case of SN-12867 the proton-exchange was incomplete even in 18 M sulfuric acid, but the change in spectrophotometric absorption was in the direction of that exhibited by the other compounds. The addition of a third proton to these 9-aminoacridine derivatives is a reversible process as demonstrated by the complete reversal of the spectrophotometric changes by dilution of the sulfuric acid solutions with water. A "medium effect," consisting principally of a small increase in the molecular absorption coefficients at all wave lengths, was observed at the lower range of sulfuric acid concentrations (0.1 to 5 M), below the range of the proton-exchange. Another medium effect, consisting of a slight, progressive shift to lower wave lengths (the maximum shift being 3 mμ) of the peaks of the absorption band of the species $^+HB{-}B'H^+$ in the visible range of the absorption spectrum, was observed throughout the range from 6 M to 17 M sulfuric acid. Corrections for these medium effects in the evaluation of $pK_{(H_2SO_4)}$ were made essentially as described by Flexser, *et al.*[9]

The agreement of the experimental data for SN-390 and SN-12868 with the theoretical relationship of equation 2 is shown in Fig. 3. The values of $pK_{(H_2SO_4)}$ determined for these compounds are -6.49 and -5.95, respectively. An accurate evaluation of $pK_{(H_2SO_4)}$ for SN-12867 [2 - methoxy - 6 - chloro - 9 - (2' - diethylamino-1'-methyl-ethylamino)-acridine] was not feasible inasmuch as the proton-exchange for this compound was incomplete even in 17.5 M sulfuric acid. However, an approximate value of -9.2 was calculated from the spectrophotometric data for solutions of the compound in sulfuric acid of concentrations ranging to 17.5 M by rectification of the data by the logistic analysis of Reed and Berkson.[12,13] The progressive decrease in $pK_{(H_2SO_4)}$ with shortening of the side-chain in this series of compounds can be attributed to the increase in the electrostatic repulsion of the third proton by the positive charge on the diethylamino group of the side-chain as the distance of separation is shortened. No attempt has been made to analyze quantitatively the increase in the electrostatic effect, which accompanies the shortening of the side-chain, in terms of the extended theory of Bjerrum.[15] The lack of accurate data on the dielectric constant of sulfuric acid and of concentrated solutions of sulfuric acid in water prevents quantitative application of the Bjerrum theory to the present case, but the semi-quantitative aspects of the effect are in agreement with the theory.

Summary

In concentrated aqueous solutions of sulfuric acid a reversible proton-exchange involving the 9-amino nitrogen atom of quinacrine, and of two homologs of this compound, has been studied, and the ionization exponents have been evaluated spectrophotometrically in terms of the extended pH scale of Michaelis and Granick. The difficulty in adding the third proton to these molecules is attributed to electrostatic and resonance effects.

(15) Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

BALTIMORE, MD. RECEIVED NOVEMBER 21, 1949

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Sorption by Organic Substances. I. Krypton and Nitrogen on Polyethylene, Nylon and Collagen[1]

BY A. C. ZETTLEMOYER, AMIR CHAND AND ERNEST GAMBLE

The adsorption of non-polar gases on organic solids presents a field that has been little developed. This situation contrasts sharply with the field of the adsorption of gases on inorganic solids. In the latter case considerable progress has been made in developing a fundamental understanding of the adsorption phenomenon, and a large body of data is available in the literature.

Previous adsorption work on organic solids reported in the literature includes a few exploratory measurements of nitrogen adsorption by Emmett and co-workers on dried bacteria[2a] and on paper[2b]; the point B method was employed for the first and the BET equation for the second to estimate the surface areas. The BET method was also used by Shaw[3] on egg albumen, by Benson and Ellis[4] on various proteins, by Assaf, Haas and Purves[5] on cellulose, by Palmer, Shaw and Ballantyne[6] on sodium pectate and by Zettlemoyer, Schweitzer and Walker[7] on hide powder.

These few studies have not demonstrated thoroughly that the BET method is applicable to organic surfaces. In this study adsorption isotherms on polyethylene, nylon and collagen were measured with both krypton and nitrogen so that

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(1) Presented before the 116th meeting of the American Chemical Society in Atlantic City, N. J., September, 1949.

(2) (a) S. Brunauer and P. H. Emmett, THIS JOURNAL, **59**, 2682 (1937); (b) P. H. Emmett and T. DeWitt, *I. E. C., Anal. Ed.*, **13**, 28 (1941).

(3) T. M. Shaw, *J. Chem. Phys.*, **12**, 391 (1944).

(4) S. W. Benson and D. A. Ellis, THIS JOURNAL, **70**, 3563 (1948).

(5) A. G. Assaf, R. H. Haas and C. B. Purves, *ibid.*, **66**, 66 (1944).

(6) K. J. Palmer, T. M. Shaw and M. Ballantyne, *J. Polymer Science*, **2**, 318 (1947).

(7) A. C. Zettlemoyer, E. Schweitzer and W. C. Walker, *J. Am. Leather Chem. Assoc.*, **41**, 253 (1946).

the BET method could be adequately tested. Measurements were also made at several temperatures so that isosteric heats of adsorption at various coverages could be calculated. The three substances include all degrees of organic complexity from the simple hydrocarbon polyethylene to the complex protein structure provided by collagen.

Experimental

Materials.—*Polyethylene* was obtained as a fine, white powder from E. I. du Pont de Nemours and Company, Inc., as sample number A-8269. Its molecular weight was approximately 9000, and it has a viscosity of about 30 poises at 125°. A high surface area sample was prepared from a 2% solution in thiophene-free, dry benzene. This solution was frozen and then the benzene was pumped off under vacuum over a period of twenty-four hours. After storing in a vacuum over phosphorus pentoxide for ten days, the sample was finally again evacuated on the adsorption apparatus for several hours at 1 × 10^{-5} mm. at room temperature. Repeated isotherm measurements according to the adsorption–desorption method of Harned[8] checked each other, apparently indicating that the surface was clean. When Zettlemoyer, Schweitzer and Walker[7] measured a different sample of collagen earlier, this method of Harned was found essential for obtaining reproducible results; the apparent area increased until after the sixth isotherm was measured.

Electron microscope pictures showed that this sample consisted of a wide variety of particle sizes and that the average particle size was approximately one micron.

Nylon was also obtained from du Pont as unoriented yarn, code 1152-85-B. A high surface area sample was obtained from a 10% solution in 85% formic acid. This solution was poured into a large volume of distilled water with vigorous stirring to avoid lumps being formed. The resulting fine pulp was filtered through a fine muslin cloth and washed a dozen times until the washings were neutral to litmus. The pulp was dried in air, powdered, and dried over phosphorus pentoxide in a vacuum for a month. Finally, the sample was degassed in the adsorption apparatus at 1 × 10^{-5} mm. for twenty hours at room temperature. The adsorption–desorption technique was applied several times before the actual measurements were made.

Collagen was prepared from fresh cowhide according to the methods described by Highberger[9] and by Risley, Buffington and Arnow.[10] The sample was further degreased by Soxhlet extraction with chloroform and acetone separately. The resulting white, fibrous material gave a *p*H of 4.85 in distilled water. After drying in a vacuum over phosphorus pentoxide for three months, it was further degassed in the adsorption apparatus for twenty hours at room temperature. This treatment yielded a sample not subject to large changes in BET area when the adsorption–desorption technique was applied. Furthermore, the area was only one-tenth of that reported by Zettlemoyer, Schweitzer and Walker.[7]

Apparatus.—For the nitrogen adsorption measurements, the usual BET type of apparatus was employed. Details were described elsewhere.[11] For the krypton adsorption measurements, the Wooten and Brown apparatus was employed. Except for minor changes, the apparatus was the same as they have described.[12] A cathetometer was employed in reading the McLeod gage and readings were taken every five minutes until three successive readings were constant. A minimum of one hour was usually required to attain equilibrium.

Discussion of Results

Nitrogen and krypton adsorption isotherms at the temperature of liquid nitrogen for polyethylene, nylon, and collagen are plotted in Figs. 1, 2 and 3, respectively. These curves are typical Type II isotherms although they do not possess a sharp break characteristic of adsorption on most inorganic solids. It would be difficult to obtain a "B point" on these isotherms. More points were obtained for these adsorption isotherms than are plotted in Figs. 1, 2 and 3; this

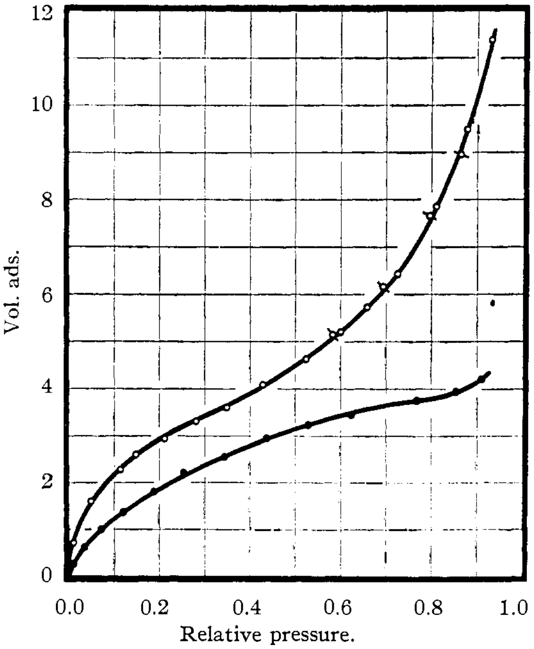

Fig. 1.—Nitrogen ○ and krypton ● adsorption isotherms on polyethylene at the temperature of liquid nitrogen: ø nitrogen desorption points.

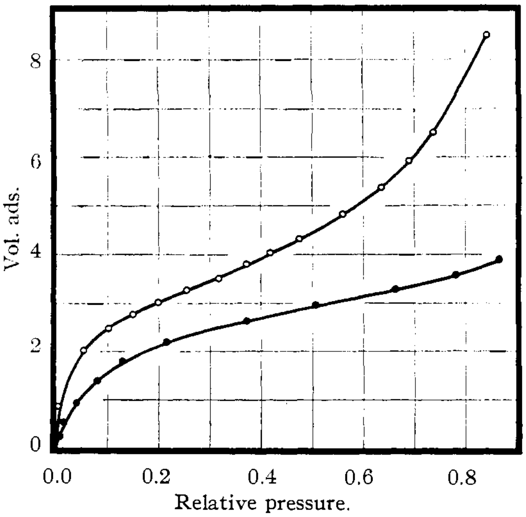

Fig. 2.—Nitrogen ○ and krypton ● adsorption isotherms on collagen at the temperature of liquid nitrogen.

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(8) H. S. Harned, THIS JOURNAL, **42**, 372 (1920).

(9) J. H. Highberger, *J. Am. Leather Chem. Assn.*, **31**, 93 (1936).

(10) E. A. Risley, A. C. Buffington and L. E. Arnow, THIS JOURNAL, **66**, 398 (1944).

(11) A. C. Zettlemoyer and W. C. Walker, *Ind. Eng. Chem.*, **39**, 69 (1947).

(12) W. A. Wooten and C. Brown, THIS JOURNAL, **65**, 113 (1943).

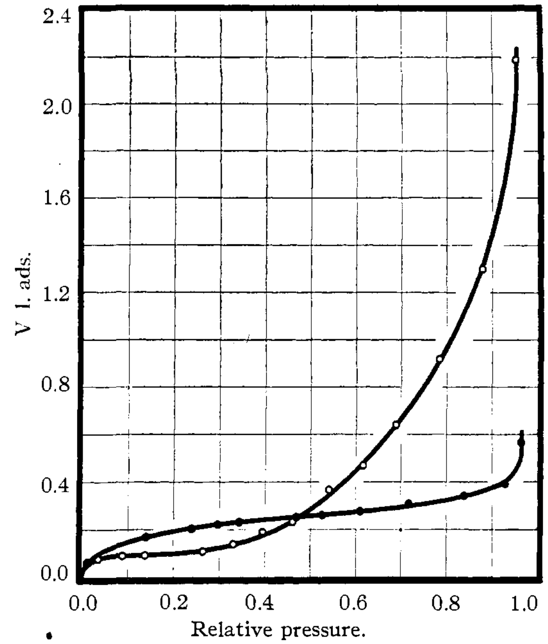

Fig. 3.—Nitrogen ○ and krypton ● adsorption isotherms on collagen at the temperature of liquid nitrogen.

was particularly true of the isotherms below 0.1 relative pressure. In each case the isotherms were first determined by a run obtaining a few points and then the isotherms were rerun obtaining many more points.

Plotted on the nitrogen adsorption curve for polyethylene are a number of desorption points. Since the desorption points fall on the same curve as obtained from the adsorption, it is evident that no hysteresis occurs.

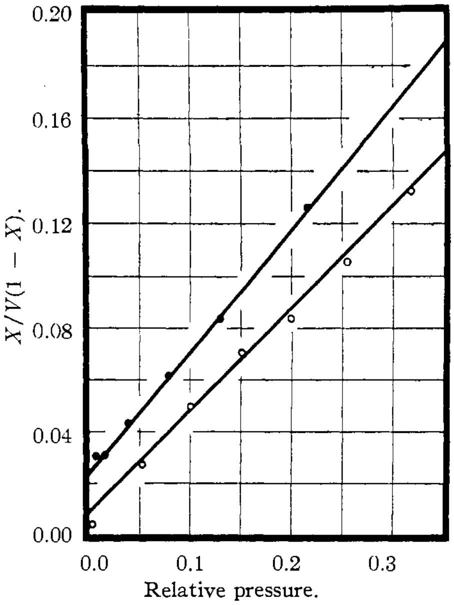

Fig. 4.—BET plots for nitrogen ○ and krypton ● adsorption on polyethylene.

The adsorption curves for krypton at the temperature of liquid oxygen are similar to those plotted for krypton at the lower temperature.

Typical BET plots are presented in Figs. 4, 5 and 6. These BET plots are good straight lines in the interval from 0.05 to 0.35 relative pressure. Table I presents the v_m and c values obtained from these plots. From the v_m values, using the appropriate factors for each temperature, surface areas were calculated. It is evident that excellent

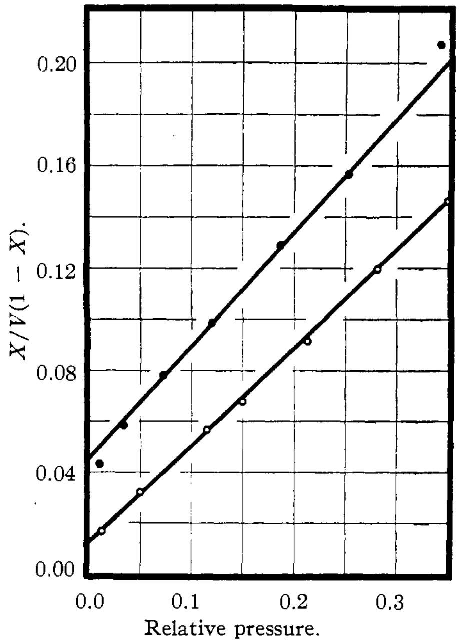

Fig. 5.—BET plots for nitrogen ○ and krypton ● adsorption on nylon.

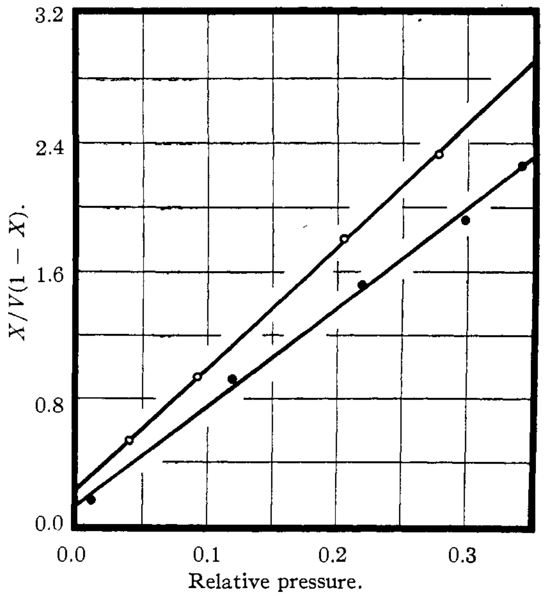

Fig. 6.—BET plots for nitrogen ○ and krypton ● adsorption on collagen.

TABLE I

KRYPTON AND NITROGEN ADSORPTION ORGANIC SUBSTRATES

Adsorbent	Adsorbate	Temp., °K.	v_m	c	Area factor sq. m./ml. of v_m	Surface area sq. m./g.	Dole ψ_1	BET E_1
Polyethylene	Krypton	90.0	2.03	9.1	5.361	10.9	2810	3070
		79.0	2.09	10.1	5.291	11.0		3040
	Nitrogen	79.4	2.54	31.0	4.408	11.2	4260	1875
		78.4	2.59	44.1	4.381	11.3		1920
Nylon	Krypton	90.0	1.93	19.6	5.361	10.4	2670	3219
		79.0	2.03	19.4	5.291	10.7		3140
	Nitrogen	78.4	2.48	42.8	4.381	10.8		1915
Collagen	Krypton	90.0	0.192	24.0	5.361	1.02	2690	3220
		81.9	0.190	20.6	5.310	1.01		3170
	Nitrogen	78.4	0.127	34.2	4.381	0.6		1880

agreement was obtained both at the two temperatures studied and between determinations for the different gases. Only in the case of collagen is there a large difference between surface areas obtained by nitrogen and by krypton adsorption. The difference may be ascribed to the inaccuracy of the BET apparatus for determining low surface areas by nitrogen adsorption. It is concluded that the BET theory provides an acceptable and useful method for estimating the surface areas of organic solids.

The surface areas in Table I were obtained from the v_m's using for the base areas of nitrogen and krypton at liquid nitrogen temperature, 16.2 and 19.5 sq. Å., respectively. The value for krypton is the one proposed by Beebe.[13] The excellent checks obtained with this value serve to substantiate its use rather than the much smaller values calculated from the density of the solid or liquid on the basis of close-packing.

The c values in Table I are all lower than 50; these values are much lower than those found for inorganic solids. From the c values E_1 values for the average heat of adsorption in the first layer were calculated assuming the constant term in the equation relating c to $E_1 - E_L$ to be equal to one.

The ψ_1 values are heats of adsorption calculated from the c values at two temperatures according to the method proposed by Dole.[14]

Thermodynamic Functions.—From the isotherms at two temperatures, the isosteric heats of adsorption were calculated by means of the Clausius–Clapeyron equation. Considering the gases to be ideal, these differential heats of adsorption apply to the total change in state from gas at p_0 to the adsorbed gas on the solid at p

$$\text{Kr}(P_0) + \text{solid} \longrightarrow \text{Kr on solid } (p) \qquad (1)$$

A similar equation applies for nitrogen. Figures 7, 8, 9 and 10 illustrate the variation in ΔH and ΔF for this change in state plotted against v/v_m, which is approximately the fraction of the surface covered.

From the ΔH of adsorption, using the average T, the ΔS of adsorption from a gas at p to adsorbed gas at p can be readily calculated. The Sackur–Tetrode equation provides the absolute entropy of the gas at p. Therefore, if the entropy of the solid is assumed to remain constant during the adsorption, the entropy of the adsorbate can be calculated by adding the entropy of the gas at p to ΔS. These entropies of the adsorbate are also plotted against v/v_m.

The heat of adsorption curve for nitrogen on polyethylene, Fig. 7, descends in a typical manner as the surface becomes covered. The peak in the curve at $v/v_m = 1.5$ remains unexplained. The ψ_1 value appears to be a better average heat of adsorption for the first layer than does the E_1 value.

Results for the entropy of the adsorbed nitrogen at low coverages were scattered and therefore considered unreliable. Above the first layer, however, it is clear that the entropy rises toward a limit.

For krypton adsorption on polyethylene, Fig. 8, the heat of adsorption rises from lowest values at low coverages and appears to form two maxima, one at $v/v_m = 0.4$ and one at $v/v_m = 1$. The rise in the heat curve is unusual but has been reported occasionally as in the work of Orr[15] for inert gases on alkali halides. A reasonable explanation is that the increased lateral interaction of adsorbed krypton molecules as the coverage is increased is responsible for the rise. Orr found an initial decrease in the heat curve which he believed to be due to crevices in the crystal where the heat of adsorption would tend to be larger. Amorphous polyethylene would be expected not to show this effect. Both E_1 and ψ_1 appear to be too high although again ψ_1 is the more nearly representative value.

The curve for the entropy of the adsorbed krypton falls through the entire range investigated. The dotted line marked $_2$S indicates the value calculated[16] assuming two degrees of translational freedome at $v/v_m = 1$. The measured entropy curve levels off at this value when about half the surface is covered but then falls somewhat below at higher coverages. The adsorbed krypton be-

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(13) R. A. Beebe, J. B. Beckwith and J. M. Honig, THIS JOURNAL, **67**, 1555 (1945).

(14) M. Dole, *Annals. N. Y. Acad. of Sci.*, **51**, 705 (1949).

(15) Wm. J. C. Orr, *Proc. Roy. Soc. (London)*, **A173**, 349 (1939).

(16) C. Kemball, *ibid.*, **187A**, 73 (1946).

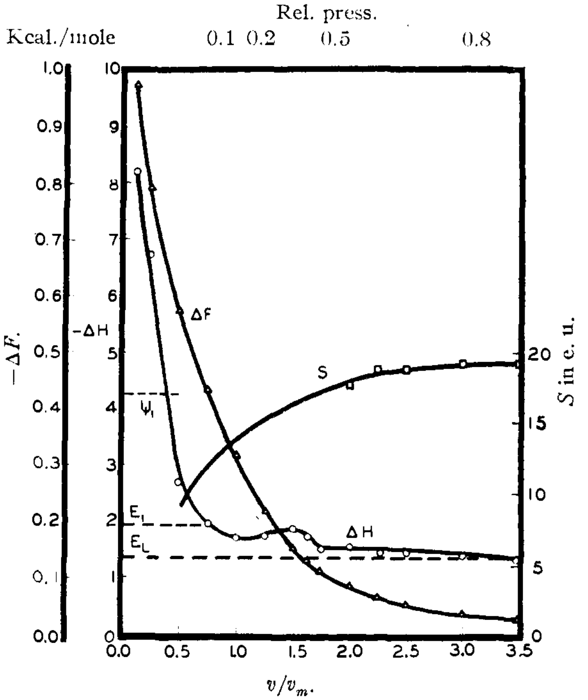

Fig. 7.—Thermodynamic functions *versus* v/v_m for nitrogen adsorption on polyethylene.

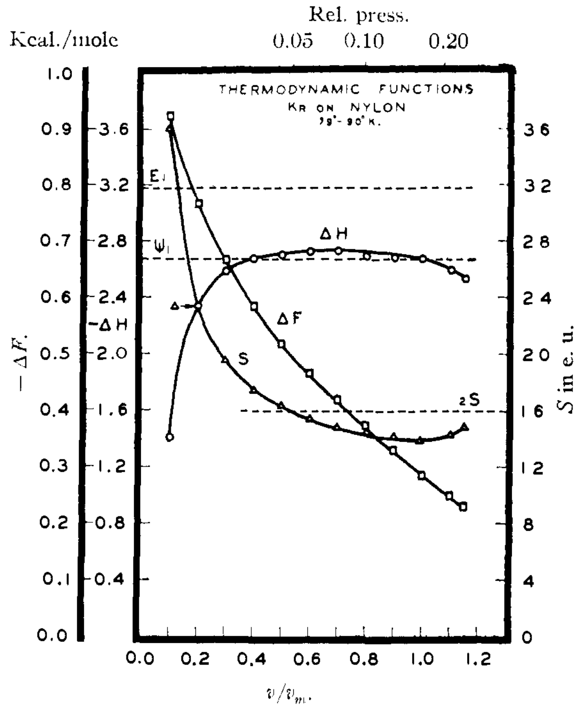

Fig. 9.—Thermodynamic functions *versus* v/v_m for krypton adsorption on nylon.

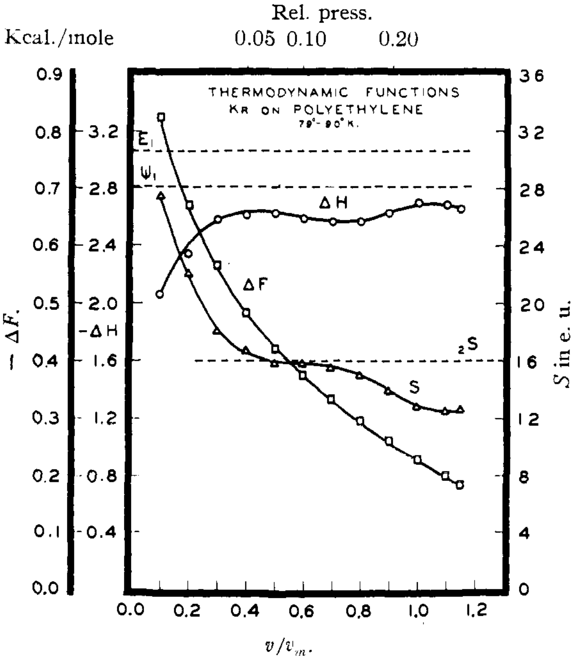

Fig. 8.—Thermodynamic functions *versus* v/v_m for krypton adsorption on polyethylene.

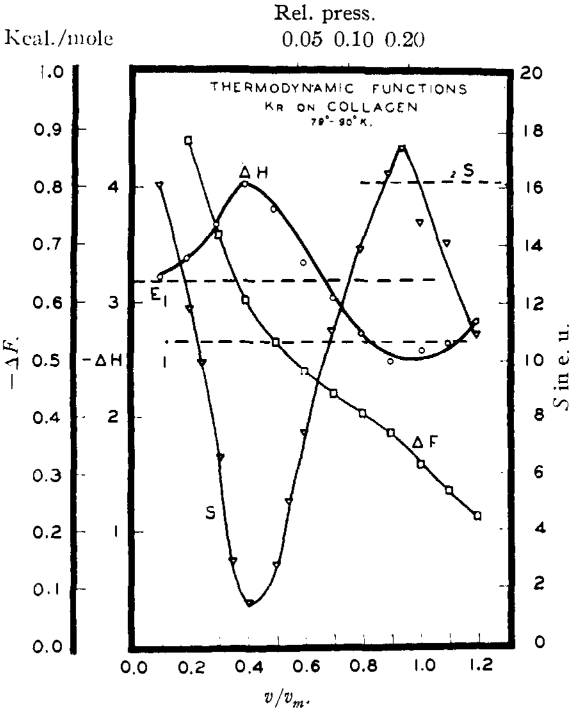

Fig. 10.—Thermodynamic functions *versus* v/v_m for krypton adsorption on collagen.

haves very much like a two-dimensional gas during formation of the first layer.

For krypton adsorption on nylon, Fig. 9, curves for the thermodynamic functions are somewhat dissimilar, to those for polyethylene. Only one broad maximum, however, appears in the heat of adsorption curve and the entropy curve only displays a minimum at $v/v_m = 1$. The ψ_1 value is quite representative of the heat of adsorption in the first layer, and again the E_1 value is too high. The entropy curve again falls somewhat above the two-dimensional gas values at low coverages and somewhat below near $v/v_m = 1$.

For krypton adsorption on collagen, Fig. 10, the heat of adsorption curve again rises to form a broad maximum which then decreases as the monolayer is approached. Here the E_1 value is far too low while the ψ_1 value is much more usual. Very unusual results were obtained for the entropy of the adsorbed krypton. This curve shows a distinct minimum at $v/v_m = 0.4$ and then a maximum where the monolayer is completed. It seems extremely unlikely that this entropy curve represents the actual facts because the minimum entropy is of the order of 2 entropy units which is only about one-fifth of the entropy of solid krypton at the same temperatures. One of the following two possible explanations may be responsible for this situation: The first is that heats of adsorption cannot be considered constant or that a discontinuity in the heat curve with temperature occurs in the range studied. This seems unlikely but other isotherms are being measured at interval temperatures to check this point. In the second place, it may be incorrect to consider that the entropy of the collagen is not changed during the adsorption. This assumption was implicit in the calculations of the entropy of the adsorbed krypton.

In order to establish the certainty of the entropy curve for collagen, the entire series of adsorption measurements and calculations therefrom, were done a second time. These results were similar to those originally obtained. Furthermore, it was estimated from extensive calculations made from the data that the probable error in the entropy curve, allowing the assumptions made, was about ±1 entropy unit at the minimum. Certainly, these unusual results for collagen warrant further investigation.

Summary

The adsorption of nitrogen and krypton has been measured on a simple hydrocarbon surface, polyethylene, at both liquid nitrogen and liquid oxygen temperatures. For nylon and collagen, krypton adsorption has been measured at the two temperatures and nitrogen adsorption at one temperature. The adsorption isotherms are typical Type II except for a rather gradual break where the monolayer is completed. The adsorption data yielded to BET analysis and gave surface areas of reasonable magnitude which agreed very well for the two gases at different temperatures on the same sample. It is concluded that the BET theory provides a satisfactory method for investigating the surface areas of organic solids with nonpolar gases.

The thermodynamic functions for the adsorptions have been calculated. For krypton, the heat of adsorption curves rise as more gas is added to the surface, and then fall off again after one monolayer is completed. The entropy curves for krypton on polyethylene and nylon fall toward limiting values as one layer is completed. For collagen, on the other hand, an extremely low minimum was obtained at a low coverage and a maximum where one layer was completed. These unusual results for collagen have not been explained.

BETHLEHEM, PENNA. RECEIVED DECEMBER 20, 1949

[CONTRIBUTION FROM THE UNIVERSITY OF MISSOURI]

Vapor Pressure Determination by Comparison with a Standard Liquid[1]

BY H. E. BENT AND C. A. KRINBILL, JR.

The purpose in developing a comparison method of determining the vapor pressure of a liquid is to economize on time through the simplification of the method and to take advantage of high precision in the determination of the vapor pressure of a single standard without having to repeat the precautions necessary for such high precision with each succeeding liquid. This paper develops the method and presents the results obtained with bis-(2-chloroethyl) sulfide, so called mustard gas, and diphenyl ether.

From the equation

$$n_2/n_1 = P_2/P_1 = a_2P_2^0/a_1P_1^0 \qquad (1)$$

in which n is the number of moles in the condensate from vapor in equilibrium with solution, P the partial pressure, a the activity in the original solution and P^0 the vapor pressure of the pure liquid, it is evident that one can obtain the vapor pressure of one pure component from the vapor pressure of the other component, the ratio of the activities and the composition of the condensate.

A useful equation for describing deviations from Raoult's law expresses the deviations by means of a single constant for both components,[2] thus

$$\log a_1/N_1 = \beta' N_2^2 \text{ and } \log a_2/N_2 = \beta' N_1^2 \qquad (2)$$

in which N is the mole fraction. These equations are applicable not only to systems which Hildebrand classifies as regular but also to some systems which show negative deviations from Raoult's law.[3a,b]

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[1] Submitted as a thesis in partial fulfillment of the requirements for a Master's Degree at the University of Missouri.

(2) J. H. Hildebrand, "Solubility," Reinhold Publ. Corp., New York, N. Y.

(3) (a) C. W. Porter, *Trans. Faraday Soc.*, **16**, 336 (1921); (b) H. E. Bent and J. H. Hildebrand, THIS JOURNAL, **49**, 3011 (1927).