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# The Rate of Adsorption of Ethylene by Silica and Nickel

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The adsorption of ethylene by silica has been investigated from 20 to 300°C. Over this range equilibrium is reached practically instantaneously in all cases. The adsorption of ethylene by reduced nickel has been investigated from -80° to 150°C. Definite slow effects and

temperature hysteresis were observed. Since diffusion into the crystal lattice ("solubility") is extremely unlikely in this case, more definite conclusions can be drawn than have been possible in previous investigations.

## INTRODUCTION

IN recent years numerous cases have been observed in which "adsorption" equilibrium is attained only slowly. Such slow effects are usually accompanied by temperature hysteresis, and frequently the adsorption is found to increase with increasing temperature.<sup>1</sup>

To explain these phenomena Taylor suggested "activated" adsorption and assumed that all such slow effects were purely attributable to the surface. Without entering into any discussion of the validity of Taylor's fundamental postulates, objections have been raised to his interpretation of observed cases on the grounds that the behavior could be equally well explained by solubility and grain boundary diffusion.<sup>2, 3</sup>

Any attempt to show unequivocally the existence of activated adsorption is complicated by the fact that when a gas is admitted to a vessel containing a solid several slow processes are possible, *viz.*, activated adsorption, grain-boundary diffusion, solubility and chemical reaction. In many systems the amount of chemical reaction is negligible. In almost all previous investigations in which slow effects occurred, solubility was definitely known to exist.

Solubility of gases in solids is known to be confined to very simple molecules (almost invariably to diatomic molecules). The only cases in which such slow "adsorption" effects had been found involved such molecules. It therefore seemed of interest to investigate the rate of adsorption on a solid of a gas which is sufficiently

complicated to make solubility extremely unlikely. We have therefore investigated the rate of adsorption of ethylene by silica and nickel.

## EXPERIMENTAL

The usual method for the measurement of adsorption at constant volume was employed. A measured quantity of gas was introduced into a vessel containing the adsorbent. By previous calibration the pressure which would be exerted by this quantity of gas if no adsorption took place was known. The difference between this pressure and the pressure actually observed was a measure of the amount of gas taken up. The apparatus was similar to that previously described by Pease.<sup>4</sup>

The adsorbents were contained in Pyrex bulbs having a capacity of about 10 cc in the case of silica and about 40 cc with nickel. All parts of the apparatus containing gas, except the adsorption vessel and connecting tubing, were immersed in a thermostat. For runs between -80°C and -30°C the adsorption bulb was placed in a Dewar flask containing solid carbon dioxide and acetone. For runs at 0°C a Dewar flask containing ice and water was used. For 20°C and 50°C a water thermostat was employed. For higher temperatures an electric furnace was used, the bulb being packed in with iron filings to ensure uniformity of temperature. In all cases the temperature could be maintained constant to within  $\pm 0.5^\circ\text{C}$  or better. Temperatures were measured with standard alcohol or mercury thermometers or by means of a chromel-alumel thermocouple, the choice depending on the temperature.

Nitrogen was employed for calibrating the apparatus, as is customary. There were indications of a small adsorption of nitrogen under

<sup>1</sup> See Taylor, *J. Am. Chem. Soc.* **53**, 578 (1931), and various papers in Faraday Society Symposium on Adsorption, 1932, etc.

<sup>2</sup> Steacie, *J. Phys. Chem.* **35**, 2112 (1931); *Trans. Faraday Soc.* **28**, 617 (1932).

<sup>3</sup> Ward, *Proc. Roy. Soc. (London)* **A133**, 506 (1931); *Trans. Faraday Soc.* **28**, 399 (1932).

<sup>4</sup> Pease, *J. Am. Chem. Soc.* **45**, 1197 (1923).

certain conditions. By making calibrations at various temperatures and pressures, however, it was possible to eliminate most of the effect. In any case an error due to the adsorption of nitrogen would affect only the absolute magnitude of the adsorption, and would have no effect on that portion of the adsorption which occurs slowly.

The description of the method of preparation of the adsorbents is given in the following section.

Ethylene was obtained in cylinders from the Ohio Chemical and Manufacturing Co. It was stated to be 99.5 percent ethylene. By fuming sulphuric acid it was found to be 99.7 percent  $C_2H_4$  and by ignition 99.2 percent.

Nitrogen was obtained from cylinders. It was bubbled through alkaline pyrogallate to remove oxygen and dried with phosphorus pentoxide.

Hydrogen was also obtained from cylinders. Oxygen was removed by passage over hot copper. It was then dried by passage over phosphorus pentoxide.

Between runs the system was thoroughly evacuated by using a mercury vapor condensation pump backed up by a Hyvac oil pump. Pressures during evacuation were followed by means of a McLeod gauge. The evacuation was always carried on for at least 8 hours. After the first two or three hours the pressure was always less than  $10^{-3}$  mm.

As a check on the method blank runs were made with a bulb containing no adsorbent. These indicated a very small slow drop in pressure amounting all told to not more than 0.07 cc at a pressure of 400 mm. This amount is practically negligible compared with the amounts of gas adsorbed. Most of the gas disappearing under these conditions was probably taken up by stop-cock grease.

## EXPERIMENTAL RESULTS

### I. Silica

Runs were first made with a 10 gram sample of ground quartz tubing, passing an 80-mesh sieve. There was no measurable adsorption of ethylene.

A sample of precipitated silica was therefore prepared. To 10 cc of sodium silicate solution (sp. gr. 1.170) were added 100 cc of 10 percent hydrochloric acid at a temperature of 50°C. The precipitate was broken up and washed by

decantation with hot distilled water until the wash water gave no milkiness with N/10  $AgNO_3$ . The precipitate was pressed between filter paper and dried at 100°C. It was then pulverized and ignited for 2 hours at a red heat. A 2-gram sample was used.

In all cases equilibrium was reached practically instantaneously. The data obtained are summarized in Table I.

TABLE I. *The adsorption of ethylene by silica.*

Temp. °C	Pressure, cm	Adsorption, cc at N.T.P.
23.8	9.81	1.23
23.7	26.70	2.24
23.7	46.27	3.10
23.7	70.84	4.00
51.0	4.96	0.39
51.0	24.52	1.23
51.0	51.27	2.05
51.0	71.15	2.59
100.6	10.55	0.23
100.7	33.25	0.50
100.7	47.30	0.67
100.7	66.84	0.92
185.6	12.35	0.06
185.5	38.47	0.07
185.5	54.30	0.14
185.7	76.85	0.14
296.0	13.63	0.03
296.0	42.41	—
296.1	84.58	—

If the data are plotted we obtain typical adsorption isotherms. As is usually the case a log-log plot gives good straight lines.

The main conclusion to be drawn is that the adsorption of ethylene by silica is entirely of the van der Waals type, with no indication of any slow processes.

### II. Nickel

An investigation was made of the adsorption of ethylene by nickel hydrogenation catalysts. The method of preparation was essentially that of Taylor and Burns.<sup>5</sup> Nickel nitrate (Merck) was heated to 400°C for 17 hours in a muffle furnace. The material was transferred to a Pyrex tube 2.5 cm diameter and 10 cm long. The tube was heated to 300°C in an electric furnace and hydrogen was passed through slowly for 15 hours. At the end of this period a calcium

<sup>5</sup> Taylor and Burns, J. Am. Chem. Soc. **43**, 1276 (1921).

chloride tube on the exit side showed no gain in weight in 3 hours. The furnace was then removed, the hydrogen flow stopped and the exit tube immediately sealed off and removed. The bulb was then evacuated to 0.001 mm at 300°C for 24 hours. On standing for 9 hours the pressure increased to only 0.005 mm. Three 30-gram samples of nickel were used.

#### Nickel I

This was prepared as above. Preliminary runs showed that the catalyst decomposed ethylene rapidly at temperatures above 100°C. At 20°C, in addition to a rapid adsorption there was also a definite slow drop in pressure. The data from a typical run are given in Table II.

It is apparent that about one-half the adsorption occurs immediately, the remainder being taken up very slowly. The same behavior was noted in other runs.

#### Nickel II

This series of runs was made on the previous sample of nickel after it had been heated to 520°C for about 1 hour. This treatment resulted in a general diminution in the activity.

Runs were made at -80, -30, 0, 20, and 50°C. At the lower temperatures equilibrium was reached practically instantaneously. At temperatures above 0°C, the initial rapid drop in pressure was followed by a slow decrease.

*Runs at low temperatures.* The data for -80, -30, and 0°C are given in Table III. Values marked *D* were obtained by withdrawing a definite part of the gas.

*Runs at higher temperatures.* Runs at 0°C showed traces of a slow effect, while at 20°C and 50°C the effect was marked. The complete data for a typical run at each temperature are given in Table IV.

It is apparent from Table IV that the rapid adsorption falls off with increasing temperature in the usual way. The slow effect, however, increases decidedly as the temperature rises. Thus at 50°C, the slow effect at the end of 9 hours amounts to 50 percent of the total adsorption. This is in accord with the usual behavior of systems which show slow adsorption effects.

Hysteresis effects were also noticeable. Thus a

TABLE II.

Time min.	Pressure, cm	Adsorption, cc at N.T.P.
1	19.66	1.73
3	19.38	1.95
10	19.08	2.18
32	18.64	2.52
59	18.35	2.75
155	17.84	3.14
186	17.73	3.24
240	17.58	3.35
365	17.32	3.55
569	17.04	3.76
651	16.95	3.84
736	16.87	3.90

TABLE III. Nickel II. Runs at low temperatures.

Pressure, cm	Adsorption, cc at N.T.P.	Pressure, cm	Adsorption, cc at N.T.P.	Pressure, cm	Adsorption, cc at N.T.P.
Temperature, -85.1°C		Temperature, -30°C		Temperature, 0°C	
6.19	4.72	2.00	0.81	0.49	0.41
15.60	5.09	9.02	1.67	9.76	0.93
18.51	5.12	20.25	2.73	21.73	1.33
25.80	5.22 <i>D</i>	26.10	2.62	22.24	1.52 <i>D</i>
35.67	5.09	51.29	3.02	35.33	1.60
40.78	5.23 <i>D</i>	54.46	3.11 <i>D</i>	41.46	1.92 <i>D</i>
53.11	5.40 <i>D</i>	71.83	3.18	59.11	2.05
54.07	5.32				
71.22	5.71				

TABLE IV. Nickel II. Rate of adsorption.

Time min.	Adsorption, cc at N.T.P.	Time min.	Adsorption, cc at N.T.P.	Time min.	Adsorption, cc at N.T.P.
Initial pressure cm (calc.) 23.33 Temperature, 0°C		Initial pressure cm (calc.) 19.25 Temperature, 20°C		Initial pressure cm (calc.) 11.52 Temperature, 50°C	
3	1.33	2	0.81	2	0.44
7	1.37	5	0.85	6	0.50
33	1.41	18	0.89	15	0.54
62	1.44	36	0.95	50	0.64
124	1.46	108	1.01	75	0.67
218	1.51	190	1.04	190	0.76
380	1.54	255	1.08	343	0.82
514	1.55	475	1.12	532	0.88
580	1.56	660	1.16	677	0.90

run was made at 50°C. The initial rapid adsorption was 0.64 cc. The adsorption in the next 10 hours was 0.59 cc, giving a total of 1.23 cc. The adsorption bulb was then cooled to 0°C and a total adsorption of 2.17 cc was found. The normal value from a run at 0°C would have been 1.78 cc, at the corresponding pressure. There is thus a hysteresis effect leading to an excess

adsorption of 0.39 cc. There was no sign of desorption of this excess amount over a period of 2 hours.

### Nickel III

Nickel III was a new sample prepared in the same way as nickel I. The time required for complete reduction was considerably greater and amounted to  $4\frac{1}{2}$  days. It was then evacuated for 24 hours.

Runs were made at  $-80^\circ$ ,  $0^\circ$ ,  $20.8^\circ$ ,  $50^\circ$ ,  $142^\circ$ , and  $250^\circ\text{C}$ . At  $250^\circ\text{C}$  there was a rapid increase in pressure due to decomposition of ethylene. At all temperatures slow adsorption effects were noticeable, although the effect was small at  $-80^\circ\text{C}$ . The results were in general very similar to those obtained with nickel II although the sample was more active. Some typical adsorption-time curves are given in Fig. 1.

Hysteresis effects were very pronounced. Thus in one run at  $142^\circ\text{C}$  the total amount adsorbed after 10 hours was 7.83 cc. Virtually all of this was the slow type, the ordinary van der Waals adsorption having fallen to a low value at this high temperature. The bulb was then cooled to  $-80^\circ\text{C}$ . The total adsorption at this temperature was 12.39 cc. The normal adsorption at  $-80^\circ\text{C}$  would have been 5.5 cc. There is thus an excess adsorption of 6.89 cc, which is of the same order of magnitude as the slow adsorption at  $142^\circ\text{C}$ .

### DISCUSSION

It is apparent that the ethylene-nickel system resembles a number of other systems involving gases and catalytically active solids which have been previously investigated. It shows slow adsorption effects, adsorption hysteresis with changing temperature and, in certain temperature ranges, the adsorption increases with increasing temperature.

The ethylene-nickel system therefore shows all the criteria of activated adsorption. In virtually all previously investigated cases of this type solubility has been a likely complication.

In a few cases it is possible that the effects of

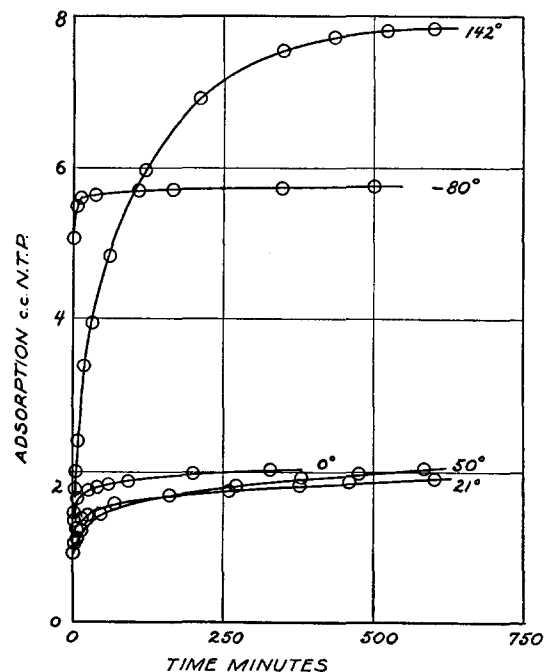


FIG. 1

solubility and adsorption have been successfully disentangled.<sup>6, 7</sup> In our opinion, however, this investigation represents the first case in which the criteria of activated adsorption have been obtained in a system in which solubility is exceedingly unlikely to be a complicating factor.

It is, of course, possible to calculate isosteric heats of activation for the ethylene-nickel system from the data given above, by using the method given by Taylor and Williamson.<sup>8</sup> The method, however, is open to criticism and it is very doubtful if calculations made in this way have any real meaning.

In any discussion of the bearing of activated adsorption on hydrogenation catalysis, it is apparent that it is necessary to take into account the slow adsorption of the substance being hydrogenated as well as that of the hydrogen.

<sup>6</sup> Benton and Drake, J. Am. Chem. Soc. **56**, 255 (1934).

<sup>7</sup> Drake and Benton, J. Am. Chem. Soc. **56**, 506 (1934).

<sup>8</sup> Taylor and Williamson, J. Am. Chem. Soc. **53**, 2168 (1931).