were carried out in an unsilvered Pyrex Dewar of about 250 cc. capacity, surrounded by an eutectic mixture of $CaCl_2$–H_2O. A rubber stopper covered with tin foil closed the neck of the Dewar. Through this stopper projected the thermocouple tube, a hand stirrer of glass and a tube for admitting nitrogen or dry air. It was found best to employ a mixture of about 3 parts of carbon tetrachloride to 1 part of methanol, by weight, since this gave a mixture which was about 50% solid and 50% liquid at the transition point. About 75 cc. of this mixture, previously cooled into the transition, was introduced into the Dewar and slowly stirred while readings were taken on the thermocouple. Three determinations gave −47.67, −47.68 and −47.65°, respectively, as compared with the accurate value of −47.66°. The deviations are barely greater than the limits of reproducibility of the thermocouple and are certainly within the limits of error with this simple apparatus. The melting point of the carbon tetrachloride employed in these determinations was also measured in a nearly similar piece of apparatus,[24] and found to be −22.86°, in good agreement with our previous more accurate determination.

The work described in the preceding pages was begun with the assistance of Mr. Sidney J. Simkins, who purified the carbon tetrachloride and assembled a portion of the apparatus. We also wish to acknowledge the able mechanical assistance of Mr. John F. Betz, who constructed the vacuum calorimeter. In particular, we wish to thank Dr. F. G. Brickwedde of the Cryogenic Division of the United States Bureau of Standards who very kindly provided us with calibrations on our thermocouples C and K.

Summary

The transition and melting points of carbon tetrachloride have been measured by an accurate procedure and found to be −47.66 (±0.05)° and −22.87 (±0.05)°, respectively.

The transition has also been measured in a suspension of solid carbon tetrachloride in methyl alcohol and found to be in agreement with the value given above.

Heats of transition and of fusion of carbon tetrachloride have been measured, calorimetrically, and found to be 1080.8 (±3) cal./mole and 577.2 (±1), cal./mole, respectively.

The purity of the carbon tetrachloride employed in the above investigations was tested by the measurement of heat capacities just below the melting point. It was found that the impurity present did not exceed 1×10^{-3} mole per cent.

The transition in solid carbon tetrachloride was found to be both sharp and reproducible. It is concluded that the carbon tetrachloride transition provides a satisfactory secondary fixed point for the calibration of thermometric instruments and a simple procedure for employing it in practical laboratory standardizations is described.

COLUMBUS, OHIO RECEIVED AUGUST 18, 1933

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[24] Kanolt, Scientific Papers, U. S. Bureau Standards, No. 520, p. 622 (1926).

[CONTRIBUTION FROM THE FERTILIZER INVESTIGATIONS UNIT, BUREAU OF CHEMISTRY AND SOILS, DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.]

The Adsorption of Nitrogen by Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND STEPHEN BRUNAUER

Experimental research carried on by various workers[1] to ascertain the mechanism by which ammonia is synthesized from hydrogen–nitrogen mixtures over iron catalysts has culminated in the idea that the nitrogen molecules enter into some sort of adsorptive or chemical combination with the iron atoms in the catalyst surface and are thereby made capable of reacting with gaseous or adsorbed hydrogen to form ammonia.[2] As yet, however, no data have been published to indicate[3] whether or not the actual rate at which nitrogen is taken up by the catalyst surface is sufficiently fast to permit this adsorption to constitute an essential step in the actual synthesis. The present work has, accordingly, been undertaken to measure (1) the rate of adsorption of nitrogen at one atmosphere pressure on active as well as on rather inactive synthetic ammonia catalysts at 200 to 450°, (2) the variation of the vol-

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[1] See Emmett, *J. Chem. Ed.*, **7**, 2571 (1930).

[2] Frankenburger, Ullmans "Enzyklopädie der Technischen Chemie," 1928.

[3] Emmett and Brunauer, THIS JOURNAL, **55**, 1738 (1933).

ume of gas adsorbed with pressure and with temperature, and (3) the variation of the amount of adsorption with pressure at −189°. The activities of the catalysts for ammonia synthesis were determined immediately after some of the rate measurements.

Experimental

(a) **Low Pressure Experiments.**—All experiments relative to the rate and quantity of adsorption at pressures of one atmosphere or less were carried out in the apparatus shown in Fig. 1. The 10 cc. of catalyst in bulb A was reduced in hydrogen at temperatures between 350 and 450° until the water yield was less than 0.1 mg. per hour. Throughout the work liquid air was always kept on trap G or H during reductions to prevent any possible contamination of the catalyst by traces of volatile matter from the stopcock through which the hydrogen entered.

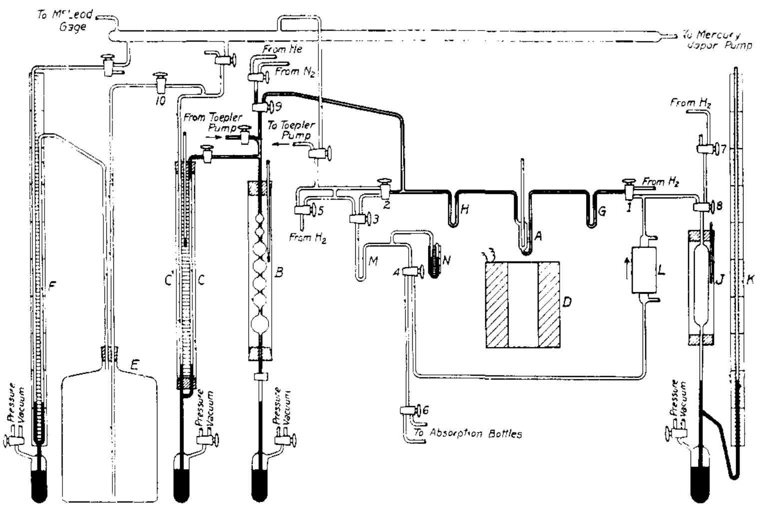

Fig. 1.—Adsorption apparatus.

Before each run the final reduction stage always consisted in circulating 30 or 40 cc. of hydrogen by an all-glass pump L through stopcock 1, liquid air trap G, catalyst A, trap H kept at −78°, stopcocks 2 and 3, liquid air trap M, stopcock 4, and then back to the catalyst again. This circulation was continued until the ammonia frozen out in M per half hour was equivalent to less than 0.02 cc. of nitrogen, as determined by interrupting the flow every half hour, pumping out the trap between stopcocks 3 and 4, closing these again, removing liquid air from trap M and noting the pressure exerted by ammonia on manometer N. One mm. on this manometer was equivalent to about 0.005 cc. of nitrogen.

A uniform procedure was used in evacuating the catalyst before an adsorption run. At the end of each reduction described above, the catalyst was evacuated with a mercury vapor pump for one-half hour at 450°, after which the adsorption measurements were carried out. It is not claimed, of course, that the catalysts were freed completely from dissolved hydrogen, for past experience has shown that many hours of degassing will hardly suffice for this. Nevertheless, by the uniform procedure observed the surfaces are believed to have been rendered comparable in the various runs.

Buret C was 60 cm. long and had a capacity of 5 cc.; the bulbs in buret B were so chosen that any amount of gas up to 50 cc. could be held in the two burets. The uncertainty in each adsorption reading at atmospheric pressure was about 0.05 cc. Throughout each rate of adsorption run the mercury column in C was kept at the same height as in C′. The rates were thus always measured at constant pressure. In the adsorption measurements at less than one atmosphere pressure, C′ was maintained by bottle E at the desired low pressure. Furnace D was equipped with an aluminum block fitting closely around catalyst tube A. The temperature could be kept within ±1° during a run.

The activity of the catalyst for synthesizing ammonia was measured at the end of each particular rate of adsorption run with which comparison was desired by passing 3:1 hydrogen–nitrogen mixture at known rates over the catalyst and through absorption bottles. The ammonia was caught in distilled water and titrated.

(b) **High Pressure Experiments.**—In the high pressure experiments 10 cc. of catalyst 931 was reduced completely in an externally heated nichrome steel bomb[4] and then exposed at high pressure to pure nitrogen or to a very slow stream of pure[5] 3:1 hydrogen–nitrogen gas for one hour at a given temperature. The adsorption equilibrium was then "frozen" by quickly cooling the catalyst bomb to room temperature. Cooling was so rapid that within five minutes the temperature dropped from 450 to about 150°. The pressure was then lowered to one atmosphere and the adsorbed ammonia flushed out with dry nitrogen at 100°. Finally adsorbed nitrogen was removed as ammonia by passing a stream of dry hydrogen at one atmosphere pressure over the catalyst at temperatures that were increased according to a regular schedule up to 450°; the amount of ammonia so formed was determined by titration. Reduction was continued until the exit ammonia concentration was equal to the blank value produced by traces of nitrogen in the hydrogen. The nitrogen adsorption values determined in this manner must of course be only relative; furthermore, because of unavoidable differences between the high and the low pressure procedures, they are not to be compared quantitatively with those obtained in the low-pressure adsorption experiments already described.

Doubly promoted catalyst[6] 931 contained 1.3% Al_2O_3 and 1.59% K_2O; singly promoted catalyst 921 contained 1.31% Al_2O_3. "Pure iron" catalyst 973 was not purposely promoted; it was found however to contain about 0.15% Al_2O_3. Nevertheless it behaved essentially as a pure iron catalyst, giving a conversion of only 3–4% ammonia

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[4] Emmett and Brunauer, This Journal, **52**, 2682 (1930)

[5] Larson and Dodge, *ibid.*, **45**, 2918 (1923).

[6] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

at 450°, 5000 space velocity and 100 atmospheres in contrast to 12–13% for 931, and 8–10% for 921.

Results

The rates of adsorption of nitrogen by catalyst 931 at various temperatures are shown by curves in Fig. 2. Runs 5, 9 and 11 made at about 330°, runs 2 and 3 at about 450° and runs 4 and 10 at about 400° illustrate the reproducibility of the adsorption measurements. Sufficiently accurate values for the energy of activation E_1 involved in the adsorption of nitrogen can be obtained from these data with the help of the equation

$$\log t_1/t_2 = \frac{E_1}{2.303\,R}(1/T_1 - 1/T_2) \qquad (1)$$

t_1 and t_2 being the times required for the adsorption of a given volume of gas at T_1 and T_2, respectively. Plots of log t *vs.* $1/T$ for the runs on catalyst 931 for the adsorption of 1.7, 2.0, 2.3, 2.8, 3.2 and 3.6 cc. of nitrogen indicate energies of activation of 14,400, 14,500, 15,400, 17,100, 18,000 and 16,000 calories, respectively. Similar rate curves for catalysts 921 and 973 are illustrated in Fig. 3. The decrease in activity of catalyst 973 was rapid enough to make the determination of the dependence of rate of adsorption upon temperature impossible. In the rate runs on catalyst 921, some unknown irregularity or poisoning factor caused the last run at 356° to be considerably slower than a previous one at 358°; unfortunately time did not permit us to ascertain definitely the temperature coefficient of adsorption on this catalyst.

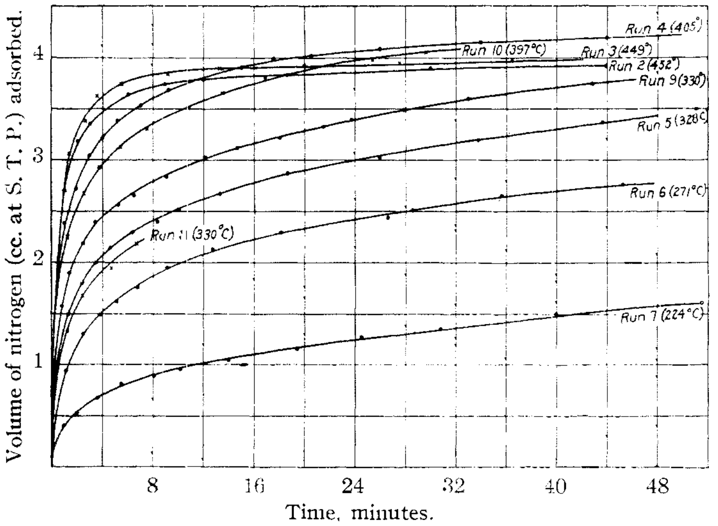

Fig. 2.—Rate of nitrogen adsorption by 16.46 g. (10 cc.) of Fe–Al_2O_3–K_2O catalyst 931 as a function of temperature.

Adsorption isotherms were taken at about 400 and 450° on both catalysts 931 and 921. They are shown in Fig. 4. The curves are, of course, taken from lower to higher pressures, for the desorption of nitrogen was too slow to permit points to be established readily by desorption. In making the individual adsorption determinations for these isotherms sufficient time was allowed at each pressure to permit the equilibrium to be approached so closely that during one-half hour less than 0.05 cc. of gas was adsorbed, an amount approximately equal to the possible experimental error in each reading. From the data of these isotherms pressures p_1 and p_2 corresponding to the adsorption of a given volume of gas at temperatures T_1 and T_2, respectively, can be obtained and the heat of adsorption, Q, calculated. Q is about 35,000 calories per mole of nitrogen for both catalysts for all volumes of adsorbed gas between 2.6 and 3.6 cc.

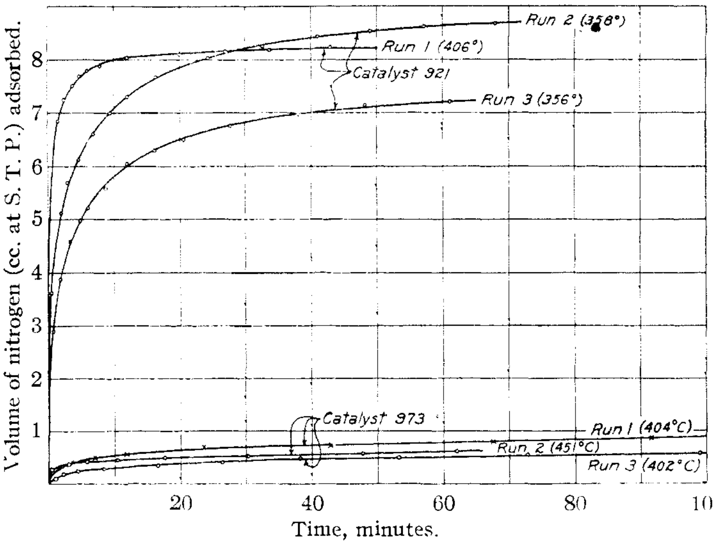

Fig. 3.—Rate of nitrogen adsorption by 18.3 g. (10 cc.) of Fe–Al_2O_3 catalyst 921 and 17.4 g. of pure iron catalyst 973.

Adsorption runs were also made at various pressures with the catalyst at −189°. Equilibration from both the adsorption and desorption sides was almost instantaneous at atmospheric pressure though at 25 mm. pressure it required about nine minutes. These low temperature isotherms shown in Fig. 5 are clearly of the physical type of adsorption. The portion of each isotherm between 100 and 750 mm. is linear, the amount of adsorption being proportional to the pressure. The adsorption was readily reversible, the points taken from the desorption side agreeing well with those taken from the adsorption side.

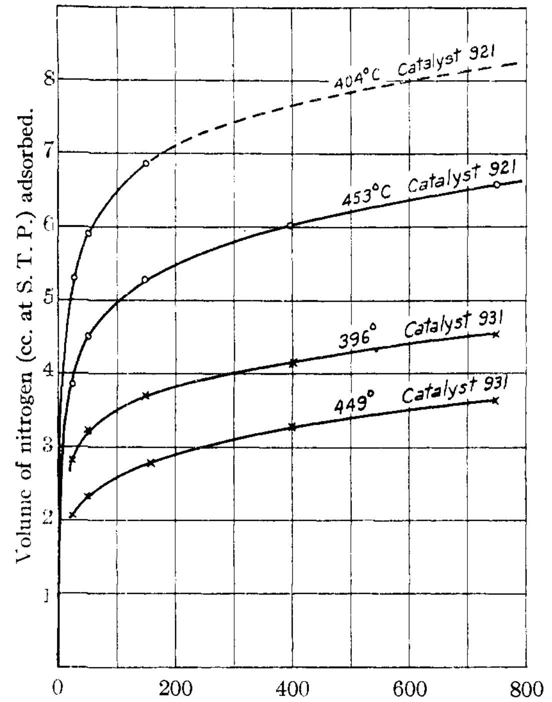

Fig. 4.—Isotherms for the adsorption of nitrogen on catalysts 921 and 931.

Comparison of the rates of ammonia synthesis at a given temperature on different catalysts was made difficult by the fact that in the particular apparatus used the large amount of capillary tubing introduced a considerable resistance to flow so that the maximum rate of gas passage was about 800 cc. per minute. The percentage ammonia in the exit gas from the catalyst at about 400° and a flow of 800 cc. of gas per minute was 0.026 for catalyst 973, 0.178 for catalyst 931 and 0.33 for catalyst 921. Equilibrium at this temperature corresponds to 0.46% ammonia. These rate determinations were made immediately after run 1 on catalyst 973; run 10, catalyst 931; and run 1, catalyst 921, respectively.

The results of the high pressure adsorption experiments on catalyst 931 at 450° are shown in Fig. 6. Part of the experiments were carried out by passing 3:1 hydrogen–nitrogen gas over the catalyst at a space velocity of 100 or less and part of them by using pure nitrogen. The amount of nitrogen adsorbed was approximately the same from pure nitrogen as from an equivalent equilibrium hydrogen–nitrogen–ammonia mixture. The departure of some of the points from the smooth curve can be attributed to unavoidable experimental error attending the determination of the adsorbed nitrogen. The experiments indicate about a two and one-half fold increase in the amount of nitrogen adsorbed by the catalyst when the pressure is increased from 1 to 50 atmospheres of nitrogen.

Discussion

The amount of data obtained in the present experiments does not appear to warrant a lengthy discussion of the approximations involved in the derivation or use of equation 1. It will suffice to point out that its use is equivalent to neglecting the rate of desorption compared with the rate of adsorption in the present experiments, and that the increase of E_1 as V increases from 1.7 to 3.2 cc. is presumably real and would be even greater than observed if corrections were applied for the simplifying assumptions of equation 1. This gradual increase in the value of E_1 with an increase in the volume of gas adsorbed is consistent with similar observations already reported for various gas-solid systems;[7] it would seem to indi-

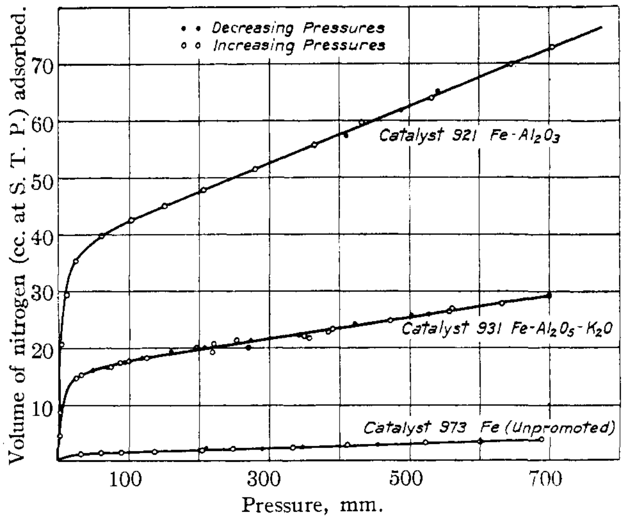

Fig. 5.—Isotherms for the adsorption of nitrogen on catalysts 921, 931 and 973 at −189°.

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(7) Taylor and Williamson, This Journal, **53**, 2168 (1931).

cate that the portions of the surface adsorbing the nitrogen more quickly are those for which a small E_1 value is required.

The heat of adsorption Q calculated from the isotherms, as pointed out above, is about 35,000 calories for catalyst 931. From the relation $Q = E_2 - E_1$, where E_1 is about 16,000 calories, one can calculate E_2, the energy of activation of the desorption process, to be about 51,000 calories. This is in agreement with at least two indirectly estimated values. Winter[8] in studying the decomposition of ammonia over iron concluded that the slow step involved in the decomposition was the escape of nitrogen from the surface. The 50,000 calorie energy of activation found by him for the decomposition would therefore correspond approximately to the energy of activation of the desorption process. Furthermore,[9] recent experiments on the temperature coefficient of the decomposition of Fe_4N prepared by passing ammonia over a doubly promoted catalyst similar to catalyst 931, indicate that the energy involved in the escape of nitrogen from the iron surface is about 50,000 calories.

The isotherm data represented by Fig. 4, agree with the equation of Freundlich, the volume of nitrogen adsorbed increasing in proportion to $(P_{N_2})^{1/6}$; it does not agree with the Langmuir isotherm equation.

A comparatively simple calculation will show that the rate at which ammonia is synthesized by the catalysts used in the present experiments is of the same magnitude as the observed rate at which nitrogen is taken up by the catalyst. Thus, for example, in the case of the pure iron catalyst 973 at 400° at a flow of 800 cc. per minute the exit ammonia concentration was 0.026%. This corresponds to the synthesis of 0.21 cc. of ammonia per minute. On the same catalyst 0.13 cc. of nitrogen, equivalent to 0.26 cc. of ammonia was adsorbed in the first minute. This calculation is very approximate but indicates that the slow step in the synthesis of ammonia may be the adsorption of nitrogen.

The relative activities of the three catalysts at 400° and 1 atmosphere pressure places them in the same relative order as their initial rates of nitrogen adsorption at 300–450°, and as the relative volume of nitrogen adsorbed at −189° or at 300–450°. The present experiments do not, however, reveal any explanation for the well-known fact that at 100 atmospheres pressure doubly promoted catalyst 931 is much more active toward a pure hydrogen–nitrogen mixture than is catalyst 921.

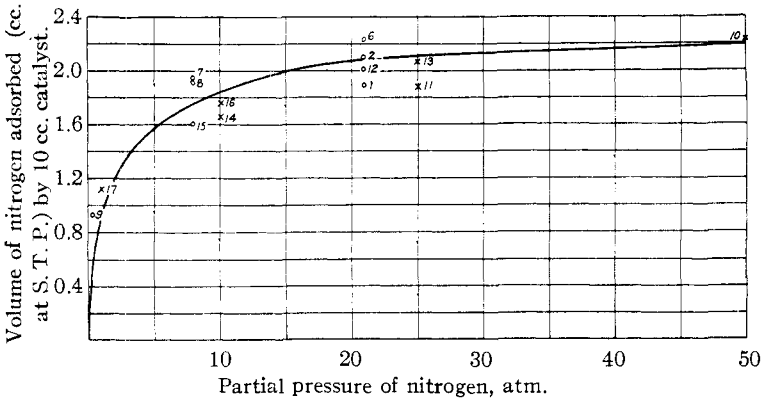

Fig. 6.—High pressure nitrogen adsorption isotherms on catalyst 931 at 450°. Crosses (×××) represent adsorption from pure nitrogen; circles (○○○), from equilibrium H_2–N_2–NH_3 mixtures in which the hydrogen–nitrogen ratio was 3:1 and the partial pressures of nitrogen were those plotted as abscissa.

Thus far we have referred to the nitrogen taken up by the iron catalysts at high temperature as nitrogen adsorbed upon the catalyst surface. However, there is some indirect evidence that part of this nitrogen may actually be dissolved in the iron. Engelhardt and Wagner[10] have studied the kinetics of the reaction

$$Fe + NH_3 = N \text{ (dissolved in } \alpha \text{ Fe)} + 3/2\ H_2 \quad (4)$$

by passing ammonia–hydrogen mixtures over a heated iron foil 0.01 mm. thick and measuring the rate of change in the conductivity of the foil. From the observed kinetics they conclude that the reaction of ammonia with the surface iron atoms is the slow step in the reaction and that only two or three seconds are required for the nitrogen atoms to diffuse throughout the foil at 490°. They further point out that this rate of diffusion is to be expected if the value of the diffusion coefficient is about 2×10^{-8} sq. cm. per second as reported by Eilender and Meyer.[11]

By means of the integrated form of the Fick diffusion equation one can calculate the time t

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[8] Winter, *Z. physik. Chem.*, **B13**, 401 (1931).

[9] Emmett and Love, THIS JOURNAL, **55**, 4043 (1933).

[10] Engelhardt and Wagner, *Z. physik. Chem.*, **B18**, 369 (1932).

[11] Eilender and Meyer, *Arch. Eisenhüttenwesen*, **4**, 343 (1930–1931).

$$\frac{C_0 - C}{C_0} = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-y^2}\,dy$$

necessary for the nitrogen concentration to reach the concentration C at distance x cm. below the surface of a particle of iron catalyst when in the outer few layers of atoms the concentration is C_0. Using 2×10^{-8} sq. cm. per second for k, the diffusion coefficient, one finds that the time required for the concentration C to become equal to $^1/_2$ C_0 is 5×10^{-5} second for $x = 10^{-6}$ cm.; 5×10^{-3} second for 10^{-5} cm.; 0.5 second for 10^{-4} cm.; and 50 seconds for 10^{-3} cm. From these values it would seem that during the one to two hours duration of the present adsorption experiments the nitrogen concentration C at a distance 0.01 cm. below the surface could become half as great as at the surface of the catalyst. Definite conclusions as to the importance of this solubility factor in the iron–nitrogen adsorption measurements must, however, await additional experimental data.

The present experiments yield no conclusive evidence as to whether the nitrogen taken up by the catalyst in the temperature range 250 to 450° is present as atoms or molecules. The following experimental observations seem strongly to suggest, however, that at least part of the surface nitrogen[12] is present as atoms:

(1) The nitrogen in Fe_4N is present in the atomic form according to crystal structure determinations, the nitrogen atoms being about 3.79 Å. apart[13] rather than 1.10 Å. as in the normal molecule.

(2) The nitrogen on the iron surface is chemically active, being reducible by hydrogen at 200° or less to form NH_3. Though a chemically active complex between surface iron atoms and molecular nitrogen could be imagined, the known iron–nitrogen compounds Fe_4N and Fe_2N contain nitrogen in the atomic rather than the molecular form.

(3) The same amount of surface nitrogen is formed by a given pressure of pure nitrogen as by an equivalent partial pressure of nitrogen in a nitrogen-hydrogen-ammonia equilibrium mixture (see Fig. 6, for example).

It is interesting to compare the observed rates of adsorption of nitrogen at 450° with the rate that would result if every nitrogen molecule striking the catalyst surface with an energy of 16,000 calories or more were adsorbed. The ratio of the volume of nitrogen that should have been adsorbed during the first minute by catalyst 931 to the volume actually observed is about 10^6, the surface of 10 cc. of catalyst 931 being estimated as 390,000 sq. cm. by assuming that 16 cc. of nitrogen was needed to form a monomolecular layer (see Fig. 5). The enormously large ratio of calculated to observed rates has already been noted by Taylor[14] in connection with the rate of adsorption of hydrogen by ZnO.

In conclusion it may be well to call attention to a few peculiarities of the adsorption experiments carried out at −189°. Benton and White[15] have carried out experiments similar to our own on catalyst 973. In their nitrogen adsorption curve for −183° a change in slope was obtained at a point corresponding to about 4 cc. of gas adsorption per 10 cc. of catalyst. This was interpreted as being the point at which a monomolecular layer of nitrogen was formed on the catalyst surface. Our own experiments on catalyst 973 show no such break. However, our apparatus was not so well adapted to accurate isotherm measurements at liquid air temperature so that possible experimental errors might have obscured such a break in our run on the pure iron catalyst. Curves representing our adsorption data on catalysts 931 and 921 at −189° likewise show no such breaks. However, in these cases the total adsorption at 760 mm. is a little less than twice the amount corresponding to the extrapolation of the straight line portion of the curves back to zero pressure; it is possible that adsorption measurements carried to a slightly higher pressure might show up a break similar to the one mentioned by Benton and White.

Summary

The rates of adsorption of nitrogen by promoted and by pure iron catalysts have been measured over the temperature range 273 to 450°. The energy of activation of the adsorption process is about 16,000 calories. Isotherms at 400 and 450° indicate a heat of adsorption of about 35,000 calories. Isotherms for adsorption at −189° are

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[12] Either the terminology "surface nitride" (Frankenburger, *loc. cit.*) or "activated adsorption" [Taylor, THIS JOURNAL, **53**, 578 (1931)] appears permissible and adequately descriptive in the present experiments.

[13] Emmett, Hendricks and Brunauer, *ibid.*, **52**, 1456 (1930).

[14] Taylor, *Trans. Faraday Soc.*, **28**, 131 (1933).

[15] Benton and White, THIS JOURNAL, **54**, 1820 (1932).

linear with respect to pressure between 100 mm. and 760 mm.

The rate of nitrogen adsorption is of the right magnitude to be the slow step in the catalytic synthesis of ammonia.

WASHINGTON, D. C. RECEIVED AUGUST 21, 1933

[CONTRIBUTION FROM THE LABORATORY OF COLLOID SCIENCE, CAMBRIDGE UNIVERSITY, ENGLAND]

Monomolecular Films of the Polyesters

BY SANFORD A. MOSS, JR.

Monolayers of substances of high molecular weight such as derivatives of cellulose and of rubber form either condensed or (apparently) liquid expanded films on various substrates. It has recently been shown that monolayers of proteins on aqueous solutions can exist in three characteristic states: two fluid and one gel-like, compatible with the assumption that polypeptide chains are flexible and extend on the water surface.[1] A transition in the properties of monolayers of simple molecules, such as fatty acids and those of substances which exist normally in the colloidal state, is to be anticipated in films of compounds of large and increasing molecular weight that form true solutions, the eucolloids of Staudinger. It appeared of some interest to examine the properties of films of a typical series of such eucolloids. Thanks to the kindness of Dr. W. H. Carothers of E. I. du Pont de Nemours Company, we were provided with specimens of acidic ethylene succinates.[2] These are identified as follows:

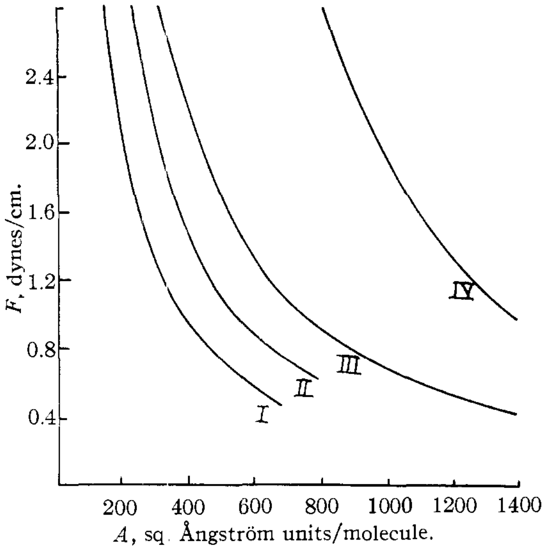

Fig. 1.—Monomolecular films of the polyesters.

No.	M. p., °C.	Mean mol. wt.	Name	Film formation from chloroform
I	73	1070	Acidic ethylene succinate	Yes
II	82	1380–1400		Yes
III	90	1580–1800		Yes
IV	98	3110–3400		Yes
V	103	3000	Neutral ethylene succinate	Yes
VI	...	15,000		Yes
VII	130	300	Cyclic dimeric ethylene succinate	Does not spread

The general formula for the first four is

$$HO—OC—(CH_2)_2—CO—[—O—(CH_2)_2—O—OC—(CH_2)_2—CO—]_n—OH$$

where n is 6, 9, 12 and 23, respectively; of V and VI:

$$H—[—O—(CH_2)_2—O—OC—(CH_2)_2—CO—]_n—O—(CH_2)_2—OH$$

where n is 22 and 100, respectively

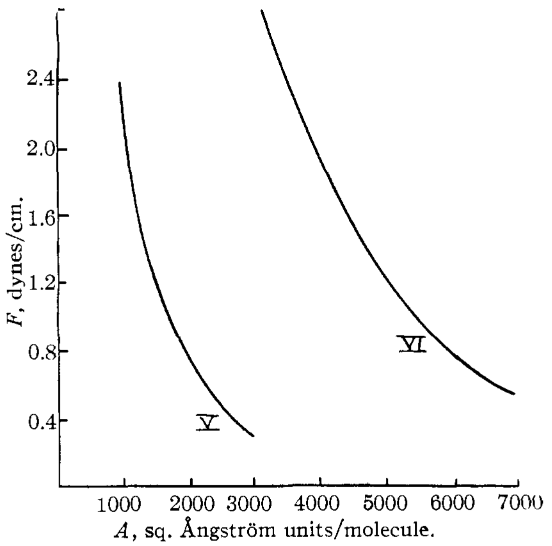

Fig. 2.—Monomolecular films of the polyesters.

With the exception of the cyclic dimeric ethylene succinate, all of the substances when dissolved in chloroform and spread by means of

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(1) Hughes and Rideal, *Proc. Roy. Soc.* (London), **A137**, 62 (1932).

(2) Carothers *et al.*, THIS JOURNAL, **52**, 711 (1930).