sites as the same calorimetric results may result from a number of site distributions.

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