

### Summary

It is shown by the study of the solid-liquid phase diagrams that diphenyl sulfoxide and selenone, dibenzyl selenoxide and sulfone, diphenyl selenoxide and sulfone form continuous

mixed crystal series of the minimum type (type III).

Diphenyl sulfone and selenone give a mixed crystal series of the ascendant type (type I).

SÃO PAULO, BRAZIL

RECEIVED OCTOBER 25, 1946

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

## The Sorption of Water Vapor by High Polymers

BY SHERMAN E. SMITH<sup>1</sup>

The remarkable extent to which the properties of textile fibers, protective films, and many plastics are modified by the sorption of water vapor has long maintained an interest in the subject.<sup>2,3,4,5</sup> The sorption of water by cellulose has received detailed consideration from Urquhart,<sup>6</sup> Peirce,<sup>7</sup> Assaf, Haas and Purves<sup>8</sup> and others.<sup>9</sup> In general, the more detailed discussions assume either special structural features for the cellulose or special types of association between cellulose and water. The necessity of such assumptions is questionable, since isotherms of virtually identical (usually sigmoid) form are obtained from many other systems in which such special considerations are out of the question. Such a relatively unorganized subject as sulfuric acid, for example, gives the sigmoid moisture-sorption isotherm characteristic of many high polymeric substances.

Several lines of evidence point clearly to a distinction between two principal classes of sorbed water: (1) that which is in some way bound on the inner or outer surface of the solid adsorbent by forces in excess of the normal forces responsible for condensation of water to the liquid state and (2) that which is normally condensed within the gel. The distinction is particularly noteworthy in the case of water sorbed by a somewhat polar sorbent. It is permissible, on statistical grounds, to divide the regain,<sup>10</sup>  $\alpha$ , into two fractions, thus

$$\alpha = \alpha_b + \alpha_c \quad (1)$$

Here  $\alpha_c$  is specifically defined as that portion of the regain which is condensed with a normal heat of condensation, while  $\alpha_b$  comprises that fraction which is bound by excessive forces. Peirce<sup>7</sup> and Filby and Maass<sup>11</sup> refer to these portions of the

regain as separate (though contiguous) phases. It is to be expected that these fractions will depend on the relative vapor pressure in quite different ways. While  $\alpha_b$  may be expected to reach a virtual maximum at a vapor pressure well short of saturation,  $\alpha_c$  must increase progressively toward the saturation vapor pressure. The isotherm for  $\alpha_b$  will be concave, and that for  $\alpha_c$  convex, toward the axis of relative vapor pressures. The summation of the isotherms for the two fractions results in the sigmoid isotherm typical of high polymer sorption.

The interpretation of any conventional sorption isotherm depends on the assumption that  $m$ , of the  $x/m$  ratio, is a mass of sorbent presenting a definite and invariant surface. The same consideration is implicit in the use of the regain,  $\alpha$ , which is equivalent to  $x$  when  $m$  is one gram. With sorption, however, high polymers usually undergo either limited or unlimited swelling, which must inevitably result in an increase in the number of sorptive points exposed within the structure. The assumption of such an increase in the effective surface has been employed by Urquhart,<sup>6</sup> and more concretely by Filby and Maass,<sup>11</sup> to explain the phenomenon of sorption hysteresis in cellulose. Here, precisely arises the principal difficulty in rationalizing the sorption isotherms for substances capable of gross swelling, for the regain is dependent not only on the relative vapor pressure, but also on the progressive effect of sorption on the structure of the swelling gel. The problem may be simplified by considering first the case of a hypothetical, non-swelling gel.

**The Sorption of Water Vapor by a Non-swelling Gel.**—The dependence of  $\alpha_b$  on the relative vapor pressure may be expected to follow approximately the formulation of the Langmuir adsorption isotherm. Especially when the sorbent and sorbate are polar,  $\alpha_b$  should achieve its maximum value at a vapor pressure well short of saturation. Even so non-polar a sorbate as nitrogen vapor approaches completion of the first or bound layer at  $p/p_0 = 0.1$ .<sup>12</sup> In a non-swelling gel, therefore, some characteristic relative vapor pressure,  $p_b/p_0$ , well short of saturation, will be

(1) Present address: University of New Mexico, Albuquerque, N. M.

(2) F. T. Peirce, *J. Text. Inst.*, **15**, T501 (1924).

(3) A. C. Walker, *Textile Research*, **7**, 229, 289 (1937).

(4) G. H. Argue and O. Maass, *Can. J. Research*, **13B**, 156 (1935).

(5) K. C. Brown, J. C. Mann and F. T. Peirce, *J. Text. Inst.*, **21**, T186 (1930).

(6) A. R. Urquhart, *ibid.*, **20**, T125 (1929).

(7) F. T. Peirce, *ibid.*, **20**, T133 (1929).

(8) A. G. Assaf, R. H. Haas and C. B. Purves, *THIS JOURNAL*, **66**, 66 (1944).

(9) See Stamin, "Colloid Chemistry of Cellulosic Materials," U. S. Dept. Agric. Misc. Publ., No. 240, 1936.

(10) The regain is the weight ratio of sorbate to dry sorbent.

(11) E. Filby and O. Maass, *Can. J. Research*, **7**, 162 (1932).

(12) S. Brunauer, P. H. Emmett and E. Teller, *THIS JOURNAL*, **60**, 309 (1938).

sufficient to bring the bound fraction virtually to completion.

The normally condensed fraction,  $\alpha_c$ , theoretically begins to form at the outset of the sorption process, though obviously it can form only in those regions where the bound water molecules are already in place or where the force field of the polymer surface is equivalent to that of a liquid water surface. This phase consists of multiple layers of condensed water molecules, although in the early stages of sorption at least, the layers are presumably not continuous. The dependence of  $\alpha_c$  on the relative vapor pressure may be expressed by means of an equation, the derivation of which, with appropriate modifications, follows closely an earlier treatment by Peirce.<sup>7</sup>

Let  $\alpha'$  be defined as the weight of normally condensed vapor (per gram of sorbent) required to saturate the first layer of the  $\alpha_c$  fraction.  $\alpha'$  comprises those molecules which are normally condensed directly on the bound water molecules or on equivalent positions (in point of binding energy) on the polymer surface. Additional water molecules condense in multiple layers on those of the  $\alpha'$ -fraction, but each molecule of the top-most layer replaces an equivalent molecule in the  $\alpha'$ -fraction which is prevented by its overburden from evaporating. For this reason, additional layers superimposed upon the first do not materially augment the evaporating surface. Hence  $\alpha'$  is also a measure of the total potential evaporating surface of the gel. The  $\alpha'$ -fraction is complete only at the saturation vapor pressure.

Since, by definition, molecules of the  $\alpha'$ -set are bound with common average forces of attraction and have the same tendency to evaporate as have the molecules of liquid water, it follows that at any stage of the sorption the completed fraction of  $\alpha'$  is  $p/p_0$ , while the uncompleted fraction is  $(1 - p/p_0)$ . If it may be assumed that positions in the  $\alpha'$  and succeeding layers are, throughout most of the range of sorption, equally accessible to condensing water molecules, an increment of condensing vapor,  $d\alpha_c$ , will be distributed uniformly over the completed and the uncompleted areas of the  $\alpha'$ -layer. On the completed fraction of  $\alpha'$ ,  $d\alpha_c$  will condense to develop multiple layers, while only on the uncompleted fraction will it condense in such a way as to increase the content of  $\alpha'$  and thereby augment the vapor pressure of the system. The effective increment for the  $\alpha'$ -layer will thus be  $(1 - p/p_0)d\alpha_c$ . Provided all increments in  $\alpha'$  are equally effective in augmenting the vapor pressure, it follows that

$$(1 - p/p_0)d\alpha_c/\alpha' = dp/p_0 \quad (2)$$

That is, the increment in  $\alpha'$  bears the same ratio to the total capacity of  $\alpha'$  as the increment of vapor pressure which results bears to the total pressure at saturation. On integration, equation (2) becomes

$$\alpha_c = -\alpha' \ln(1 - p/p_0) \quad (3)$$

the constant of integration being fixed by the consideration that  $\alpha_c = 0$  when  $p = 0$ .<sup>13</sup>

The total regain is the sum of the bound and the normally condensed fractions. Thus

$$\alpha = \alpha_b + \alpha_c = \alpha_b - \alpha' \ln(1 - p/p_0). \quad (6)$$

For all values of  $p/p_0 > p_b/p_0$ , at which the bound fraction is complete,  $\alpha_b$  should be constant and independent of  $p/p_0$ . In the case of a non-swelling gel, a plot of  $\alpha$  vs. the dimensionless pressure function  $-\ln(1 - p/p_0)$  should therefore be linear beyond  $p/p_0 = p_b/p_0$ .

**The Sorption of Water Vapor by a Swelling Gel.**—Equation (6) fails to take into account the progressive enlargement of the effective sorbing surface of the gel which accompanies

(13) The development of equation (2) provides inferentially for the successive layers condensed on  $\alpha'$ , since the fraction  $p/p_0$  is so condensed. The special dependence of the extent of each layer on that of every other by the theory of polymolecular condensation of Brunauer, Emmett and Teller<sup>14</sup> is not considered. Rather this treatment assumes, simply, that after the completion of the bound layer the condensation of water molecules on each available element of area is equally probable, regardless of the number of layers already condensed. It is interesting to compare the results of the two concepts.

For the special case in which an adsorbent treated according to the BET theory has a surface indistinguishable from that of liquid water, the ratio  $v/v_m$  is readily identified with the ratio  $\alpha_c/\alpha'$ . In this case,  $\gamma$ , the ratio of  $s_1$  to  $s_0$  would not differ from  $x$ , the generalized ratio of  $s_i$  to  $s_{i-1}$ ,  $c$  would equal unity, and  $v/v_m = x/(1 - x)$ . Having shown the identity of  $x$  with  $p/p_0$ , we may recognize  $x/(1 - x)$  as the sum of an infinite geometric progression in  $x$ , and write, for this special case

$$v = v_m [p/p_0 + (p/p_0)^2 + (p/p_0)^3 + \dots] \quad (4)$$

Expansion of the logarithmic term of equation (3) leads to the statement

$$\alpha_c = \alpha' [p/p_0 + 1/2(p/p_0)^2 + 1/3(p/p_0)^3 + \dots] \quad (5)$$

The BET theory identifies the successive terms in (4) with the contents of the first, second, and higher layers. If, only for the sake of comparison, one so identifies the terms of (5), it is apparent that in (5) the development of the higher layers is progressively limited.

In justification of this general result, a doubtful assumption of the BET theory may be pointed out.<sup>14</sup> The summation of the contents of the multimolecular layers is accomplished through the simplifying assumption that "the evaporation-condensation properties of the molecules in the second and higher adsorbed layers are the same as those of the liquid state." This cannot, in fact, be correct, as brief consideration will show.

In order that a surface partially covered by normally evaporating molecules should develop under equilibrium conditions a vapor pressure less than  $p_0$ , the covered fraction must be highly dispersed in small patches on the total area. The pyramiding of multimolecular layers, each progressively smaller in extent than the one below it, will result in the exposure, at the edges of each successive layer, of an increasing proportion of the molecules of that layer. These exposed "edge" molecules will be bound by diminished forces and will consequently tend to evaporate preferentially. In equivalent terms one may predict that  $E_L > E_2 > E_3 > \dots > E_i$ , where  $E_L$  is the normal heat of liquefaction, and point out that surface tension may be expected to restrict the pyramiding of the layers. The effect will be particularly important in the condensation of a sorbate of high surface tension, such as water.

The simple form of the BET isotherm predicts weights of condensed sorbate which are usually much too high at the higher relative vapor pressures. The BET equation may be fitted to the experimental data by the introduction of a pragmatic factor which sets a limit on the number of layers which can be formed one above the other. The quantitative result of such a limitation is in general similar to that which would be obtained by applying a progressively increasing restriction on the formation of each successive layer without limit, as is done in equation 5.

(14) See also Harkins and Jura, *THIS JOURNAL*, **66**, 919 (1944).

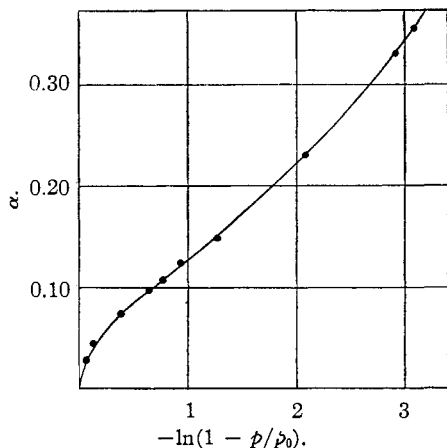


Fig. 1.—Adsorption isotherm for cellophane at 24.8°.

swelling. Figure 1 shows that in the case of unplasticized, non-moistureproofed cellophane<sup>15</sup> the suggested plot is non-linear, and has, beyond the point of inflection, a steadily increasing slope. As a result of the gradual enlargement of the sorbing surface, neither  $\alpha_b$  nor  $\alpha'$  of equation (6) is constant. New points capable of attaching molecules of the  $\alpha_b$  fraction are produced by the swelling so long as it continues, though they are immediately saturated at all relative vapor pressures above  $p_b/p_0$ . In order to express the effect of swelling it is convenient to replace the weight ratio of sorbate to sorbent,  $\alpha$ , by the ratio  $\alpha/[1 + f(\alpha)]$ , where  $f(\alpha)$  represents the effective increase in the sorptive capacity of the swollen gel in terms of an undetermined general function of the regain. In view of the considerable variety of gel structures resulting from varying degrees of micellar aggregation and other types of inhomogeneous dispersion, cross-linking and variable structural flexibility, it is unlikely that the nature of  $f(\alpha)$  can readily be predicted on *a priori* grounds. If, however, the shape of  $f(\alpha)$  can be discovered empirically, the task of representing the sorption data and differentiating the  $b$  and  $c$  fractions of the sorbate may be accomplished with no less certainty.

One special case is significant. If it is assumed that swelling proceeds by the development of additional discrete pores within the gel structure, rather than by the progressive enlargement of those originally present, so that a fairly constant concentration of pores is maintained, the effective sorbing surface will, at all stages of the sorption, be approximately proportional to the volume of the sorbing gel. Under these circumstances, since the true density of the gel is not greatly altered by moderate swelling,<sup>16</sup> the number of

(15) V. L. Sinril and Sherman Smith, *Ind. Eng. Chem.*, **34**, 226 (1942).

(16) The extent of the deviation of the true density of a swollen gel may be evaluated by considering an extreme case, that of cotton cellulose, whose density is, at most, 1.4. At  $p/p_0 = 0.977$ , soda-boiled cotton adsorbs water to the extent of 18% of its dry weight.<sup>17</sup> At least one-sixth of the sorbed water is, to judge from the shape of

sorptive points exposed within the swollen structure will be proportional to its total mass, and  $[1 + f(\alpha)]$  may be replaced by  $(1 + \alpha)$ . In all cases which permit this simplification, the rather awkward formulation  $\alpha/[1 + f(\alpha)]$  reduces to  $\alpha/(1 + \alpha)$  which is identical with the weight fraction,  $\bar{w}$ , of sorbate in the swollen gel. Equation (6) may then be rewritten

$$\bar{w} = \bar{w}_b + \bar{w}_c = \bar{w}_b - \bar{w}' \ln(1 - p/p_0) \quad (7)$$

where the definitions of the various weight fractions parallel those of the regains of equation (6).

The foregoing derivation is not general and equation (7) is not expected to apply in all cases of polymer sorption. However, as will appear in the following discussion, this equation represents successfully a considerable variety of situations in which the substitution of  $(1 + \alpha)$  for  $[1 + f(\alpha)]$  is valid, for whatever reason. The use of the weight fraction in place of the regain may be regarded as an approximate method of including, implicitly, the effect of swelling on the sorptive capacity of the gel.

**Application of the Method to Sorption Data. Sorption by Cellophane.**—In Fig. 2 the weight fraction of water adsorbed by unplasticized,

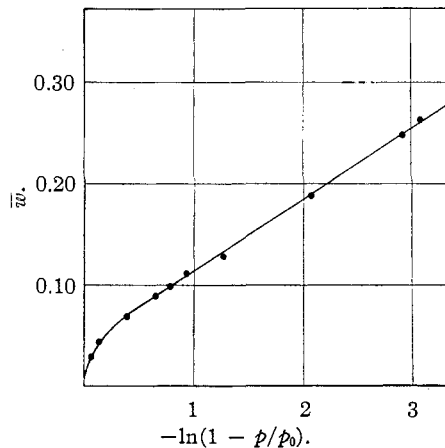


Fig. 2.—Adsorption isotherm for cellophane at 24.8°.

non-moistureproofed cellophane (the data are the same as those of Fig. 1) is plotted against the negative value of the natural log of  $(1 - p/p_0)$ . The curve is linear beyond the point at which  $p/p_0$  is approximately 0.4. At all higher relative the isotherm, tightly bound. To the bound water, Filby and Maass<sup>11</sup> have ascribed an augmented density of approximately 2.5. Assuming that five-sixths of the water exhibits its normal density, the mean density of all the water adsorbed would be 1.25. Moreover, the disparity between the density of the adsorbent and the mean density of the adsorbate affects the density of the whole only through that fraction of the mass which is contributed by the sorbate. The mean density of the cellulose with its adsorbed water in this instance is 1.38, which does not differ materially from the density of dry cellulose. At lower relative vapor pressures with correspondingly smaller regains and especially when the density of the adsorbent is nearer that of water, the deviation is of still less consequence. In general it may be expected that those polymers which manifest unusually high densities will present adsorbing surfaces of such high polarity as to produce an enhanced density in a part of the adsorbed water.

vapor pressures these data are satisfactorily represented by equation (7) in the form

$$\bar{w} = 0.044 - 0.069 \times 2.303 \log(1 - p/p_0)$$

The solid line of Fig. 3 shows the part of the conventional adsorption isotherm which may be calculated from the above equation. The points in Fig. 3 are taken from the original data.

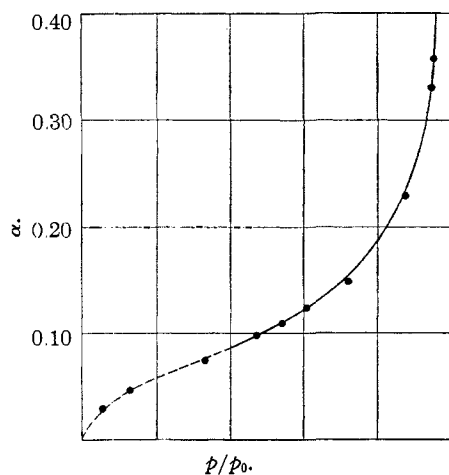


Fig. 3.—Conventional adsorption isotherm for cellophane at 24.8°.

**The Hysteresis Phenomenon.**—Figure 4 shows both the desorption and adsorption isotherms for the cellophane under discussion, plotted as hitherto suggested. The two lines are in this case strictly parallel throughout their lengths, indicating that  $\bar{w}'$  is independent of the sorption history of the adsorbent. A striking distinction between the adsorption and desorption processes is found in the variation in the intercepts for the two lines. In this instance  $\bar{w}_b$  on absorption is 0.044, on desorption, 0.057. The adsorption and desorption lines apparently meet at infinity, which would be the value of  $-\ln(1 - p/p_0)$  at the saturation vapor pressure.

Urquhart<sup>6</sup> attributed the hysteresis in the sorption of water by cellulose to an irreversible uncoupling of hydroxyl groups within the cellulose structure, the uncoupling occurring during adsorption and the recoupling occurring at a relatively delayed stage in the desorption process. Filby and Maass<sup>11</sup> have concluded that there is a greater proportion of bound water in cellulose on desorption than on adsorption. A mechanism for the development of hysteresis which is in accord with both ideas is suggested by the present treatment.

Additional points of attachment for water molecules of the bound fraction are developed, as a result of swelling, throughout all of the adsorption process. (Note that while  $\bar{w}_b$  is constant, the weight of bound water increases in proportion to the weight of the swollen sample.) Above the critical relative vapor pressure  $p_b/p_0$  these points are saturated as rapidly as they ap-

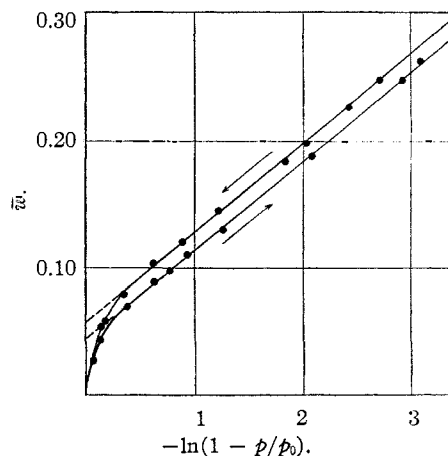


Fig. 4.—Complete sorption isotherm for cellophane at 24.8°;  $w' = 0.069$ ,  $w_b(\text{adsorption}) = 0.044$ ,  $w_b(\text{desorption}) = 0.057$ .

pear. On desorption the regression of these centers of attraction is delayed by the persistence of a portion of the bound water which intervenes to block the collapse of the structure. Since both the bound and the normally condensed phases are in equilibrium with the vapor phase at all stages of the sorption, the evaporation of individual water molecules of the bound layer can and must occur at any relative vapor pressure, the evaporation being less probable when the molecule is tightly bound. However, when the collapsing structural elements of the shrinking gel are large enough to accommodate a number of water molecules on their faces, the probability of the simultaneous evaporation of all of these molecules is minute except at the lowest relative vapor pressures. The presence of rigid structural elements of appreciably greater dimensions than those of the sorbate molecules is thus a necessary condition for the development of sorption hysteresis. The phenomenon is not to be expected in sorption by liquids or by those polymers possessing a high degree of structural mobility, since the individual structural collapses would be hindered by so few molecules of the bound sorbate that the recoupling of the structure would be essentially probable at all relative vapor pressures.

**Sorption by Soda-boiled Cotton.**—The applicability of the method is further demonstrated in Fig. 5. The sorbent is soda-boiled cotton; the data are those of Urquhart and Williams.<sup>17</sup> The values of  $\bar{w}_b$  for this sample are lower than those for cellophane, suggesting that the native cellulose is less disperse than the regenerated. The lower value for  $\bar{w}'$  probably results in part from a more perfect orientation in the native cellulose, with a resulting decrease in the number and size of the interspaces on whose bounding surfaces the  $\bar{w}'$  layer condenses. Hys-

(17) A. R. Urquhart and A. M. Williams, *J. Text. Inst.*, **15**, T433 (1924), Table I.

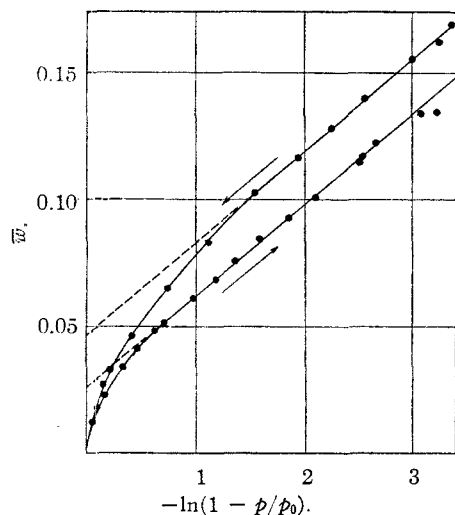


Fig. 5.—Sorption isotherm for soda-boiled cotton at 25°;  $w' = 0.036$ ,  $w_b(\text{adsorption}) = 0.026$ ,  $w_b(\text{desorption}) = 0.047$ .

teresis is more pronounced than in the case of cellophane.

**Sorption by Wool.**—The data plotted in Fig. 6 are those of Shorter and Hall<sup>18</sup> for the mean sorption of a group of yarns. A rapidly fluctuating relative humidity resulting from an oscillation in the temperature of these experiments gives an average of the adsorption and desorption isotherms, so that the wide hysteresis normally exhibited by wool does not occur. The sorption is characterized by an unusually high proportion of bound water.

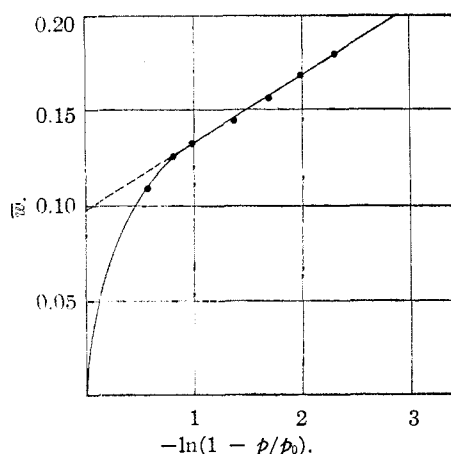


Fig. 6.—Sorption isotherm for wool at 22.2°;  $w' = 0.036$ ,  $w_b(\text{mean}) = 0.098$ .

**Sorption by Nylon.**—Figure 7 represents the sorption of water vapor by a sample of experimental nylon film.<sup>19</sup> The striking feature of this

(18) S. A. Shorter and W. J. Hall, *J. Text. Inst.*, **15**, T316 (1924), Table IV.

(19) V. L. Simril, "The Sorption of Water Vapor by Polymers," dissertation, University of North Carolina (1942). The experimental method is described in ref. 17.

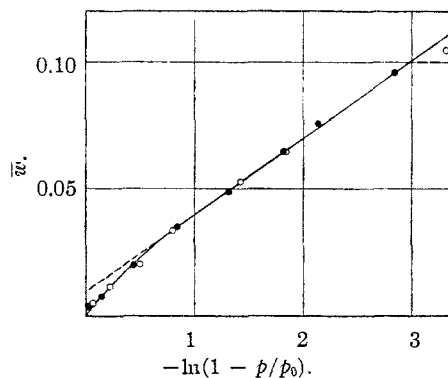


Fig. 7.—Sorption isotherm for nylon at 25°;  $w' = 0.030$ ,  $w_b = 0.009$ ; O = adsorption, ● = desorption.

isotherm is the absence of an appreciable hysteresis. This is probably attributable to the mobility of the polar amido groups which are spaced at intervals along the flexible hydrocarbon chains of the polymer. The very low value for  $\bar{w}_b$  suggests that the polar points to which water molecules might be bound are mutually saturated, probably through hydrogen bonds between amido groups in adjacent chains.

Figures 4 to 7 illustrate some of the variations of which high polymer sorption data are capable. A plot of the weight fraction *vs.*  $-\ln(1 - p/p_0)$  is linear in each case. The method applies successfully to sorption data on all of the varieties of cellulose which have been treated, as well as to such diverse systems as starch, zein, chitosan and polyvinyl alcohol polymers with water as the sorbate. In general the curves are linear between relative vapor pressures of 0.5 and 0.95. One of the advantages of the method lies in the fact that this is the region in which precise sorption data are most readily obtained. At values of  $p/p_0 > 0.95$  the function  $-\ln(1 - p/p_0)$  is highly sensitive to small absolute errors in the measurement of  $p$ .

**Comparison with the Method of Brunauer, Emmett and Teller.**—Some points of similarity between the mathematical bases of this treatment and that of Brunauer, Emmett and Teller have been discussed in an earlier section. The two methods differ materially in one respect. In the BET theory, the contents of the second and all higher layers are related to each other and to the content of the first layer through the constants  $\gamma$  and  $\alpha$ . In the present treatment that portion of the sorbate which has the condensation properties of liquid water is isolated on the basis of the manner of its dependence on the relative vapor pressure. The remainder,  $\bar{w}_b$ , is designated the bound fraction. This treatment thus avoids the complicating effects of irreversible or chemisorption and the probable persistence of the binding forces of the primary surface beyond the first adsorbed layer.

In the present method,  $\bar{w}'$  is, at each stage of the sorption, the weight fraction of water re-

quired to complete the first layer of normally condensed water. It is thus a measure of the effective surface of the polymer for the condensation of such water. As the several plots demonstrate,  $\bar{w}'$  may be either larger or smaller than  $\bar{w}_b$ . In this connection it is interesting to compare the values of the constants already listed with related values obtained by the BET method.

In employing BET equation (A),<sup>12</sup>  $\alpha$  and  $\alpha_m$  may be substituted for  $v$  and  $v_m$ , respectively, without affecting the validity of the equation. Here  $\alpha$  is defined as the total regain and  $\alpha_m$  as that portion of the regain required to saturate the first layer. The equation then reads

$$p/\alpha(p_0 - p) = 1/\alpha_m c + [(c - 1)/\alpha_m c] \{p/p_0\} \quad (8)$$

Values of  $\alpha_m$  have been calculated by plotting  $p/\alpha(p_0 - p)$  vs.  $p/p_0$  to obtain the slope,  $(c - 1)/\alpha_m c$ , and the intercept,  $1/\alpha_m c$ . The table below compares the values of  $\bar{w}'$ ,  $\bar{w}_b$  and  $\alpha_m$  on both adsorption and desorption for the samples of cellophane, soda-boiled cotton and nylon heretofore described. The data for wool are inadequate for the graphical determination of  $\alpha_m$ .

TABLE I

Adsorbent	$\bar{w}'$	$\bar{w}_b$	$(\bar{w}' + \bar{w}_b)/2$	$\alpha_m$ (BET)
Adsorption				
Cellophane	0.069	0.044	0.056	0.055
Cotton	.036	.026	.031	.029
Nylon	.030	.009	.019	.018
Desorption				
Cellophane	.069	.057	.063	.067
Cotton	.036	.047	.042	.044
Nylon	.030	.009	.019	.018

The term  $\bar{w}'$  represents a ground layer for the normally condensed water and its definition is roughly comparable to that of  $\alpha_m$ .  $\bar{w}_b$  may be

regarded as the measure of a tightly bound substratum of water molecules which paves the sorbing surface of the polymer and effectively reduces the intensities of the surface forces of attraction to the level of the forces in a liquid water surface.

There is striking concordance between the values of  $\alpha_m$  and the values of the mean of  $\bar{w}'$  and  $\bar{w}_b$ . The differences are insignificant. It may be inferred that the BET method obtains, as the surface area in these cases, an average between that covered by the tightly bound water molecules and that covered by the first normally condensed layer.

### Summary

A method for the graphic analysis of data on the sorption of water vapor by high polymers is presented. The method subdivides the weight fraction of sorbed water into a bound and a normally condensed fraction. It is shown that hysteresis in the sorption isotherm is a consequence of variation in the fraction of bound water present in the adsorption and desorption processes, the bound fraction being always larger on desorption than on adsorption. A mechanism for the development of hysteresis is suggested. Conditions for the development of hysteresis are: (1) an enlargement of the sorptive surface as a consequence of swelling and (2) the presence of rigid structural elements in the polymer having dimensions relatively large compared to those of the sorbate molecules. The method is compared and contrasted with that of Brunauer, Emmett and Teller.

ALBUQUERQUE, NEW MEXICO

RECEIVED<sup>20</sup> OCTOBER 14, 1946

(20) Original manuscript received November 4, 1944.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY, AND FROM E. I. DU PONT DE NEMOURS AND CO.]

## The Free Energy, Heat and Entropy of Sorption of Water Vapor by Proteins and High Polymers

BY MALCOLM DOLE AND A. D. McLAREN<sup>1</sup>

### Introduction

Bull<sup>2</sup> has recently published data for the gain of weight of a number of proteins and nylon when exposed to atmospheres of different relative humidities at 25 and 40°, from which he calculated "the free energy required to transfer water molecules from the vapor state to the solid surface," using the equation

$$\Delta F = -RT \int_0^1 n \, d \ln x \quad (1)$$

where  $n$  is the number of moles of water sorbed per 100 g. of protein and  $x$ , equal to  $p/p_0$ , is the relative vapor pressure of the water.<sup>3</sup>

Simril and Smith<sup>4</sup> in studying the sorption of water by cellophane wrote for the over-all change in free energy for the process water at the saturation pressure  $p_0$  transferred to cellophane at pressure  $p$  the equation

$$\Delta F = nRT \ln x \quad (2)$$

(1) Present address: Polytechnic Institute of Brooklyn.

(2) H. B. Bull, THIS JOURNAL, **66**, 1499 (1944); Bull's graphical method for calculating the free energy was suggested by G. E. Boyd and H. K. Livingston, *ibid.*, **64**, 2383 (1942).

(3) The negative sign was omitted from Bull's equation, but it was given correctly in his table of data.

(4) V. L. Simril and Sherman Smith, *Ind. Eng. Chem.*, **34**, 226 (1942).