

## The Nature of Silica-Alumina Surfaces. I. Thermodynamics of Adsorption of Ammonia

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The adsorption of ammonia on eleven silica-alumina gels ranging in composition from pure alumina to pure silica has been studied. Isothermic heats and differential surface entropies have been determined from adsorption isotherms at 50-degree intervals in the range 100-400°C. The adsorption data are correlated satisfactorily by means of the Freundlich equation. Isothermic heats drop off sharply with increasing coverage for all the gels. Compositions in the range of 55-90% silica have the largest fraction of weak adsorption sites. This is the region which exhibits high catalytic activity for various acid-type reactions. The magnitude of the differential surface entropies indicates that in this range most of the adsorbed molecules are in a highly mobile state.

### I. INTRODUCTION

In this paper an account is given of the thermodynamics of adsorption of ammonia on eleven silica-alumina gels ranging in composition from pure alumina to pure silica. Isothermic heats of adsorption and differential surface entropies are stressed. In a second paper, this thermodynamic information will be related to catalytic properties in a group of reactions carried out over gels of the same compositions. In a third paper, a detailed statistical-mechanical interpretation of the adsorption of ammonia on alumina will be given.

Basic work on the clarification of adsorption thermodynamics, especially adsorption entropies, was carried out by de Boer and Kruyer (1). Numerous reports (2-5) on the adsorption of ammonia or other nitrogen-containing bases on alumina and silica-alumina have appeared in the literature. Very few of them cover broad enough ranges of temperatures and surface concentrations to allow significant thermodynamic information to be obtained. Most of them are concerned with silica-alumina gels having compositions in the limited region of good cracking catalysts. It is one

of the primary objectives of this work to show the trends in thermodynamic properties as a function of adsorbent composition.

We have used differential thermodynamic quantities throughout the paper in accord with the views of Everett (6). In our opinion, differential quantities have a more direct bearing on the interpretation of catalytic phenomena than integral molar quantities. Furthermore, they are easier to obtain experimentally.

### II. EXPERIMENTAL

#### *Materials*

Eleven adsorbents ranging in composition from pure alumina to pure silica were prepared. The silica-alumina compositions were coprecipitated from solutions of sodium silicate and sodium aluminate as described previously (7). Silica gel was made by a similar procedure from sodium silicate. Alumina was obtained by heat treatment of high purity  $\beta$ -alumina trihydrate from Davison Chemical Corporation; the resulting material was  $\eta$ -alumina.

All adsorbents were heated in granular form for 16 hours at 550°C in a stream of

dry air and stored prior to use under dry conditions. Each sample received a further heat treatment at 500°C for one hour under diffusion-pump vacuum in the adsorption apparatus just before use. Physical and chemical properties of these adsorbents are given in Table 1. The compositions

a small diameter quartz fiber. The sample was enclosed by a Pyrex furnace tube, 1½-inch OD and 20 inches long, attached to the lower side of the balance case by means of a tapered joint. The balance case was connected by 5/8-inch OD glass tubing to a vacuum manifold consisting of a

TABLE 1  
COMPOSITION AND PROPERTIES OF SILICA-ALUMINA CATALYSTS

Composition (% SiO <sub>2</sub> )	Na (%)	SA. (m <sup>2</sup> /g)	Pore volume (ml/g)	Avg. pore dia. (Å)	Tamele activity <sup>a</sup> (meq/m <sup>2</sup> × 10 <sup>3</sup> )	Protonic acidity <sup>b</sup> (meq/m <sup>2</sup> × 10 <sup>3</sup> )
0	<0.002	303	0.56	74	0.51	0
8	0.003	292	0.46	63	1.44	0.14
15	0.008	358	0.51	57	1.02	0.18
40	0.18	309	0.49	63	1.05	0.48
55	0.17	249	0.42	68	1.33	0.99
70	0.22	296	0.32	43	1.37	1.55
82	0.036	397	0.58	58	0.89	1.78
90	0.010	510	0.52	41	0.75	1.45
95	0.004	562	0.52	37	0.60 <sup>c</sup>	1.18 <sup>c</sup>
98	0.003	564	0.59	42	—	0.63 <sup>c</sup>
100	0.026	344	0.59	68	0.06 <sup>c</sup>	0.27 <sup>c</sup>

<sup>a</sup> Determined by titration with *n*-butylamine in dry benzene (?).

<sup>b</sup> Determined by base exchange with neutral ammonium acetate solution (?).

<sup>c</sup> Denotes results on similar compositions but different preparation batches.

given in this table are approximate; they are within 1% of the actual analyses. Pore volumes were sufficiently large that no indications of slow diffusion were obtained during adsorption measurements. In the compositions 40, 55, and 70% silica, the sodium contents are higher than desired, but they did not appear to affect the general trends of the results obtained. Other metal impurities were present only in trace quantities.

Ammonia was obtained from the Matheson Company, and its specified purity (99.99%) was verified. Extreme precautions were taken to maintain ammonia samples moisture free.

#### *Adsorption Equipment*

Adsorption measurements were made with a vacuum microbalance similar to one described by Gray and Jennings (8). The adsorbent sample of about 0.2 g, contained in a small quartz bucket, was suspended from one arm of the balance by means of

manometer, triple-range McLeod gauge, liquid nitrogen trap, three-stage mercury diffusion pump, and suitable connections and stopcocks for admitting gas to the system. The sensitivity of the balance under the conditions of use was between 1 and 2 μg.

The furnace tube was specifically designed to minimize the effect of convection currents which otherwise would have proved bothersome at the higher temperatures. A short length of 7/8-inch OD tubing, closed at the bottom, was placed within the furnace tube. It was supported by the thermocouple well which was attached to the bottom of the furnace tube and extended upward a short distance through the bottom of the inner tube. The quartz bucket, suspended by the quartz fiber, was situated in the quiescent zone within the inner tube. Convection corrections never exceeded 10% of the total weight of adsorbed phase. Maximum corrections oc-

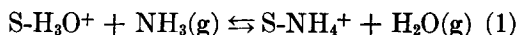
curred at a pressure of about 0.1 mm of mercury and at the highest temperature (400°C) of adsorption measurements. At higher and lower pressures and at lower temperatures, corrections rapidly declined to zero. Convection corrections were established by using an inert material, sand, in the sample bucket and making weighings in vacuo and at various ammonia pressures over the temperatures covered by the adsorption measurements.

#### *Adsorption Technique*

All adsorbents were heated for one hour at 500°C under diffusion-pump vacuum prior to adsorption measurements. After adjustment of the temperature to 400°C, the pressure was of the order of  $10^{-6}$  mm of mercury, and the weight of the sample was stable. The total water contents of the stabilized samples varied between 0.8 and 2.5%. Future work will include the effect of water content on the adsorption characteristics of the various adsorbents. A predetermined amount of ammonia was admitted into the system. After periodic weighings indicated that equilibrium had been reached, a pressure reading was made and the temperature adjusted to 350°C for equilibrium measurements at this level. The procedure was repeated at 50-degree intervals down to 100°C. Similar runs were made using different amounts of ammonia. Thus adsorption data were obtained at each temperature level for various pressures up to 15 mm of mercury.

The sorption of ammonia by all eleven compositions of the adsorbents proved fully reversible over all the temperatures studied, and it was possible to evaluate thermodynamic functions over a broad range of coverages. Isotherm points could be duplicated within the limits of sensitivity of the balance by approaching the points from the high temperature side as described above or from the low temperature side. Similar techniques for ensuring the attainment of equilibrium were used by Frankenburger (9) and by Sweett and Rideal (10) in other systems. Excellent agreement among isotherm points was obtained in duplicate

runs with fresh samples of adsorbents. It was also shown that gas uptake represented true adsorption and not an equilibrium of the type:



where a product is displaced from the surface upon adsorption of ammonia. In one case, using alumina as the adsorbent, 1420  $\mu\text{g}$  of ammonia was introduced into the adsorption system at 100°C. The increase in weight after equilibrium had been reached was 1398  $\mu\text{g}$  and the equilibrium gas pressure was 0.006 mm which corresponds to 17  $\mu\text{g}$  of ammonia. Thus, no more than 1.5% of the ammonia could have been adsorbed according to Eq. (1) if all of the residue gas were considered to be water vapor. In another case, using  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (70:30) as adsorbent, 821  $\mu\text{g}$  of ammonia was introduced into the adsorption system at 100°C; 813  $\mu\text{g}$  was adsorbed at an equilibrium gas pressure of 0.0013 mm which corresponds to 4  $\mu\text{g}$  of ammonia. Thus, no more than 1% of the ammonia could have been adsorbed according to Eq. (1) if all the residual gas were water vapor. Under all conditions and with all adsorbents, the sum of the weights of residual (equilibrium) and adsorbed gas checked closely the weight introduced into the system, and no changes in pressure readings were observed when the measurements were made at more than one compression ratio.

### III. RESULTS AND DISCUSSION

#### *Isotherms*

The results of ammonia adsorption measurements were plotted on large-scale graphs for each adsorbent. A typical set of isotherms for 70%  $\text{SiO}_2\text{-30% Al}_2\text{O}_3$  is shown in Fig. 1. It was found that the data for all adsorbents except silica gel and 98% silica-2% alumina conformed well to the Freundlich equation,  $N = Ap^c$ , where  $A$  and  $c$  are functions of temperature only,  $N \times 10^{14}$  is the number of adsorbed ammonia molecules per  $\text{cm}^2$  of surface, and  $p$  is the equilibrium gas pressure in mm of mercury. The values of the constants,

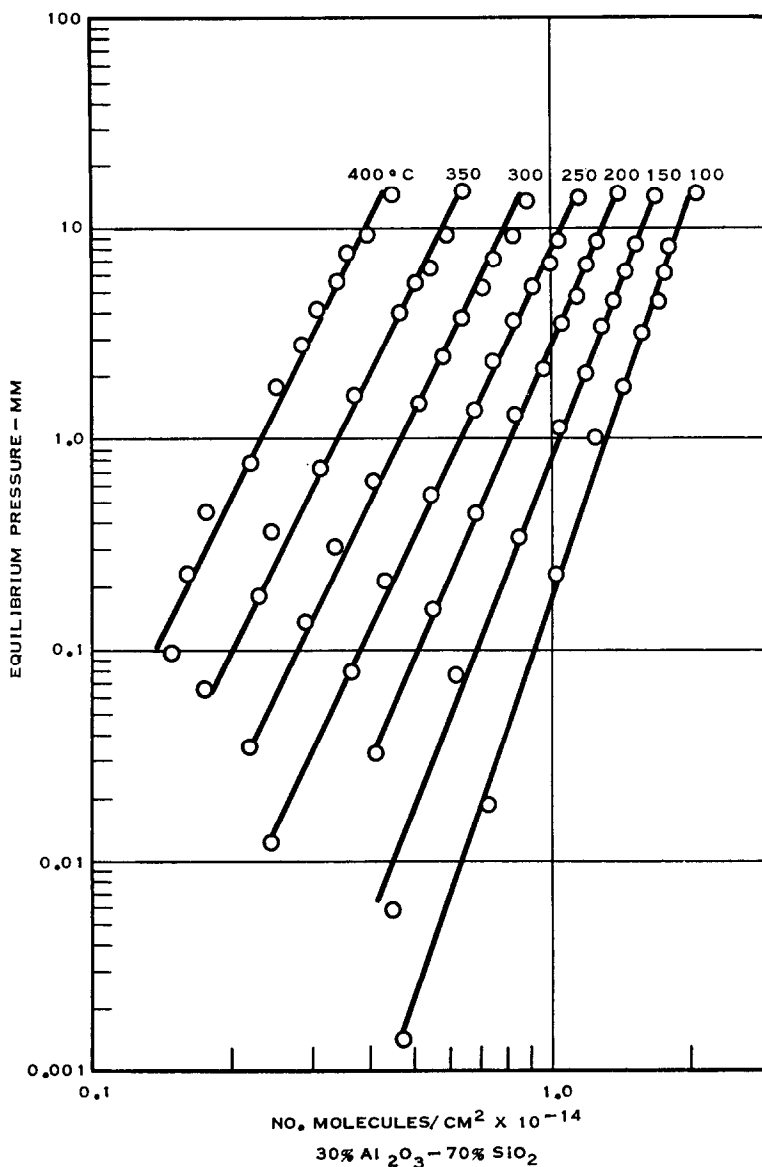


Fig. 1. Freundlich plot of  $\text{NH}_3$  adsorption.

$A$  and  $c$ , are presented in Table 2 for the various adsorbents. The two compositions which did not conform very well to the Freundlich equation had such low total adsorption at the temperatures investigated that good experimental accuracy was difficult to attain.

The isotherms for the adsorbents show steep initial rises and then enter a region of slow rise. The surface coverage at the

onset of slow rise depends sharply on temperature. This behavior is typical of surfaces which possess a spectrum of sites ranging in adsorption energy from strong to weak.

Figure 2 shows how the adsorption of ammonia varied with adsorbent composition for selected levels of temperature and equilibrium pressure. The curves at  $400^\circ\text{C}$  reveal essentially a gradual decrease in

TABLE 2  
 FREUNDLICH CONSTANTS IN THE EQUATION,  $N = Ap^c$ , FOR  $\text{NH}_3$  ADSORPTION  
 ON SILICA-ALUMINAS AT VARIOUS TEMPERATURES

% SiO <sub>2</sub>	T°C													
	100		150		200		250		300		350		400	
	A	c	A	c	A	c	A	c	A	c	A	c	A	c
0	1.625	0.094	1.300	0.102	1.013	0.122	0.836	0.134	0.660	0.141	0.508	0.150	0.384	0.154
8	1.600	0.107	1.225	0.104	0.960	0.128	0.740	0.148	0.580	0.161	0.460	0.189	0.315	0.209
15	1.500	0.175	1.125	0.126	0.880	0.144	0.680	0.151	0.540	0.156	0.410	0.165	0.300	0.171
40	1.500	0.145	1.150	0.157	0.900	0.176	0.660	0.209	0.490	0.226	0.340	0.240	0.230	0.253
55	1.550	0.192	1.200	0.165	0.960	0.195	0.700	0.228	0.530	0.243	0.360	0.274	0.250	0.261
70	1.325	0.158	1.050	0.183	0.820	0.199	0.630	0.221	0.470	0.224	0.350	0.230	0.230	0.232
82	1.075	0.155	0.860	0.155	0.680	0.169	0.520	0.174	0.395	0.170	0.300	0.176	0.225	0.161
90	0.840	0.129	0.650	0.127	0.510	0.123	0.400	0.124	0.320	0.117	0.255	0.104	0.195	0.127
95	0.640	0.107	0.480	0.116	0.380	0.118	0.310	0.111	0.250	0.120	0.220	0.114	0.165	0.108
98	—	—	—	—	0.230	0.09	0.190	0.095	0.165	0.091	0.135	0.092	0.115	0.088

<sup>a</sup>  $N \times 10^{14}$ , the number of ammonia molecules adsorbed per cm<sup>2</sup>;  $p$ , equilibrium pressure in mm mercury. Based on experimental isotherms up to 15 mm pressure.

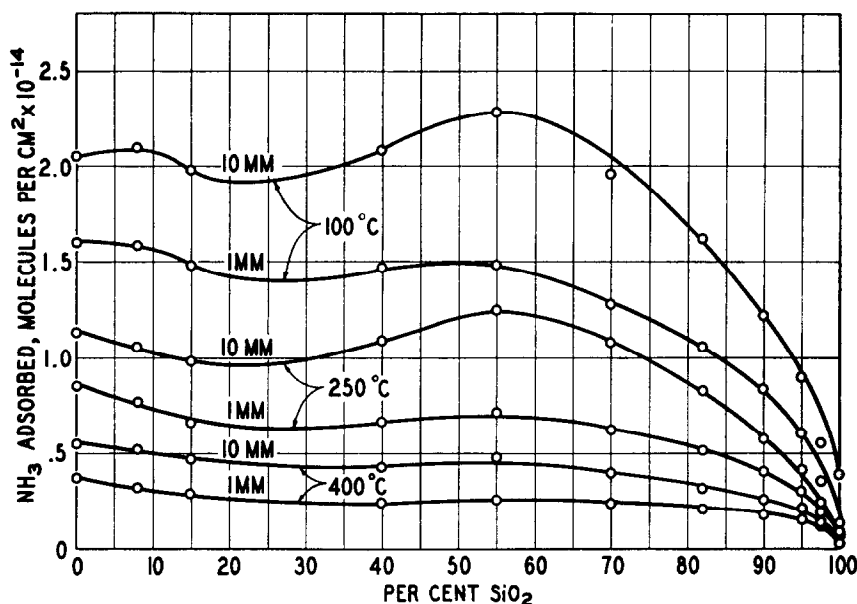


FIG. 2. Variation of ammonia adsorption with silica-alumina composition at three temperatures for two pressures.

adsorption as the composition varies from pure alumina to pure silica. However, at 250°C and 100°C, particularly at ammonia pressures of 10 mm, the curves show maxima in the neighborhood of 55% silica. This certainly is related to the familiar acidic properties developed in this system by the combination of the two materials, silica and alumina. In fact, the curve for adsorption at 100°C and 10 mm pressure is remarkably similar to the one obtained by plotting the acidity of the same adsorbents determined by butylamine titration in dry benzene (7).

#### Isosteric Heats of Adsorption

The isosteric heats of adsorption,  $q_{st} = -\Delta\bar{H}$ , were obtained in the usual manner from the integrated form of the Clausius-Clapeyron equation, for a constant number of molecules adsorbed per unit area. Areas were determined by the BET method. It was not possible to obtain experimental points on each isostere covering the entire temperature range, 100°–400°C. The temperature ranges were broad enough on each isostere, however, to show the constancy of

$q_{st}$  at constant surface coverage within the limits of experimental accuracy. It was assumed that small extrapolations of isosteres could be made without introducing significant errors in the real picture.

Calculations of isosteric heats were made at adsorption level intervals of  $0.02 \times 10^{14}$  molecules per cm<sup>2</sup>. Many adsorption measurements were made at temperatures within the 50-degree intervals selected for complete study. Isosteric heats calculated from these measurements agreed well with those determined over the 50-degree intervals.

Smooth curves of the average values of  $q_{st}$  for each adsorption level are plotted against surface coverage for the eleven adsorbent compositions in Figs. 3 and 4. Deviations of the unaveraged isosteric heats from the smoothed curves did not exceed 8% of the smoothed curve values for the initial points on the very steepest portion and 3% at higher coverages. All curves show a rapid initial drop. Silica gel and the high silica adsorbents show the sharpest drops and have the smallest total adsorption. Curves for alumina and high-alumina adsorbents drop less rapidly. Their

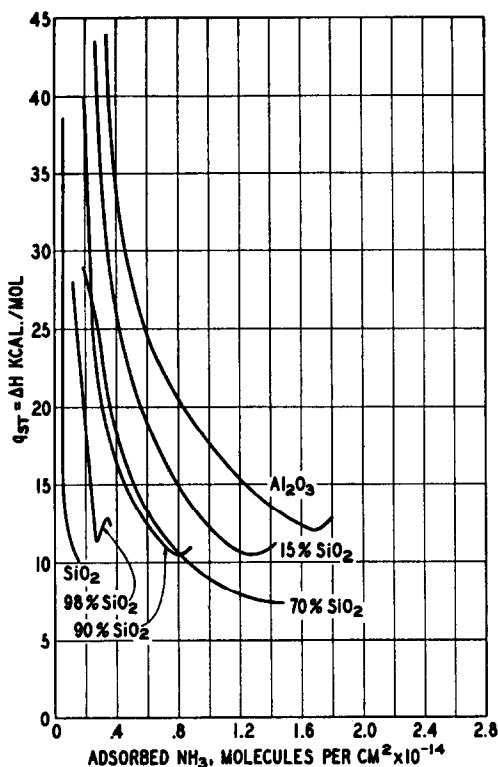


FIG. 3. Variation of isosteric heats of adsorption with coverage for ammonia on  $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalysts of various compositions.

total adsorption is greater and they have a much larger fraction of high energy sites. The curves for intermediate compositions, 55 to 90% silica, reach lower heats and show a large amount of low energy adsorption. This is the range of composition in which silica-alumina catalysts are known to develop the highest activity for such acid-type reactions as olefin polymerization, skeletal isomerization, cracking, and hydrogen transfer.

Some of the curves reach minima and then increase. The upswing is attributed to exothermal interactions between near-neighbor adsorbed molecules of ammonia. For some compositions, 98% silica-2% alumina, for example, the upswing occurs at rather low coverage. This might indicate a nonuniform distribution of sites in small "islands."

As mentioned above, isosteric heats were determined at a constant number of mole-

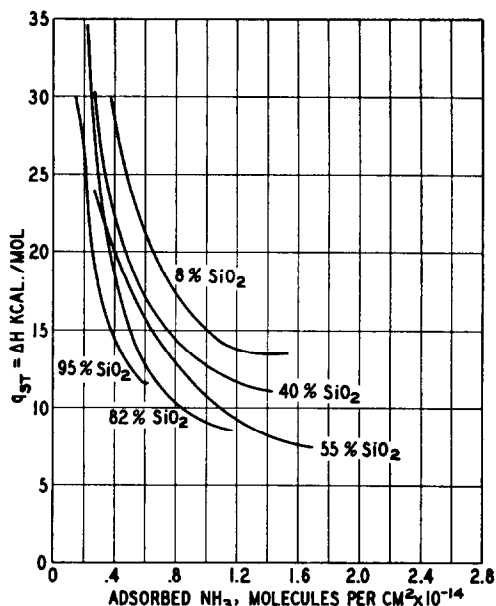


FIG. 4. Variation of the isosteric heats of adsorption with coverage for ammonia on  $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalysts of various compositions.

cules adsorbed per  $\text{cm}^2$ . Another procedure often described in the literature (10) is to determine a saturation value assumed independent of temperature and then calculate isosteric heats as a function of the fraction of saturation value. The methods are equivalent. Both rely on the invariance of the total number of sites or surface area with temperature in order to be consistent with the Clausius-Clapeyron equation,

$$\left(\frac{\partial \ln p}{\partial T}\right)_{\Gamma} = \frac{q_{st}}{RT^2}$$

where the partial derivative is taken with  $\Gamma$ , the true concentration, constant. The invariance of  $q_{st}$  and, as will be shown later, the differential molar entropy with temperature at constant number of molecules adsorbed per  $\text{cm}^2$  is strong evidence that no marked change in the number or nature of adsorption sites or in surface area occurs with change of temperature. For specific models of the adsorbed state this is easily shown. Assume fixed adsorption of the ammonia molecule with no rotation and no interaction of adsorbed species with one another. Assume further that the internal

vibrational energy of the ammonia molecule is not appreciably changed upon adsorption. If there is no change in potential energy of adsorption,  $U_0$ , (heat of adsorption per mole at absolute zero) with temperature at constant coverage, we are concerned only with the average change in energy with temperature of the six modes of vibration with respect to the surface. Using the harmonic oscillator approximation, the vibrational energy per mole in excess of the zero-point vibrational level at any given  $q_{st}$  is:

$$\bar{E}_v = \frac{6RT\bar{\nu}/kT}{[\exp(\hbar\bar{\nu}/kT)] - 1}$$

where  $\bar{\nu}$  is an average frequency of the six modes of surface vibration and varies with  $q_{st}$ . Isothermal plots of  $\bar{E}_v$  against  $\bar{\nu}$  show an essentially constant drop in molar energy per 50-degree C drop in temperature over the range 100°C to 400°C at constant  $\bar{\nu}$ . At  $\bar{\nu} = 2 \times 10^{13}$  sec<sup>-1</sup>, the drop is approximately 450 cal/mole and increases to a maximum of approximately 500 cal/mole at lower frequencies. For  $\bar{\nu} > 2 \times 10^{13}$  sec<sup>-1</sup>,  $\bar{E}_v$  (for all temperatures between 100° and 400°C) rapidly approaches zero, and therefore does not continue to balance

the change in energy of the gas phase with decrease in temperature. Thus  $q_{st}$  can vary with temperature at constant coverage at high values of  $\bar{\nu}$  (high  $q_{st}$ ) even though  $U_0$ , the potential energy of adsorption, does not. Calculations which will be given in a later paper indicate that  $\bar{\nu} = 2 \times 10^{13}$  sec<sup>-1</sup> is just about the highest frequency attained in these systems. In Fig. 5, the interrelationships of  $U_0$ ,  $q_{st}$ , and  $\bar{E}_v$  for temperatures  $T_1$  and  $T_2$  ( $T_2 > T_1$ ) between 100° to 400°C are shown schematically.

For the gas phase, we are concerned with the changes in energy with temperature of those degrees of freedom which are transformed upon adsorption. These are the energies of translation and rotation. If both are assumed classical in behavior, they amount to  $\frac{1}{2}RT$  for each mode, or a total of  $3RT$ . Since  $q_{st}$  is an enthalpy term,  $RT$  must be added (for a perfect gas) to obtain a total of  $4RT$ , or a decrease in energy of approximately 400 cal/mole per 50-degree drop in temperature. The difference between this figure (400 cal/mole) and those for the adsorbed phase (450–500 cal/mole) is within the limits of accuracy of  $q_{st}$  determinations over the range 100°–400°C. No significant change of  $q_{st}$  with temperature

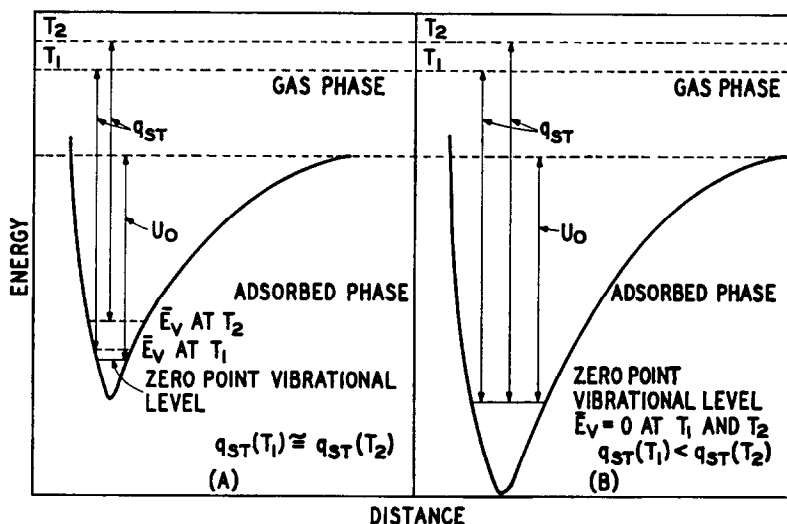


Fig. 5. Energy relationships between  $U_0$ ,  $q_{st}$ , and  $\bar{E}_v$  (fixed adsorption). Schematic: (A)  $q_{st}$  independent of temperature at constant surface coverage at moderate values of  $q_{st}$ ; (B)  $q_{st}$  dependent on temperature at constant surface coverage at high values of  $q_{st}$ .



would be observed so long as  $\bar{v}$  does not exceed  $2 \times 10^{13} \text{ sec}^{-1}$  approximately.

Similar arguments may be developed for other models of the adsorbed phase with approximately the same results. It is therefore reasonable to conclude that the invariance of  $q_{st}$  and differential molar entropy of adsorption with temperature at constant number of molecules per  $\text{cm}^2$  indicates that no marked change in the mode of adsorption occurs with change of temperature.

### Differential Entropies

Taking gaseous ammonia at 1 atm as the standard state and ignoring deviations from the perfect gas laws, the partial molar free energy of adsorption is given by:

$$\Delta\mu_{\Gamma} = RT \ln p_{\Gamma}$$

at a surface concentration  $\Gamma$ , at which the equilibrium pressure is  $p_{\Gamma}$ . The differential molar entropy of adsorption relative to the standard state was then obtained from the equation:

$$\Delta\mu_{\Gamma} = \Delta\bar{H}_{\Gamma} - T\Delta\bar{S}_{\Gamma}$$

where  $-\Delta H_{\Gamma} = q_{st}$  is the isosteric heat of adsorption whose determination was described in the preceding section. The differential molar entropy,  $S_{\Gamma}$ , of the adsorbed molecules was obtained from the relation:

$$\Delta\bar{S}_{\Gamma} = \bar{S}_{\Gamma} - S_G$$

where  $S_G$  is the molar entropy of gaseous ammonia at 1 atm. Values of  $S_G$  for temperatures between  $100^{\circ}$ – $400^{\circ}\text{C}$  were obtained from the literature (11). A typical calculation of isosteric heat, partial molar free energy, and entropy is given as follows:

For the adsorbent  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (82:18) the equilibrium pressures at a coverage of  $0.72 \times 10^{14}$  molecules/ $\text{cm}^2$  and temperatures  $300^{\circ}$ ,  $250^{\circ}$ ,  $200^{\circ}$ ,  $150^{\circ}$ , and  $100^{\circ}\text{C}$  are 14, 5.16, 1.60, 0.36, and 0.058 mm, respectively. Using the pressures for  $300^{\circ}$ – $250^{\circ}\text{C}$ ,  $250^{\circ}$ – $200^{\circ}\text{C}$ ,  $200$ – $150^{\circ}\text{C}$ , and  $150$ – $100^{\circ}\text{C}$ , the following values of  $\Delta\bar{H} = -q_{st}$  are calculated from the Clausius-Clapeyron equation:  $-11700$ ,  $-11520$ ,  $-11870$ ,  $-11460$  cal/mole, respectively. The average of these values is 11637 cal/mole. Similar averages

are obtained for other coverages and a smoothed curve drawn of average  $\Delta\bar{H}$  vs. coverage. The smoothed value of  $\Delta\bar{H}$  for  $0.72 \times 10^{14}$  molecules/ $\text{cm}^2$  is 11200 cal/mole, and is taken as the heat of adsorption over the temperature range investigated. The partial molar free energies,  $\Delta\mu_{\Gamma} = RT \ln p_{\Gamma}$ , are calculated for the five temperatures and corresponding equilibrium pressures in atmospheres (standard state: gas at 1 atm). The values are:  $-4570$ ,  $-5190$ ,  $-5790$ ,  $-6440$ , and  $-7210$  cal/mole at  $300^{\circ}$ ,  $250^{\circ}$ ,  $200^{\circ}$ ,  $150^{\circ}$ , and  $100^{\circ}\text{C}$ . The differential molar entropies of adsorption determined from  $\Delta\mu_{\Gamma} = \Delta\bar{H}_{\Gamma} - T\Delta\bar{S}_{\Gamma}$  are found to be:  $-11.50$ ,  $-11.49$ ,  $-11.44$ ,  $-11.25$ , and  $-11.26$  eu at  $300^{\circ}$ ,  $250^{\circ}$ ,  $200^{\circ}$ ,  $150^{\circ}$ , and  $100^{\circ}\text{C}$ . From  $\Delta\bar{S}_{\Gamma} = (\bar{S}_{\Gamma} - S_G)$ , using the literature values: 52.3, 51.2, 50.3, 49.3, 48.1 eu for  $S_G$  at  $300^{\circ}$ ,  $250^{\circ}$ ,  $200^{\circ}$ ,  $150^{\circ}$ , and  $100^{\circ}\text{C}$ , the values of the differential surface entropies are found to be 40.80, 39.81, 38.86, 38.05, and 36.84 eu.

In Fig. 6, values of  $\bar{S}_{\Gamma}$  are plotted against the number of molecules adsorbed per  $\text{cm}^2$  for various compositions of adsorbents. To conserve space, only six of the eleven adsorbents studied are shown. Those not shown also fall in line with the trends discussed below.

To serve as rough guides, the molar entropies of gaseous ammonia and the differential molar entropies of the perfect two-dimensional adsorbed gas have been plotted for corresponding temperatures. The latter,  $\bar{S}_{\Gamma m}$ , were calculated by statistical mechanical methods on the assumption (12) that the integral molar entropy,  $S_{\Gamma m}$ , of the adsorbed layer is given by:

$$S_{\Gamma m} = S_{2t} + S_R + S_v$$

where  $S_{2t}$  is the integral molar entropy of two degrees of translational freedom,  $S_R$  is the molar rotational entropy, and  $S_v$  the molar entropy of internal vibrations of the ammonia molecule. The expression assumes that the only loss accompanying the process of adsorption is one translational degree of freedom. The entropy of vibration with respect to the surface has been neglected. The translational entropy (13) is given by:

$$S_{2t} = R \ln MTA + 65.8$$

where  $M$  is the molecular weight of ammonia, and  $A$  the area occupied per molecule—a function of the number of moles ( $n$ ) adsorbed. Rotational and vibrational entropies are readily calculated by well-known statistical methods (13). Multiplying the expression for  $S_{r,m}$  by  $n$  to get the total entropy,  $\bar{S}_{r,m}$ , and then taking the derivative,  $\partial \bar{S}_{r,m} / \partial n = \bar{S}_{r,m}$ , gives the desired expression:

$$\begin{aligned} \bar{S}_{r,m} &= \bar{S}_{2t} + S_R + S_v \\ &= R \ln MTA + 63.8 + S_R + S_v \end{aligned}$$

which is not much different from  $S_{r,m}$ . Essentially, the expression gives the *maximum* differential molar entropy of a mobile adsorbed layer of ammonia. Other physical models of the adsorbed state may be selected and the entropies calculated.

As mentioned in the preceding section, the experimentally determined differential molar entropy of adsorption relative to the standard state,  $\Delta \bar{S}_r$ , is independent of temperature at constant coverage within the limits of experimental accuracy. The differential molar entropy of the adsorbed molecules,  $\bar{S}_r$ , as may be seen from Fig. 6, varies with temperature at constant coverage. Approximately, the isotherms of  $\bar{S}_r$  plotted against the number of molecules adsorbed per  $\text{cm}^2$ , are equally displaced from one another in the vertical direction. In all cases, the initial entropies,  $\bar{S}_r$ , at low coverages are small and are rising rapidly. They then level out; if adsorbate-adsorbate interaction occurs, they fall again. They behave conversely to  $\Delta \bar{H}_r$ . The fact that some of the curves rise above the values for a two-dimensional adsorbed gas is interpreted to mean that vibration with respect to the surface in the vertical direction is beginning to make a significant contribution to the entropy (13).

It is in the intermediate range, 55–90% silica, that the highest entropies are obtained, that is, the greatest mobilities. On either side, the maximum entropies are significantly lower, much closer to the maximum values calculated for a perfect two-dimensional gas.

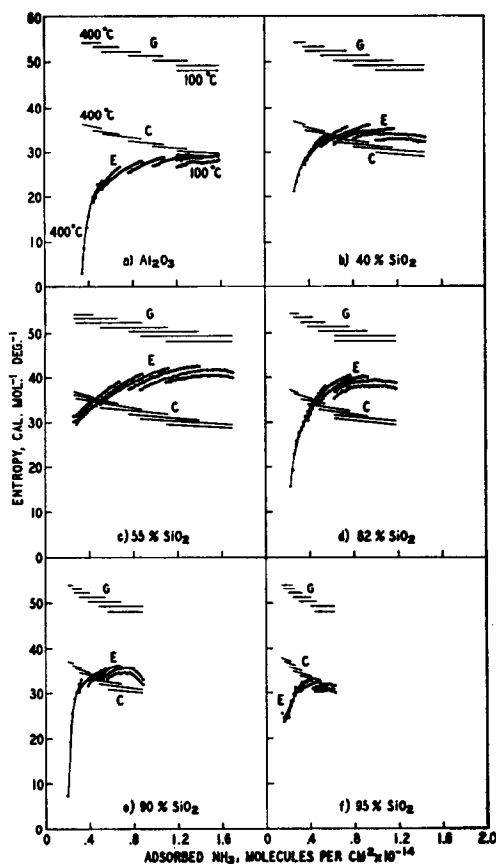


FIG. 6. Differential entropies for ammonia adsorbed on silica-alumina gels at various compositions. Experimental differential surface entropy curves—E ( $\bar{S}_r$ ). Entropies of gaseous ammonia at 1 atm—G ( $S_0$ ). Calculated maximum differential entropies for perfect two dimensional gas—C ( $\bar{S}_{2t} + S_R + S_v$ ). Temperature interval in sets of curves (G, E, C) is 50°C.

On alumina (Fig. 6a) at low coverage the differential molar entropy sinks as low as 2.7 eu per mole at 400 C. A molecule of ammonia in this state must be essentially immobilized—no rotation and no translation.

#### Types of Adsorption Sites

Thermodynamic studies alone provide very little information about the types of sites present on silica-alumina surfaces. In conjunction with other studies (7), they may throw some light on this question. In nonaqueous butylamine titrations, for ex-

ample, both typical silica-alumina cracking catalyst and pure alumina indicate an appreciable number of acid sites. Pure alumina, however, shows no activity for propylene polymerization, or hydrogen transfer, whereas the silica-alumina is quite active. On the other hand, if the acidities are determined by base exchange (7) with aqueous ammonium acetate solution, pure alumina shows no acidity whereas the silica-alumina shows about the same amount as indicated by butylamine titration. This brings up the question of the occurrence of two types of acidity, the so-called Lewis and protonic (Brönsted), in these catalysts, and suggests that for the reactions mentioned, protonic acid sites are more important than Lewis acid sites. If protonic acid sites are formed by interaction of water with Lewis acid sites, the adsorption energies of the resulting sites are probably lower than those of the parent Lewis acid sites. Our thermodynamic studies, therefore, may indicate that for any given composition the weakest adsorption sites are protonic and the strongest ones Lewis acids. For different compositions, Lewis acid sites probably have different energy distributions, and the relative adsorption energies of protonic sites may well reflect the energies of the particular Lewis sites on which they were formed.

#### IV. CONCLUSION

The data reported in this paper show that considerable information on the nature of silica-alumina surfaces can be obtained by studying a wide range of compositions. They show that broad distributions of adsorption energies are encountered with each composition, and that there are im-

portant differences between them. In catalytic reactions on these surfaces, we believe that adsorption energy distributions are just as significant as the amount of adsorption. Only when the ranges of compositions studied are narrow and of approximately equal adsorption energy distributions is the amount of adsorption alone a measure of catalytic activity.

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