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## DETERMINATION OF SURFACE HETEROENERGENEITY IN CATALYSTS BY GAS ADSORPTION CHROMATOGRAPHY

### ADSORPTION OF HYDROGEN FLUORIDE ON CHROMIC FLUORIDE

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#### SUMMARY

The adsorption of hydrogen fluoride on anhydrous chromic fluoride (a catalyst for the conversion of  $\text{CCl}_4$  into  $\text{CCl}_3\text{F}$ ) was studied by gas adsorption chromatography. The isotherms obtained were non-linear, showing an isosteric heat of adsorption which increased with increasing coverage. This is an implausible description of the process, considering that the adsorption probably occurs by the formation of a hydrogen bond and that the maximal coverage under investigation was less than 10%. Simulation of the trailing edge of the adsorption peaks (and to the isotherms) was achieved in a two-site, heteroenergetic surface model in which the majority of the adsorbing surface had a heat of adsorption of  $7.8 \text{ kcal mole}^{-1}$ , consistent with the adsorption occurring by hydrogen bond formation. Analysis of the second site showed it to be composite, comprising more than one heat. This description of the adsorption has direct application to the catalytic situation where the conversion of  $\text{CCl}_4$  into  $\text{CCl}_3\text{F}$  has been shown to be successively first order, zero order and negative order, on increasing the partial pressure of HF.

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#### INTRODUCTION

While it is axiomatic that chemisorption is important in catalysis, most kinetic studies of catalytic performance ignore any explicit determination of the heats of adsorption of either reactants or products. In a kinetic study of the chromic fluoride-catalysed hydrofluorination of carbon tetrachloride, the reaction was found to be successively first order, zero order and then negative order on increasing the partial pressure of hydrogen fluoride<sup>1</sup>. An explanation of this behaviour is provided by assuming that the HF is strongly adsorbed on the catalyst, thereby preventing the catalytic halogen exchange reaction.

The adsorption studies of HF on chromic fluoride reported here were therefore undertaken as a test of the hypothesis. The technique employed for measuring the heats of adsorption was gas adsorption chromatography<sup>2,3</sup>, as the measurements could be made at conditions approximating to those used catalytically.

## EXPERIMENTAL

The apparatus was a conventional gas chromatograph employing a katharometer detector. Owing to the reactive nature of HF, all of the piping, the column which contained the adsorbent/catalyst and the injection device (a six port-valve accommodating a calibrated loop of 1.17 ml) were made of PTFE, which, at the temperatures of interest, did not adsorb and was not corroded by HF. The filaments of the katharometer were also coated with PTFE.

The adsorbent/catalyst was prepared by passing pure HF over granular (60–80 mesh) chromic oxide at 623°K for at least 10 h. The resulting material was characterized by elemental analysis and comparative X-ray diffraction as anhydrous chromic fluoride having a crystallite size of 500–1000 Å (10 Å = 1 nm); its surface area was 4.7 m<sup>2</sup> g<sup>-1</sup>.

The helium carrier gas and HF adsorbate were supplied by Air Products (New Malden, Great Britain); they were 99.995% and 99.8% pure, respectively, and so were used direct. The carrier gas flow-rate of 60 ml min<sup>-1</sup> was maintained at that level by the use of needle valves and a Flowstat automatic flow controller.

As it was possible that, in the transfer of the chromic fluoride to the chromatographic column, some water could have been adsorbed, resulting in the possibility that a fraction of the surface might have been hydrolysed, prior to all adsorption experiments the adsorbent was pre-treated with pure HF at 373°K. Ten pulses of the HF (4.4 · 10<sup>-4</sup> mole) were injected in rapid succession from the sample loop. This amount was more than sufficient to saturate all of the fluoride ions of the surface of the catalyst, the latter quantity having been determined by "titration" with CCl<sub>4</sub>, measuring the CCl<sub>3</sub>F produced; a value of 10.2 Å<sup>2</sup> per surface fluoride ion was obtained. The total number of moles of surface fluoride of the catalyst (5.479 g, 4.7 m<sup>2</sup> g<sup>-1</sup>) was 4.2 · 10<sup>-4</sup>. After pre-treatment, the adsorbent was left overnight under a flow of helium at 373°K.

## RESULTS AND DISCUSSION

The adsorption peaks in Fig. 1 were obtained by injecting a single pulse from the loop on to the column at 318, 343 and 368°K. The tail shapes were all superimposable when larger amounts of HF were injected at these temperatures, confirming that equilibrium had been achieved. These peaks were then transformed to the isotherms (Fig. 2a) by horizontal integration<sup>3</sup>. The isosteric heats listed in Table I were calculated from these using the Langmuir equation:

$$\ln(1/C) = (E_d - E_a)/RT + \ln(A_d/A_a) - \ln[\theta/(1 - \theta)] \quad (1)$$

where

*C* is the equilibrium concentration of HF at a given coverage;

*A<sub>d</sub>* and *E<sub>d</sub>* are the Arrhenius *A* factor and activation energy, respectively, for desorption;

*A<sub>a</sub>* and *E<sub>a</sub>* are the Arrhenius *A* factor and activation energy, respectively, for adsorption;

*θ* is the fractional coverage.

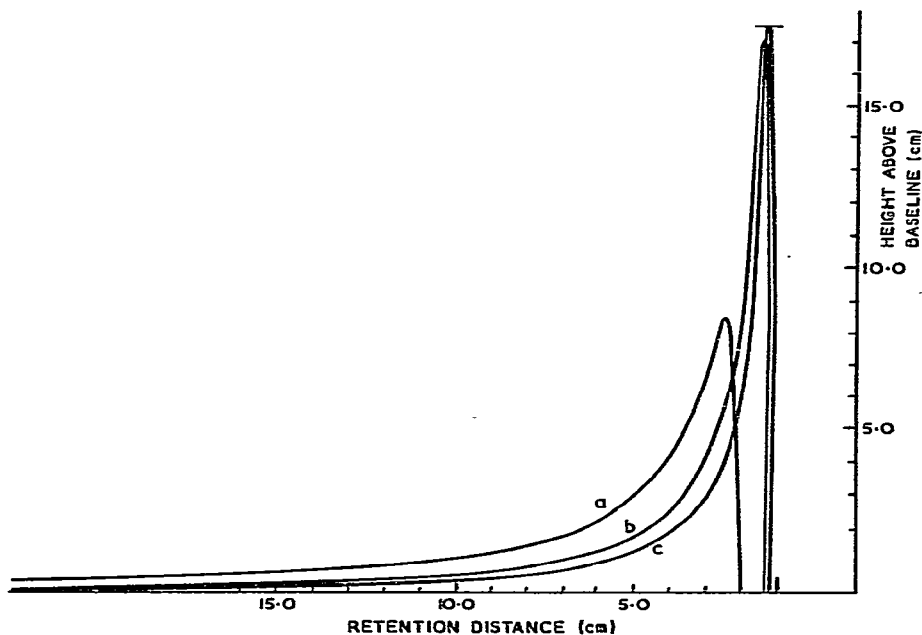


Fig. 1. Gas adsorption peaks of hydrogen fluoride on chromic fluoride: (a) 318°K; (b) 343°K; (c) 368°K.

Therefore

$$E_d - E_a = \Delta H \text{ (heat of adsorption)}$$

As HF would be expected to bond to the chromic fluoride by a hydrogen bond, the dependence of the coverages on the heats, at such low coverages, can be accounted for neither in the boundary layer type of description, usually applied to adsorption on semiconductors<sup>4</sup>, nor in a model envisaging repulsion between the adsorbed species<sup>5</sup>.

HF is known to dimerize in the gas phase and so the non-linearity of the isotherm could be accounted for in Freundlich terms, *i.e.*  $\theta = K'p^{1/2}$ , resulting from the dissociative adsorption of the (HF)<sub>2</sub> dimer. The ratio of the concentrations of the HF dimer to monomer can be calculated from a knowledge of the equilibrium constant. It is given by<sup>6</sup>

$$K = e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT} \quad (2)$$

where

$$\begin{aligned} \Delta S^\circ &= -40 \pm 4 \text{ eu (1 eu} = 4.182 \cdot 10^{-3} \text{ kJ } ^\circ\text{K}^{-1}\text{)} \\ \Delta H^\circ &= -6800 \text{ cal mole}^{-1} \text{ (1 cal} = 4.182 \cdot 10^{-3} \text{ kJ)} \\ R &= 1.987 \text{ cal mole}^{-1} \text{ } ^\circ\text{K}^{-1} \end{aligned}$$

and the (HF)<sub>2</sub> and HF concentrations are given by

$$[(\text{HF})_2] + [\text{HF}] = Q \quad (Q = P/RT) \quad (3)$$

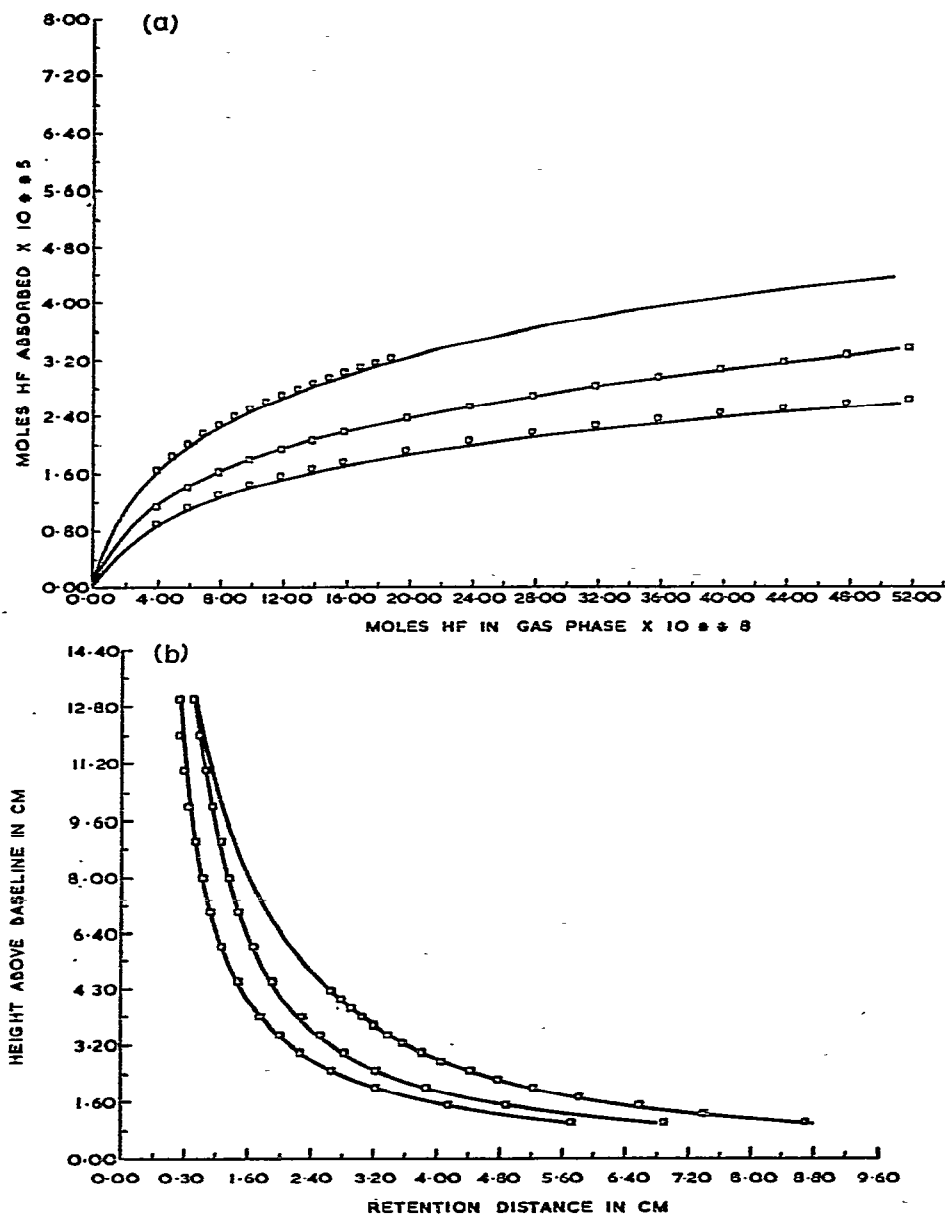


Fig. 2. (a) Adsorption isotherms of hydrogen fluoride obtained by horizontal "strip-wise" integration of the adsorption peaks: points ( $\square$ ), experimental; lines, prediction. (b) The fit to the trailing edge of the adsorption peaks: points ( $\square$ ), experimental; lines, predicted shapes for the best fit values  $\alpha = 0.71$ ,  $K_1 = 10^{1.1} e^{7480/RT}$ ,  $K_2 = 10^{4.5} e^{9060/RT}$ ,  $\sigma = 15\%$  of the total surface (these values are used to calculate the isotherms in Fig. 2a).

Substitution of  $K[\text{HF}]^2$  for  $[(\text{HF})_2]$  in eqn. 3 and solution of the resulting quadratic gives

$$[\text{HF}] = 2Q / [(1 + 4KQ)^{1/2} + 1] \quad (4)$$

TABLE I

ISOSTERIC HEATS OF ADSORPTION AND  $A$  FACTOR RATIOS AT DIFFERENT COVERAGES

Surface coverage	$E_d - E_a$ , i.e., $\Delta H$ (kcal mole <sup>-1</sup> )	$A_d/A_a$ (cm <sup>3</sup> mole <sup>-1</sup> )	Temperature range (°K)
1.0·10 <sup>-2</sup>	3.4	6.0·10 <sup>3</sup>	343-368
2.0·10 <sup>-2</sup>	3.1	8.3·10 <sup>3</sup>	
3.0·10 <sup>-2</sup>	3.3	3.9·10 <sup>3</sup>	
4.0·10 <sup>-2</sup>	4.2	9.1·10 <sup>2</sup>	
5.0·10 <sup>-2</sup>	5.0	1.7·10 <sup>2</sup>	
1.0·10 <sup>-2</sup>	4.8	8.6·10 <sup>2</sup>	318-343
2.0·10 <sup>-2</sup>	6.3	7.2·10 <sup>2</sup>	
3.0·10 <sup>-2</sup>	8.1	3.7	
4.0·10 <sup>-2</sup>	9.5	3.3·10 <sup>-2</sup>	
5.0·10 <sup>-2</sup>	10.3	1.2·10 <sup>-2</sup>	

Table II lists the equilibrium constants at the three temperatures, together with the HF and (HF)<sub>2</sub> concentrations calculated from eqn. 4 at the maximal HF partial pressures of the isotherms. The maximum [(HF)<sub>2</sub>]/[HF] ratio was 6·10<sup>-4</sup>, from which it must be concluded the dimer would make a negligible contribution to the curvature of the isotherm.

TABLE II

VALUES OF THE EQUILIBRIUM CONSTANT AND HF, (HF)<sub>2</sub> CONCENTRATIONS CALCULATED FROM EQNS. 2 AND 4, RESPECTIVELY

Temperature (°K)	$e^{AS_0/R}$ (cm <sup>3</sup> mole <sup>-1</sup> )	$K$ (cm <sup>3</sup> mole <sup>-1</sup> )	[HF] (mole cm <sup>-3</sup> )	[(HF) <sub>2</sub> ] (mole cm <sup>-3</sup> )	[(HF) <sub>2</sub> ]/[HF]
318	3.6·10 <sup>-2</sup>	1.7·10 <sup>3</sup>	3.4·10 <sup>-7</sup>	2.0·10 <sup>-10</sup>	6·10 <sup>-4</sup>
343	3.9·10 <sup>-2</sup>	8.3·10 <sup>2</sup>	3.6·10 <sup>-7</sup>	1.1·10 <sup>-10</sup>	3·10 <sup>-4</sup>
368	4.2·10 <sup>-2</sup>	4.5·10 <sup>2</sup>	3.6·10 <sup>-7</sup>	6.0·10 <sup>-11</sup>	2·10 <sup>-4</sup>

Giddings and Eyring<sup>7</sup> suggested that the tailing shown in Fig. 1 could be the result of the existence on the surface of a second site (a tail-producing site) in addition to the site responsible for the main chromatographic effect; this second site should be scarce and therefore does not adsorb molecules very often, but, following such adsorption, it holds the adsorbate molecules very strongly. The expression of this two-site surface heterogeneity in Langmuir terms<sup>8</sup> is

$$\text{No. of moles adsorbed} = \sigma \left[ \frac{\alpha K_1 C}{(1 + K_1 C)} + (1 - \alpha) \cdot \frac{K_2 C}{(1 + K_2 C)} \right] \quad (5)$$

where

$\sigma$  is the total number of moles of adsorption sites;

$K_1$  is the equilibrium constant for site 1 =  $10^{A_1} e^{\Delta H_1/RT}$ ;

$K_2$  is the equilibrium constant for site 2 =  $10^{A_2} e^{\Delta H_2/RT}$ ;

$\alpha$  is the fraction of the surface having heat of adsorption  $\Delta H_1$ ;

$C$  is the equilibrium concentration of HF.

TABLE III  
 COMPARISON OF PREDICTED AND EXPERIMENTAL RETENTION DISTANCES FOR THE "BEST FIT" PARAMETERS  
 $\alpha = 0.71$ ;  $K_1 = 10^{1.1} e^{2600/RT}$ ;  $K_2 = 10^{4.8} e^{1000/RT}$ ;  $\sigma = 15\%$  of total surface.

Height above baseline (cm)	Retention distance (cm)		Height above baseline (cm)		Retention distance (cm)		Height above baseline (cm)		Retention distance (cm)	
	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
1.0	8.2	8.80	6.90	6.82	1.0	6.82	5.72	5.67	1.0	5.67
1.25	7.4	7.44	4.88	4.95	1.5	4.95	4.16	4.17	1.5	4.17
1.50	6.58	6.48	3.87	3.91	2.0	3.91	3.24	3.27	2.0	3.27
1.75	5.81	5.77	3.24	3.27	2.5	3.27	2.67	2.68	2.5	2.68
2.00	5.23	5.22	2.84	3.83	3.0	3.83	2.28	2.28	3.0	2.28
2.25	4.77	4.78	2.53	2.51	3.5	2.51	2.02	2.00	3.5	2.00
2.50	4.43	4.41	2.30	2.28	4.0	2.28	1.77	1.77	4.0	1.77
2.75	4.06	4.10	1.92	1.93	5.0	1.93	1.49	1.47	5.0	1.47
3.0	3.82	3.84	1.69	1.70	6.0	1.70	1.28	1.27	6.0	1.27
3.25	3.58	3.60	1.50	1.52	7.0	1.52	1.14	1.13	7.0	1.13
3.50	3.39	3.40	1.38	1.38	8.0	1.38	1.05	1.03	8.0	1.03
3.75	3.21	3.22	1.28	1.26	9.0	1.26	0.95	0.94	9.0	0.94
4.00	3.06	3.05	1.16	1.16	10.0	1.16	0.86	0.88	10.0	0.88
4.25	2.92	2.90	1.07	1.08	11.0	1.08	0.79	0.82	11.0	0.82
4.50	2.79	2.77	0.99	1.00	12.0	1.00	0.75	0.78	12.0	0.78
4.75	2.66	2.64	0.92	0.94	13.0	0.94	0.73	0.74	13.0	0.74

The retention distance of the trailing edge of the adsorption peak is equal to the differential of eqn. 5 with respect to concentration, appropriate constants relating to the chart speed and carrier gas flow-rate being included. A fit was therefore made to the trailing edges of the adsorption peaks in Fig. 1 by varying the six parameters  $\sigma$ ,  $A_1$ ,  $\Delta H_1$ ,  $A_2$ ,  $\Delta H_2$  and  $\alpha$  of eqn. 6 using a Gauss-Newton weighted least-squares programme:

$$\text{Retention distance (cm)} = \frac{s\sigma}{F} \left[ \frac{\alpha K_1}{(1 + K_1 C)^2} + (1 - \alpha) \cdot \frac{K_2}{(1 + K_2 C)^2} \right] \quad (6)$$

where  $s$  is the chart speed and  $F$  is the carrier gas flow-rate. The best fit parameters are as follows:

$$\begin{aligned} \alpha &= 0.71 \pm 0.02; \\ A_1 &= 1.1 \pm 0.2 \text{ cm}^3 \text{ mole}^{-1}; \\ \Delta H_1 &= 7.84 \pm 0.3 \text{ kcal mole}^{-1}; \\ A_2 &= 4.8 \pm 0.4 \text{ cm}^3 \text{ mole}^{-1}; \\ \Delta H_2 &= 4.06 \pm 0.7 \text{ kcal mole}^{-1}; \\ \sigma &= 15.0\% \text{ of the total number of surface sites.} \end{aligned}$$

The fit to the tail shapes is shown in Fig. 2b and to the isotherms in Fig. 2a (the boxes are experimental values and the lines the prediction), and Table III lists the experimental and predicted retention distances. The correspondence between the prediction and experiment is extremely good and well within experimental error (the sum of the squares of the differences between the predicted and experimental values was consistent with a random distribution).

The parameter correlation matrix (Table IV) shows that  $\sigma$ , the total number of surface sites, and  $\alpha$ , the fraction having heat of adsorption  $\Delta H_1$ , are independent variables. As expected, the Arrhenius pre-exponential terms and the heats of adsorption are strongly correlated.

The values obtained do not obviate the premises of the model. The major fraction, 71% of the adsorbing surface, has a heat of adsorption of 7.8 kcal mole<sup>-1</sup>. On the remaining 30% the adsorption equilibrium constant is larger [ $K_2$  (343°K) =

TABLE IV  
PARAMETER CORRELATION MATRIX

	$\alpha$					
$\alpha$	1.0					
$10^{41}$	0.082	$10^{41}$ 1.0				
$\Delta H_1$	0.084	-0.99	$\Delta H_1$ 1.0			
$10^{42}$	0.009	0.98	-0.99	$10^{42}$ 1.0		
$\Delta H_2$	0.012	0.98	0.99	0.99	$\Delta H_2$ 1.0	
$\sigma$	0.35	0.06	0.009	0.04	0.03	$\sigma$ 1.0

$2.44 \cdot 10^7$ ,  $K_1 (343^\circ\text{K}) = 1.25 \cdot 10^6$ ] although the predicted heat of adsorption is lower. As there is a unit correlation between the pre-exponential terms and the heats of adsorption and as the pre-exponential term should relate to the adsorption collision

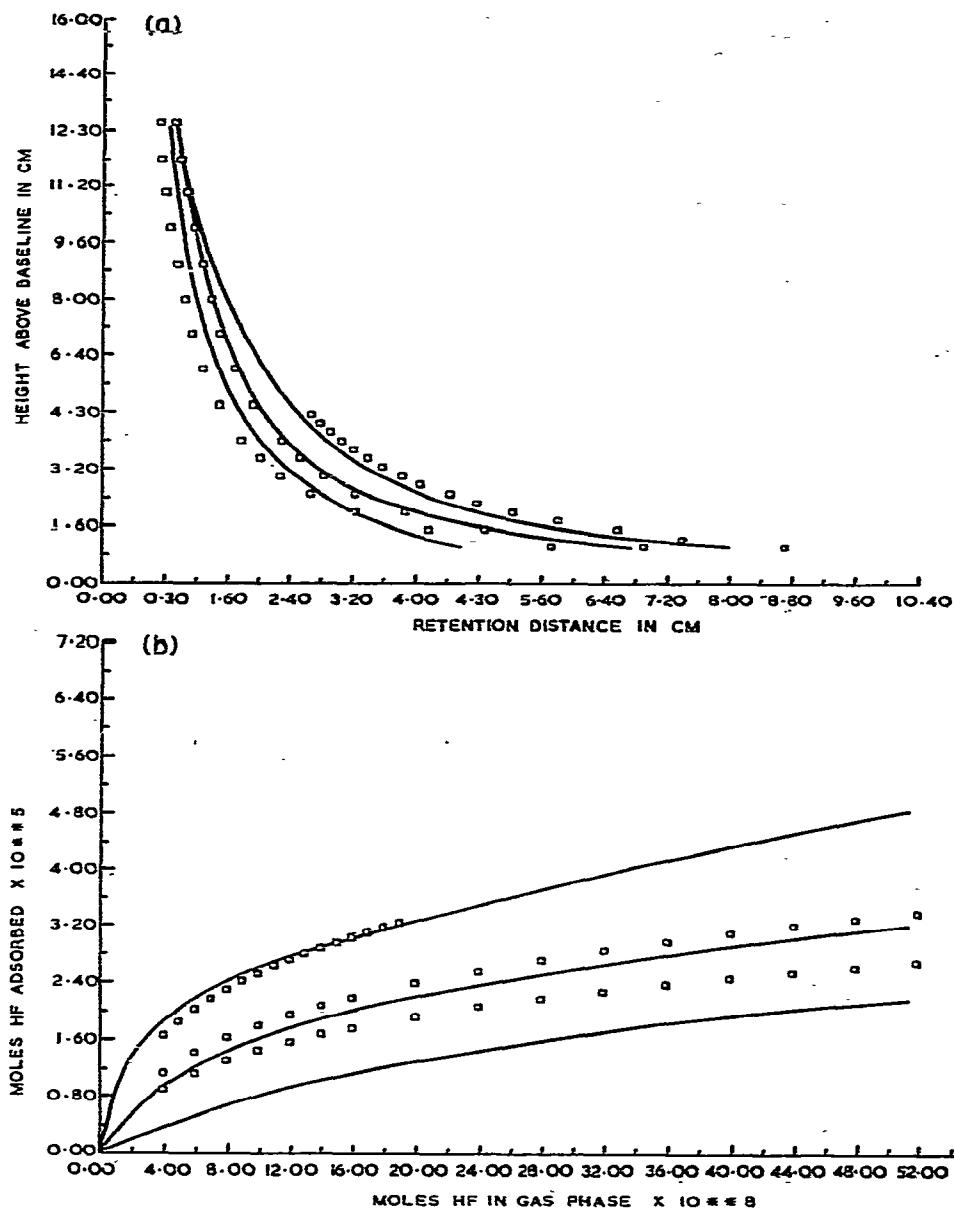


Fig. 3. (a) Fit to the trailing edge of the adsorption peaks: points ( $\square$ ), experimental; lines, predicted shapes for a model in which only  $\Delta H_2$  was varied,  $\alpha$ ,  $\sigma$ ,  $A_1$ ,  $\Delta H_1$  being kept constant at 0.71, 15% of the surface, 1.1 and 7.84 kcal mole $^{-1}$ , respectively, with  $A_2$  set equal to  $A_1$ . The best fit value of  $\Delta H_2$  was 9.87 kcal mole $^{-1}$ . (b) Lines, predicted isotherms for the values of the parameters listed in Fig. 3a; points ( $\square$ ), experimental values.



cross-section (which would not be expected to vary greatly in the two bonds),  $A_2$  was set equal to  $A_1$  and a fit was made to  $\Delta H_2$ . The expectation was that a higher heat of adsorption would be predicted and that the fit would be identical with that shown in Fig. 2. The best fit value obtained was  $9.87 \pm 0.5$  kcal mole<sup>-1</sup> but, as can be seen from Fig. 3 (confirmed also by the sum of the squares of the residuals), there was a systematic difference between the predicted and experimental points at the highest temperature. The conclusion to be drawn from this model is that the adsorption process is more complex than can be described in two sites, the high-energy adsorption probably being a composite of two or more sites.

Finally, the model is also predicting that the maximal number of surface sites on which adsorption can occur is only 15% of the total number of surface sites, a point which will be enlarged upon below.

As it had been anticipated that the HF would have been capable of being adsorbed on all of the surface fluoride ions (the adsorption probably being hydrogen bond formation), a five-parameter model was examined in which the parameter  $\sigma$  was held constant at a value obtained by dividing the total surface area by 10.2 Å (the area per surface fluoride ion). Otherwise the model was identical with that described by eqns. 5 and 6. The best fit parameters obtained from this model are as follows:

$$\begin{aligned} \alpha &= 0.94 \pm 0.001; \\ A_1 &= 0.27 \pm 0.26; \\ \Delta H_1 &= 7.82 \pm 0.04 \text{ kcal mole}^{-1}; \\ A_2 &= 4.86 \pm 0.52; \\ \Delta H_2 &= 3.57 \pm 0.09 \text{ kcal mole}^{-1}. \end{aligned}$$

As can be seen from Fig. 4a and b, which show the fit to the tail shapes and the isotherms, respectively, the predicted and experimental tail shapes show reasonable correspondence, there being a systematic difference only at the large retention time point. The fit to the isotherms, however, is not good, reflecting this lack of correspondence at the low concentration point. Here again, as  $K_2$  was larger than  $K_1$  and as the model really required that  $\Delta H_2$  be larger than  $\Delta H_1$ ,  $A_2$  was set equal to  $A_1$  and the fit was made to  $\Delta H_2$ . The value obtained was  $\Delta H_2 = 11.56 \pm 0.01$  kcal mole<sup>-1</sup> but, as before in the six-parameter model, the fit to the tail shapes and the isotherms was worse (Fig. 5a and b, respectively), indicating again that the high-energy site is composite.

Although the six-parameter model gives a better fit to the experimental data than the five-parameter model (as evinced by the lower sum of the squares of residuals), a choice between the two models should not be made on statistical grounds alone; it is necessary to take cognizance of the physical/chemical aspects of the bonding of the HF to the chromic fluoride surface. Both the five- and six-parameter models predict a heat of adsorption of 7.8 kcal mole<sup>-1</sup> on the majority of the adsorbing surface, consistent with the adsorption being by hydrogen bonding. On this basis, therefore, in spite of the poor fit to the adsorption isotherms resulting from the poor fit to the low concentration, large retention time point, the model in which all of the fluorided surface is capable of adsorbing the HF is probably a better representation of the physical situation. Indeed, although the adsorption peaks and the iso-

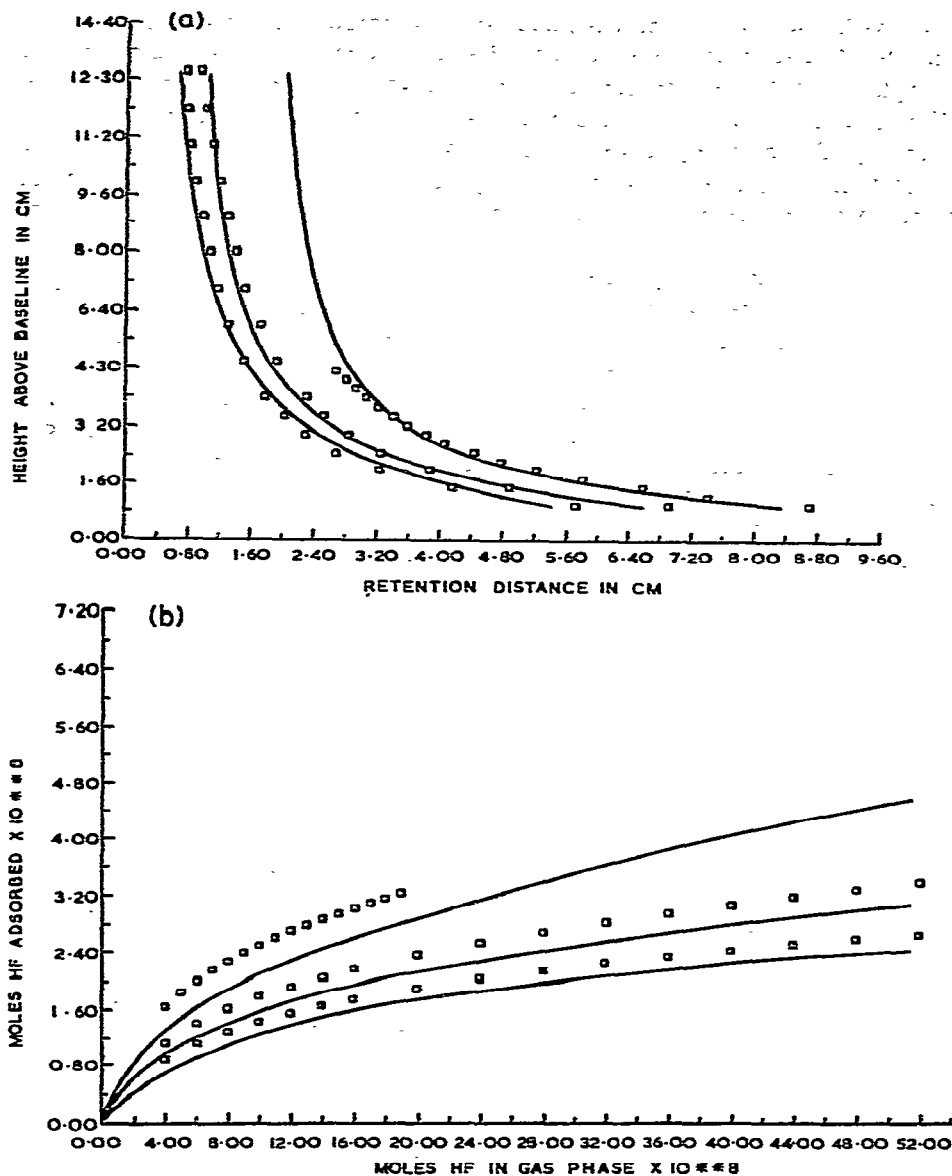


Fig. 4. (a) Fit to trailing edge of the adsorption peaks: points ( $\square$ ), experimental; lines, predicted shapes for a model in which all of the surface was assumed capable of adsorbing the hydrogen fluoride. The best fit parameters are  $\alpha = 0.94$ ,  $K_1 = 10^{-0.3} e^{7820/RT}$ ,  $K_2 = 10^{4.56} e^{4860/RT}$ . (b) Lines, predicted isotherms for the values of the five-parameter models listed in Fig. 4a; points ( $\square$ ), experimental values.

therms can be fitted exactly in a two-site, six-parameter model, it has been shown that the surface is energetically more heterogeneous than this, the large retention time points resulting from more than one heat of adsorption.

For completeness, a single-site model was tested fitting to three parameters,

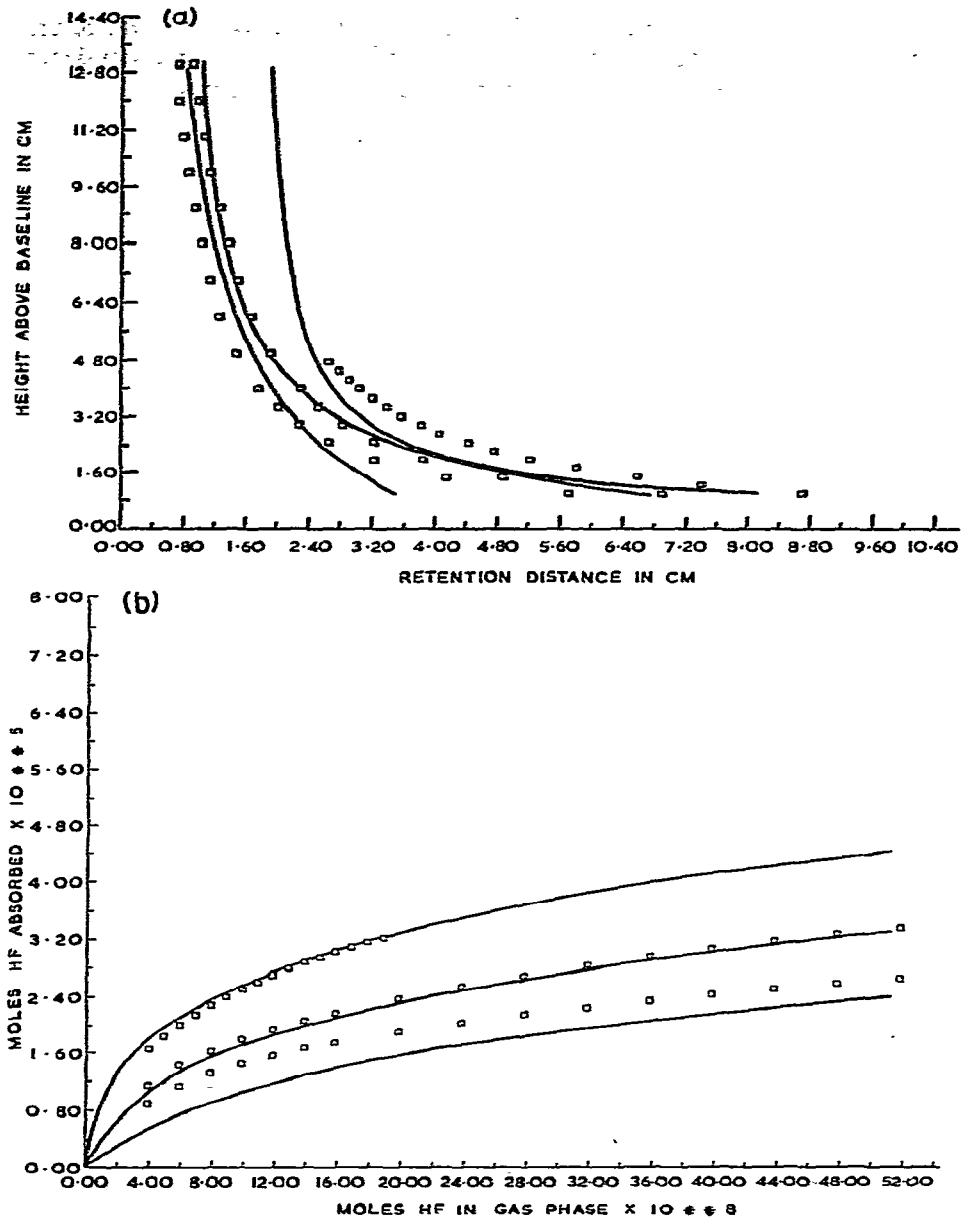


Fig. 5. (a) Fit to the trailing edge of the adsorption peaks: points ( $\square$ ), experimental; lines, prediction for a five-parameter model in which only  $\Delta H_2$  was varied,  $\alpha$ ,  $A_1$  and  $\Delta H_1$  being kept constant at 0.94,  $-0.3$  and  $7.84$  kcal mole $^{-1}$ , respectively, with  $A_2$  set equal to  $A_1$  (all of the surface was assumed to be capable of adsorption). The best fit value of  $\Delta H_2$  was  $11.6$  kcal mole $^{-1}$ . (b) Lines, predicted isotherms for the values of the parameters listed in Fig. 5a; points ( $\square$ ), experimental values.

the number of surface sites and  $A$  and  $\Delta H$  of the equilibrium constant. Whereas a curved isotherm was obtained when 9.6% of the surface sites only were capable of adsorbing the HF, the curvature was found in the high concentration region and

not in the low region observed experimentally. The best fit value of the equilibrium constant was  $10^{4.1} e^{4150/RT}$  but, as can be seen from Fig. 6, there was no correspondence between the prediction and experimental adsorption peaks or isotherms.

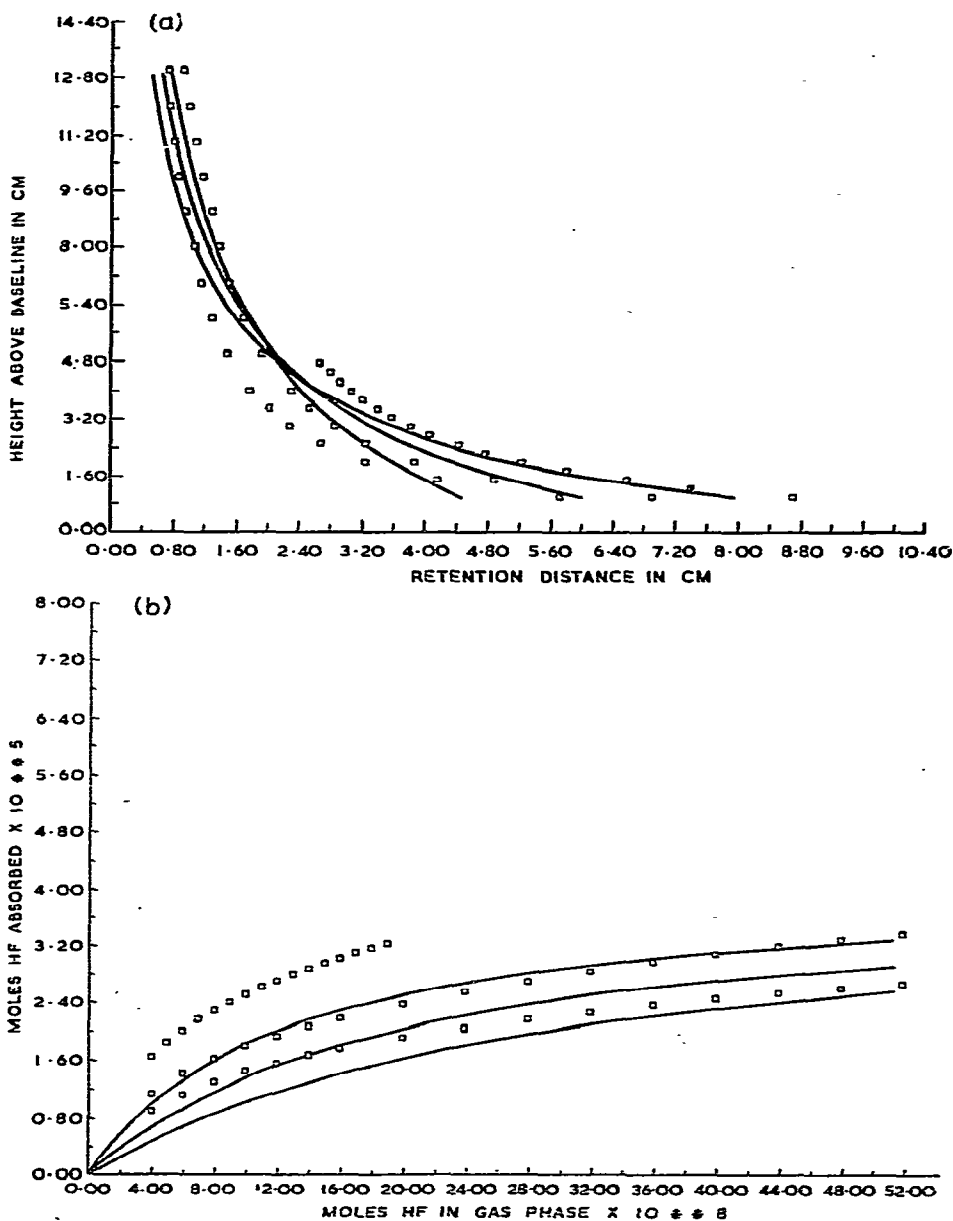


Fig. 6. (a) Fit to the trailing edge of the adsorption peaks using a three-parameter single-site model: lines, predicted shape for the best fit values  $K = 10^{4.1} e^{4150/RT}$ ,  $\sigma = 9.6\%$  of the total surface; points ( $\square$ ), experimental values. (b) Lines, predicted isotherms for the values of the single-site model listed in Fig. 6a; points ( $\square$ ), experimental values.

## CONCLUSIONS

(1) Chromic fluoride subtends on an energetically heterogeneous surface for the adsorption of HF.

(2) The adsorption process can be described by a minimum of two heats of adsorption, although the results suggest that the higher energy bond, associated with only a small fraction of the adsorbing surface, is a composite of two or more heats.

(3) The heat of adsorption of HF on the majority of the surface is  $7.8 \text{ kcal mole}^{-1}$ , a value which is consistent with the adsorption occurring by hydrogen bond formation.

(4) These results are capable of explaining the observations of a kinetic analysis of the  $\text{CrF}_3$ -catalysed hydrofluorination of  $\text{CCl}_4$  in which the reaction was found to be first order, zero order and negative order with respect to HF concentration.

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