THE KINETICS
OF THE
SORPTION OF GASES
BY
SOLID SUBSTANCES

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INTRODUCTION.

INTRODUCTION

In recent years certain investigators have postulated the existence of more than one type of adsorption of a gas by a solid.

Langmuir (1.), after making measurements of the adsorption of gases by glass, mica and platinum, concluded that, "The adsorption of these gases by platinum is clearly due to very strong chemical forces of the type represented by primary valence. The action with oxygen seems to be wholly irreversible, so that this gas can be removed from the platinum only by reaction with carbon monoxide, hydrogen, etc. With carbon monoxide, the gas is partly driven off by heating but only with relative difficulty. This behavior is in marked contrast with that observed in the adsorption of gases by mica and glass, where forces involved are of the secondary valence type." Further, "It is evident from these data that at liquid air temperature platinum adsorb~~e~~s carbon monoxide in much the same way that glass does, that is, by secondary valence forces. With a moderate rise in temperature this gas is released, but in the neighborhood of room temperature the reaction velocity becomes sufficient for the platinum to react (primary valence) with the carbon monoxide to form a much more stable adsorbed film".

Thus we see definitely introduced the concept of more than one type of adsorption for the same system.

These two types of adsorption have been variously termed by different authors. What Langmuir considered as due to primary valence has been called 'primary' or 'chemical' adsorption, while the other type has been referred to as 'secondary', 'physical', 'molecular', 'reversible' or 'van der Waals'' adsorption.

In the past adsorption studies have been concerned chiefly with secondary adsorption. This process possesses characteristics which usually distinguish it from other phenomena. Such characteristics need not be mentioned here since they have received thorough treatment at various times (2).

More recently, and with the object of throwing some light on the important and difficult problem of contact catalysis, many systems with catalytically active metal or metallic oxide as the solid phase have been investigated. In a number of such systems it has been found that under certain conditions the gas is taken up by the solid with measurable velocity; that the amount taken up at equilibrium increases with increase in temperature; that it is difficult if not impossible to recover the gas by evacuation; and that marked temperature hysteresis occurs.

Benton(3) measured the adsorption of various gases on a number of different oxide surfaces. It was found that on each of the oxides used at temperatures as low as -79° the order of adsorption of the different gases was in the order of their melting points. Furthermore, the gas taken up was readily recovered by evacuation at the same temperature. This behavior is characteristic of secondary adsorption. At higher temperatures, however, on certain of the oxides, carbon monoxide was taken up in abnormally large amounts, and was recovered by evacuation only with difficulty. He considered that primary adsorption caused this abnormality, and estimated the amount of it on each adsorbent. This amount was found to parallel the catalytic activity of the oxide toward the oxidation of carbon monoxide. On the other hand, the extent of neither secondary, nor total adsorption, bore any such relationship.

Benton and White (4) admitted hydrogen to previously evacuated nickel and measured the pressure changes which resulted. They found that the rate of approach to equilibrium depended greatly on the experimental temperature and pressure, and that the amount of gas taken up was a maximum at about -110°, and a minimum at somewhat below -150°. They also found temperature hysteresis to the extent that more hydrogen was taken up by the metal if the gas was admitted at 0° and then the temperature was reduced to -190°, than if the measurement was made exclusively at the lower temperature.

They explained the greater part of their experimental results by assuming that at the lowest temperatures secondary adsorption of hydrogen molecules took place, with little or no change of their configuration, whereas at temperatures above -100° only primary adsorption occurred, involving marked activation, and perhaps even complete dissociation of the molecule.

Benton and Elgin (5) found more oxygen taken up by silver at 110° and at 26°. Their measurements showed that the first small amounts were taken up rapidly, but after further additions of gas a long-continued decrease in pressure occurred. They concluded that, "If such cases are to be classified as adsorption, it is evident that the customary postulate of a rapid attainment of adsorption equilibrium must be revised."

The same authors found that the oxygen and gold system behaved in a similar manner (6).

Taylor (7) recently drew attention to the fact that phenomena such as described in the above cases could be caused by the operation of more than one adsorption process in the same system, that is adsorption of a given molecular species producing more than one form of adsorbed product, each process possessing its own particular heat of adsorption and energy of activation. In addition, he outlined in some detail the possibilities which such a condition would give rise to on the basis of the Langmuir concept of adsorption as a time lag between condensation and evaporation.

In discussing the equilibrium conditions on the above basis, he considers a gas which may be adsorbed on a surface by either of two different processes. It may then be assumed, for a particular case, that Q" is greater than Q', and that E" is very much greater than E', where Q' and Q" represent the heats of adsorption, and E' and E" the activation energies for the two processes. On this assumption the activation energies for the processes of vaporization will be $E' + Q'$ and $E'' + Q''$.

The Langmuir theory has the average time which the molecules occupy the surface depending on the ratios of the rates of adsorption and desorption, which ratio on the above assumption may be written

$$\frac{A'e^{-E'/RT}}{B'e^{-(Q'+E')/RT}} = \frac{A'e^{Q'/RT}}{B'}$$

for the one process and

$$\frac{A''e^{Q''/RT}}{B''}$$

for the other. He then suggests that the variations in A' and A", B' and B" will be minor compared with the variation of the exponential for different values of Q' and Q", and thus, therefore, the relative magnitudes of Q' and Q" will determine largely the positions of the adsorption-temperature isobars for the two processes. In this connection he points out that in the Langmuir theory A' and A" are the rates at which molecules strike unit surface inelastically and are identical, and that the B factors for the evaporation process are similar to the unimolecular equation factor C, in $dx/dt = Ce^{-E/RT}$, which Polanyi and Wigner (8) have shown varies to a very small extent in the available experimental data. The result obtained is, then, that the isobar for the process which has the largest heat of adsorption will be above the isobar for the other process.

On this basis of two adsorption processes for a given system, each with a characteristic activation energy, it might happen that, due to the magnitudes of the activation energies, the velocity of the process having the higher activation energy will be negligibly slow at low temperatures compared with the velocity of the other process. With increasing temperature, however, there will be the normal decrease in the extent of adsorption due to the process predominate at low temperature. Simultaneously, there will be an increase in the velocity of the process having the higher activation energy until at sufficiently high temperature the adsorption will be due practically entirely to this latter process. Between the two temperature extremes, it follows that there may occur rising values of adsorption, at a given pressure, with increase in temperature.

From the above point of view a temperature hysteresis effect is to be anticipated. At low temperature very little adsorption due to the process having a high activation energy is to be expected. On raising the temperature, however, the velocity of this process is increased and gas is taken up. If subsequently the temperature is again reduced, the velocity not only of adsorption but also of desorption again falls off so that an adsorption value will be found greater than that originally attained at the lower temperature due to the low activation energy process only.

In general, the values of the heats of adsorption and the activation energies will vary from system to system. The temperatures at which the velocities of the processes become measurable will depend upon the magnitudes of the activation energies. It may then happen that with a given adsorbate, and within the temperature range covered, by varying the adsorbent the number of processes observed to occur will also vary.

Increase in gas pressure should also increase the extent of adsorption because the number of molecules striking the surface and, therefore, the probability of a collision with the necessary activation energy present at the place of collision, will be increased.

In considering the effect of a non-uniform surface, Taylor claims that this results in a steadily falling value for the heat of adsorption, with increase in surface covered, due to the adsorptions involving high heats of adsorption occurring first and being succeeded by processes of lower and lower heat of adsorption. The effect of this would be to increase the rate of evaporation by increase in the term

$$e^{-(Q+E)/RT}$$

He suggests, however, that the activation energy of the adsorption process becomes larger, the less active the surface area. This increase in E with surface covered would tend to offset to some extent the effect of diminishing Q.

For such a case it is evident that the curve obtained by plotting the heat of adsorption against amount of gas adsorbed might show a descending portion for each process occurring, with transition values between. Furthermore, with suitable values for Q and E, one or more portions of such a curve would be eliminated. For example, in the case of two processes both with low values for the activation energy, the curve obtained would be entirely for the process having the higher activation energy, and would then show continuously falling values.

If the heat of adsorption and energy of activation for one process are considerably greater than for another, it is obvious that a smaller value for the heat of adsorption will be obtained at low than at high temperature, if no complications such as the dissociation of the molecule into atoms during the activation process arise.

It also follows, for a non-uniform surface, that with certain Q and E values, and in a suitable temperature range, very little adsorption will occur due to the process having the higher activation energy. Also, in the same temperature range, the adsorption due to the other process may be negligible.

Since the velocity of evaporation depends on the values of E and Q, it is evident that there might be two adsorption processes with equal values of Q, but with great differences in velocities of evaporation because of unequal values of E.

Finally, Taylor notes an important bearing of his concept on surface chemical reactions. As pointed out by Hinshelwood (41), the equations giving the true energy of activation of a surface chemical reaction, in terms of the observed energy of activation and the heats of adsorption and desorption, presuppose that the establishment of adsorption equilibrium is rapid in comparison with any disturbance of it due to the removal of the molecule in chemical change. If, however, owing to the necessity of an activation energy, the rate of adsorption leading to activation is very materially decreased, this condition may no longer hold, and the equations derived will be inapplicable.

In a later paper, Taylor and Sickman (9) have indicated a method for evaluating certain isobaric adsorption factors. Essentially this is as follows.

Consider adsorption taking place at constant pressure on a plane uniform surface with an activation energy E and a heat of adsorption Q, which are assumed constant independent of the amount adsorbed. The rate of condensation of the gas molecules on the surface will be proportional to the number of molecules striking the surface per unit time with an energy greater than E, that is, roughly, the rate of condensation is $k'e^{-E/RT}$. The rate of evaporation will be proportional to $e^{-(E+Q)/RT}$, and to the fraction of the surface covered or, roughly, rate of evaporation is $k_2ve^{-(E+Q)/RT}$, where v is the volume adsorbed after time t. The total rate of adsorption will be

$$\frac{dv}{dt} = k'e^{-E/RT} - k_2ve^{-(E+Q)/RT} \qquad \text{.................(1)}$$

At equilibrium $dv/dT = 0$, and

$$v_o = \frac{k'}{k_2} e^{Q/RT} \qquad \text{..................................(2)}$$

where v_o = quantity adsorbed at equilibrium at the given pressure.

Equation (1) integrated, with the condition that $v = 0$ when $t = 0$, gives

$$v = \frac{k'}{k_2} e^{Q/RT}\left(1 - e^{-k_2 t e^{-(E+Q)/RT}}\right) = v_0\left(1 - e^{-k_2 t e^{-(E+Q)/RT}}\right). \quad (3)$$

which may be put into the logarithmic form

$$\log_e (v_0 - v) = \log_e v_0 - k_2 t e^{-(E+Q)/RT}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Thus the graph of $\log_e(v_0 - v)$ as a function of t is a straight line whose slope is $-k_2 e^{-(E+Q)/RT}$. This affords a convenient graphical method of determining v_0 by assuming values for v_0, and plotting $\log_e(v_0 - v)$ as a function of t until a satisfactory straight line is obtained. If k_2 is known $E + Q$ may be calculated, or conversely if E and Q are known, k_2 may be calculated. By plotting the logarithm of the negative of the slope of equation (4) as a function of $1/T$, a straight line should again be obtained whose slope obviously allows $E + Q$ to be calculated independent of any assumption of the order of magnitude of k_2.

The temperature of maximum isobaric adsorption may be obtained from equation (3) by solving $dv/dT = 0$ for T.

By means of the hypothesis outlined above Taylor explained slow attainment of equilibrium, increase in amount of gas taken up with increase in temperature, and temperature hysteresis effects in a collection of existing experimental data. Among such data were those of Benton and White (4) and Benton and Elgin (5)(6) mentioned above. The others will now be summarised.

Garner and Kingman (10) stated that hydrogen or carbon monoxide adsorbed on zinc chromium oxide and hydrogen adsorbed by copper oxide at room temperature at an equilibrium pressure of 10^{-3} - 10^{-4} cm. were evolved on raising the temperature to 100° - 120°, but in 20-30 minutes were readsorbed. On further raising the temperature no gas was evolved until at about 350° when water and carbon dioxide were given off. De Hemptinne (11) found at -78° the adsorption of hydrogen on platinum and palladium, and also of carbon monoxide on palladium decreased with decrease in temperature. Firth (12) reported that at liquid air temperature massive palladium foil did not take up hydrogen, but palladium saturated at room temperature did not evolve the gas on cooling to this low temperature. Later (13) he found for hydrogen and palladium black temperature hysteresis and a minimum in the adsorption temperature curve. Gutbier, Gebhardt and Ottenstein (14) also detected a minimum adsorption of hydrogen on palladium black. Harris' measurements (15) showed a maximum for the adsorption of hydrogen on copper between 0° and 100°. There was also some evidence of temperature hysteresis. Bone and Wheeler (16) recorded that quartz at 650° took up considerable quantities of hydrogen. Taylor and Burns stated that above 180° carbon monoxide is reversibly adsorbed by nickel, while above 270° it is irreversibly adsorbed. They also reported less adsorption of carbon monoxide on platinum at 25° than at 110° (17).

Furthermore Taylor showed that heats of adsorption which are large, that is, too large presumably to be ascribed to a process involving only van der Waals' forces, and which decrease in value with increase in amount adsorbed, are quite in accordance with his concept. Heats of adsorption having such values, he points out, have been found by Fryling (18), G. B. Taylor, Kistiakowsky and Perry (19), Taylor and Kistaikowsky (20) Flosdorf and Kistiakowsky (21), Keyes and Marshall (22), and Garner and co-workers (23).

Taylor considered the finding of Bonhoeffer and Harteck (24) that charcoal catalyses the conversion of ortho to para hydrogen at liquid hydrogen temperature, as evidence that even at such low temperature hydrogen adsorbed on charcoal is to some extent activated.

Because of the quantities of gas involved and because of the importance of surface rather than volume where adsorption is concerned, Taylor did not consider that solubility could be the cause of the slow processes.

He then decided that his theoretical conclusions were "abundantly verified by practical experience". In this respect he appears to have been somewhat hasty.

Steacie (25), while not questioning the possibility that Taylor's theory might be true in some cases, showed that practically all the evidence which had been brought forward in support of it was completely explained by the known solubility of the gases in the solids concerned. He emphasized the fact that the surface-volume ratio will not differentiate between solubility and adsorption, in the case of gases and metals, at low temperatures because at such temperatures solubility equilibrium is not reached in reasonable periods of time.

With the hydrogen-copper system Ward (26) found that a certain amount of gas was taken up instantaneously and that this was followed by a slow drop in gas pressure. The slow pressure decrease he ascribed to solubility, the nature of which he considered to be grain boundary diffusion rather than lattice diffusion. The rate of this solution was measured and found proportional to the amount of gas adsorbed on the surface. This rate is therefore related to the gas pressure by the same form of equation as the adsorption isotherm. Neither, then, will mere conformation with the adsorption isotherm distinguish between a surface phenomenon and solubility. The failure of the Langmuir equation as a criterion had been demonstrated by Hitchcock (27) previously from other considerations. In a later communication Ward (28) stated that if diffusion was to take place through the lattice it would be expected to become measurable at some critical temperature. Grain boundary diffusion, he said, should occur at lower temperatures and the energy of activation will be that necessary for lateral diffusion. He also pointed out that, conventionally, the term"adsorption" is used only with reference to surfaces which are directly subject to bombardment from the gas phase, as distinct from those surfaces at which the gas may arrive only by diffusion inwards along the surface.

Tronstad has drawn attention to the fact that X-ray photographs have been obtained which show, in some cases at least, that nitrogen and ammonia may diffuse into the crystal lattice of a metal (37).

Taylor continued to insist with the utmost tenacity that the quantities of gas taken up slowly were one or two orders greater in magnitude than the well-determined solubility data. He reproduced comparative tables of figures (29) to show this. Unfortunately, however, in these tables he compared with solubility data the total quantity of gas taken up rather than the amount taken up slowly. This error was pointed out by Steacie (30).

Burrage (53) and Allmand and Chaplin (54) have suggested that slow adsorption of gases by metals and oxides may be due to a gas displacement effect. This, apparently, is the cause of a similar phenomenon which occurs with charcoal. Several authors, however, consider that the experimental technique which they have employed has obviated this possibility.

The situation was, then, that almost all the evidence of the existence of activated adsorption could be criticised on the basis of solubility or chemical reaction. Hence, in order to obtain direct proof of the existence of activated adsorption, the other processes must be corrected for quantitatively or, better still, elminated entirely.

In the case of oxygen and gold, as pointed out by Steacie

(25), solubility was not likely to be the cause of the increase in the amount of gas taken up with increase in temperature since it had been shown by Toole and Johnson (52) that oxygen is not appreciably soluble in gold. In only one system, however, in which solubility was quite unlikely, had activated adsorption actually been sought. This system, ethylene and manganous-chromic oxide, was investigated by Taylor and Williamson (42) but no evidence for activated adsorption was found. This was significant.

It was thought, then that experiments with a gas composed of molecules sufficiently complex to make solubility extremely unlikely would be interesting. After some preliminary measurements, the systems chosen for investigation were silica-ethylene and nickel-ethylene. These substances could be studied under such conditions that no chemical reaction occurs. Furthermore, solubility was not to be expected because an exhaustive survey of the literature by Steacie (43) revealed the fact that the only gases which had been found to dissolve in solids were composed of simple molecules, almost invariably diatomic.

The desirability of making this investigation has not been lessened by more recently published data. For example, it should be noticed with reference to the heat of adsorption figures cited by Taylor, as mentioned above, that of late some carefully made measurements have indicated constant differential heats of adsorption. Such measurements have been made by Ward (26), Maxted (31) and Beebe (32). In addition, Schwabe and Brennecke (33) have drawn attention to experimental errors which would cause apparent variation in the heat of adsorption.

It was mentioned above that Taylor considered the conversion of ortho to para hydrogen catalysed by charcoal as evidence that charcoal adsorbed hydrogen in an activated form. In following this up, Taylor and Sherman (34) made measurements on nickel and several metallic oxides. They found a decided parallelism between the capacity of such surfaces to show activated adsorption of hydrogen and their capacity to induce the spin-isomerisation of hydrogen. Later, however, Taylor and Diamond have found (35) that there is no connection whatever between activated adsorption and the ortho para hydrogen change. Harkness and Emmett (36), on the other hand, found that high temperature adsorption actually inhibited the change and concluded from this that the phenomenon referred to as activated adsorption is actually a surface phenomenon.

Taylor and co-workers (42)(56)(57)(75) have investigated the cases of hydrogen and carbon monoxide with palladium, manganous oxide, manganous chromium oxide, zinc oxide, zinc chromium oxide, zinc molybdenum oxide, and water with zinc oxide. Williamson (58) has reported on the systems carbon monoxide with manganous oxide and manganous oxide promoted with chromium. Russell and Ghering (77) measured the sorption of oxygen by nickel. In all these cases increase in the amount of gas taken up with increase in temperature, temperature hysteresis, and slow attainment of equilbrium were abserved and interpreted to mean the existence of activated adsorption. McKinney (59) reported that on palladium oxide there was no adsorption of oxygen but that carbon dioxide was adsorbed physically and that carbon monoxide showed activated adsorption, being recoverable only as carbon dioxide for the most part. It will be noticed that in all the above cases solubility or chemical reaction may have given rise to the observed phenomena.

Garner and Kingman (60) reported that with hydrogen or carbon monoxide and zinc chromium oxide the gases were first evolved on raising the temperature, then readsorbed, and finally removable only as water vapour.

Kingman (61) working with the hydrogen-zinc chromium oxide system found that the adsorbent underwent reduction and concluded that there were three types of adsorption, physical, slow adsorption having an activation energy, and a third type removable only as water vapour.

The nitrogen taken up slowly by iron synthetic ammonia catalysts was referred to by Emmett and Braunauer (62) as adsorbed. They gave evidence, however, that actually it may be in solution.

Harkness and Emmett (63) in a note to the editor announced that they had obtained evidence of one type of physical and two types of activated adsorption of hydrogen on promoted iron.

Maxted and Hassid (64) found with hydrogen and platinum or nickel temperature hysteresis but no indication of more than one adsorption type. Later (65) for the same systems they have determined the relative magnitudes of the fast and slow components of the adsorption. The same authors (66) have studied the kinetics of the adsorption of small quantities of oxygen on platinum black and calculated an activation energy for the slow process.

Smittenburg (67) reported that adsorption of hydrogen by nickel was of two types, a slow process at pressures below 10 mm. and a rapid reversible process at higher pressures. In a later paper (68) he deals further with this work.

Benton and White (69) used a copper adsorbent. Nitrogen showed physical adsorption only. Hydrogen and carbon monoxide gave the usual indications of two types of adsorption and in addition gas appeared to be taken up in a third manner which they had little doubt was solubility in the case of hydrogen and probably also in the case of carbon monoxide. Benton and White have also studied the adsorption of nitrogen, carbon monoxide and hydrogen on iron (70). They found for all three gases physical adsorption below -183° and activated adsorption at higher temperatures. Above 110° hydrogen appeared to be taken up by a third process which they suggested was solution.

Iijima (71) obtained velocity curves which he claimed indicated that the sorption of hydrogen by nickel is due to adsorption followed by diffusion.

Benton and Drake (72) found with oxygen and silver the usual criteria for physical adsorption at low temperatures and for activated adsorption at temperatures and pressures at which they claimed oxide formation and solubility were not appreciable.

Drake and Benton (73) have reported for a clean silver surface that carbon dioxide showed physical adsorption only, which was measurable below 179°. Hydrogen showed reversible adsorption at -183° and was taken up by activated adsorption at 300°. On an oxygen covered silver surface they found that carbon dioxide gave physical adsorption at 0° and 200°. On the same surface there was an indication that hydrogen was adsorbed at 0°. Similar results were obtained for a silver oxide surface although the results with hydrogen were not definite.

Alyea (49) reported that the amount of hydrogen taken up by Pyrex glass increased with increase in temperature above 450°. Using this fact as a basis, he explained the upper explosion limit of the oxygen hydrogen reaction. He stated that not all the gas was recovered and that the glass became darkened. Later Williamson (50) measured the adsorption of hydrogen on quartz and Pyrex glass. He, too, found a positive temperature coefficient for the amount of gas taken up. Since an isotherm at 542° using Pyrex glass as the adsorbent corresponded to the Langmuir equation, he concluded that the principal process taking place was adsorption. That this is not necessarily so was emphasized above. In addition he showed that the rate at which the hydrogen was removed from the gas phase was negligibly slow compared with the rate necessary for Alyea's explosion limit explanation. Reyerson (51), using silica gel rigorously purified by electrodialysis, found no adsorption of hydrogen even in the temperature range, 400° to 600°, investigated by Alyea and by Williamson. He did, however, find that the gas was taken up by Pyrex glass which during the process became darkened. He concluded that it is not likely that hydrogen is adsorbed by the silica in the glass but rather by some reduction product such as boron. He could not reconcile his results with those of Williamson on quartz, and regretted that Williamson did not state the source and purity of his material, since it is known that impurities make it possible for samples of this substance to adsorb additional small quantities of gas.

Reference will now be made to some recent experiments in which more complex gases have been used. In the reports of these experiments, which, however, it must be admitted, do not seem to be very detailed, there is no definite indication that the usual criteria of activated adsorption have been found for any system in which neither solubility nor chemical reaction may be a complicating factor.

Durau and Teckentrup (44) using iron as the solid phase found that for O_2, CO_2, C_2N_2, HCl, NH_3, NO, and SO_2 equilibrium was attained only slowly and that desorption was difficult. They stated that pure adsorption occurred with A, H_2, N_2, CO, N_2O, CH_4, C_6H_6, C_3H_8, C_2H_4, C_3H_6, and CH_3Cl.

Hollings and Griffith in a note (45) reported activated adsorption of hydrogen on tin, cadmium and the oxides of molybdenum, chromium, tungsten and vanadium. They also found that adsorption of hexane, cyclohexane and benzene at temperatures up to 450° took place with every metal or metallic oxide tried. They used Cr, Ti, Fe, Cu, Mo, Zn, Cd, Ca, Zr, Mg, Sn, Co, Al, Mn and W. They stated that the velocity and extent of adsorption varied greatly in different cases and were considerably influenced by the presence of impurities. No further account of this work appears to have been published.

Magnus and Klar (46, 47) compared the adsorption of carbon dioxide and ethylene on gold and iron with the adsorption of these gases on charcoal. They stated that hydrogen was taken up slowly over a long period of time but did not mention that any such phenomenon was observed when using ethylene.

Later Klar (48), reporting the adsorption of ethylene, ethane and hydrogen by iron, referred to a measurable adsorption rate in the case of hydrogen only.

McKinney (74) has measured the adsorption of hydrogen on manganous chromic oxide at constant volume and at constant pressure. As was to be expected, he found the rate at constant pressure to be greater than at constant volume.

Taylor and Strother (75) examined the systems hydrogen-zinc oxide, hydrogen-zinc chromium oxide and hydrogen-zinc molybdenum oxide at constant pressure. They found a second maximum on the isobar in the case of zinc oxide.

The evidence that the adsorption of hydrogen by charcoal is an example of activated adsorption (79, 80) is not very convincing and will not be gone into here.

Blodgett and Langmuir (76) announced that in one of their experiments a film adsorbed hydrogen atoms but not molecules.

Howard (78) has reported that activated adsorption of hydrogen and nitrogen by a chromium oxide gel diminished physical adsorption to a marked extent.

An interesting observation has been made by Barry and Barrett (81). During the progress of some accurate calorimetry a heat evolution, which continued over a long period of time, occurred when gold was exposed to water vapour. They considered that this was certainly not due to adsorption in the ordinary sense of the term, but that it might be the result of occlusion following initial adsorption. Later Barrett (82) has announced that W. R. Ham has found that the rate of diffusion of water through gold is easily measurable at 400°.

Some recent theoretical papers have referred to activated adsorption (79, 83, 84). Magid and Roginskii (85) have discussed the possibility of activated adsorption on molecularly plane surfaces. Sherman and Eyring (86) have made some quantum mechanical calculations.

EXPERIMENTAL APPARATUS

and

PROCEDURE.

EXPERIMENTAL APPARATUS AND PROCEDURE

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.

Apparatus.

The apparatus employed was of type often used (39) somewhat modified to meet the present requirements. It is shown in Figure 1.

Referring to this figure, A is a tube containing the adsorbent. Small bore capillary tubing was used to connect the tube A to the constant volume manometer B and gas burette C. Thus the dead space between the tube and manometer was of small volume. The adsorption tubes were made of Pyrex glass and were connected to the rest of the apparatus, which consisted of soft glass, by means of de Khotinsky cement. They measured 1 cm. in diameter by 10 cm. long in the case of the ones containing silica, while those used for nickel measured 2.5 cm. in diameter by 10 cm. long. When first put in place, each of the tubes containing nickel had sealed to its lower end a U-tube. One arm of this appendage was of such length that it protruded above the electric furnace used for heating, and from it issued the gases during reduction of the adsorbent. After it had served its

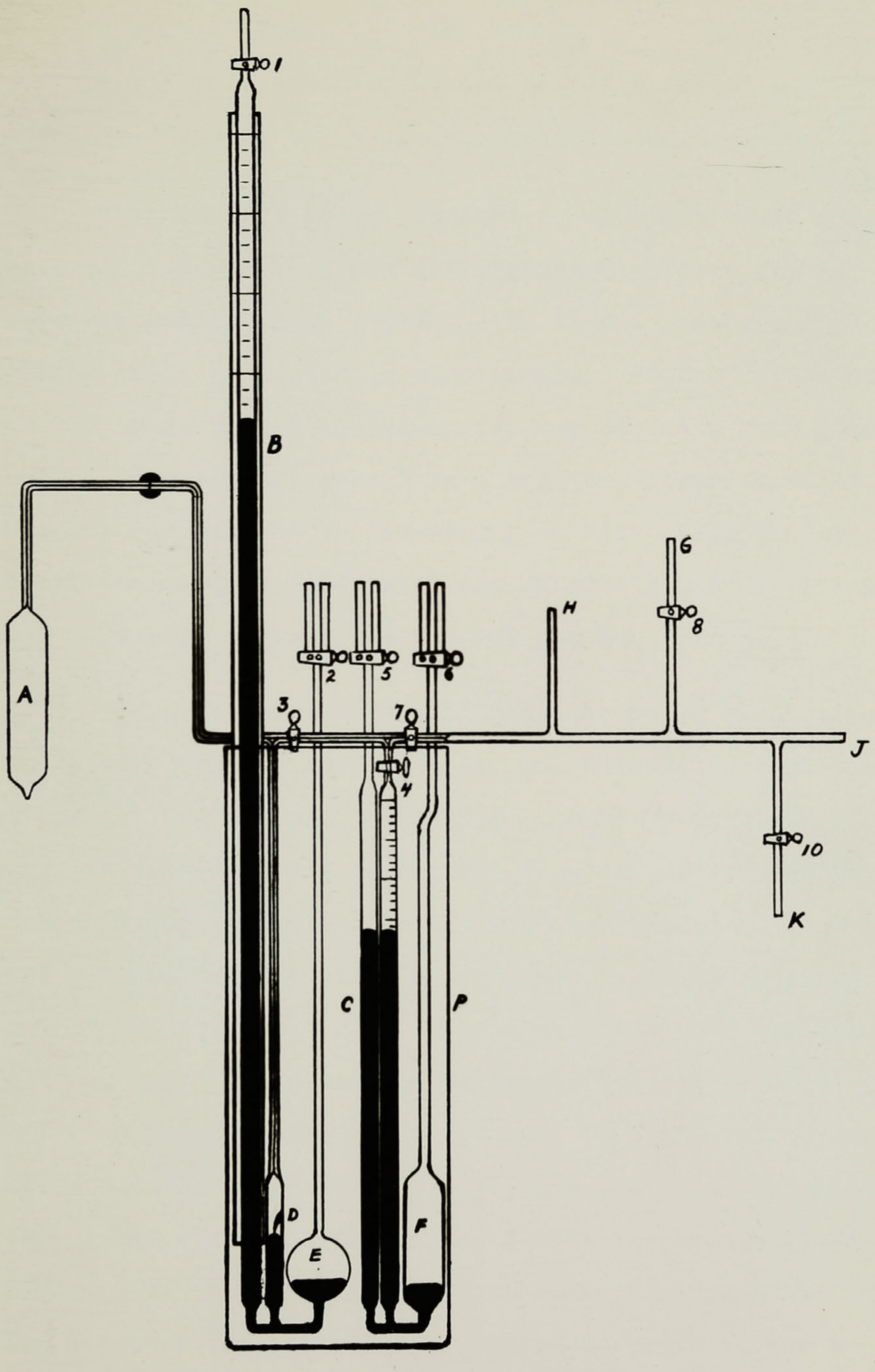

FIGURE I

ADSORPTION APPARATUS

purpose the exit tube was sealed off at a point, previously constricted, just below the adsorption tube.

The constant volume manometer was constructed from 1.2 cm. tubing. The long arm was evacuated through tap 1. Behind this arm and in close contact with it was placed a 100 cm. mirror scale graduated in millimeters. To the inner surface of the short arm of the manometer was sealed a blue glass pointer D. This pointer served as a constant level to which the mercury was brought by increasing or decreasing the air pressure above the mercury surface in the reservoir E by applying pressure or vacuum through the two way tap 2.

The adsorption bulb and manometer which were directly connected, communicated with the gas burette through the taps 3 and 4. The burette, which had a capacity of about 35 ml., had one arm fashioned out of a piece of good quality eudiometer tubing having a 1.2 cm. bore. This was graduated to 0.1 ml. and when calibrated using mercury was found to be accurate to within the reading error. The other arm of the burette was of 1.2 cm. bore tubing and was connected so that it stood parallel and very close to the graduated arm. The gas volume was read off after the mercury in the two arms had been brought to the same level with the two way tap 5 open to the atmosphere. Leveling of the mercury was brought about through the two way tap 6 connecting with the burette reservoir F in the manner described for the manometer. The graduated arm of the burette could be evacuated without the mercury entering tap 4 by evacuating also the reservoir through tap 6 and the plain arm through tap 5. For evacuation taps 2, 5 and 6 led to a water aspirator. The other arms of taps 2 and 6 led to a 10 l. bottle which in turn was connected to a compressed air line. This was found convenient when greater than atmospheric pressure was required to level the mercury. Somewhat greater than the required pressure was allowed to build up in the 10 l. reservoir and then adjustment of the burette or manometer was readily accomplished by control of taps 6 or 2.

Evacuation of the adsorbent took place through taps 3, 7 and 8 and the tubing G which led through a phosphorous pentoxide tube to a Langmuir mercury vapour condensation pump backed up by a Hyvac oil pump.

The tubing H led to a McLeod guage on which the first 0.5 cm. of the scale represented 0.001 mm. pressure.

Gas storage bulbs were connected to the rest of the apparatus through tubing J.

By means of the open tube K and tap 10 gas could be introduced into the apparatus.

The gas burette and lower part of the manometer were immersed in water contained in a Pyrex glass jar P 22 cm. in diameter and 46 cm. in depth. The water was heated to 38° by a spiral of resistance wire through which was passed an electric current of about 2 amperes. This heating element was contained in a soft glass U-tube filled with oil. A smaller similar heater drawing a current of 6 amperes was used to bring the bath up to temperature more rapidly. To conduct the heat away from the wire the tube containing this second heater contained about 20 ml. of butyl phthalate which boiled vigorously but refluxed completely from the upper portions of the tube before reaching the level of the surface of the water. The temperature of the water bath was maintained constant to within about 0.1° by means of a toluene thermoregulator of the usual type in conjunction with a circuit breaker. The water was efficiently stirred. Its temperature was observed by means of a mercury thermometer.

The tubing between the adsorption tube and the tap 3 was wound with resistance wire. This part of the dead space could then be heated electrically.

Only a very small portion of the dead space was not under direct temperature control. This portion, between the surface of the water and the tubing connecting the adsorption bulb to tap 3 was made as short as possible. With this equipment it was possible to maintain the dead space at sufficiently high temperature so that easily condensable vapours, such as methyl formate could be employed.

Temperature Control.

The temperature of the adsorbent was maintained by placing around the adsorption tube an electric furnace for temperatures above 100°, an electrically heated water bath controlled by the usual form of mercury thermoregulator for temperatures between 20° and 50°, while for 0° and -81°.5, a Dewar flask containing ice and water or solid carbon dioxide and acetone respectively was used. For the runs made at -30°, temperature was maintained by surrounding the adsorption tube with a Dewar flask containing acetone, agitated by bubbling air, and cooled by adding, as required, small pieces of solid carbon dioxide. The compressed air for agitation of the acetone, before entering the tube contained in the Dewar flask, was dried by traversing another tube contained in a second Dewar flask containing solid carbon dioxide and acetone, in which the water vapor was frozen out. This was found necessary since passing the air through a considerable length of tubing containing phosphorus pentoxide or bubbling it through a wash bottle containing concentrated sulphuric acid did not suffice. This procedure was found satisfactory. When the temperature desired had been obtained, it was found necessary to add a small piece of carbon dioxide about every twenty minutes.

The electric furnace used was of a type which has been described before (40). It consisted of a piece of iron pipe 2½ inches in diameter and 12 inches in length wrapped with two layers of asbestos paper and wound with 18 gauge Nichrome resistance wire, the spirals of which were separated by about ¼ inch. This heating element was placed in a sheet-iron container about 1 foot in diameter and 15 inches deep with flake asbestos packing. The furnace would maintain a temperature of 1000° C. when drawing a current of 6 amperes at 110 volts.

When constant temperature was required, the space remaining in the core of the furnace after it had been placed around the adsorption tube was well packed with 80 mesh iron filings. The top of the furnace was then closed by pieces of asbestos board and covered to a depth of about 4 inches with flake asbestos. The temperature was then controlled by means of hand adjusted resistance to within less than half a degree.

When removal of the furnace was necessary it was found that the iron filings were readily transferred to a trap placed in a suction line from a water aspirator, even though a temperature of 550° had been attained and a temperature of 400° had been maintained for many periods of 8-10 hours.

Temperature Measurement.

Higher temperatures were measured by means of a Chromel vs. Alumel thermocouple in conjunction with a potentiometer supplied by Leeds and Northrup, using conversion tables published by these manufacturers. The temperature of the cold junction was read off on a mercury thermometer placed close to the cold junction in oil, in a Dewar flask.

The temperatures of the two water baths were measured by means of mercury thermometers.

For the lower temperatures an alcohol thermometer was used.

Comparison with a sub-standard showed that all the mercury thermometers used were correct to within 0°.2.

Gases

Commercial tank nitrogen was used for calibration. When silica adsorbents were used the nitrogen was dried before entering the apparatus by passing through a 2.5 foot tube of phosphorous pentoxide. For calibration of the nickel adsorbent, the nitrogen was first passed in a fine stream through a wash bottle containing alkaline pyrogallate to remove oxygen, and then over phosphorous pentoxide.

The hydrogen used for reduction of the nickel adsorbents was taken from a commercial tank. Oxygen was removed by leading the gas first through a heated silica tube well packed with copper and then over phosphorous pentoxide.

Ethylene from a tank supplied by The Ohio Chemical and Manufacturing Company was passed over phosphorous pentoxide before entering the apparatus. Analysis of this gas showed it to be sufficiently pure and was as follows: by fuming sulphuric acid 99.7%, by ignition 99.2%.

Before filling the apparatus with gas the storage bulbs, gas burette, and connecting tubing were evacuated to 0.001 mm. and then flushed twice with the gas to be used.

Vacuum Treatment.

Between each run and the next one the adsorbent was evacuated for about 8 hours at 400° in the case of silica and at 300° for the nickel adsorbent. On turning off the pumps after such treatment the pressure in the apparatus was found to build up to only about 0.003-0.004 mm.

Blank Runs.

Runs were made with an empty bulb which was exactly similar to those which contained the adsorbents. Two such runs were made with methyl formate and in each case after admitting the gas a slow but long-continued drop in pressure occurred which finally amounted to a few centimeters. It was concluded that the gas was dissolving in the Lubriseal tap grease used. Runs made with ethylene resulted in a negligible drop in pressure amounting to only about 1 mm. at a pressure of about 500 mm.

Calibration of Apparatus.

The amount of gas adsorbed was calculated from the difference between the actual gas pressure observed and the calculated pressure which would have been exerted if no gas had been taken up by the adsorbent. In order to make this calculation the volume of the apparatus containing the adsorbent had to be known. This volume was calculated, using the simple gas laws, from the pressures exerted by known quantities of nitrogen at certain temperatures. This method has been commonly employed for this purpose. The assumption involved is that no nitrogen is adsorbed. This is not strictly true, but, with many adsorbents and in certain regions of temperature and pressure, the error is not serious. Use may, of course, be made of helium, which is adsorbed to a smaller extent than nitrogen, or, more accurate still, some absolute method.

If no nitrogen is removed from the gas phase, the gas laws would of course be obeyed. In the present determinations the gas laws were found to hold to well within the experimental error when the silica adsorbents were used. In the case of the first sample of silica used, however, an extended series of determinations were made including numerous check runs. In the values of the volumes calculated from these data there was found to be a very small but definite trend of such nature that it may have been caused by a very slight amount of adsorption of the gas.

During calibration with nickel, however, sorption of nitrogen was very definitely indicated. Below 100° the deviation from the gas laws was very appreciable. At temperatures as high as 300° admission of the gas was followed by a long-continued fall in pressure which took place with quite appreciable velocity. This indicated that at such temperatures the gas was being taken up slowly by the metal. This was confirmed by the finding of a very definite hysteresis with change in temperature between 200° and 375°. A calculation of the amount of gas taken up was made.

At 100° and 200°, however, the gas laws were closely adhered to and data obtained at these temperatures was used for the necessary volume calculations. The effect of more accurate calibration would be to change by a small amount the absolute values of the adsorptions to be calculated, but would not affect the more important findings of this investigation.

The purpose of the calibration is to determine the volume of those parts of the apparatus which contain the gas in contact with the adsorbent. This volume must be known in order to calculate the amount of gas adsorbed. The parts of this volume are the adsorption tube and the dead space. Practically all of the latter is contained in the water thermostat. We have then a volume of gas the different parts of which are at different temperatures, but which is all at the same pressure. For such a mass of gas the gas laws state that

$$\sum \frac{pV}{T} = K .$$

If we represent the volume and temperature of the adsorption bulb by V' and T' respectively, and the volume and temperature of the dead space by V" and T" respectively, we may then write

$$p \left\{ \frac{V'}{T'} + \frac{V''}{T''} \right\} = K \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

which, on rearrangement, gives

$$\frac{K}{p} - \frac{V'}{T'} = \frac{V''}{T''} = \text{a constant}$$

since V" and T" are both constant. We will then have for different quantities of gas at different temperatures of the adsorption bulb

$$\frac{K'}{p'} - \frac{V'}{T'} = \frac{K''}{p''} - \frac{V'}{T''},$$

where K' and K" are the constants of the different masses of gas which exert the pressures p' and p" when the temperatures of the adsorption bulb are T' and T''' respectively. This may obviously be rearranged to give

$$V' = \left\{ \frac{K''}{p''} - \frac{K'}{p'} \right\} \frac{T'T'''}{T' - T'''} \quad .$$

Equation (1) may also be written

$$V'' = \left\{ \frac{K}{p} - \frac{V'}{T'} \right\} T'' \quad .$$

We have then V' and V'', which are the quantities sought, expressed in terms of quantities which were determined by experiment. Such experiments consisted in allowing various known quantities of gas into the dead space and adsorption tube, while the latter was maintained at various constant temperatures, and observing the resultant pressures.

In this way the values of V' and V'' had to be determined for each tube of adsorbent.

The temperature of the dead space was taken as the temperature of the water bath containing the lower part of the manometer. This gave rise to no error, however, since that part of the dead space which was outside the thermostat was such a small part of the total that accurate temperature control of it was not necessary.

Experimental Procedure

After the adsorbent had been evacuated sufficiently, and the different parts of the apparatus were brought to the required temperatures a run was commenced. With tap 4 open, again referring to Figure I., and taps 3 and 7 closed, the mercury in the gas burette was leveled, as described above, and the volume of gas noted. Not long after this the barometric pressure was observed. Tap 3 was then opened until the amount of gas desired had entered the adsorption tube and dead space. As soon as possible after closing tap 3 the mercury in the short arm of the manometer was brought to the level pointer D, as described above, and the scale reading of the mercury level in the long arm taken. This first pressure reading was obtained usually about one minute after the gas had come in contact with the adsorbent. Further pressure readings were taken at intervals varying from one minute to two hours depending on the rate at which the pressure was changing. Rate measurements were continued on the average for about 10 hours. Soon after the run had been started the gas burette mercury was again leveled and the gas volume again read off. This procedure was used for measuring the rate at which the gas was taken up.

For the determination of an isotherm additional measured amounts of gas were allowed to pass through tap 3. The pressure in the adsorption tube was noted after each addition of gas and after an interval dependent upon the time necessary for establishment of equilibrium.

For the investigation of temperature hysteresis, the temperature of the adsorption tube was varied while it and the dead space contained a constant amount of gas.

After completion of a run the adsorbent was evacuated as described above under vacuum treatment.

Sample Calculation

As an illustration, the calculation in detail of the amount of ethylene taken up by Nickel II when apparent equilibrium had been attained at -81°.5 is given. The necessary data for the representative run 5E11 is:

Barometric pressure	76.22 cm.
Reduction of volume of gas in burette	25.89 cm.^{3}
Temperature of water bath	311° K.
Temperature of adsorbent	192° K.
Pressure at apparent equilibrium	15.60 cm.

It is known from previous calibration that the volume of the adsorption tube V' = 55.37 cm.^{3}, and that the volume of the dead space V" = 8.66 cm.^{3}.

Equation (1) above here reproduced for convenience is

$$p\left\{\frac{V'}{T'} + \frac{V''}{T''}\right\} = K$$

Substituting in this equation and evaluating K, from the above data, assuming Dalton's law, we get

$$p\left\{\frac{55.37}{192} + \frac{8.66}{311}\right\} = K = \frac{76.2 \times 25.89}{311}$$

from which

$$p = 20.07,$$

which is the pressure which would have been exerted by the gas if no adsorption had taken place. The difference between this and the actual pressure observed is

$$20.07 - 15.60 = 4.47 \text{ cm.},$$

which is the pressure which would have been exerted in the adsorption tube and the dead space by the amount of gas adsorbed. This amount of gas is, by the gas laws,

$$55.37 \times \frac{4.47}{76.0} \times \frac{273}{192} + 8.66 \times \frac{4.47}{76.0} \times \frac{273}{311} = 5.09 \text{ cm.}^3 \text{ at N.T.P.}$$

EXPERIMENTAL RESULTS.

EXPERIMENTAL RESULTS

I. Silica

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

A sample of precipitated silica was therefor prepared. To 100 c.c. of sodium silicate solution (sp. grav. 1.170) were added 100 c.c. of 10 per cent 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 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.

Temperature, °C.	Pressure cm.	$P_N - P_E$	Adsorption c.c. at N.T.P.
24	9.81	4.54	1.23
24	26.70	8.32	2.24
24	46.27	11.46	3.10
24	70.84	14.81	4.00
51	4.96	1.12	0.29
51	24.52	4.78	1.23
51	51.27	7.94	2.05
51	71.15	10.05	2.59
101	10.55	0.96	0.23
101	33.25	2.08	0.50
101	47.30	2.82	0.67
101	66.84	3.81	0.92
186	12.35	0.28	0.06
186	38.47	0.30	0.07
186	54.30	0.64	0.14
186	76.85	0.67	0.14
296	13.63	0.13	0.03
296	42.41	-0.18	-
296	84.58	-0.14	-

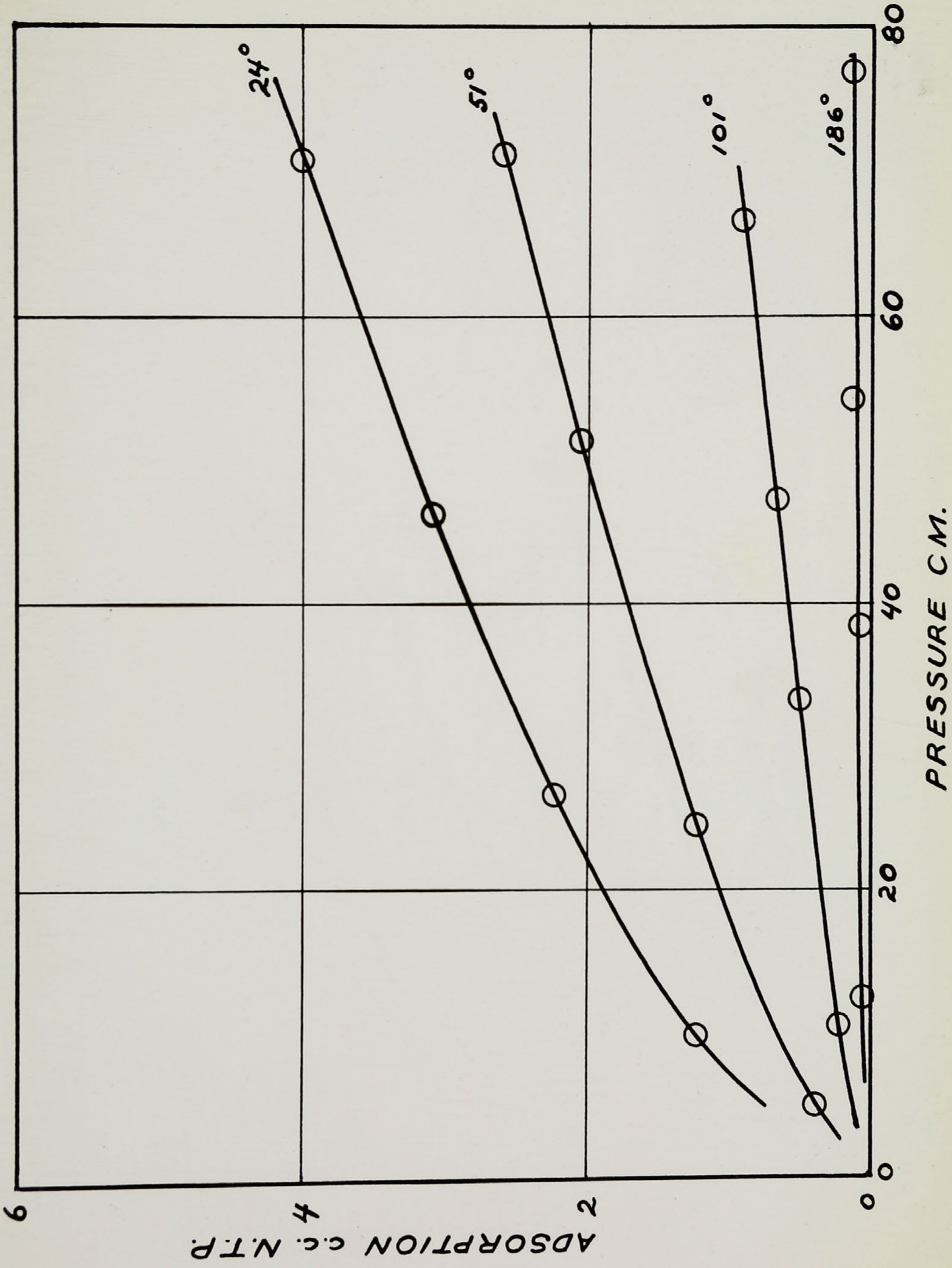

FIGURE 2

ADSORPTION ISOTHERMS SILICA

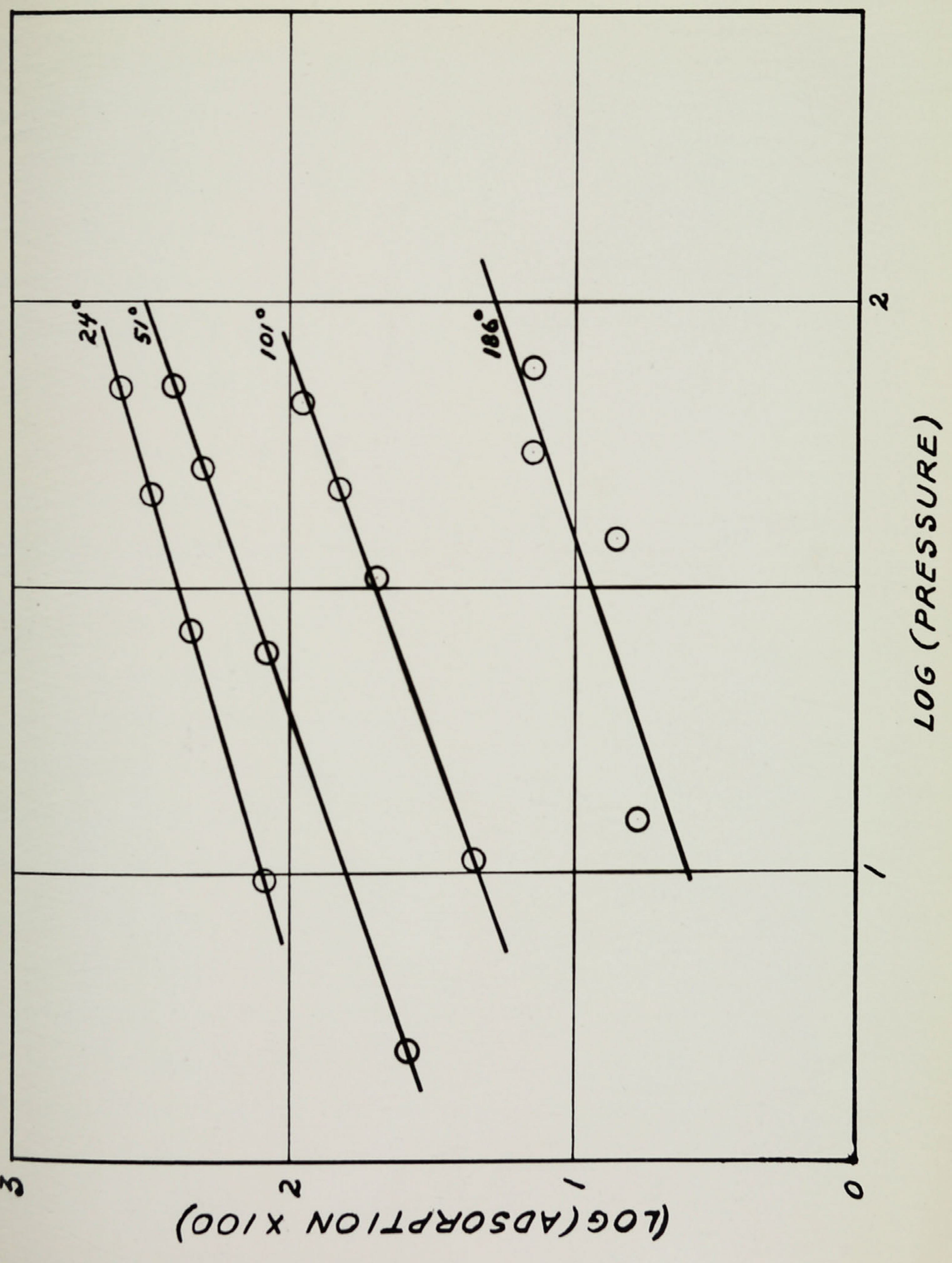

FIGURE 3

ISOTHERMAL ADSORPTION SILICA

The values given in the column headed $P_N - P_E$ represent the difference between the pressure which would have been produced by the same volume of nitrogen and the observed pressure with ethylene.

The data contained in Table I. are plotted in Figure 2. giving typical adsorption isotherms. Figure 3. shows the data in the form of a log-log plot. Good straight lines are obtained as is usually the case.

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 (38). 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 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 was 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 typical runs are given in Table II.

TABLE II.

Nickel I. Rate of Adsorption.

Temperature °C.	21		21		21	
Initial Pressure cm. (calc.)	11.39		21.89		40.90	
	Time min.	Ads. c.c. at N.T.P.	Time min.	Ads. c.c. at N.T.P.	Time min.	Ads. c.c. at N.T.P.
	2	1.72	1	1.73	6	1.90
	5	1.93	3	1.95	14	2.04
	9	2.05	10	2.18	36	2.24
	15	2.18	32	2.52	61	2.37
	40	2.48	59	2.75	99	2.54
	58	2.60	155	3.14	163	2.68
	115	2.84	186	3.24	243	2.79
	239	3.11	240	3.35	282	2.85
	312	3.24	365	3.55	361	2.91
	389	3.30	569	3.76	397	2.96
	1010	3.71	651	3.84		
	1095	3.73	736	3.90		

Data from runs at temperatures above 100° C. are not given. At these temperatures decomposition of the ethylene occurred with rapid pressure increase.

It is apparent that about one-half of the adsorption occurs immediately, the remainder being taken up very slowly. Adsorption-time curves plotted from the data in Table II. are

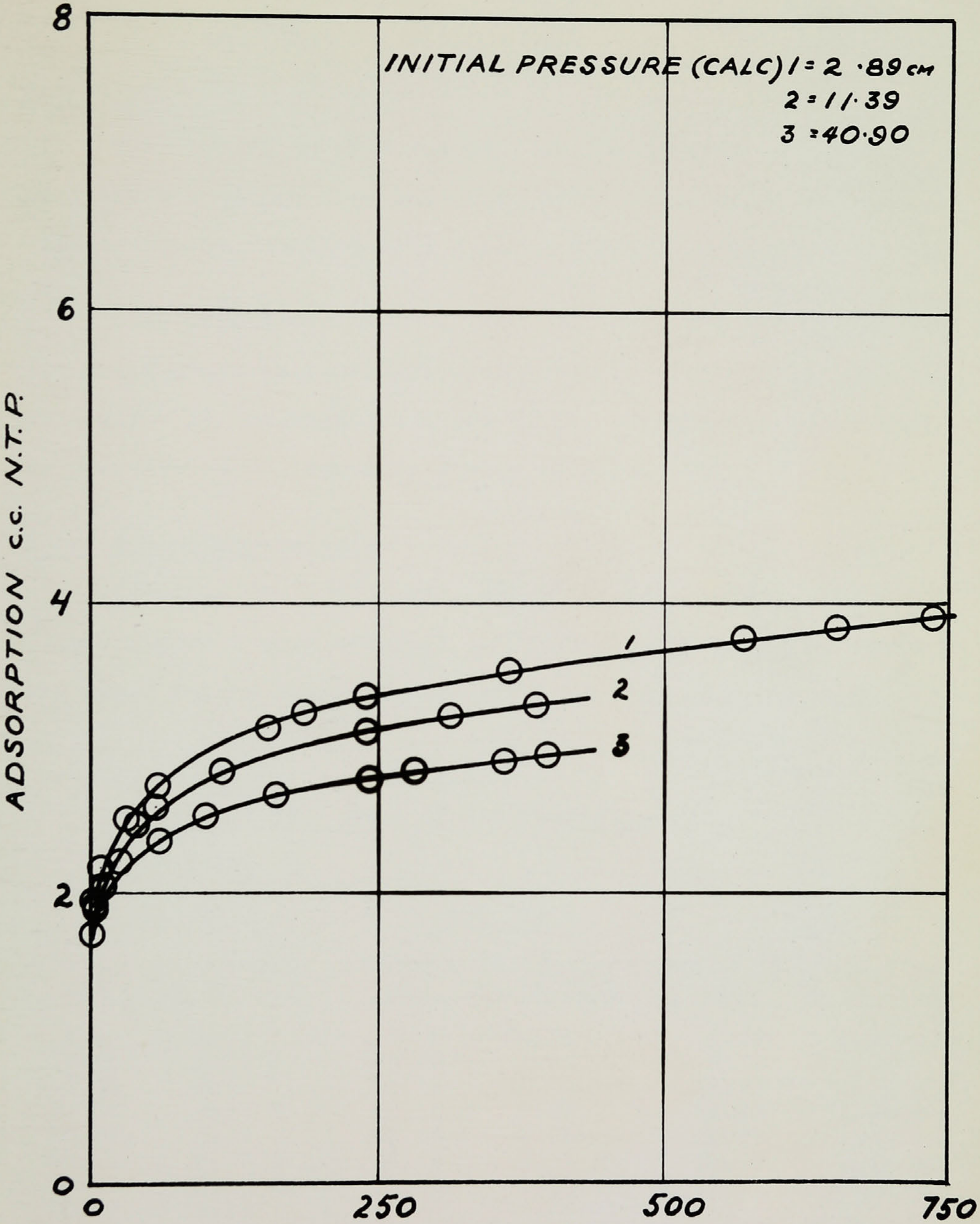

FIGURE 4

RATE OF ADSORPTION AT 21° NICKEL I

given in Figure 4.

Nickel II

This series of runs was made on the previous sample of nickel after it had been heated to 520° C. for about one 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. Values marked X were obtained from separate runs.

TABLE III

Nickel II. Runs at Low Temperatures

Temperature

-82° C.		-30° C.		0° C.	
Pressure cm.	Adsorption c.c. at N.T.P	Pressure cm.	Adsorption c.c. at N.T.P	Pressure cm.	Adsorption c.c. at N.T.P
6.19	4.72	2.00	0.81	0.49	0.41
15.60	5.09 X	9.02	1.67	9.76	0.93
18.51	5.12	20.25	2.73 X	21.73	1.33 X
25.80	5.22 D	26.10	2.62	22.24	1.52 D
35.67	5.09	51.29	3.02	35.33	1.60
40.78	5.23 D	54.46	3.11 D	41.46	1.92 D
53.11	5.40 D	71.83	3.18	59.11	2.05
54.07	5.32				
71.22	5.71				

The above values are plotted in Figure 5. It will be seen that the low temperature adsorption is of the van der Waals'

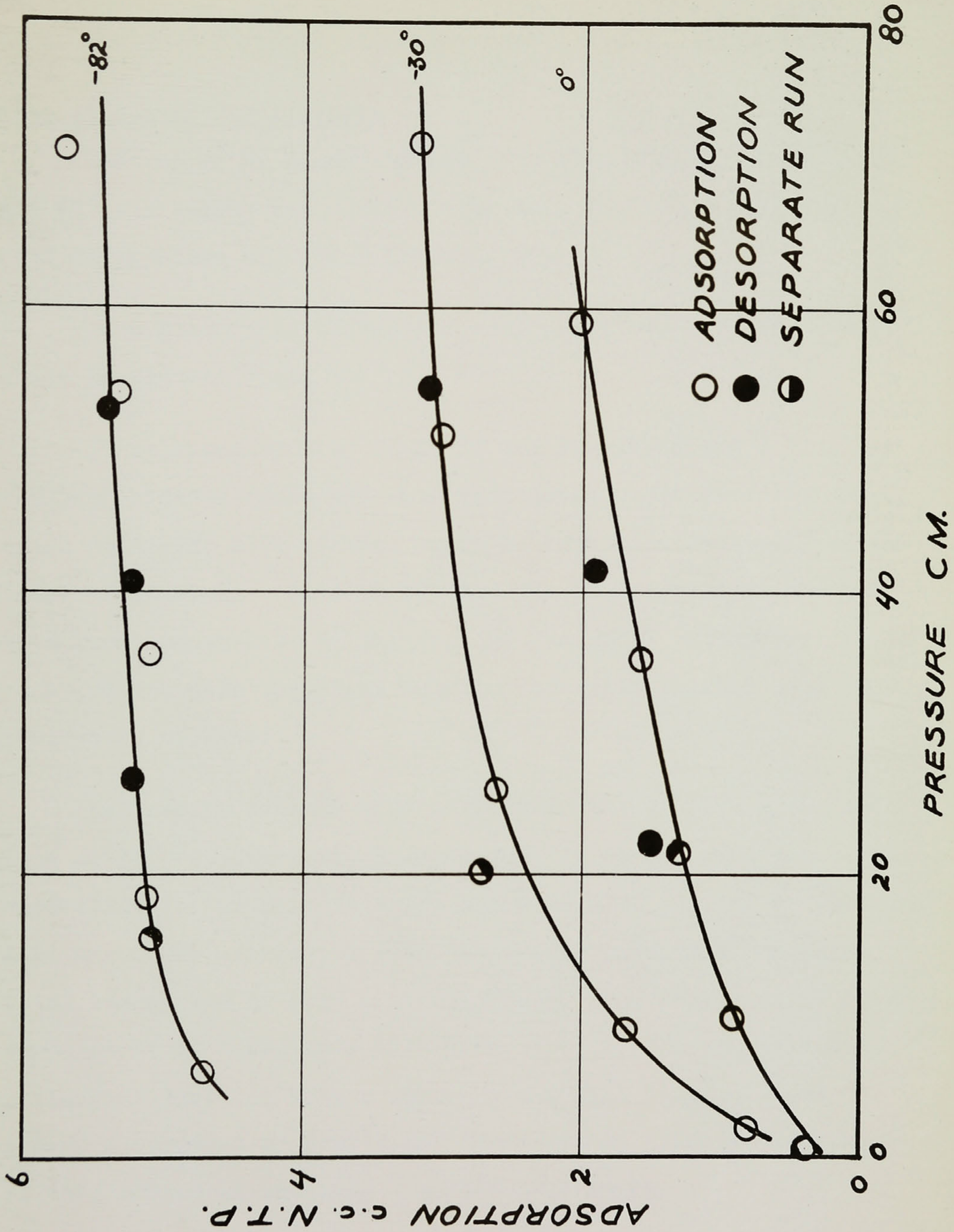

FIGURE 5

ADSORPTION ISOTHERMS NICKEL II

type, and gives typical adsorption isotherms.

Runs at Higher Temperatures

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

Adsorption time curves for runs at 20° C. and 50° C. are given in Figures 6 and 7.

It is apparent from Table IV and Figures 6 and 7 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 per cent 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 run was made at 50° C. The initial rapid adsorption was 0.64 c.c. The adsorption in the next 10 hours was 0.59 c.c., giving a total of 1.23 c.c. The adsorption tube was then cooled to 0° C. and a total adsorption of 2.17 c.c. was found. The normal value from a run at 0° C. would have been 1.78 c.c., at the corresponding pressure. There is thus a hysteresis effect leading to an excess adsorption of 0.39 c.c. There was no sign of desorption of this excess amount over a period of 2 hours.

TABLE IV.

Nickel II. Rate of Adsorption.

Temperature °C.	0°		20		20		20		20		50		50		50	
Initial Pressure cm.(calc.)	23.33		6.47		19.25		49.30		67.41		11.52		38.87		52.07	
	Time min.	Ads. c.c.at N.T.P.	Time min.	Ads. c.c.at N.T.P.	Time min.	Ads. c.c.at N.T.P.	Time min.	Ads. c.c.at N.T.P.	Time min.	Ads. c.c.at N.T.P.	Time min.	Ads. c.c.at N.T.P.	Time min.	Ads. c.c.at N.T.P.	Time min.	Ads. c.c.at N.T.P.
	3	1.33	2	0.49	2	0.81	5	1.12	7	2.20	2	0.44	2	0.63	5	0.74
	7	1.37	6	0.52	5	0.85	10	1.14	13	2.23	6	0.50	5	0.70	13	0.80
	33	1.41	21	0.57	18	0.89	20	1.17	20	2.26	15	0.54	10	0.72	31	0.86
	62	1.44	42	0.60	36	0.95	60	1.22	61	2.34	50	0.64	30	0.80	100	0.97
	124	1.46	69	0.61	108	1.01	127	1.26	122	2.36	75	0.67	60	0.87	202	1.06
	218	1.51	167	0.68	190	1.04	193	1.27	186	2.39	190	0.76	108	0.96	289	1.12
	380	1.54	357	0.71	255	1.08	315	1.32	322	2.43	343	0.82	196	1.02	480	1.20
	514	1.55	533	0.75	475	1.12	408	1.33	494	2.48	532	0.88	319	1.09	537	1.21
	580	1.56	860	0.77	660	1.16	484	1.35	618	2.51	677	0.90	483	1.15	610	1.22

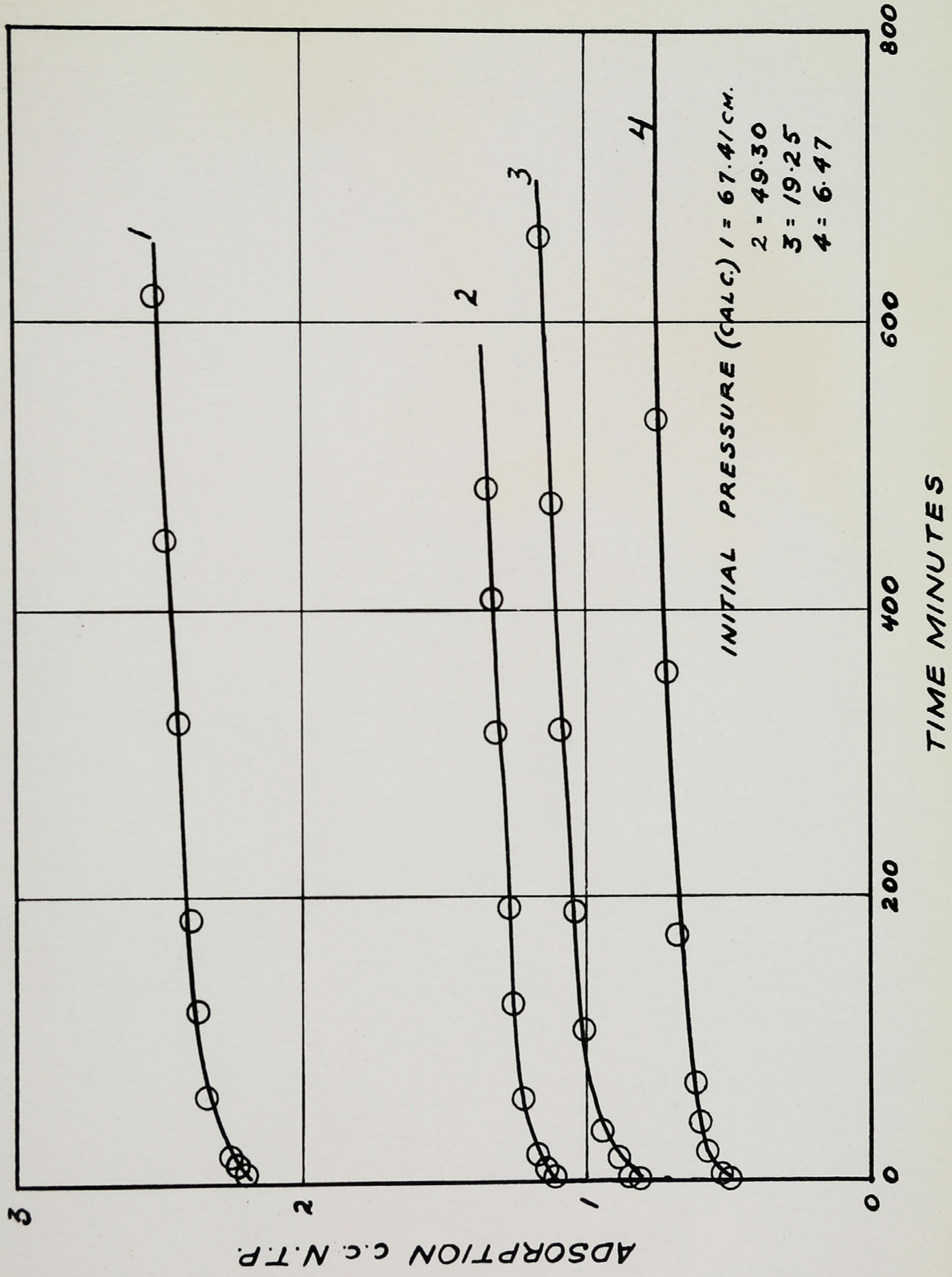

FIGURE 6

RATE OF ADSORPTION AT 20° NICKEL II

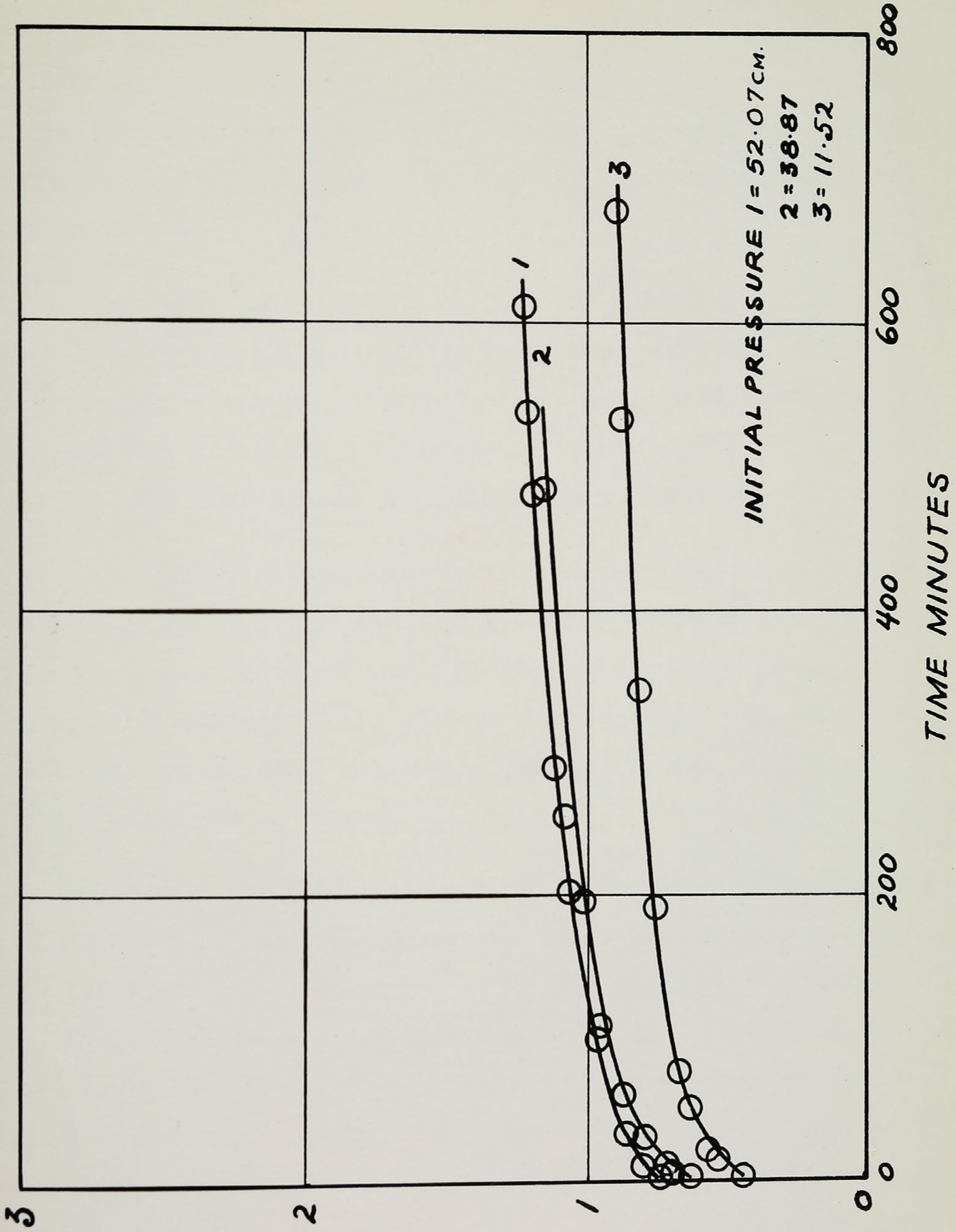

FIGURE 7

RATE OF ADSORPTION AT 50° NICKEL II

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 4½ days. It was then evacuated for 24 hours.

Runs were made at -80°, 0°, 21°, 50°, 142°, and 250° C. At 250° 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°. The data for some typical runs are given in Table V.

It will be noticed, for example in the data for runs at 21°, that the amount of gas adsorbed does not increase regularly with pressure. This was due to a gradual decrease in the adsorptive capacity of the nickel. The runs were made not in order of increasing or decreasing pressure so that such an effect would not be masked.

The data given in the third 50° column and the second 142° column are from runs which were made after the other runs. In the meantime the apparatus had stood idle for some time and it is thought that some air leaked in, oxidising the catalyst. This would account for there being much less adsorbed at 50° in these latter runs. At 142° less gas was adsorbed at first but finally the amount of gas taken up was even greater than in former runs. This was probably due to some reduction of the oxidised adsorbent taking place.

TABLE V.

Nickel III. Rate of Adsorption.

Temperature -82° C.		-82° C.		-82° C.		0° C.	
Initial Pressure (calc.) 11.91 cm.		24.62 cm.		42.64 cm.		23.97 cm.	
Time Min.	Ads. c.c.	Time min.	Ads. c.c.	Time min.	Ads. c.c.	Time min.	Ads. c.c.
1	5.31	1	5.06	8	5.16	2	1.45
3	5.38	3	5.32	14	5.20	7	1.64
15	5.41	6	5.50	27	5.25	15	1.17
68	5.49	12	5.60	62	5.28	25	1.75
123	5.50	38	5.64	124	5.32	41	1.80
180	5.50	108	5.69	183	5.32	60	1.83
273	5.51	165	5.71	268	5.34	91	1.87
		299	5.74			199	1.98
		500	5.75			329	2.03

Temperature 21° C.		21° C.		21° C.		21° C	
Initial Pressure (calc.) 5.38 cm.		22.18 cm.		48.20 cm.		71.80 cm.	
Time	Ads.	Time	Ads.	Time	Ads.	Time	Ads.
1	1.26	2	1.06	5	1.81	6	1.74
3	1.41	5	1.25	14	1.98	22	1.82
6	1.50	15	1.37	45	2.16	48	1.97
16	1.65	25	1.43	60	2.22	64	1.99
69	1.88	67	1.57	199	2.46	121	2.12
248	2.08	259	1.74	262	2.54	215	2.22
438	2.20	377	1.83	375	2.62	303	2.30
562	2.22	458	1.87	432	2.63	455	2.38
615	2.24	600	1.90	601	2.75	641	2.48

Temperature 50° C.		50° C.		50° C.		142° C.		142° C.	
Initial Pressure (calc.) 20.36 cm.		38.44 cm.		24.91 cm.		39.78 cm.		43.40 cm.	
Time	Ads.	Time	Ads.	Time	Ads.	Time	Ads.	Time	Ads.
1	0.93	2	0.77	2	0.25	1	1.35	2	0.97
5	1.11	7	0.96	6	0.30	2	1.72	5	1.42
13	1.22	30	1.16	13	0.35	6	2.40	10	1.89
46	1.44	108	1.41	30	0.46	18	3.39	20	2.45
160	1.68	184	1.54	105	0.57	31	3.95	57	3.60
271	1.82	297	1.65	221	0.62	60	4.83	120	4.76
379	1.93	399	1.75			120	5.97	194	5.74
475	1.98	496	1.84			210	6.90	288	6.56
584	2.04	636	1.92			434	7.72	470	7.59
						600	7.83	600	7.96

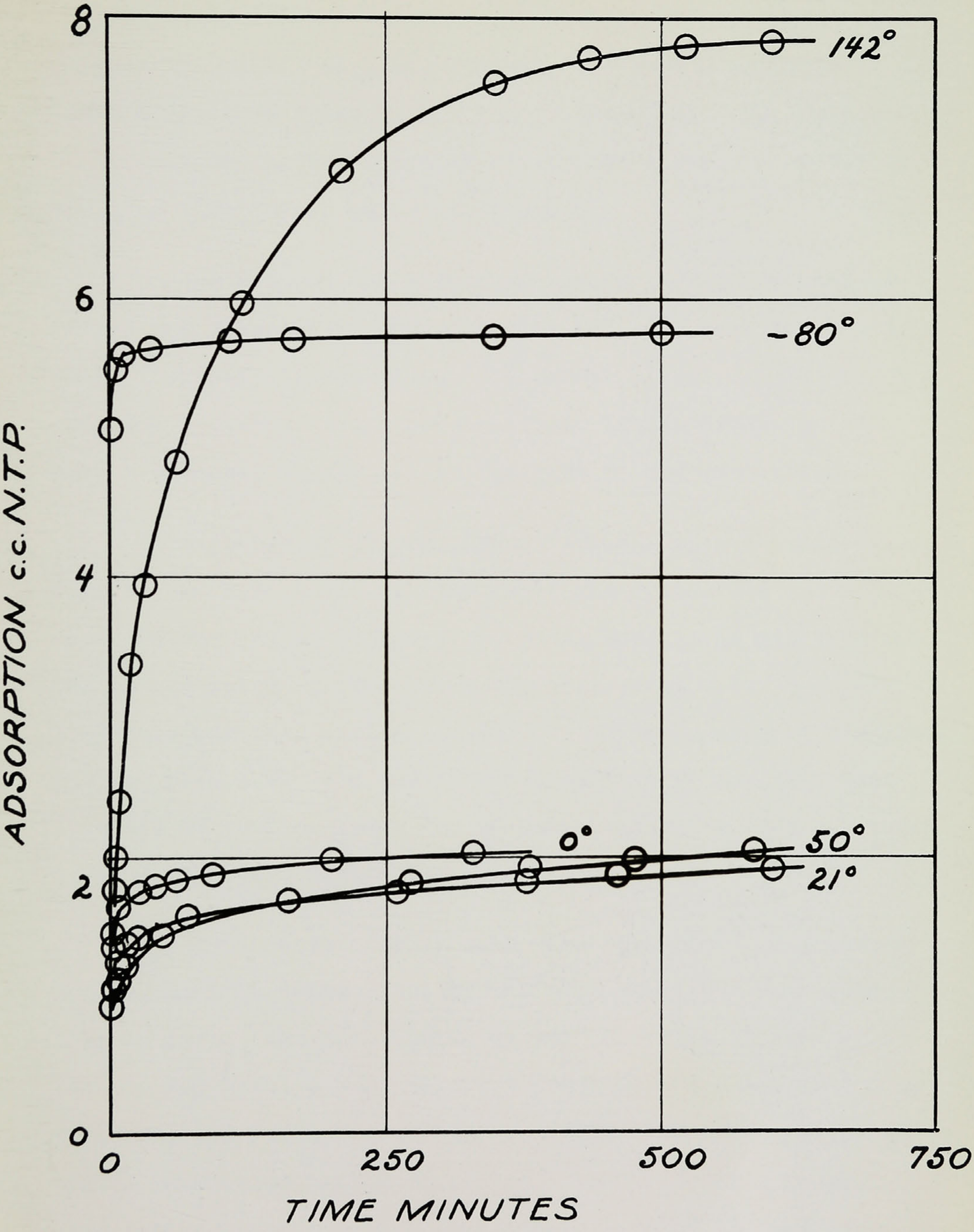

FIGURE 8

RATE OF ADSORPTION NICKEL III

It will be seen that at -80° C. the slow effect is comparatively small. At 142°, however, the slow adsorption is at least 5 times as great as the rapid adsorption. The relative magnitudes of the two types of adsorption are shown by the adsorption time curves given in Figure 8.

Figure 9 shows the effect of pressure on the amount adsorbed and the rate of adsorption at 20°. It will be seen that while increasing pressure has the normal effect on the amount adsorbed rapidly, it has comparatively little effect on the amount adsorbed slowly, or on the rate of its adsorption.

As with Nickel II, hysteresis effects were noticeable. Thus in one run at 21° C., the rapid adsorption was about 1.58 c.c. At the end of 10 hours the total adsorption was 2.75 c.c. The amount taken up slowly was therefore 1.17 c.c. The adsorption tube was then cooled to -80° C. The total amount adsorbed was now 6.28 c.c. The amount which would have normally been adsorbed at -80° C. under these conditions was 5.60 c.c. There is thus an excess adsorption of about 0.68 c.c.

The hysteresis effects were very pronounced if a sample were brought to equilibrium at 142° C., where the slow adsorption is large, and then cooled to -80° C. Thus in one run at 142° C. the total amount adsorbed after 10 hours was 7.83 c.c. 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 tube was then cooled to -80° C. The total

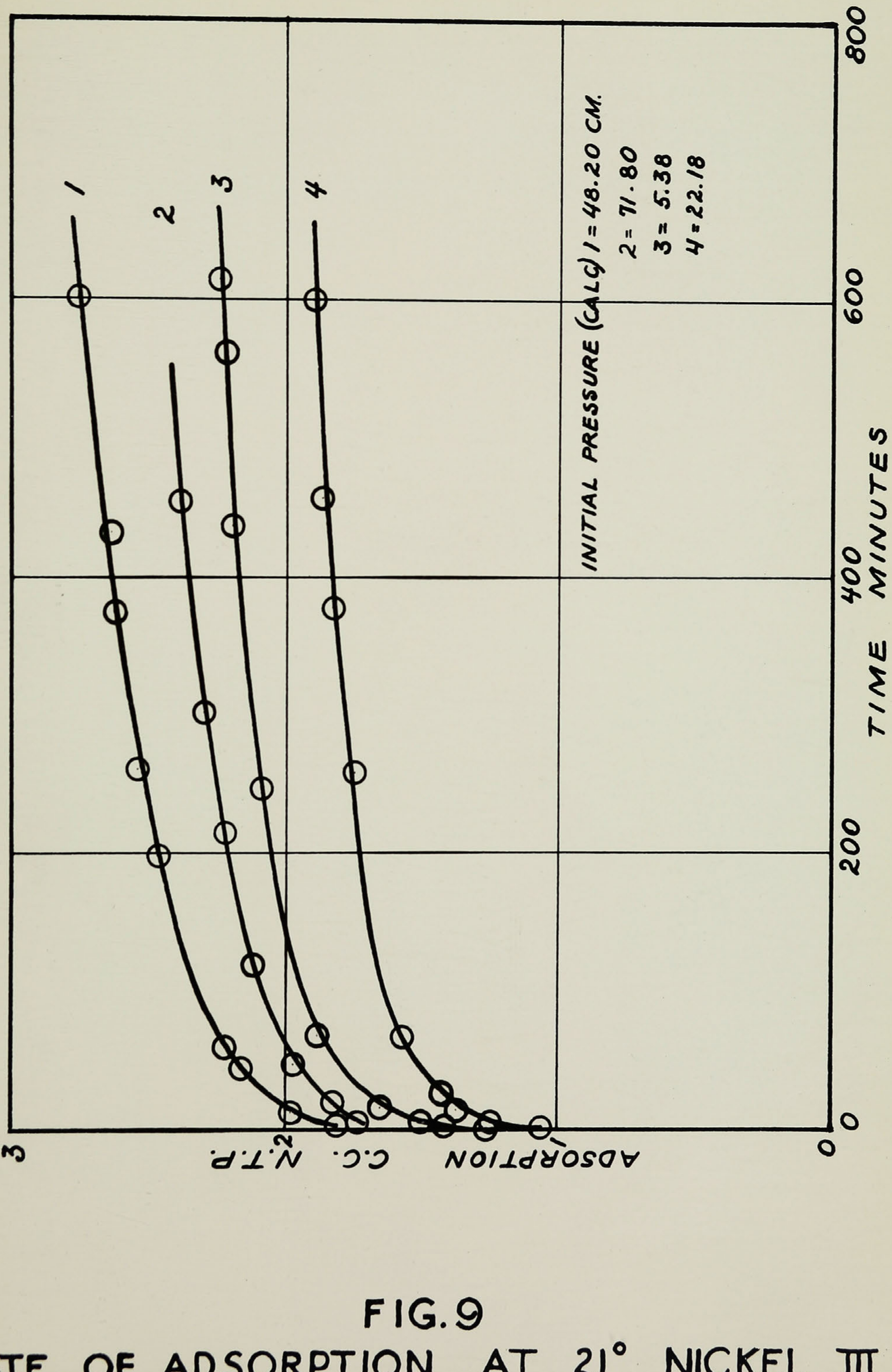

FIG. 9

RATE OF ADSORPTION AT 21° NICKEL III

adsorption at this temperature was 12.39 c.c. The normal adsorption at -80° C. would have been 5.5 c.c. There is thus an excess adsorption of 6.89 c.c., which is of the same order of magnitude as the slow adsorption at 142° C.

DISCUSSION.

DISCUSSION.

Adsorption of nitrogen by silica was indicated. Adsorption by nickel was appreciable below 100°. Above 200° the gas was taken up with moderate velocity.

Very satisfactory evidence of van der Waals' adsorption of ethylene by a sample of precipitated silica was obtained. After each addition of gas equilibrium was attained almost instantly. Over the entire temperature range investigated only steady decrease in adsorption with increase in temperature was observed. For temperatures between 24° and 101° smooth curves resulted when the amounts adsorbed at constant temperature were plotted against the corresponding values of the gas pressure (Figure 2). When, for the same data, the logarithm of the adsorption was plotted as a function of the logarithm of the pressure (Figure 3) the points fell on straight lines to well within the experimental error. It is indicated then that the amount of gas taken up was related to the pressure by some equation having the form:

$$a = kp^{1/m}$$

in which a represents the amount adsorbed at the equilibrium gas pressure p, k is a constant, and 1/m is a fraction, the value of which depends on the circumstances. This equation, it is well known, approximately represents the facts in virtually all cases in which secondary adsorption is the predominate process occurring. The amount adsorbed was small at 186° and was within the experimental error at 296°.

Below 296° there was no indication of the occurrence of a second adsorption process.

At the lower temperatures the actual amount adsorbed was quite appreciable. Under pressures of about 1 atmosphere it amounted per gram of adsorbent to approximately 2 c.c. and 0.5 c.c. at 24° and 101° respectively.

The surface area of the precipitated silica was probably considerable since the two gram sample used had an apparent volume equal to that of 10 grams of 80 mesh fused quartz.

An approximate value of the heat of adsorption of ethylene by silica may be obtained using the Clausius-Clapeyron equation

$$\frac{d \ln p}{dT} = \frac{Q}{RT^2}$$

which on integration yields the relation

$$\ln\frac{p'}{p''} = Q\frac{T'-T''}{RT'T''} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1).$$

Figure 2. indicates that 2 c.c. of gas would have been adsorbed under a pressure of 22 cm. at 297° K. and under a pressure of 50 cm. at 324° K. Substituting these figures and the appropriate value of the gas constant in equation (1) an approximate value of 5700 calories per gram molecule is obtained for the heat of adsorption. Magnus and collaborators (87) obtained by direct measurement the value of 7500 calories for the adsorption of ethylene by silica gel.

With the nickel-ethylene system an instantaneous adsorption was found to be followed by a slow taking up of the gas. This effect was observable in the case of the more active Nickel III. at temperatures as low as -82°. No slow effect occurred with Nickel II. below -30°. The heat treatment received by Nickel II. seemed to diminish the slow effect relatively more than the instantaneous adsorption. Practically the same amount of gas was taken up by Nickel II. and Nickel III. at -82°. As will be seen, however, from a comparison of Figures 4,6 and 9 the magnitude of the slow adsorption was much greater on the nickel which had not been heated to above the temperature of reduction.

As will be seen in Figures 5 and 8 the rapid adsorption decreased steadily with increase in temperature. At temperatures of 50° and above, however, the velocity of the slow adsorption became so great that within 10 hours more gas was taken up than in the same period at 21°. This effect became greater with rise in temperature and a rate curve for -80° is crossed by one for 142° within 2 hours. This evidence does not establish that the amount of gas taken up at equilibrium would be less at lower temperatures than at higher. It appears simply that the rate of the slow adsorption is very small at the lower temperatures. Whether or not this is the case, the so-called hysteresis effects described above in the experimental results could have occurred.

These same hysteresis effects do not appear to show any connection between the two types of adsorption in the nickel-ethylene system. Howard (78), as stated above, reported that on a chromium oxide gel high temperature adsorption inhibited rapid adsorption. In the work described here, of course, the conditions or accuracy to show this effect may not have been attained. Howard does not yet appear to have published details of his experiments.

At temperatures of 0° C. and below the rate of slow adsorption by Nickel II. was negligible. Adsorption isotherms for 0°,-30° and -82° C. which appear in Figure 5 were determined. Assuming that these curves represent values for only van der Waals' adsorption data was taken from them to calculate the heat of adsorption. 1 c.c. of gas would be adsorbed at pressures of 3.6 cm. and 12.0 cm. at temperatures of -30° and 0° C. respectively. Substituting these figures in equation (1) above, a value of 5300 calories per gram molecule is obtained for the adsorption of ethylene by Nickel II. This is in satisfactory agreement with the value 5845.6 calories found by Foresti (88).

The extent of rapid adsorption increased with increase in pressure in the usual manner as appears from the isotherms in Figure 5 and the rate curves in Figure 6. This is not apparent in Figures 4 and 9 because the adsorptive capacity of Nickel I. and Nickel III. decreased somewhat with each run and the runs were not made in order of decreasing or increasing pressure. Nickel II, however, was much more stable.

The effect of pressure on the rate of slow adsorption seemed to be negligible.

A satisfactory calculation of the heat of high temperature adsorption could not be made from the data.

It is usual to calculate isosteric energies of activation for the slow adsorption process by the method used by Taylor and Williamson (42). They substitute observed data in an integrated form of the Clausius-Clapeyron equation

$$\ln \frac{V''}{V'} = \frac{E}{R}\frac{(T''-T')}{(T'T'')}$$

in which V''/V' is the ratio of the average velocities of adsorption of equal amounts of gas at the temperatures T' and T''.

This may be done for the ethylene-nickel system taking data from runs with Nickel III. at 142° and 50°. At these temperatures rapid adsorption had fallen to a negligible amount. Figure 8 indicates that the first 1.72 c.c. were taken up in 2 minutes at 415° K. and in 175 minutes at 323° K. The next 0.30 c.c. were taken up in 2 minutes at 415° K., and in 375 minutes at 323° K. Since the ratio of the required lengths of time is the inverse ratio of the average velocities of adsorption, these data may be substituted directly in the above equation. This yields a value for the energy of activation of 13000 calories per gram molecule for the first 1.72 c.c. adsorbed and 15000 calories per gram molecule for the next 0.30 c.c. adsorbed.

Values of the isosteric activation energies of the adsorption of hydrogen by manganous oxide and by manganous-chromic oxide calculated by Taylor and Williamson (42) increased with increase in amount of gas taken up. Values for oxygen and silver given by Benton and Drake (72) are fairly constant.

This calculation of activation energy is open to criticism and it is very doubtful that it has any real meaning. In most cases the values obtained increase with increase in surface covered. Taylor considers that this is due to the first portions of gas being taken up by the most active parts of the surface and subsequent amounts being adsorbed by less active regions. This does not account for the fact that if calculations are made for equal amounts of gas at two temperatures the value obtained for the activation energy suddenly becomes infinitely great when the amount of gas considered is greater than the saturation value at one of the temperatures. Actually, however, the value is certainly not infinitely great unless it is a static equilibrium which is attained,in which case Langmuir's condensation evaporation concept would have to be discarded as the basis for the theory of slow adsorption, if not of rapid adsorption as well. It is likely that if an activation energy is to be calculated what should be compared is the adsorption, not of equal quantities of gas, but of equal fractions of the saturation value. As to the significance of the value obtained, Hinshelwood (89) has pointed out that a distinction should be drawn between those temperature effects which really depend upon activation of the molecules and those which depend simply upon changes with temperature in the state of the solid. These latter changes he found to give rise to such large temperature coefficients that very little significance could be attached to heats of activation calculated for processes involving the decomposition of solid substances.

With reference to heterogeneous catalysis it has for some years now been suspected that adsorption at a surface is a condition precedent to reaction at such surface. Until recently, however, the only generally recognized correlation between adsorptive capacity and catalytic activity was that all the metals adsorbed to some extent those gases the interaction of which they were able to promote. Taylor and Burns (17) found that at the optimum temperature, 130° to 150°, for the hydrogenation of ethylene catalysed by nickel the adsorption of ethylene by nickel was considerably less than at the temperature at which the reaction commences. That high temperature adsorption occurring at measurable rates may be used as a basis for the satisfactory explanation of catalysis has been dealt with by Taylor (90). He pointed out that the velocities with which hydrogen is adsorbed on several surfaces are consistent with the hydrogenation and dehydrogenation catalytic effects. Emmett and Braunauer (62) found that the initial rates of nitrogen adsorption by synthetic ammonia catalysts were in accordance with the rates of ammonia synthesis.

During the investigation described in this thesis it was found, contrary to the results of Taylor and Burns referred to above, that at 142° the adsorption of ethylene by nickel was much greater than at 50°, the rate of adsorption being about four times greater at the higher temperature. A considerable amount of data for the adsorption of hydrogen by metals has been previously recorded but this is the first report not only of a definite measurement of the rate of adsorption, but also of a maximum adsorption in the optimum temperature range for reaction, by a hydrogenation catalyst of the component to be hydrogenated. Hence, valuable data for one example are here presented which may be used in seeking a correlation between adsorption characteristics and rate of reaction in a number of cases. It is studies of this nature, as has, in effect, been pointed out by Hinshelwood (91), that promise to lead to a more thorough understanding of the hitherto mysterious phenomenon of catalysis.

More important, however, is the fact that this is the first case in which the usual criteria of activated adsorption have been definitely obtained in a system in which solubility is exceedingly unlikely to be a complicating factor. To this extent, then, the first unequivocal proof of the existence of such adsorption is provided.

SUMMARY.

SUMMARY.

An apparatus for measurement of the adsorption of high boiling point gases has been devised.

Adsorption of nitrogen by silica and nickel has been detected.

The ethylene-silica system has been investigated at pressures up to one atmosphere and at temperatures between 24° and 296°. Adsorption is of the van der Waals' type only. A value for the heat of adsorption has been calculated.

The ethylene-nickel system has been investigated at pressures up to one atmosphere and at temperatures between -82° and 250°.

In the lower temperature range adsorption is principally of the van der Waals' type. In addition a slow adsorption occurs, the rate of which increases with increase in temperature.

After a period of ten hours the pseudo-equilibrium values for isobaric adsorption are a minimum at about 21° and then increase rapidly to values at 142° which are considerably greater than at -82°.

If there is any effect of pressure on the adsorption rate it is very slight.

The heat of adsorption in the low temperature region has been calculated.

Isosteric activation energies for the slow adsorption have

been calculated by the usual method, but the method is criticised.

Measurement of the rate of adsorption, and a maximum adsorption in the optimum temperature range for reaction, by a hydrogenation catalyst of the component to be hydrogenated are reported for the first time.

Definite occurrence of the criteria of activated adsorption in a system in which solubility is exceedingly unlikely have been found. To this extent the first unequivocal proof of the existence of activated adsorption is provided.

This investigation has been carried out at McGill University under the direction of Dr. E. W. R. Steacie, whose unfailing interest and sympathetic criticism have been a source of encouragement and inspiration.

McGill University,
Montreal, Quebec,

April 25th, 1934.

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