neglect of intramolecular cross-linking can be expected to occur at the gel point, this error diminishing with increasing displacement in either direction from the gel point. This conclusion, which is particularly well demonstrated by the above calculations based on the present treatment, also can be deduced from molecular size distribution equations, which display a diminution in the abundance of highly complex finite species with increasing cross-linking beyond the gel point. The physical reasons for this course of affairs beyond the gel point are evident apart from statistical theory.

According to this analysis, statistical calculations beyond the gel point are vitiated less by the disregard of intramolecular connections than is the calculation of the gel point under the same approximation.[1,5] The discrepancies between calculated and observed gel points[1,7] furnish an indication of the magnitude of the error introduced. Presumably its correction would require a distortion of the ρ scales in Figs. 1, 2, 4 and 5, the gel points occurring at somewhat higher values of ρ and the magnitude of the distortion factor diminishing in either direction from the gel point.

The assumption that the units are cross-linked at random should apply satisfactorily to cases where the cross-linkages are introduced by a reaction which occurs subsequent to and independent of the process of polymerization of the chains (*e.g.*, a vulcanization reaction). In the polymerization of dienes, or in the copolymerization of vinyl and divinyl compounds, cross-linkages are formed simultaneously with the main chain polymerization process. Here, according to the most plausible mechanisms for such processes, it can be shown that the distribution of cross-linked units may not be precisely random; the probability that a given structural unit is cross-linked is not entirely independent of the number of other cross-linked units in the same polymer chain.[17] The departure from random cross-linking appears not to be serious, so far as application of the above theory is concerned, unless the polymerization is carried to high conversion.[17]

Whether or not the cross-linking reaction is such as to permit a given unit to enter into more than one cross linkage is of no particular concern provided the degree of cross linking ρ is small.

Polymers in which the cross linkages are formed by a reversible process also may be treated by the present theory. Whether the abundance and disposition of cross linkages is governed by equilibrium, kinetic or stoichiometric factors is irrelevant, so long as they occur at random, or approximately so.

Summary

The constitution of randomly cross-linked polymers containing a sufficient concentration of cross linkages to produce a gel fraction has been treated statistically by a method which avoids the use of molecular size distribution equations. The treatment is sufficiently general to cover any distribution of "primary" polymer chain lengths.

The new theory has been applied, for purposes of illustration, to two arbitrarily selected primary chain length distributions. Results are similar to those previously deduced in a less direct manner from size distribution equations. Limitations imposed by the basic assumptions relating to the absence of intramolecular cross-linking in finite molecular species (sol) and to the random occurrence of cross-linked units are discussed.

[17] Unpublished work.

AKRON, OHIO RECEIVED SEPTEMBER 6, 1946

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, SINCLAIR REFINING COMPANY]

Adsorption–Desorption Isotherm Studies of Catalysts. II. A Comparison of Low Temperature Isotherms of Ammonia and Nitrogen[1]

BY HERMAN E. RIES, JR., ROBERT A. VAN NORDSTRAND AND WILLIAM E. KREGER

As part of a program for the study of adsorption–desorption isotherms of gases on catalysts experiments have been performed with ammonia as the adsorbate. A comparison of the complete isotherms of ammonia with those of nitrogen, which is generally used, is of interest with respect to surface area values, pore volumes, pore radii and general hysteresis effects since the two adsorbates are quite different. The boiling point of ammonia is considerably higher than that of nitrogen, its surface tension is much greater and its molecule is smaller and of higher dipole moment.

Earlier work in these laboratories has demonstrated that nitrogen adsorption–desorption hysteresis effects are remarkably similar for both the pellet and powder forms of two supported cobalt catalysts, H-G and H-A, which are alike in chemical composition but considerably different in area.[1a] The pelleted form of the catalyst of greater area, H-G, was selected for the present ammonia study.

I. Experimental

Apparatus and Materials.—General methods for the study of adsorption isotherms have been described by Em-

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[1] Presented before the Petroleum Division of the American Chemical Society, Atlantic City, April, 1946.

[1a] Ries, Van Nordstrand, Johnson and Bauermeister, THIS JOURNAL, **67**, 1242 (1945).

mett and Brunauer[2,3] and the particular apparatus and procedure employed in these laboratories have been previously reported.[1,4] During the ammonia adsorption experiments thermostating is achieved by use of a liquid ammonia bath (−33°). Temperature variation of the bath is greatly reduced by preserving an ammonia atmosphere above the liquid. This is accomplished by means of relatively tight packing of the Dewar. The saturation pressure, p_0, for these experiments approximates 760 mm.

The adsorbate ammonia, which is obtained from the Ohio Chemical Company, is better than 99% pure (99.95% at the source according to the manufacturer). After transferring ammonia to the all glass isotherm system noncondensable gases are removed by repeated vacuum degassing of the ammonia solidified in liquid nitrogen. A barium oxide drying tube introduced later caused no apparent change in the adsorption isotherms. The purified adsorbate ammonia is also used to fill an ammonia vapor pressure thermometer which provides continuous p_0 readings and the temperature of the liquid ammonia bath in which the catalyst bulb is immersed.

Before each adsorption experiment the catalyst sample is degassed at 340° for sixteen hours by means of a mercury diffusion pump system. The "dead space" volumes are measured with helium of 99.9% purity obtained in Pyrex flasks from the Ohio Chemical Company. These measurements are performed at liquid ammonia temperatures. Ammonia vapor present in the "dead space" is corrected for its deviation from the perfect gas law, 2.64% at 760 mm. and −36°.[5]

The H-G pelleted catalyst studied earlier in nitrogen adsorption-desorption experiments[1a] is the adsorbent for the ammonia studies. The particular catalyst used in this adsorption study was prepared by the reaction between sodium carbonate and a cobalt salt in the presence of suspended diatomaceous earth. The method of preparation was very similar to that described by J. W. Teter.[6] The catalyst was calcined at 350° for two hours.[6a] Diatomaceous earth constitutes approximately fifty per cent. by weight of the supported material. The catalyst is studied in the form of one-eighth inch pellets that have an initial nitrogen area of 229 sq. m./g. Slight sintering, however, takes place at the degassing temperature, 340°, and consequently nitrogen area values are determined frequently throughout the study (see Table III).

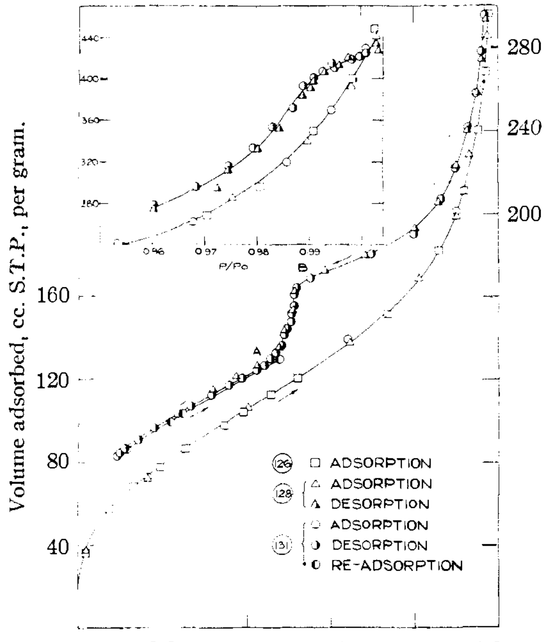

Fig. 1.—Ammonia adsorption-desorption isotherms for H-G pellets at liquid ammonia temperatures.

Adsorption Equilibrium at Low Relative Pressures.—Difficulty was experienced in obtaining adsorption equilibrium in the ammonia experiments. In the low relative pressure range, 0.05 to 0.25, used for Brunauer-Emmett-Teller (BET) area calculations nitrogen adsorption equilibrium at liquid nitrogen temperatures was practically instantaneous. However, in a typical ammonia experiment of this study the fall-off rate in this pressure range was approximately 1 mm. per hour during the first five to ten hour period. Following this initial fall-off a continuous but considerably slower rate of fall of about 0.2 mm. per hour was observed during the next forty hours. Perhaps two different processes are represented by these two rates. For most of the points in the ammonia experiments described here the adsorption system was allowed to stand about twenty-four hours before final readings were made. Less time was permitted in certain portions of the isotherm in which readings were made for relatively small pressure increments. Data obtained in this manner were quite reproducible (see Fig. 1).

Several processes that may be responsible for the slow equilibration have been considered. Activated adsorption[7] or slow surface reaction[8] are reasonable possibilities even

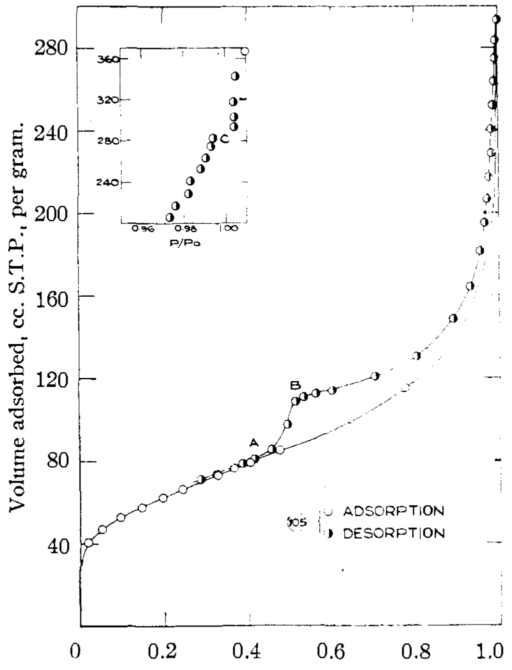

Fig. 2.—Nitrogen adsorption-desorption isotherm for H-G pellets at liquid nitrogen temperatures.

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(2) Emmett and Brunauer, This Journal, **59**, 310 (1937).

(3) Emmett, "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942.

(4) Ries, Van Nordstrand and Teter, *Ind. Eng. Chem.*, **37**, 310 (1945).

(5) Emmett and Brunauer, This Journal, **59**, 1553 (1937).

(6) J. W. Teter, U. S. Patent 2,381,473 (August 7, 1945); *C. A.*, **39**, 5253 (1945).

(6a) Catalyst preparation procedures were supervised by Dr. L. E. Olson of these laboratories.

(7) Taylor, This Journal, **53**, 578 (1931). See also Dew and Taylor, *J. Phys. Chem.*, **31**, 277 (1927), for a discussion of ammonia adsorption at somewhat elevated temperatures.

(8) Frankenburger and Hodler, *Trans. Faraday Soc.*, **28**, 229 (1932).

at −33° since decomposition of ammonia has been detected after adsorption experiments at slightly elevated temperatures. Presumably the catalytic decomposition of ammonia is preceded by activated adsorption.[9] Another explanation of the equilibrium difficulty may be the slow diffusion of ammonia into the small pores of the catalyst. A third factor considered is the polarity of the ammonia molecule which may result in a low surface mobility in the monolayer[10] or a slow re-orientation or packing of the molecules as adsorption proceeds. Displacement of a strongly adsorbed gas[11] is unlikely since the slow rate was observed repeatedly on the same sample. Solution[12] of the ammonia in the high area catalyst is also an unlikely possibility. Slow removal of ammonia by Pyrex surfaces, mercury or stopcock grease has been eliminated as a possible explanation by simple experiments performed in the absence of the catalyst. Interference to adsorption by impurities in the adsorbate has been effectively excluded since mass spectrometer analyses of the ammonia disclose negligible contamination.

Adsorption Equilibrium at High Relative Pressures.—In the high relative pressure region data for both ammonia and nitrogen adsorption are shown slightly above p_0 in the expanded inset plots of Figs. 1 and 2. Pressure in the catalyst bulb system has been found to be consistently 2 to 3 mm. higher than that of the vapor pressure thermometer in this region. The discrepancy cannot be attributed to the uncertainty of the measurement because of the consistent character of the difference. Furthermore the manometers of the catalyst and thermometer systems have been connected and checked satisfactorily against each other. In addition a nitrogen experiment was performed in which the liquid nitrogen containing bulb of the vapor pressure thermometer was sealed inside the catalyst bulb in order to check differences that might be ascribed to nonuniformity of the bath temperature. The "inside" and "outside" thermometer readings were in good agreement.

A thermal transpiration effect arising from the "cold" catalyst bulb and "warm" manometer portion separated by a capillary was considered as a possibility but an unlikely one. In an experiment in which the catalyst bulb contained no catalyst the p_0 values for both the empty catalyst bulb and the thermometer were in almost perfect agreement. Thus the catalyst bulb manometer system with its connecting capillary is not causing observable thermal transpiration.

A possible explanation may be that the vapor pressure in the vapor pressure thermometer is that of a quiescent liquid whereas that in the catalyst system is the vapor pressure of the liquid disturbed by addition and removal of adsorbate gas and the presence of the porous catalyst (acting as ebullition stones). The liquid nitrogen or ammonia in the thermometer may be in an effectively superheated state and thus give a slightly subnormal vapor pressure. Pumping or agitation of the vapor pressure thermometer by repeatedly raising and lowering the mercury column was tried without success however in raising the indicated vapor pressure. Perhaps such agitation was much too mild.

Experiment 105 (Fig. 2) was one of the early studies carried to high relative pressures and the unusually high relative pressure point of 1.01 may have resulted from relatively poor experimental conditions or measurements (*e. g.*, failure to allow sufficient time for equilibrium).

Results and Discussion

Because of the difficulties which were experienced in obtaining equilibrium and because the ammonia adsorption was not reversible at liquid ammonia temperatures certain portions of the following discussion are necessarily qualitative. However, the three adsorption isotherms shown in Figure 1 are in close agreement as are the two desorption curves of the same figure. The sample was thoroughly degassed at 340° before each adsorption experiment plotted in Fig. 1. Additional confirmatory data were obtained but are not shown. Thus good reproducibility is demonstrated in spite of the difficult equilibrium problem.

Area.—Nitrogen areas[13] were determined at intervals during the ammonia studies since slight sintering is observed at 340°, the degassing temperature (see Table III). The average loss in area is, however, less than 1% during a sixteen hour evacuation at 340°. The nitrogen area obtained in Experiment 124 (217 sq. m./g.) may be compared with that determined with ammonia shortly thereafter in Experiment 126 (238 sq. m./g.). The data of these two experiments are plotted according to the BET equation in Fig. 3 and fall on good straight lines between 0.05 and 0.25 relative pressures.

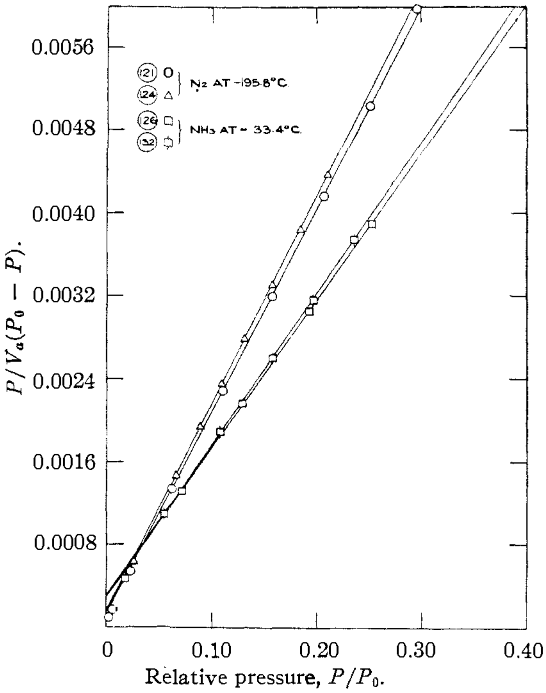

Fig. 3.—Adsorption of nitrogen and ammonia by catalyst H-G according to BET equation.

The adsorbate molecular areas used for the surface area calculations are those suggested by Emmett and Brunauer using liquid densities: nitrogen, 16.2 sq. Å., and ammonia, 12.9 sq. Å.[5] Since these values give a greater catalyst area by ammonia adsorption (approximately 10%) more pore surface may be available to the smaller ammonia molecule than to the nitrogen. However, assuming the total surface reached by the nitrogen and ammonia adsorbates to be identical the ef-

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[9] Love and Emmett, THIS JOURNAL, **63**, 3297 (1941).

[10] Gleysteen and Dietz, *J. Research Natl. Bur. Standards*, **35**, 285 (1945).

[11] Allmand and Chaplin, *Trans. Faraday Soc.*, **28**, 223 (1932).

[12] Ward, *ibid.*, 399 (1932).

[13] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

fective area of the ammonia molecule may be calculated from the catalyst area (nitrogen, BET) and the number of ammonia molecules in the monolayer (BET). The ammonia molecular area thus calculated is 11.8 sq. Å. The area of the ammonia molecule calculated from the density of solid ammonia (−80°) is 11.7 sq. Å.[5]

Another factor that may be important is activated adsorption.[7] If activated or slow irreversible adsorption is appreciable below 0.3 relative pressure it may complicate the adsorption isotherm by giving too great an area in a manner similar to that of Emmett and Brunauer's rapid "chemisorption."[2] Physical adsorption will take place over the chemisorbed or activatedly adsorbed molecules. The relatively good agreement between the BET ammonia and nitrogen areas indicates that activated adsorption is not extensive during the period required to reach 0.3 relative pressure. However, the area calculated from the ammonia desorption isotherm (experiment 131) is 286 sq. m./g. as compared with 238 sq. m./g. calculated from the adsorption curve. Thus during the course of an ammonia experiment, which may extend three to four weeks, approximately one-fifth of a monolayer is irreversibly adsorbed at liquid ammonia temperatures.

To exclude the factor of ordinary hysteresis[1a] from this particular irreversible effect an adsorption–desorption experiment was performed below 0.4 relative pressure since it is believed that ordinary hysteresis does not occur in this low relative pressure region. The fact that the desorption points fell above those of adsorption indicates that irreversible adsorption is occurring below the point at which hysteresis is generally attributed to pore structure characteristics. The occurrence of this slow "chemisorption" below 0.4 relative pressure is supported also by the fact that the adsorption and desorption branches of the complete isotherms of Fig. 1 are closer at 0.4 than at 0.1 relative pressure. Nevertheless any ammonia that is irreversibly adsorbed at liquid ammonia temperatures is removed during the sixteen hour evacuation at 340° since good reproducibility in the adsorption isotherms is obtained after such treatments. If adsorbed ammonia were not completely removed by this degassing treatment less would be adsorbed in the succeeding experiments.

Hysteresis, Pore Structure and Pore Volume.—A pronounced adsorption–desorption hysteresis effect is observed in the ammonia isotherms (Fig. 1) and there is great similarity in the contours of the ammonia and nitrogen hysteresis curves (Fig. 2). A sharp break in the desorption curves at 0.5 relative pressure is common to both, and both desorption curves approach linearity at 0.4 relative pressure. At 0.4 relative pressure the nitrogen desorption curve rejoins the adsorption branch; the ammonia desorption isotherm, however, remains above its adsorption branch. Nevertheless an equilibrium is apparently reached at this lower portion of the ammonia desorption curve since re-adsorption data (Fig. 1, experiment 131) are in good accord with the desorption points.

Application of the simple Kelvin equation to the steepest portion of the ammonia desorption isotherm (0.5 relative pressure) gives a pore radius value of 15 Å. as compared with 13 Å. obtained in the nitrogen experiments. Pore radii thus calculated do not include the thickness of the adsorbed film. The Kelvin equation and the values used for the nitrogen and ammonia calculations are given in Table I. The values in Table I indicate the rather wide differences in the physical properties of the adsorbates. The pore radii calculated are of preliminary interest only since many assumptions are inherent in the application of the Kelvin equation to adsorption isotherms.

TABLE I

NITROGEN AND AMMONIA VALUES USED FOR CALCULATIONS WITH THE KELVIN EQUATION, $\ln p/p_0 = -2V\sigma/rRT$

V is the molal volume of the liquid adsorbate, σ its surface tension, r the capillary radius, R the gas constant, T the absolute temperature, p the equilibrium pressure and p_0 the saturation pressure.

	Nitrogen (−195.8°)	Ammonia (−33.4°)
σ	8.4 dynes/cm.[a]	41.2 (−29°)[b]
d^t_4	0.808 g./cc.[c]	0.682[c]
V	35.0 cc./mole	25.0
R	8.314×10^7 egs/mole degree	8.314×10^7
T	77.4°K.	239.8° K.
p/p_0 (used)	0.5	0.5
r (calcd.)	13 Å.	15 Å.

[a] Landolt–Börnstein "Physikalisch-chemische Tabellen," Vol. I, Julius Springer, Berlin, 1923, p. 242. [b] "International Critical Tables," Volume IV. [c] "International Critical Tables," Volume III.

The desorption curve at p_0 is used to obtain the V_s value from which the pore volume (P_g, cc. per g.) is calculated.[1a] The ammonia isotherm gives a V_s value of 424 cc. (see Table II) or a P_g value of 0.47 cc./g. A liquid ammonia density of 0.682 g./cc. is used in the pore volume calculations. Although the P_g value obtained with ammonia, 0.47 cc./g., is a little greater than that found with nitrogen, 0.45 cc./g., it is in agreement with the helium-mercury displacement measurements (0.47 cc./g.). The smaller size or greater polarity of the ammonia molecule may account for a P_g value greater than that obtained with nitrogen. Activated adsorption may also be responsible for closer packing.

The pore volume emptying in the 0.5 relative pressure region is also slightly greater for ammonia than for nitrogen. As shown in Table II the $V_B - V_A$ value gives a volume of 0.047 cc./g. emptying in the ammonia experiments (0.53 to 0.43 relative pressure) whereas only 0.042 cc./g. empties in the nitrogen experiments (0.52 to 0.42 relative pressure). It is of interest that these values, 0.047 and 0.042 cc./g., are very close to

10% of their respective total P_g values, 0.47 and 0.45 cc./g.

The approximate number of layers deposited at p_0 are 5.8 for nitrogen and 6.2 for ammonia (Table II). Since there is a great difference in polarity between the two adsorbates the polar forces are less significant than the pore structure in determining the amount adsorbed at the saturation pressure on this type of porous solid. Evidence of a different nature supporting this viewpoint has been presented previously.[1a]

TABLE II

H-G PELLETS, NITROGEN AND AMMONIA ISOTHERM CHARACTERISTICS

	Adsorbate	
	Nitrogen	Ammonia
V_m, cc./g. (monolayer)	49.8 (exp. 124)	68.6 (exp. 126)
Area, sq. m./g.	216.7 (exp. 124)	237.9 (exp. 126)
V_s, cc./g. (at p_0)	290 (exp. 105)	424 (exp. 131)
P_g, cc./g. (from V_s)[a]	0.45	0.47
V_A, cc./g.	82 (0.42 p_0)	125 (0.43 p_0)
V_B, cc./g.	109 (0.52 p_0)	167 (0.53 p_0)
$V_B - V_A$, cc./g.	27	42
P_g', cc./g. (from $V_B - V_A$)	0.042	0.047
V_s/V_m (approximate number of layers at p_0)	5.8	6.2
r, Å. (Kelvin pore radius at 0.5 p_0)	13	15

[a] P_g by the helium–mercury displacement method = 0.47 cc./g.

Heats of Adsorption.—A preliminary statement may be made at this time on the heat of adsorption, ΔH_a, of ammonia on the H-G catalyst. Heat of adsorption values are calculated from the available adsorption data by two methods, the Clausius–Clapeyron equation and the "c" constant method of Brunauer, Emmett and Teller.[13] The BET "c" term is defined as $(a_1b_2/a_2b_1)e^{(E_1 - E_L)/RT}$; where E_1 is equal to the average heat of adsorption for the monolayer, E_L is equal to the heat of liquefaction and a_1b_2/a_2b_1 is a constant term assumed to be unity. Because of various assumptions which need not be discussed here both methods give only approximations. Application of the Clausius–Clapeyron equation is further strained because of the wide temperature range used, -33 to 0°, and the possibility of combined activated and physical adsorption. The -33 and 0° isotherms at an adsorption value of 60 cc./g. give, by the Clausius–Clapeyron relation, a ΔH_a of 7580 cal./mole and at an adsorption of 70 cc./g. (68.6 = V_m) a value of 7110 cal./mole. A ΔH_a value of 7390 cal./mole is obtained from the BET "c" constant for the -33° isotherm.

Dr. P. H. Emmett has suggested that if chemisorption is occurring probably more would be observed at 0° than at -33°.[14] Consequently the ΔH_a values calculated by means of the Clausius–Clapeyron equation would be too small. In a recent discussion of the BET equation by Cassie[15] the constant term, a_1b_2/a_2b_1, in the expression for "c" is changed to yield higher ΔH_a values. The increase in the heat of adsorption according to Cassie is approximately $RT \ln 50$ calories per mole.

These heat of adsorption values may appear somewhat high for physical adsorption. However the heat of liquefaction of ammonia is of considerable magnitude, 5570 cal./mole at -33.4°. The heat of adsorption values for ammonia as well as the comparisons of the ammonia and nitrogen isotherms included in the preceding sections of this discussion support the viewpoint that the ammonia adsorption is substantially of the physical type.

Note on Harkins–Jura Area Calculations.—There is considerable current interest in the comparison of area values calculated by the Brunauer–Emmett–Teller (BET) and Harkins–Jura (HJ) methods.[16,17,18] Excellent agreement between the two methods is found in the nitrogen isotherm series for the H-G catalyst presented in Table III. The difference in the area values as calculated by the two methods is in every case less than 2%. Since the HJ method is presumably independent of the molecular area of nitrogen, the effective area of the nitrogen molecule on H-G closely approximates the 16.2 sq. Å. value recommended by Emmett and Brunauer.[5]

TABLE III

BET AND HJ NITROGEN AREAS OF H-G PELLETS

Expt. no.	Nitrogen areas, sq. m./g. BET[a]	HJ[b]
101	229	226
103	227	223
104	225	222
105	224	224
121[c]	223	224
124	217	218
138	208	204

[a] Ref. 13. [b] Ref. 16. [c] Second sample.

In the HJ method a plot of $1/V_a^2$ *vs.* $\log p/p_0$ is used (see Fig. 4). The best straight line is drawn through the points in the relative pressure range 0.1 and 0.4[19] and the slope "s" of this line substituted in the equation

$$\Sigma = ks^{1/2}$$

in which Σ is the area (sq. m./g.) and the constant, "k," has a value of 4.06 for nitrogen at liquid nitrogen temperatures. Points not on the straight lines in Fig. 4 deviate in the direction of the expected trend.

In order to apply the HJ method to ammonia experiments it is necessary to determine the

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[14] Emmett, private communication.

[15] Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).

[16] Harkins and Jura, THIS JOURNAL, **66**, 1366 (1944).

[17] Emmett, *Ind. Eng. Chem.*, **37**, 639 (1945).

[18] Beebe, Beckwith and Honig, THIS JOURNAL, **67**, 1554 (1945).

[19] Jura, private communication.

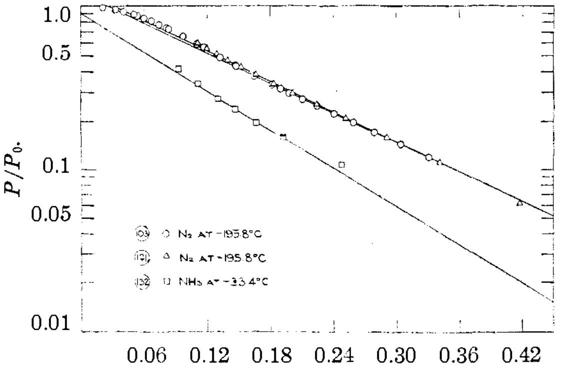

Fig. 4.—Nitrogen and ammonia adsorption by catalyst H-G according to Harkins–Jura equation.

"*k*" constant for ammonia. This is best accomplished by careful ammonia adsorption measurements on a non-porous titanium oxide sample of known area (BET or HJ "absolute" method). However, since the BET and HJ areas are in excellent agreement for nitrogen on the H-G catalyst a preliminary value of "*k*" for ammonia at liquid ammonia temperatures is calculated from the nitrogen area of H-G and the slope of the ammonia HJ plot. The value obtained is 3.46. It is assumed in the calculation of "*k*" that pore structure and surface composition factors are not significant.

Acknowledgment.—The authors wish to thank Mr. E. C. Herthel and Mr. J. W. Teter for their interest and advice, Mr. M. F. L. Johnson and Mr. J. Melik for suggestions and assistance, Miss Sarah Siebenmorgen for calculating and plotting, and Mr. R. D. Duncan for preparing the figures. The authors are also grateful to Dr. P. H. Emmett for his valuable criticism of the original manuscript.

Summary

Adsorption–desorption isotherms of ammonia on a high area supported cobalt catalyst at liquid ammonia temperatures have been studied and are compared with those obtained using nitrogen at liquid nitrogen temperatures. The results are discussed with respect to surface area values, hysteresis characteristics, pore volumes, pore radii and heats of adsorption. Experimental methods for the ammonia studies are described along with an outline of possible explanations for the slow rate of approach to adsorption equilibrium. Adsorption data obtained with the two adsorbates are quite similar except for the failure of the desorption branch of the ammonia isotherm to rejoin the adsorption curve. The Brunauer–Emmett–Teller and Harkins–Jura area values calculated from the nitrogen isotherms of this study differ by less than two per cent.

EAST CHICAGO, INDIANA RECEIVED SEPTEMBER 3, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

A Mechanism for the Hydrolysis of Cyanamide in Acid Solution

BY MARY L. KILPATRICK

The mechanism here proposed for the hydrolysis of cyanamide in acid solution is offered with the view that it may throw light upon some of the anomalies which have been observed in the hydrolysis of nitriles. It is based upon kinetic measurements with water as solvent, already reported,[1] and upon unpublished results obtained in this Laboratory with alcohol as solvent.[2] In water, the product of solvolysis is urea, in alcohol, the salt of the alkyl isourea.[3] The results of the kinetic measurements are summarized below.

With water as solvent: (i) The rate of hydrolysis of cyanamide is the same in dilute solutions of various strong acids, very different in concentrated solutions. (ii) In nitric acid solution, the rate increases continuously as the acid concentration increases, and the measured energy of activation shows no change with acid concentration. (iii) In hydrochloric and in hydrobromic acid solution, the rate increases to a maximum, and thereafter drops off, as the acid concentration increases. The energy of activation increases with acid concentration in both cases. (iv) In trichloroacetic acid solution, and in dichloroacetate and acetate buffers, the hydrolysis is more rapid than is anticipated from the hydrogen ion concentration. The catalytic constant for the trichloroacetic acid molecule, calculated on the assumption of general acid catalysis, is greater than that for the hydrogen ion; consequently the data are to be interpreted rather as basic catalysis of the cation of cyanamide.

With methyl or ethyl alcohol as solvent: (v) The solvolysis is more rapid than in water. For instance, in 0.1 *N* hydrochloric acid solution, at 30°, the formation of methyl isourea hydrochloride is *ca.* 150 times, and that of ethyl isourea hydrochloride 50 times, as fast as the formation of urea in the aqueous acid solution. (vi) The rate drops off with increasing concentration of hydrochloric acid at quite low acid concentrations, and since

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(1) Sullivan and Kilpatrick, THIS JOURNAL, **67**, 1815 (1945).

(2) M. J. Sullivan, unpublished work.

(3) Stieglitz and McKee, *Ber.*, **33**, 810, 1518 (1900); McKee, *Am. Chem. J.*, **26**, 209 (1901).