1.57.[2] In alkaline solution[20] this band is still present, with intensity lowered to $\log \epsilon = 1.17$, while a new band appears at about $\lambda = 3175$ Å., $\log \epsilon = 1.79$. The band for our 3-methyl-2-hydroxy-Δ^2-cyclohexenone in alkaline solution is at 3120 Å., $\log \epsilon = 3.88$, and the ketone band is masked. Apparently the camphorquinone is only partially enolized. In fact, it is only about 1% enolized, as indicated by the ratio of intensities of the two bands. More accurately controlled conditions of solvent may permit a more accurate determination of the percentage of enolization, and we intend to pursue this investigation in this Laboratory. The similarity of position of the new band in the camphorquinone (which is incapable of forming a di-enol) with the band in a basic solution of our compound, we consider an indication of like chromophoric groups in the two substances, and evidence that even in basic solution the mono-enol and not the di-enol is present.

Summary

New absorption spectra are presented for the α,β-unsaturated cyclic ketones, 2-benzal-3-methylcyclohexanone, inactive and optically active, 2,6-dibenzal-3-methylcyclohexanone, 2,5-dibenzalcyclopentanone, and 3-methyl-2-hydroxy-Δ^2-cyclohexenone.

Woodward's and Gillam's generalizations are noted, and a possible extension suggested to include the influence of hydroxyl substitution at the ethylene double bond.

Absorption spectra data are used as evidence for the structure of 3-methyl-2-hydroxy-Δ^2-cyclohexenone.

Wellesley, Mass. Received October 4, 1944

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(20) French and Holden, unpublished data.

[Contribution from the Research and Development Department of the Sinclair Refining Company]

Adsorption–Desorption Isotherm Studies of Catalysts. I. Supported Catalysts in the Powder and Pellet Forms

By Herman E. Ries, Jr., Robert A. Van Nordstrand, Marvin F. L. Johnson and Herman O. Bauermeister

The pore structure characteristics of catalysts in the powder and pellet forms are of considerable importance in the study of catalytic processes. Hysteresis effects observed in adsorption–desorption isotherm experiments are related to the pore structure of the adsorbent.[1,2,3] Although there exists at present no well-established theory to account for hysteresis phenomena, sound experimental relationships may point the way to a better understanding of adsorption and desorption as related to surface forces and pore structure.

Interesting similarities have been observed in the adsorption–desorption hysteresis effects obtained with two catalysts both in the pellet and powder forms. The two catalysts, H-A and H-G, are supported catalysts similar in chemical composition. They have widely different surface areas, 120 and 225 sq. m. per g., respectively, as calculated by the Brunauer, Emmett and Teller method.[4] Both catalysts are studied in the form of 0.125-inch pellets (P) and in the form of ground pellet (GP) material (100-mesh). A sample of the unpelleted (UP) powder used in preparing H-G pellets is also studied. When time permits, this investigation will be extended to include the support, the unsupported catalyst and related materials of interest.

Experimental

The apparatus and methods employed are essentially the same as described by Emmett and Brunauer.[5,6] A brief description and a photograph of the adsorption apparatus in use in these laboratories have been previously presented.[7] Several modifications of the experimental procedure have subsequently been introduced. These apply to the studies reported in this paper with the exception of Experiments 56 and 103.

A vapor pressure thermometer using nitrogen replaces the oxygen vapor pressure thermometer formerly used. Errors in reading the saturation pressure, p_0, are thus reduced threefold. The nitrogen and helium used in these experiments are obtained from the Ohio Chemical Company. The nitrogen, of 99.8% purity, is further purified by means of copper gauze at 500°, a drying tube of phosphorus pentoxide, and a Dry Ice–acetone trap. The helium now used for the dead space measurements at liquid nitrogen temperatures is 99.9% pure and is obtained in special Pyrex flasks.

All isotherm experiments are performed at liquid nitrogen temperatures (−195°) with nitrogen as the adsorbate. Adsorption equilibrium is reached in time intervals varying from ten

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(1) Emmett and De Witt, This Journal, **65**, 1253 (1943).

(2) Cohan, *ibid.*, **60**, 433 (1938); **66**, 98 (1944).

(3) Brunauer, "The Adsorption of Gases and Vapors," Vol. 1, Princeton University Press, Princeton, New Jersey, 1943.

(4) Brunauer, Emmett and Teller, This Journal, **60**, 309 (1938).

(5) Emmett, "Advances in Colloid Science," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1942.

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

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

TABLE I

ADSORPTION-DESORPTION ISOTHERM DATA

Adsorbent	Expt.	Area, sq. m. per g., BET	V_m, cc. adsorbed in monolayer on 1 g. of adsorbent	Point A Desorption rejoins adsorption		Point B, Sharp break in desorption		V_s, gas adsorbed at p_0, cc./g.	$V_B - V_A$, cc./g. desorbed, 0.5 to 0.4 rel. press.	V_s/V_m. no. layers at p_0
				p/p_0	V_A, cc./g.	p/p_0	V_B, cc./g.			
H-G (UP)	111	217.7	50.02	0.41	82	0.52	119	327	37	6.5
H-G (UP)	112	218.6	50.22	.40	80	.52	118	332	38	6.6
H-G (P)	103	226.8	52.09	.43	(86)	.51	114	...	28	..
H-G (P)	104	224.7	51.61	..	..	.50	109	291	..	5.6
H-G (P)	105	223.7	51.39	.42	82	.52	109	290	27	5.6
H-G (GP)	107	222.6	51.13	.41	79	.51	108	297	29	5.8
H-G (GP)	108	218.1	50.10	.43	79	.53	107	278	28	5.6
H-A (P)	56	119.5	27.45	(.4)	..	(.5)	...	...	..	..
H-A (GP)	109	120.0	27.56	.39	46	.52	72	340	26	12.3
H-A (GP)	110	119.5	27.44	.40	45	.52	71	336	26	12.2

minutes to two hours, depending on the portion of the isotherm concerned, and is checked by allowing the system to remain at the same point a comparable length of time. Equilibrium is confirmed at certain critical points for both adsorption and desorption by allowing the system to stand for sixteen hours.[8] Temperature variation of the liquid nitrogen bath during a single hysteresis experiment, usually extending over a period of five to six days, is generally not more than 0.4°. Attempts to reduce temperature variation are made in some experiments by bubbling nitrogen gas through the liquid nitrogen bath. The nitrogen vapor pressure thermometer, however, is used continuously and readings are made to within 0.2 mm.

All catalyst samples are degassed at 340° for sixteen hours by means of a mercury diffusion pump system. Slight sintering on successive degassing treatments is indicated by the area values listed in Table I.

In the helium-mercury displacement measurements of porosity cylinder helium of 98.2% purity is used. The mercury displacement measurements are made at atmospheric pressure. Room temperature evacuations are considered sufficient for these pore volume experiments since adsorption phenomena are not involved.

Discussion and Results

Hysteresis and Pore Structure.—Typical hysteresis curves for the catalysts of this series are plotted in Fig. 1 and the complete data are listed in Table I. The adsorption-desorption isotherms for H-G pellets (P) and ground pellets (GP) are practically identical. The original powder (UP) gives a closely corresponding adsorption curve but the desorption branch above 0.5 relative pressure is somewhat higher. Similarly the isotherms for H-A (P and GP) are essentially identical. Each desorption isotherm has a plateau ending in a sharp and reproducible break (point B) at 0.5 relative pressure (p/p_0) and then joins the adsorption branch at a relative pressure of 0.4 (point A). The high reproducibility of these two points in the desorption curves for the pellets and powders is apparent in Table I.

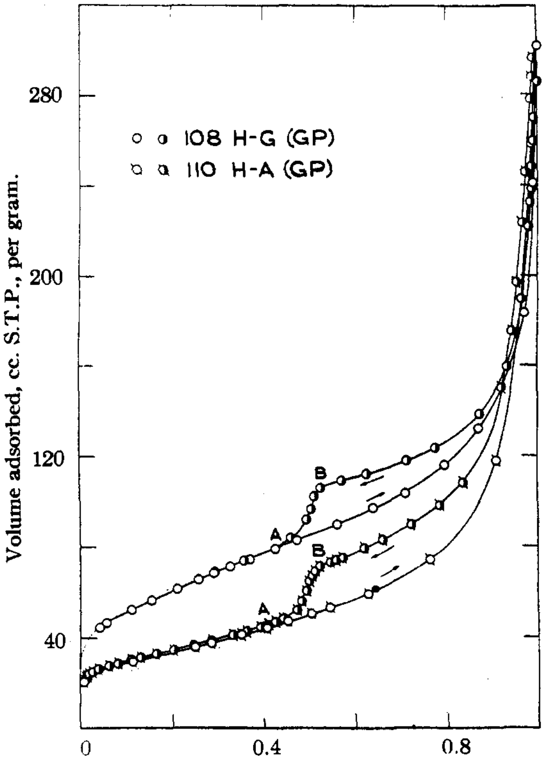

Fig. 1.—Nitrogen isotherms: adsorption and desorption.

Certain tentative conclusions may be drawn from these observations:

1. The pore structure presumably responsible for this marked and reproducible hysteresis effect is not produced by the pelleting process nor is it affected by subsequent grinding to 100 mesh

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[8] If there were no hysteresis one would expect the rate of approach to the equilibrium state to be equal on adsorption and desorption. This is not the case. Hysteresis evidently implies that there are two equilibrium states for each pressure, separated by a potential barrier. The rate of crossing such a barrier depends on the height and nature of the barrier, the temperature fluctuations of the thermostat, the absolute temperature and the nature of the adsorbate molecules. Other factors being comparable a more stable hysteresis should be observed at low temperatures.

powder. However, the pore volume of H-G emptying at 0.5 relative pressure is reduced on pelleting (see $V_B - V_A$ values, Table I), although the over-all isotherm contour remains the same. Partial collapse of the fine pore structure may account for this difference.

2. The hysteresis effect described here is not intimately associated with a specific surface area since the effects are very similar for the H-A and H-G catalysts of widely different areas. Nevertheless those portions of the solid responsible for the effect may have identical structures.

3. On desorption the relative pressure of 0.4 represents the lower limit of hysteresis, hence presumably the completion of capillary evaporation. This may indicate either a limit for hysteresis (capillary) effects for nitrogen on solids of the type studied (regardless of pore sizes), or that the solid has no pores smaller than those corresponding to 0.4 relative pressure.

However, at 0.5 relative pressure considerable pore volume is emptied (see Table I). The pronounced desorption that occurs at this point (Point B) may be related to pore structure by means of the Kelvin equation. According to the Kelvin equation

$$\ln p/p_0 = -2V\sigma/rRT$$

a relative pressure of 0.5 corresponds to a pore radius of 13 Å. V is the volume of one mole of the liquid (nitrogen), σ its surface tension, r the capillary radius, R the gas constant, T the absolute temperature and p the equilibrium pressure. V and σ are assumed to be the same as for the bulk liquid. The value of 13 Å. for the radius does not include the thickness of the adsorbed film. If a platelet structure is assumed the same value, 13 Å., is obtained at 0.5 relative pressure for the platelet separation, d (adsorbed film again not included). Radii of curvature for such a platelet meniscus are $d/2$ (or 6.5 Å.) and ∞ and therefore, yield the same equation for the vapor pressure lowering as that for cylindrical pores with r equal to d.

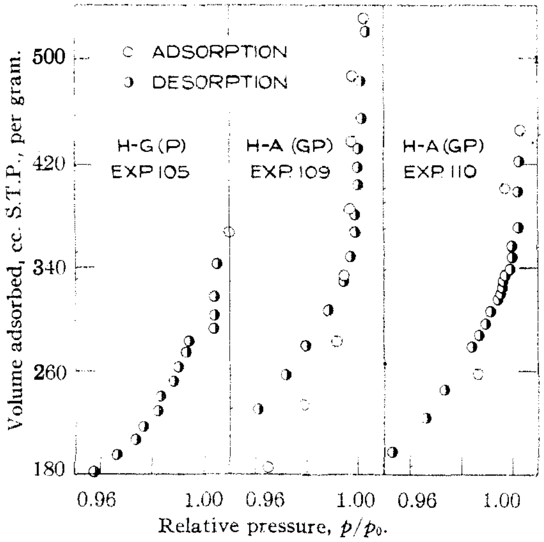

Fig. 2.—Upper portions of isotherms.

The relatively flat region of the curve immediately to the right of the sharp desorption at 0.5 relative pressure indicates that only a small portion of the pore volume consists of pores whose Kelvin radii are in the range of 15 to 40 Å.

4. Area values calculated from the pore volume emptying at 0.5 to 0.4 relative pressure and corresponding pore radii or platelet separations are considerably less than the total areas. If the areas thus calculated were greater than the measured areas the bottleneck type of structure would be indicated. Nevertheless a certain portion of the bottle-neck type of pores may be present. However, the bottle-neck picture of pore structure[9,10] is not necessary to account for the volumes emptied at 0.5 relative pressure and the open pore theory may apply.[2]

Hysteresis and Pore Volume.—Isotherms of Types I, IV and V[11] give a satisfactory measure of the volume of adsorbate, V_s, required to attain the saturation pressure. This V_s value has been interpreted as the amount of adsorbate in the liquid phase required to fill the pores of the adsorbent; that is, V_s has been used in these cases as a measure of pore volume. Isotherms of the type described in this paper, Type II,[12] have been considered not suited for this purpose because of their asymptotic approach to p_0. In the experiments reported here, however, it is found that if the desorption is performed carefully in small steps the desorption curve obtained is not asymptotic. Apparently the hysteresis extends to p_0. The isotherms thus provide a method for obtaining values of V_s.

Figure 2 illustrates the rather sharp breaks which occur on desorption in the neighborhood of p_0, apparently at the inception of the pore emptying process. The reproducibility of the V_s data is demonstrated in Table I.

Pore volumes have been calculated from these V_s values, with the assumptions that the nitrogen adsorbed in the pores has the density of liquid nitrogen, 0.800 g. per cc., and that the nitrogen adsorbed on the external area is negligible.

Table II

Pore Volumes (cc. per g.)

	Isotherm method (V_s) (P)	Isotherm method (V_s) (GP)	Helium-mercury method (P)
H-G	0.45	0.45	0.47
H-A	..	0.53	0.57

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(9) Kraemer, "A Treatise on Physical Chemistry," edited by H. S Taylor, D. Van Nostrand Co., New York, N. Y., 1931.

(10) McBain, This Journal, **57**, 699 (1935).

(11) Classification of Brunauer, Deming, Deming and Teller, *ibid.*, **62**, 1723 (1940).

(12) The Type II classification for isotherms might be broken down into two groups: those showing hysteresis (porous solids) and those not showing hysteresis (non-porous solids). The former group is treated in this paper.

These pore volumes are in agreement with the helium–mercury displacement values for the pellets as shown in Table II.

Helium–mercury displacement methods are not useful for measuring the pore volume of porous powders. The isotherm method, using V_s, may provide a method for measuring pore volumes of powders as well as pellets.

Consideration of the V_s data for the various samples suggests the following interpretation. The original powder (UP) consists of porous granules. V_s is a measure of the intra-granular pore space and does not include significant inter-granular space. In the pelleting operation these granules are packed together and crushed to some extent. Inter-granular space is effectively eliminated in the pellets. Subsequent grinding of the pellets simply forms granules again, without changing the intra-granular pore volume.

This interpretation is supported by the following observations:

(a) The pore volume of pellets measured by helium–mercury displacement agrees with the V_s value.

(b) The V_s value of the original H-G powder is decreased by only 12% on pelleting, whereas the bulk volume of the powder is reduced by more than 75%.

(c) The V_s values for the pellets and the ground pellets are in good agreement.

Estimates of the number of layers held by the adsorbent at saturation (V_s/V_m) give values for H-A and H-G of 12.3 and 5.6 layers, respectively. Chemically these catalysts are nearly identical. Hence it is not likely that the solid surface forces of H-A extend twice as far as the forces of H-G.[13] A more tenable explanation is that V_s simply represents the available volume of pores below a critical pore size and V_s/V_m is a measure of the average pore radius.

Furthermore, the number of layers held by H-G apparently changes from 6.6 to 5.6 on pelleting, and it is improbable that the chemical nature of the solid surface is altered during this process.

Summary

Nitrogen adsorption–desorption isotherm studies have been made at low temperatures with supported catalysts in the powder and pellet forms.

1. Hysteresis effects are very similar for both forms of two catalysts widely different in area. The pore structure responsible for the hysteresis effect is not produced by pelleting nor is it affected by subsequent grinding to 100-mesh powder.
2. Hysteresis extends from 0.4 relative pressure to p_0. V_s may be determined more precisely on desorption than on adsorption. Pore volumes calculated from V_s data are in agreement with those obtained in helium–mercury displacement measurements. Determinations of pore volume by the isotherm V_s method indicate that intra-granular pore volume only is measured. The isotherm method described may thus provide a technique for measuring pore volumes of particles in the finely divided state.
3. For the systems studied the number of layers deposited at p_0 is apparently limited not by solid surface forces but by the pore volume available.

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[13] Harkins and Jura, THIS JOURNAL, **66**, 919 (1944), have found that ten layers of nitrogen are adsorbed on a non-porous TiO_2 (anatase) sample. They attribute this film thickness to solid surface forces.

EAST CHICAGO, INDIANA RECEIVED APRIL 25, 1945

[CONTRIBUTION FROM PURDUE UNIVERSITY]

Heterocyclic Derivatives of Sulfamide[1]

BY ALBERT FUHRMAN[2] WITH ED. F. DEGERING

The chemistry of substituted sulfamides and their methods of preparation have been reviewed by Audrieth and collaborators.[3] Recently, Wheeler and Degering[4] described a series of substituted sulfamides, prepared by the action of dimethyl and diethylsulfamyl chlorides upon aromatic amines.

The present project deals with the preparation of heterocyclic derivatives of sulfamide and is a continuation of the work of Wheeler and Degering.

Little has been reported on the physiological action of sulfamide derivatives. Aeschliman[5] reported that tetraethylsulfamide in small doses has a slight analeptic action. In view of the antimalarial activity exhibited by certain sulfamides and the current interest in this field, the compounds prepared have been submitted for testing for antimalarial and general pharmacological activity.

The compounds described in this paper were prepared, for the most part, by the action of dialkylsulfamyl chloride on a heterocyclic amine dissolved in either benzene or pyridine. 4,4'-Sulfonyldimorpholine was prepared from sulfuryl chloride and morpholine. N-(Dimethylsulfamyl)-phthalimide was prepared from dimethylsulfamyl chloride and potassium phthalimide.

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[1] Abstracted from a thesis presented to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science, June, 1944.

[2] Du Pont Fellow, 1944–1945.

[3] Audrieth, Sveda, Sisler and Butler, *Chem. Rev.*, **26**, 49–94 (1940).

[4] Wheeler with Degering, THIS JOURNAL, **66**, 1242 (1944).

[5] Aeschliman, Festschrift Emil C. Barrel, 1936, pp. 246–254.