desoxycodeine had the melting point 184.5–185.5° (red liquid) and $[\alpha]^{26}\mathrm{D}$ −156.7° (benzene, c = 0.434).

Anal. Calcd. for $C_{18}H_{20}O_2NBr_3$: C, 41.39; H, 3.86. Found: C, 41.04; H, 3.97.

A solution of 514 mg. of tribromodihydrodesoxycodeine in 10 cc. of alcohol with Adams catalyst absorbed three moles of hydrogen. The resulting hydrobromide yielded a monobromotetrahydrodesoxycodeine, sparkling crystals from acetone or ethyl acetate, m. p. 116–117.5°, $[\alpha]^{25}\mathrm{D}$ −3.3° (alcohol, c = 0.305). It is soluble in dilute alkali, precipitated by carbon dioxide; ferric chloride test pale emerald-green. It is not the same as the bromotetrahydrodesoxycodeine obtained by bromination of tetrahydrodesoxycodeine.

Anal. Calcd. for $C_{18}H_{24}O_2NBr$: C, 59.00; H, 6.60. Found: C, 59.19; H, 6.69.

Reduction of 102 mg. of the monobromotetrahydrodesoxycodeine (m. p. 117°) in alcohol with 2 g. of sodium gave a nearly quantitative yield of crystalline base, which was sublimed twice in an oil-pump vacuum at 110°. It formed clumps of needles of m. p. 88–89°, halogen-free, structure uncertain. It is slightly soluble in alkali and is reprecipitated by carbon dioxide, ferric chloride test brown-green.

Anal. Found: C, 72.49; H, 7.90.

Bromination of Desoxycodeine-A.—To a solution of 10 g. of desoxycodeine-A in 100 cc. of glacial acetic acid, 6.5 g. of bromine in 50 cc. of glacial acetic acid was added slowly during four hours. Removal of acetic acid *in vacuo* and dilution with water gave a crystalline hydrobromide, which yielded a base of m. p. 189–189.5° (from acetone); $[\alpha]^{25}\mathrm{D}$ +10.2° (benzene, c = 0.979). Analyses showed the presence of two bromine atoms, but otherwise did not agree with any reasonable formula.

When desoxycodeine-A is treated with hydrogen bromide in glacial acetic acid, a base is obtained which contains one bromine atom, and which on further treatment with bromine yields the above-mentioned dibromo compound. The hydrogen bromide addition product has the m. p. 149–151°, $[\alpha]^{25}\mathrm{D}$ −3.8° (alcohol, c = 0.793) and likewise gives analytical data which cannot be interpreted.

Acetolysis of "dibromodihydrodesoxycodeine-A" was accomplished by heating under reflux 8.3 g. of the base with 1 g. of sodium acetate in 30 cc. of acetic anhydride. The product, isolated in the usual way and sublimed in an oil-pump vacuum, was 1-bromoacetylmethylmorphol, m. p. 163–165.5°.

Bromodihydrodesoxycodeine-D.—This compound was prepared for comparison with the other brominated desoxycodeines by treatment of dihydrodesoxycodeine-D in glacial acetic acid with the calculated amount of bromine. It likewise may be prepared using bromine water. After crystallization from acetone and methanol, it melts at 156–157° and has $[\alpha]^{26}\mathrm{D}$ −37.6° (alcohol, c = 0.985).

Anal. Calcd. for $C_{18}H_{22}O_2NBr$: Br, 21.95. Found: Br, 22.14.

Summary

1. Bromomorphine has been degraded through bromocodeine and bromoacetylmethylmorphol to 1-bromo-3,4-dimethoxyphenanthrene.
2. The synthesis of 1-bromo-3,4-dimethoxyphenanthrene and of 2-bromo-3,4-dimethoxyphenanthrene by the Pschorr method is described.
3. Reduction of bromochlorocodide with zinc and alcohol leads to a bromodesoxycodeine-C, which can be degraded by the Hofmann method to 1-bromomethylmorphenol.
4. The bromination of desoxycodeine-A, of desoxycodeine-C, and of dihydrodesoxycodeine-D has been studied.
5. The significance of the results for the question of the structure of pseudomorphine is discussed.

UNIVERSITY, VIRGINIA RECEIVED JUNE 14, 1937

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF THE MICHIGAN STATE COLLEGE]

The Heat of Wetting of Activated Silica Gel[1]

BY D. T. EWING AND GEORGE T. BAUER

The structure of silica gel has been rather definitely shown by Fells and Firth[2] and Jones[3] to consist of capillary pores creating an enormous surface and internal volume and giving to a gel the property of sorption. As this large surface has associated with it a great amount of energy, destruction of this surface by water will give a heat effect whether it is done by water vapor or water liquid. To destroy this surface partially in steps and to measure the remaining surface energy was the purpose of this work.

In this investigation special attention was given to the preparation of the hydrated gel. Unless the proper precautions are observed irregular results are found in heat effect measurements. The percentage of hydrated water does not alone define the activity of the gel. It is equally important that the water is distributed in a manner to give a uniform surface energy. As a means of partially destroying the surface of the

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(1) A portion of a Ph.D. thesis presented by Mr. George T. Bauer to the Graduate Faculty of the Michigan State College, December, 1936.

(2) Fells and Firth, *J. Phys. Chem.*, **29**, 241 (1925).

(3) Jones, *ibid.*, **29**, 327 (1925).

gel, its water content was varied by either adding or removing water at very definite vapor pressures. The surface of the gel can have active points or centers which in the equilibrium state would be covered by a deeper layer of water than the less active centers. This would allow a surface to result, any part of which has the same vapor pressure and uniformly distributed surface energy. To allow distillation from points of higher vapor pressure to those of lower vapor pressure in order to reach equilibrium with the vapor in which the gel is placed, time is required (usually several days) and interfering agencies such as air and changing temperature must be absent. A gel so constituted should have a very uniform activity as measured by heat of wetting, sorption, etc. Zsigmondy, Bachman and Stevenson,[4] van Bemmelen,[5] and Anderson[6] attempted to prepare such a gel by equilibrating it over sulfuric acid solutions of different concentration. A marked hysteresis effect was noted in their studies of adsorption and desorption of water vapor. Patrick and McGavack[7] observed no hysteresis in their investigations of the adsorption of sulfur dioxide on silica gel and ascribed hysteresis effect to the presence of air. Later, Patrick[8] observed no hysteresis in the adsorption and desorption curves for water vapor on silica gel. Ray and Ganguly[9] found a hysteresis effect with water vapor on gel in their experiments carried out at high vacuum.

In this work no hysteresis effect was noted. All gels were equilibrated over the proper sulfuric acid solutions in a vessel which was evacuated of air.

Lamb and Coolidge[10] and Harkins and Ewing[11] expressed the opinion that vapors strongly adsorbed on a surface were held there by a sufficiently strong force to cause great compression. Harkins and Ewing indicated that the surface energy of an adsorbent is the seat of great energy and calculated a value of several thousand atmospheres pressure holding adsorbed molecules on a surface of carbon. Coolidge,[12] who previously had given a value of many thousand atmospheres for the force of compression, later decided that his value for compression was too high and instead of stating that net heat of adsorption was due to compression decided on a correlation with Polanyi's theory and destruction of surface. Patrick and Grimm[13] calculated the area exposed by 1 g. of silica gel from heat of wetting measurements on the theory that the gel exhibited a water surface and the heat evolved developed from destruction of the total surface energy of this water surface. Patrick and Greider[14] determined the heat of wetting of silica gel by water vapor at saturation at 0° and results obtained were in agreement with the calculations of total surface energy yielding the net heat of adsorption.

Experimental

Apparatus.—The electrically calibrated adiabatic calorimeter including its accessories incorporated most of the features of calorimeters of previous investigators.[15] The accessories included a nichrome heating element with heavy copper lead wires, a twenty-four couple copper-constantan thermopile, a five-degree Beckmann thermometer, a metallic four paddle and blade stirrer with a glass shaft, and an especially designed support for the bulbs.

The nichrome heating element was 5 cm. in length, welded and soldered to two heavy copper lead wires which were coated with an insulating shellac. The thermopile, connected to a Leeds and Northrup wall type galvanometer indicated temperature differences between the inner calorimeter and outer bath. The thermocouples were each welded and then insulated with a thin coating of special shellac. The support for the bulbs was a very light metallic cradle with a sharpened screw for breaking them and the whole assembly held in the calorimeter by a glass tube through which a glass rod operated as a means of tightening or loosening the screw.

Two Beckmann thermometers inserted one in the inner silvered calorimeter and one in the outer copper sulfate bath were read by an adjustable eye piece clamped to their stems.

The inner and outer stirrers for the inner calorimeter cup and copper sulfate solution, respectively, were powered by an a. c. 1250 r. p. m. motor. The relative speeds of the two stirrers could be regulated by means of adjustable pulley wheels.

The calorimeter cup was turned out of a brass block giving walls 0.7 mm. thick and was silver plated to ensure against corrosion. This silvered cup was 1 cm. from the brass container which with its ground brass cover was completely submerged in a copper sulfate bath. There was at least 7 cm. of copper sulfate solution surrounding this brass container. For entry into the silvered cup the ground brass cover included five brass chimneys 15 cm. in length.

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(4) Zsigmondy, Bachman and Stevenson, *Z. anorg. Chem.*, **76**, 189 (1912).

(5) Van Bemmelen, *ibid.*, **30**, 265 (1902).

(6) Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

(7) Patrick and McGavack, THIS JOURNAL, **42**, 946 (1920).

(8) Patrick, *Colloid Symposium Monograph*, **7**, 129 (1929).

(9) Ray and Ganguly, *Trans. Faraday Soc.*, **30**, 997 (1934).

(10) Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).

(11) Harkins and Ewing, *ibid.*, **43**, 1787 (1921).

(12) Coolidge, *ibid.*, **48**, 1795 (1926).

(13) Patrick and Grimm, *ibid.*, **43**, 2144 (1921).

(14) Patrick and Greider, *J. Phys. Chem.*, **29**, 1031 (1925).

(15) Williams and Daniels, THIS JOURNAL, **46**, 903 (1924); Ewing and collaborators, *ibid.*, **54**, 1335 (1932); W. P. White, *ibid.*, **36**, 2292 (1914).

For preventing heat transfer from the inner calorimeter to the copper sulfate bath a 110-v. alternating current was passed directly through the copper sulfate solution, using its container as one electrode and a perforated insulated copper shield around the brass container as the other electrode. A stirrer in the copper sulfate bath eliminated the danger of localized heating and a water-cooled copper coil lowered the temperature of the bath when desired. This assembly was then placed in an air-bath[16] at 25° constant to 0.02°. The cabinet for the air-bath was equipped with the usual devices for constancy including a mercury thermoregulator, a dry cell relay, an air fan with motor, nichrome wire heating element No. 32, 5 cm. long, and a water-cooled copper coil and bank for cooling.

For measuring the energy of the direct current, which was supplied by two 6-v. batteries connected in parallel, used in equilibrating the heat equivalent of the calorimeter, the following pieces of equipment were used: Type "K" potentiometer, Leeds and Northrup galvanometer, Standard Weston Cell No. 56567 of 1.0186 v., 0–6 d. c. ammeter, and a Leeds and Northrup Standard resistance of 0.1 ohm and 15 amp.

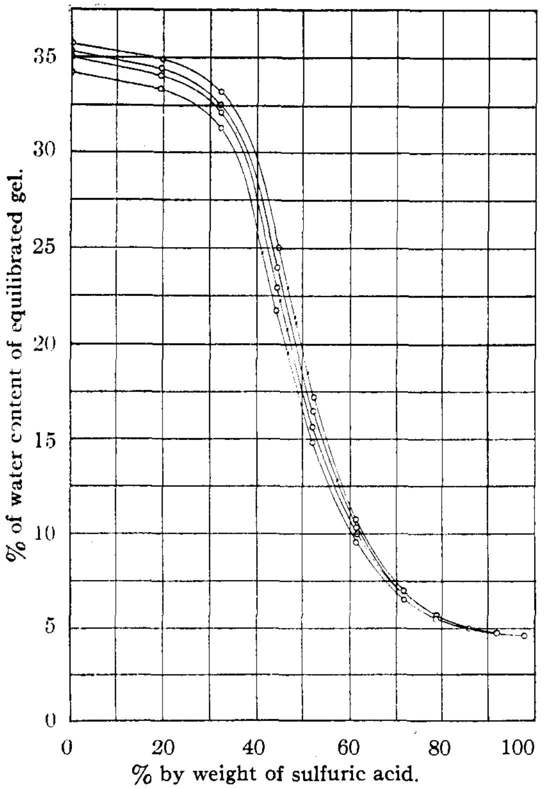

Fig. 1.—Percentage water content of silica gels equilibrated over sulfuric acid solutions at 15, 25, 40 and 60°.

Material.—Commercial samples of silica gel of a very uniform conformation and remarkably free from metallic impurities as shown by spectrograms were used throughout this investigation. The gel was sorted to pass a 3-mm. sieve and to be retained by a 2-mm. sieve. All discolored, crumbly and opalescent particles were separated from the clear transparent ones over a black surface and discarded.

The water used for the heat of wetting determinations was low conductivity grade. The sulfuric acid and phosphorus pentoxide were both of c. p. quality.

Procedure.—Three different methods for preparing silica gel with a definite water content were followed in this investigation. By these methods it was possible to prepare gels with definite water contents ranging in amounts up to 36% and to reproduce them as desired.

In the first method a procedure which was a modification of that of van Bemmelen was followed. The gel was suspended in an atmosphere of water vapor above a solution of sulfuric acid of a known definite concentration. The system was evacuated as regards air. By using a comparatively large amount of sulfuric acid solution the vapor pressure was kept sufficiently constant during the time necessary to equilibrate the gel to a definite vapor pressure and water content. Using approximately 2.4 g. of gel as received and working in quadruplicate through eleven different atmospheres of controlled vapor pressure spaced from lowest pressures to saturation and through four temperature ranges the graph Fig. 1 was obtained. These adsorption–desorption reversible curves indicating no hysteresis could be duplicated and were duplicated three years later which might indicate that the gel did not change upon standing. Three to four days were found sufficient to prepare gel whose vapor pressure under set conditions was at equilibrium with that of the acid solution over which the gel was suspended and whose water was evenly distributed over the surface of the gel as regards total surface energy exposed. By this method gels could be reproduced at any desired water content between the limits of 4.6 to 36.2%. No matter what the water content of the gel as received this method gave expected results within its range.

In the second method gels of a water content as low as 1.4% could be prepared. The sulfuric acid solution used in the above method was replaced by phosphorus pentoxide. The silica gel was suspended in a vessel containing also phosphorus pentoxide and evacuated of air. The temperature of the gel and water vapor surrounding it was regulated by an electric heating element around the gel, and its temperature was read by an iron–constantan thermocouple. The temperature of the phosphorus pentoxide on the bottom of the vessel was kept constant at about 25°. The gel prepared in this manner was tested for the presence of metallic elements by a medium quartz spectrograph with results which showed it to be remarkably free from metallic impurities.

In the third method the gel was heated in a vacuum apparatus at various temperatures to a pressure of 0.0001 mm. The gel was contained in individual spherical capsules sealed into the vacuum system and were removed by sealing off at various time intervals. This procedure required a longer time than either of the other two methods and gave results in agreement with those obtained with the gel prepared over phosphorus pentoxide.

Heat Measurements.—The gel of known water content sealed in thin-walled glass bulbs 2.5–3.0 cm. in diameter

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[16] Hendricks and Steinback, *J. Phys. Chem.*, **36**, 1279 (1932).

was placed in the silvered cup and allowed to remain until temperature equilibrium (four to six hours) was attained at 25°. The gel was wetted suddenly by shattering the bulb with a pointed plunger regulated by a compression screw. The final equilibrium temperature was attained within 0.005° in a short time, usually not exceeding five minutes.

The temperature of the calorimeter and contents was returned to 25° and electrical energy was supplied through the heating element at a rate to duplicate the temperature–time changes previously observed for the wetting effect. From this total electrical energy input the heat equivalent was calculated.

Results and Discussion

Bartell and Almy[17] studied the interrelation of water content, heat of wetting, temperature of activation and time of activation. Our results for the study of the same interrelations are expressed in Figs. 2 and 3 and indicate a general agreement with their results. It should be observed, however, that a gel activated at 260–275° in a vacuum until equilibrium is reached at about 4% water content results in a gel which has a heat of wetting of 32 calories per gram. This high value was only attained for gels heated at high temperature not exceeding 275° and held at this temperature in a vacuum for many hours. This value for the heat of wetting is 20% higher than that of Ray and Ganguly (26.7 calories per gram), which is the highest previous value we have noted.

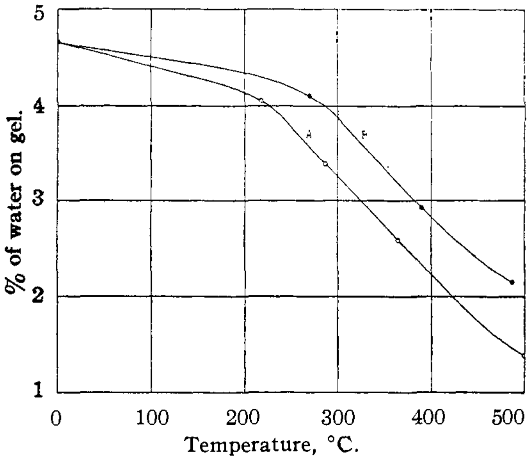

Fig. 2.—Relation of water content to temperature of activation: A, heating over phosphorus pentoxide; B, heating and evacuating.

The curves of Fig. 1 follow the same general shape for each isotherm and indicate a dropping off of adsorption capacity at higher temperatures. If a vapor pressure *vs.* % weight acid curve at 25° is compared to the above curve of the same temperature the two show great similarity in structure and forecast the shape of the vapor pressure–X/M curve to be similar to the adsorption isotherm with one portion a straight line. Such a line could indicate that, as Rideal[18] has stated, "the transition from a monomolecular layer to a polymolecular adsorbed layer, in such a bulk that its free surface would possess the free surface of the liquid in bulk, is not abrupt." Regraphing these results as a log–log curve according to Freundlich's coördinates gives a curve with three straight sections.

In the preparation of gels containing 0 to 36% of water by weight concentrated sulfuric acid was used for those as low as 4.7% water content. For samples below this water content a vacuum electric furnace was used. A 4.7% gel[19] equilibrated over concentrated sulfuric acid was heated gradually to equilibrium at fixed temperatures ranging from 25 to 500°. The results expressing the relationship between the water content and temperature of activation are shown in Fig. 2. It should be noted that the water content decreased faster with a slow increase in temperature when the percentage of water present fell somewhat below 4%. A water content below this amount produced a gel of lower activity.

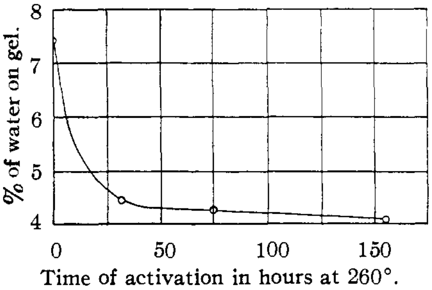

Fig. 3.—The relation of water content to time of activation.

Table I gives the experimental values at 25° for the heats of wetting per gram of silica gel containing amounts of water varying from 0 to

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[17] Bartell and Almy, *J. Phys. Chem.*, **36**, 475 (1932).

[18] Rideal, "Surface Chemistry," Oxford University Press, p. 58.

[19] A transition of color which accompanied the removal of water was interesting. With the application of heat the gel became colored ranging from light tan at first to almost black at higher temperatures. The darkest color occurred during the preparation of the 4% water content gel and that gel of lower water content. The color did not in all cases indicate a more active gel although when colored the gel was very active as measured by heat of wetting. Another observation was that if the gel remained at the same temperature long enough the color would disappear leaving at that time a gel which was the most active at that particular temperature and water content. A longer time was necessary for fading of the color at the lower temperatures.

Table I

% water on gel	Cal./g. gel	% water on gel	Cal./g. gel
35.80	0.10 (0.02)	5.35	26.50 (0.20)
34.60	.20 (.04)	4.70	28.00 (.20)
28.50	2.25 (.05)	4.40	28.80 (.20)
25.50	3.75 (.05)	4.18	30.00 (.20)
24.75	4.25 (.05)	4.00	31.60 (.20)
20.35	7.50 (.06)	3.50	29.10 (.20)
19.90	7.80 (.06)	2.98	28.90 (.10)
17.10	10.30 (.10)	2.12	27.10 (.10)
12.70	15.25 (.05)	1.90	26.55 (.10)
12.05	16.10 (.05)	1.53	25.30 (.05)
7.50	22.80 (.20)	1.42	24.50 (.05)
7.10	23.50 (.20)	0.00	00.00

35.8%. The values are the mean from at least six trials with the maximum deviations in parentheses. In the region of greatest activity the values obtained were variant due to a possibility that in this highly active condition small changes in the gel structure and manner of activation will cause a great difference in activity. The interpolated value for the heat of wetting gave 32.0 calories per gram of gel with a 4% water content. The highest experimental value obtained was 31.80 calories per gram of gel containing 4% water. Values above 30 calories were more difficult to duplicate. Below 4% water content the gel activity was reduced rapidly, probably due to the destruction of its interior active surface, while 0% water (fused gel) gave particles which seemed to be negative to wetting although the transparent particles were wetted.

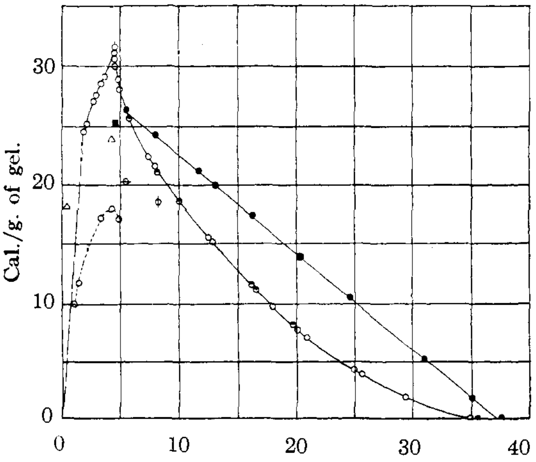

Fig. 4.—Heats of wetting of water on silica gel: ●, Ray and Ganguly; --○--, Bartell and Almy; -⊖-, Patrick and Greider; △, Bartell and Fu; ϕ, Patrick and Grimm; ■, Stenzel; ◓, Nasif; ○, Ewing and Bauer.

Figure 4 includes the graph of the above data. That portion of the curve on the right side of the 4% point represents the behavior of a gel acting reversibly while that portion to the left of the point a gel acting irreversibly. Once the gel has been activated to a water content of less than 4% the high activity of 32 cal./g. of gel cannot again be reached. In other words, when the water below 4% is once removed it cannot be replaced on the gel with a corresponding increase of activity such as to give a heat of wetting of 32 cal./g. of gel.

Fitting the equation of a circle to the experimental points of the curve of Fig. 4 the extended line crosses the % water axis at 37.7% which will be taken as the total amount of water-fillable space of the silica gel. Ray and Ganguly gave 37.5% water content as the saturation limit for their gel. Ikerman[20] found that this gel had a pore volume of 0.333 cc. Deducting 4% irreversible bound water from the amount held at saturation (37.7%), it is noted that the pore volume becomes 0.337 cc., which compares with Ikerman's value of 0.333 cc. obtained by helium displacement.

It is noteworthy that the simple relationships observed by Ray and Ganguly as to the ratio of moles of water to moles of silica were observed in these results. At the point of greatest activity (4%) the ratio is 2 moles of water to 15 moles of silica while at the saturation point the ratio becomes 30 moles of water to 15 moles of silica.

It is noted that the values for the heats of wetting given by previous investigators vary from 19 to 26 cal./g. for their most active gel. These values are given on Fig. 4 as accurately as their known water contents will permit. The various methods employed by different investigators in preparing their active gels would explain the disagreement in results. It has been found in this investigation that great care in activation must be exercised to obtain a gel to give reproducible heat of wetting results.

Ewing and Spurway[21] found a discontinuity between density and water content at approximately 8% which agrees with our first discontinuity. In their data the break comes at the 4% point but in the preparation of their gel 4% water was with the gel before the addition of their first 4% water.

The second discontinuity of the curve (cal. per g. gel *vs.* % water on gel) is a multiple of the

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[20] Ikerman, "Pore Volume of Silica Gel by Helium Displacement," M.S. Thesis, Michigan State College, 1928.

[21] Ewing and Spurway, This Journal, **52**, 4635 (1930).

first discontinuity with respect to water content, considering the 4% point as the lowest percentage water content gel obtainable without destruction of gel activity. Calculating the area covered by 0.04 g. of water one molecule thick also gives a value of about 1 × 10^6 sq. cm.

Summary

1. An adsorption–desorption curve of water vapor on silica gel showing no hysteresis was obtained.
2. The activity was evaluated for gels of varying water content as heat of wetting measurements.
3. A maximum in the heat of wetting determinations at a water content of 4% for this particular silica gel was observed.
4. The activation of the gel must be carried out in a manner that the water on the gel is evenly distributed over the surface or at least is in a state of equilibrium with the gel surface energy.
5. Silica gel can be most highly activated by holding it in a vacuum at 260 to 275° for many hours.

EAST LANSING, MICH. RECEIVED APRIL 10, 1937

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

The Use of Low Temperature van der Waals Adsorption Isotherms in Determining the Surface Area of Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND S. BRUNAUER

In a recent communication[1] we published some low temperature physical adsorption isotherms for various gases on a pure iron synthetic ammonia catalyst and pointed out that they appeared to afford a means for calculating the surface area of the catalyst. Similar isotherms have now been determined for a total of six iron synthetic ammonia catalysts. The present paper gives the detailed experimental results that have been obtained and includes in addition a discussion of the various factors involved in interpreting the isotherms in terms of relative and absolute catalyst surface areas.

Experimental

The following six iron synthetic ammonia catalysts have been used: catalyst 930, containing 1.07% K_2O; 931, 1.59% K_2O and 1.3% Al_2O_3; 954, 10.2% Al_2O_3; 424, 1.03% Al_2O_3 and 0.19% ZrO_2; 958, 0.35% Al_2O_3 and 0.08% K_2O; and two different samples of an unpromoted iron catalyst 973 containing 0.15% Al_2O_3 as impurity. In the course of the work isotherms of some or all of the following gases have been determined on the various catalysts at the indicated centigrade temperatures: nitrogen and argon at −195.8°; nitrogen, argon, carbon monoxide and oxygen at −183°; methane and nitric oxide at −140°; nitrous oxide and carbon dioxide at −78°; ammonia at −36° and *n*-butane at 0°.

The adsorption apparatus, the general procedure used, the composition and reduction schedule of five of the catalysts, the nature of the −183 and −78° baths and the preparation and purification of the hydrogen, carbon monoxide and dioxide, nitrogen and helium have been described in a preceding paper.[2] The sixth catalyst (424) was reduced for forty-eight hours at 450° and forty-eight hours at 500°. Tank butane from the Ohio Chemical Company was condensed in a liquid air trap and the non-condensable gases were removed by pumping. Part of the remaining liquid was then vaporized into a storage bulb at room temperature. Tank oxygen containing 1.5 to 3% nitrogen was used for most of the runs; for one experiment pure electrolytic oxygen was used in place of tank oxygen to show that the small percentage of nitrogen did not materially alter the shape of the low temperature oxygen isotherm. Methane was obtained through the courtesy of the Heat Division of the National Bureau of Standards. It was condensed in a liquid air trap and degassed before using. Ammonia was taken from a tank of synthetic ammonia, dried over potassium hydroxide and used without further purification after it had been shown to contain a negligible quantity of non-condensable gas. For our supply of nitric oxide we are indebted to Dr. E. Melvin of this Laboratory who prepared it from sulfuric acid and sodium nitrite according to the method described by Noyes.[3] It contained no appreciable non-condensable gas; traces of nitrogen dioxide and water were removed by adsorption on glaucosil. Nitrous oxide from a tank was frozen in a liquid air trap and, after the removal of all non-condensable gas, vaporized from a −78° bath directly into the adsorption apparatus. Argon of 99.9% purity was used after being dried by passage through a −78° bath.

The −195.8° bath consisted of tank nitrogen that had been liquefied in fresh liquid air at about 35 pounds gage pressure. The tank nitrogen contained about 1% oxygen. For obtaining a temperature of −36° a liquid ammonia bath was used. A temperature of −140 ± 0.2° was obtained with a hand regulated thermostat; petroleum ether was used as a bath liquid. Cooling was obtained by liquid air. Sufficient stirring was provided by a stream of dry nitrogen bubbling through the bath to keep the temperature gradient throughout the bath smaller than 0.05°.

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(1) Brunauer and Emmett, THIS JOURNAL, **57**, 1754 (1935).

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

(3) W. A. Noyes, *ibid.*, **47**, 2170 (1925).