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, $\overline{w}'$ may be either larger or smaller than $\overline{w}_b$. 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),[12] α and α_m may be substituted for v and v_m, respectively, without affecting the validity of the equation. Here α is defined as the total regain and α_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 α_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 $\overline{w}'$, $\overline{w}_b$ and α_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 α_m.

TABLE I

Adsorbent	$\overline{w}'$	$\overline{w}_b$	$(\overline{w}' + \overline{w}_b)/2$	α_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 $\overline{w}'$ represents a ground layer for the normally condensed water and its definition is roughly comparable to that of α_m. $\overline{w}_b$ 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 α_m and the values of the mean of $\overline{w}'$ and $\overline{w}_b$. 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.

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

BY MALCOLM DOLE AND A. D. McLAREN[1]

Introduction

Bull[2] 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.[3]

Simril and Smith[4] 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

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

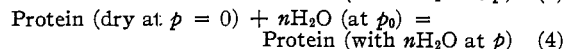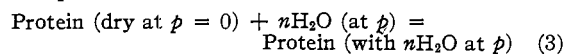(1) Present address: Polytechnic Institute of Brooklyn.

(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).

Goldmann and Polanyi[5] used an exactly similar equation to calculate "affinity curves" for such processes as the adsorption of carbon disulfide on charcoal.[6]

It is the purpose of this paper to examine in a detailed way the free energy change and heats of the processes

Protein (dry at $p = 0$) + nH$_2$O (at p) =
          Protein (with nH$_2$O at p)   (3)

Protein (dry at $p = 0$) + nH$_2$O (at p_0) =
          Protein (with nH$_2$O at p)   (4)

Process (3) is the one for which Bull calculated the integral free energy and heat changes. Here we derive equations for both processes (3) and (4) from which the free energy change can be calculated for sorption following a linear, Langmuir or Brunauer–Emmett–Teller (BET) isotherm. Similar equations for the heat of sorption will also be given and discussed in relation to data on proteins and high polymers.

General Theory

The free energy increase of process (3) or (4) may be computed from the general equation[7]

$$dF = -\sum_\alpha S^\alpha \, dT^\alpha + \sum_\alpha V^\alpha \, dP^\alpha + \sum_\alpha \sum_i \mu_i \, dn_i^\alpha$$
$$-\sum_\sigma S^\sigma \, dT^\sigma + \sum_\sigma \gamma^\sigma \, dA^\sigma + \sum_\sigma \sum_i \mu_i^\sigma \, dn_i^\sigma \quad (5)$$

where $\sum_\alpha$, $\sum_i$ and $\sum_\sigma$ signify summation over all bulk phases, components and surface phases, respectively.

For process (3) we obtain equation (1) used by Bull, and for process (4) the differential equation

$$dF/dn = \overline{\Delta F} = RT \ln x \quad (6)$$

In the case of linear sorption

$$n = \alpha x \quad (7)$$

where α is a constant, process (3) yields the free energy

$$\Delta F_{(3)} = -nRT \quad (8)$$

so that the partial molal free energy, $\Delta F/n$, is simply $-RT$, independent of the type of protein or high polymer and independent of the relative vapor pressure. In the case of process (4) the result is

$$\Delta F_{(4)} = nRT \, (\ln x - 1) \quad (9)$$

For Langmuir adsorption

$$n = \frac{\alpha x}{1 + \beta x}$$

where α and β are constants, the free energy equations for processes (3) and (4) are, respectively

$$\Delta F_{(3)} = -nRT \left[\frac{1 + \beta x}{\beta x} \ln (1 + \beta x) \right] \quad (10)$$

$$\Delta F_{(4)} = nRT \left[\ln x - \frac{1 + \beta x}{\beta x} \ln (1 + \beta x) \right] \quad (11)$$

For BET sorption[8] in which

$$n = \frac{\alpha x}{(1 - x)(1 + \beta x)} \quad (12)$$

the following free energy equations result

$$\Delta F_{(3)} = -nRT \left[\frac{(1 - x)(1 + \beta x)}{x(1 + \beta)} \ln \frac{(1 + \beta x)}{(1 - x)} \right] \quad (13)[9]$$

$$\Delta F_{(4)} = nRT \left[\ln x - \frac{(1 - x)(1 + \beta x)}{x(1 + \beta)} \ln \frac{(1 + \beta x)}{(1 - x)} \right] \quad (14)$$

The differential free energy, $\overline{\Delta F}$, may be expressed in terms of n instead of x; thus for linear, Langmuir and BET sorption, respectively, we have (for process (4))

$$\overline{\Delta F_{(4)}} = RT \ln \frac{n}{\alpha} \quad (15)$$

$$\overline{\Delta F_{(4)}} = RT \ln \frac{n}{\alpha - n\beta} \quad (16)$$

$$\overline{\Delta F_{(4)}} = RT \ln \left[\frac{[n(\beta - 1) - \alpha] + \sqrt{[n(\beta - 1) - \alpha]^2 + 4n^2\beta}}{2n\beta} \right] \quad (17)$$

It is interesting to note that the integral free energy equations for process (4) in each case differ from those for process (3) solely by inclusion of the term $nRT \ln x$; in fact it can be shown in general that

$$\Delta F_{(4)} = \Delta F_{(3)} + nRT \ln x \quad (18)$$

Figure 1 illustrates Bull's graphical estimate of $\Delta F_{(3)}$[10] for unlyophilized egg albumin and values of $\Delta F_{(4)}$ calculated from $\Delta F_{(3)}$ by means of equation (18). The essential difference between the two curves is that the slope of the top curve continually decreases as x increases whereas the slope of Bull's curve passes through an inflection point and begins to increase. This led Bull to remark "There is a gain in affinity of the protein for water as water is adsorbed." We believe that such a gain in affinity is misleading, because if water is sorbed by the protein from a standard source of constant vapor pressure, process (4), there is no point where the slope increases with x.

Bull's published ΔF values are the free energy of water sorption at saturation, for which condition there is no difference in the two methods of calculating the free energy changes.

The dotted line of Fig. 1 represents free energies calculated from equation (11) using Bull's BET constants.[10] Excellent agreement between the graphical and analytical methods of calculating the free energy of process (4) is seen to exist, but only over the range of validity of the BET equation.

Turning now to the calculation of the so-called isosteric heat of sorption,[11] q, the partial molal

(5) F. Goldmann and M. Polanyi, Z. physik. Chem., **A132**, 313 (1928).

(6) See S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943, p. 111.

(7) See, for example, E. A. Guggenheim, "Modern Thermodynamics," Methuen, London, 1933, p. 165.

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

(9) Equation (13) is identical essentially with equation (7) of the paper by H. K. Livingston, THIS JOURNAL, **66**, 569 (1944), who applied the BET theory to the calculation of surface pressures.

(10) Data kindly supplied by Professor Bull.

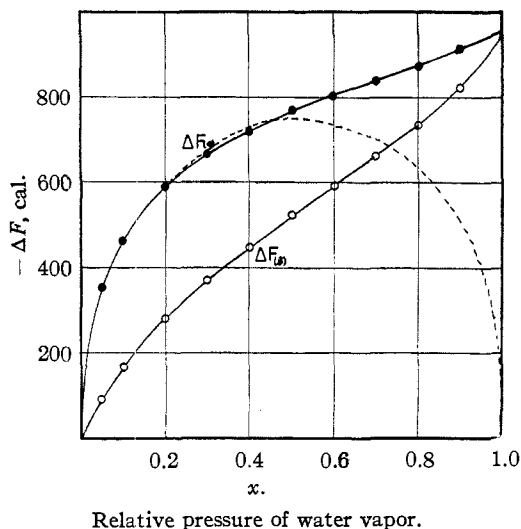(11) S. Brunauer, ref. 6, Chap. VIII.

Fig. 1.—Integral free energy of hydration of unlyophilized egg albumin from Bull's data[2] at 25°: open circles Bull's graphic estimates for process (3); closed circles, ΔF for process (4) calculated from equation (18); dotted line, ΔF for process (4) calculated from BET constants, equation (11). If the adsorption of water followed the BET equation over the whole pressure range, no such maximum in the ΔF as is exhibited by the dotted line would have been calculated. Theoretically, for pure BET sorption $-\Delta F$ should become infinite at x equal to unity.

heat of process (4) may be obtained from the well-known thermodynamic equation

$$-q = \overline{\Delta H} = \frac{\partial \Delta H}{\partial n} = r \ln \frac{x_1}{x_2} \qquad (19)$$

where $r = RT_1T_2/(T_2 - T_1)$ and x_2 is the relative vapor pressure at the higher temperature T_2 which produces the same moles of water sorption as at the lower temperature T_1. For the three types of sorption considered above, linear, Langmuir and BET, respectively, we can write

$$\overline{\Delta H}_{(4)} = r \ln \frac{\alpha_2}{\alpha_1} \qquad (20)$$

$$\overline{\Delta H}_{(4)} = r \ln \frac{\alpha_2 - n\beta_2}{\alpha_1 - n\beta_1} \qquad (21)$$

and

$$\overline{\Delta H}_{(4)} = r \ln$$

$$\left[\frac{\beta_2[n(\beta_1 - 1) - \alpha_1] + \sqrt{[n(\beta_1 - 1) - \alpha_1]^2 + 4n^2\beta_1}}{\beta_1[n(\beta_2 - 1) - \alpha_2] + \sqrt{[n(\beta_2 - 1) - \alpha_2]^2 + 4n^2\beta_2}} \right] \qquad (22)$$

In the Langmuir sorption case, the isosteric heat will be independent of n, as it is for linear sorption, if the constants α and β vary with temperature according to the same exponential function as they would in simple theory and if the surface area remains constant with temperature.

Equation (22) can be illustrated by $\overline{\Delta H}$ values calculated using the α and β constants found by Bull[10] for collagen at 25 and 40°, namely

$$\alpha_1 = 11.81 \qquad \beta_1 = 21.4$$
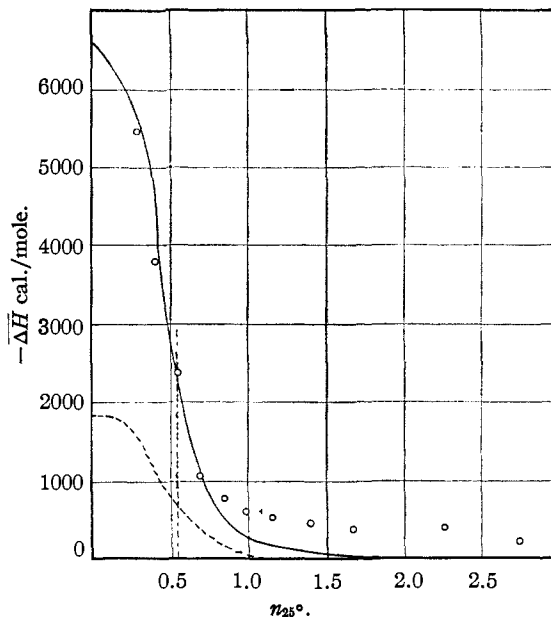$$\alpha_2 = 6.94 \qquad \beta_2 = 12.1$$

Fig. 2.—Differential net heats of sorption at 25° for collagen using Bull's BET constants in equation (22). The circles are values of $\overline{\Delta H}$ graphically estimated directly from Bull's data at 25 and 40°. The lower dashed line represents the differential net heat of sorption calculated from equation (22) using constants at 40° obtained from an exponential function from the constants at 25°, while the vertical dashed line indicates the value of n necessary for one monolayer of sorbed water.

The computed values are shown by the solid line in Fig. 2 where the circles represent more accurate differential heat values estimated graphically as described below. Over the range of validity of the BET equation, there is satisfactory agreement between the two methods of $\overline{\Delta H}$ calculation. Note that there is no break in $\overline{\Delta H}$ at the point where the amount of water sorbed is equal to that required for one monolayer (this point is shown by the vertical dotted line). As is well known the BET theory permits the onset of multilayer sorption before sorption on the first layer is complete. The lower dotted curve represents $\overline{\Delta H}$ values calculated from equation (22) using α and β constants computed at 40° from those at 25° by means of the same exponential function.

We do not give the integrated forms of equations (20), (21) and (22) as to use these equations the constants must be known accurately at the two temperatures and the sorption of the vapor must follow the equations accurately at both temperatures. Actually the integrated forms of (21) and (22) are so complicated that it is easier to integrate them graphically.

In the case of Bull's process (3) a value of $\overline{\Delta H}$ could be calculated by means of equation (19); however, the $\overline{\Delta H}$ would not be the difference between the heat of sorption on the polymer and the heat of evaporation from pure water, but the

difference between the heat of sorption and the heat of evaporation from some source of the water at pressure p, such as the sulfuric acid solutions used by Bull. As a matter of fact Bull did not use equation (19) in his calculations, preferring to calculate his ΔH values from the Gibbs–Helmholtz equation. Such a calculation implicitly assumes that the number of moles of water sorbed per 100 g. of protein at the upper and lower temperatures is the same at the same partial pressure of water vapor. Where the sorption changes materially with the temperature at constant x, a marked difference will exist, therefore, between his ΔH values and those calculated by a graphical integration of equation (19).

The total entropy of process (4) can be obtained from the integral ΔH and ΔF of the reaction while the excess differential entropy of sorption over that of condensation of the water in pure water is given by $\overline{\Delta H}$ of equation (19) divided by the absolute temperature. The actual differential entropy of sorption of the water vapor on the high polymer is obtained by adding the entropy of condensation of water in pure water to the entropy calculated from $\overline{\Delta H}$.

The Heats of Water Sorption on Nylon, Silk, Egg Albumin and Collagen

The partial molal heats of sorption are more interesting than the free energies of sorption as the $\overline{\Delta H}$ moles sorbed curves are all different and exhibit individual peculiarities. At first we attempted to compute $\overline{\Delta H}$ by means of equation (22) using BET constants at 25 and 40° given by Bull but
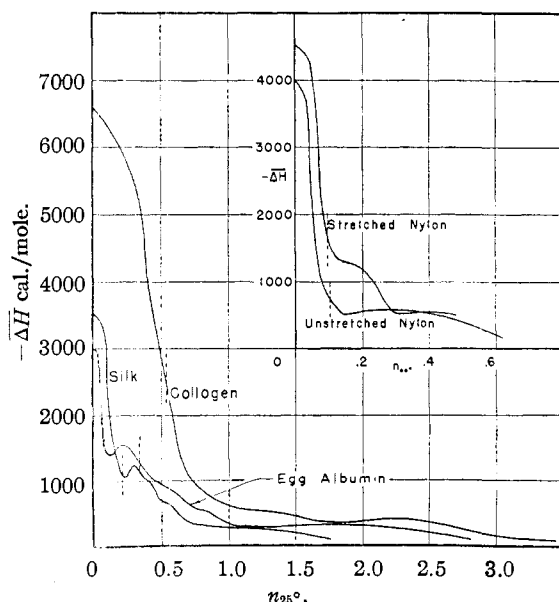

Fig. 3.—Differential net heats of water sorption at 25°, graphically estimated from Bull's data. The dotted vertical lines correspond to a value of n equal to that required for one monolayer.

on checking these data by $\overline{\Delta H}$ values estimated graphically we found that only in the case of collagen did the two methods agree and then only as far as x equal to 0.4, see Fig. 2. Apparently the BET equation is not followed with sufficient precision at the two temperatures to justify the use of equation (22). The graphic determination of $\overline{\Delta H}$ was carried out by drawing large scale isotherms at the two temperatures and determining the value of x_2 at the upper temperature necessary to produce the same number of moles of sorption as at the relative vapor pressure x_1 of the lower temperature. $\overline{\Delta H}$ was then readily calculated from equation (19). Values are shown in Fig. 3.

The initial net of heat of sorption which is large in all cases drops rapidly and then levels off at a few hundred calories at values of n greater than that required for a complete monolayer. In the BET theory the relationship between our constant β and the heat of adsorption is given by the equation

$$c = \beta + 1 = \frac{a_1 b_2}{b_1 a_2} c^{(E_1 - E_2)/RT} \qquad (23)$$

where a_1, a_2, b_1 and b_2 are constants. Taking the ratio of $a_1 b_2$ to $b_1 a_2$ as unity and using values of β at 25° supplied by Bull[10] the heats given in Table I are obtained. As has been observed before[12] the heat values calculated from the BET equation (23) are not only lower than the initial heat, third column, but lower than the heats averaged over values of n required for one monolayer, fourth column. If the ratio $a_1 b_2/a_2 b_1$, which represents the ratio of the partition function of the molecule adsorbed in the first layer to that in the higher layers is 1/50 as estimated by Cassie[13] then the heats of the second column should be increased by 2.3 RT log 50 or 2300 cal./mole. Such a correction brings about a considerable improvement between the BET theory and the graphically estimated heats of sorption. At the present time, however, calculations of partition functions of condensed molecules contain many speculative assumptions. These large initial heats may result from the chemisorption (possibly by hydrogen bond formation) on polar groups such as free carbonyl or imido groups or on the polar groups of the protein side chains as suggested by Pauling.[14] The data of Table I also indicate that the BET constant c cannot be relied upon as an indication of the initial heat of sorption, so that the conclusion of Pauling that liberated peptide carbonyl groups attract water molecules relatively weakly may not necessarily be correct. As will be demonstrated later, structural considerations have an important bearing on the energy of bonding of water.

The differential heat curve for unstretched nylon, Fig. 3, is especially interesting as $-\overline{\Delta H}$

(12) See the discussion by P. H. Emmett, THIS JOURNAL, **68**, 1784 (1946).

(13) A. B. D. Cassie, Trans. Faraday Soc., **41**, 450 (1945).

(14) L. Pauling, THIS JOURNAL, **67**, 555 (1945).

TABLE I

HEATS OF SORPTION IN CALORIES PER MOLE AT 25° CAL-
CULATED AND ESTIMATED FROM THE DATA

Substance	$[E_1 - E_L]$	$-\overline{\Delta H}$ (± 500 cal.) at $n = 0$	$-\overline{\Delta H}$ (av. up to n for one monolayer)
Unstretched nylon	934	4500	2260
Stretched nylon	1056	4400	3500
Silk	1571	4000	2600
Egg albumin (unlyo-philized)	1487	3000	1500
Collagen	1842	6600	5200
Salmin (c_1)	2550	4500	3847
Salmin (c_2)	616	4500	1650 (av. between layers)

drops rapidly from a value which is about the same for the two types of nylon, silk, salmin and egg albumin to 550 cal./mole at a water content approximately equal to that necessary to complete the first sorbed layer, and remains constant within the experimental uncertainties until roughly four layers have been covered by sorbed water. The differential heat then falls slowly up to saturation. There is no evidence among the examples shown in Fig. 3 for a rise in $\overline{\Delta H}$ mentioned by Bull[2] at high water contents. The value of $-\overline{\Delta H}$ amounting to 550 cal./mole at water contents greater than necessary for the first layer violates the assumptions of the BET theory, which is based on the idea that the heat of adsorption on layers above the first is equal to the heat of condensation in pure water. The heat of sorption on salmin is the only one which approaches this postulate of Brunauer, Emmett and Teller; see Fig. 4, which should be compared with Fig. 2.

Stretched nylon, which sorbs about 1.5 to 2 layers less water than unstretched nylon, gives $-\overline{\Delta H}$ values that seem to level off at 1250 cal./mole and 550 cal./mole over a limited water composition region. While the reduced water sorptive capacity of stretched nylon is easy to understand, because of increased crystallinity, the reason for the difference in the shape of the heat curve is not known. The curve suggests that the heats of sorption on the second and third layers are equal and greater than the heats of sorption on the fourth and fifth layers.

It is possible to interpret the nylon data in another way which involves giving up the multilayer sorption concept. Hermans and Weidinger[15] have recently related the sorption capacity to the fraction of amorphous material in recrystallized cellulose powder. Because of accurate measurements of the density of drawn and undrawn nylon carried out in this Laboratory,[16] we can calculate that the samples of nylon used by Bull (which were from the same stock of nylon as ours) were 63 and 71% crystalline in the case of

(15) P. H. Hermans and A. Weidinger, THIS JOURNAL, **68**, 1138 (1946).

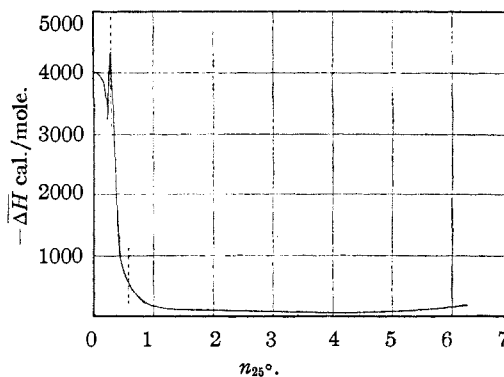(16) M. Dole and C. E. Black, III, unpublished data.

Fig. 4.—Differential net heat of water sorption for salmin at 25°, graphically estimated from the data of Bull. The dotted vertical lines correspond to values of n required for one and two monolayers, respectively.

the undrawn and drawn fibers, respectively, or 37 and 29% amorphous.[17] As there are 1.76 moles of carbonyl and imido groups total per 100 g. of nylon and as Bull[2] found 0.69 and 0.48 mole of water sorbed at saturation,[2] or 39 and 27% of the polar groups saturated for the undrawn and drawn fibers, respectively, there seems to be a direct relationship between the fraction of amorphous nylon and the fraction of total polar groups saturated with water at 100% relative humidity. This very suggestive calculation assumes only one water molecule per polar group, but any decision as to its validity must await further information and experimentation.

As Bull[2] and Pauling[14] both point out that the hydration of salmin seems to occur in such a way as to suggest that sorption takes place on two first layers, the second one of which becomes available after the first has been covered, we have calculated $-\overline{\Delta H}$ for this substance and have plotted the data in Fig. 4. Although the exact shape of the curve is quite uncertain at low water contents, there is unmistakable evidence of a maximum occurring at the point of completion of the first layer; thus the deductions of Bull and Pauling based on the BET theory are in agreement with the deductions from the differential heat curve.

With the exception of that for collagen the initial differential heats lie between -3000 and -4500 cal./mole, but the initial heat for collagen is definitely above -6000 cal./mole. Possibly the proline and hydroxyproline rings separate the layers to such an extent that the differential heat of hydration is large, i.e., less heat has to be supplied to separate the layers when water adsorption takes place, hence more is liberated. Such an effect is suggested by the high heat data for regenerated cellulose, see below.

A word should be written concerning the accuracy of the $\overline{\Delta H}$ values. Assuming the correct-

(17) This calculation was made by Dr. Black, who suggested this possible interpretation of the nylon data.

ness of Bull's data the graphical estimates are probably uncertain to about 15 to 20% at the lowest relative humidities with the uncertainty decreasing to about 5% at intermediate x values and rising again at the extreme upper limit of x. With regard to the error inherent in the experimental data we are unable to comment as Bull's published data were obtained from "smoothed" curves plotted from composite data of two separate experiments at each temperature.

The Free Energy and Heat of Hydration of Some High Polymers

The water sorption isotherms of polyvinyl alcohol, polyvinyl butyral, cellulose acetate and vinylidene chloride–acrylonitrile co-polymer[18] are all linear in the low partial pressure range becoming convex to the pressure axis at high partial pressures. Cellophane has a slight BET character to its sorption as indicated by Fig. 5 where a BET plot shows that the three lowest points approximate to a straight line well enough to calculate constants of the BET equation. From these constants it appears that 0.58 mole of water per 100 g. of polymer is required to complete the first layer; as there is 0.62 mole of glucose residues per 100 g. we can conclude that cellophane sorbs in the first layer one water molecule per glucose unit, possibly on the side-chain hydroxyl group. In the case of the other polymers mentioned there is not enough water sorbed, even at saturation, to provide one water molecule per polar group except in the case of polyvinyl alcohol, which dissolves in water. It would be interesting to compare the amount of water sorbed with the fraction of amorphous polymer in the samples.
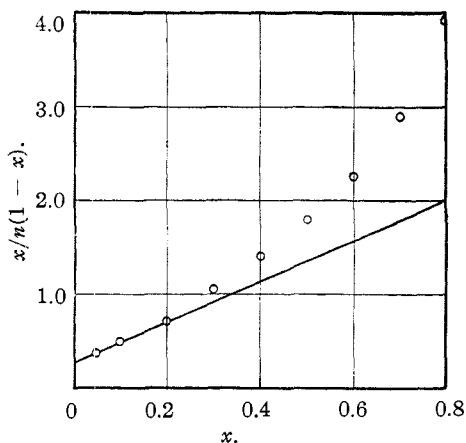
Fig. 5.—BET plot of water sorption data on cellophane at 24.8°.

(18) Cellulose acetate (91% completely substituted), polyvinyl butyral and vinylidene chloride–acrylonitrile (81% vinylidene chloride and 19% acrylonitrile) data were taken from a paper in press by P. M. Hauser and A. D. McLaren, and data on cellophane and polyvinyl alcohol from the Ph.D. thesis of V. L. Simril, University of North Carolina, 1942. The thesis of Simril also contains data for nylon practically identical with those of Bull.
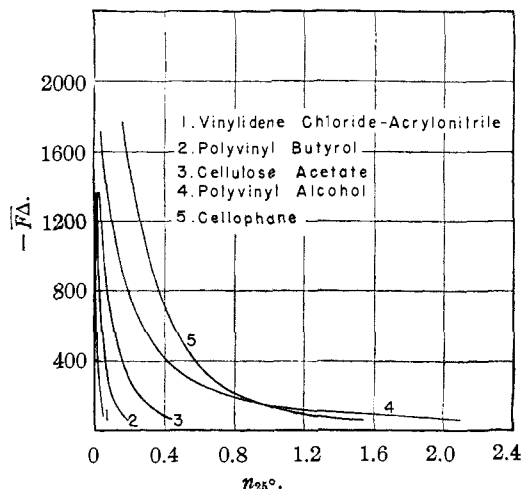
Fig. 6.—Differential free energies of sorption of water at 25°.

Figure 6 illustrates the differential free energy, $\overline{\Delta F}$, for the hydration of the polymers as a func-

TABLE II

INTEGRAL FREE ENERGIES AND NET HEATS OF SORPTION OF WATER AT SATURATION AT 25°

Substance	$-\Delta F$	$-\Delta H$ cal.
Cellophane	872	4450
Cellulose acetate	204	272
Polyvinyl alcohol	703	873
Polyvinyl butyral	93	261
Vinylidene chloride–acrylonitrile	22.8	0

tion of the water content. Cellophane has the greatest affinity for water in the low water content
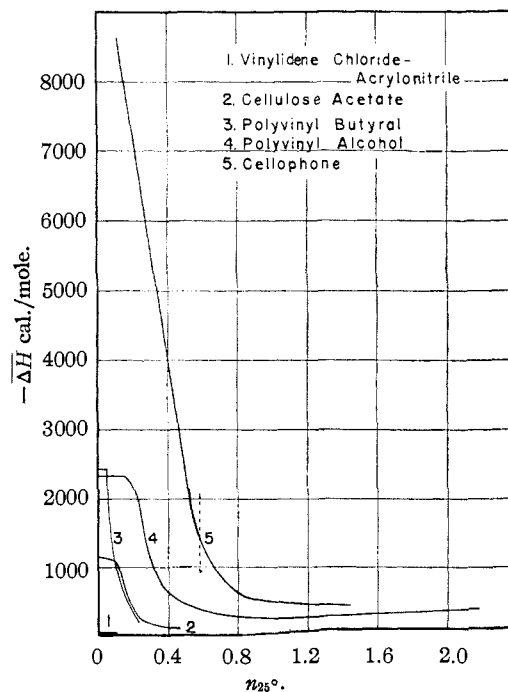
Fig. 7.—Differential net heats of sorption of water at 25°.

range, but toward saturation the affinity of polyvinyl alcohol for water becomes greatest. Using the integral free energy equation (9) over the range of its validity and graphically integrating the differential free energy curve at higher partial pressures of water, integral free energies have been calculated and are tabulated in Table II.

The $-\overline{\Delta H}$ values are shown in Fig. 7, from which the integral net heats listed in Table II were obtained.

As long as the sorption follows a linear sorption isotherm at both upper and lower temperatures the differential heats are constant with polymer composition; the curves for cellulose acetate, polyvinyl butyral and alcohol illustrate this behavior. The unusually large $-\overline{\Delta H}$ value for cellophane is noteworthy as it is a rather clear indication that the structure or internal configuration of the water-attracting polar groups must have a considerable influence on the heat of hydration, otherwise $-\overline{\Delta H}$ for cellophane would be no larger than that for polyvinyl alcohol, or cellulose itself. The increased water affinity and heat of hydration of regenerated cellulose over that for cellulose or cellulose acetate were pointed out some time ago by Sheppard and Newsome.[19] Note the slight rise in $-\overline{\Delta H}$ for polyvinyl alcohol at high partial pressures of the water vapor.

In conclusion one of us (M.D.) wishes to acknowledge (1) the help received in several stimulating discussions with Professor Bull and (2) a grant from E. I. du Pont de Nemours and Co. which defrayed part of the expense of preparing this manuscript.

(19) S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, **36**, 930 (1932) and earlier papers. The $\overline{\Delta F}$ and $\overline{\Delta H}$ curves of Simril and Smith³ for cellophane are entirely similar to ours.

Summary

1. Equations for the free energy of adsorption or sorption of any substance in terms of the constants of the linear, Langmuir and Brunauer, Emmett and Teller adsorption isotherm equations have been derived for both the differential and integral free energies.
2. Similar equations for the differential net heats (isosteric heats) are also given.
3. Data of Bull on the amount of water sorbed by proteins and nylon have been recalculated to yield differential free energies and differential and integral net heats of sorption different from those discussed by Bull, but, in the case of the integrated free energy data, equal to the previously published values of Bull.
4. The average differential heats over the first layer graphically computed from Bull's data are much higher than calculated from the constant c of the BET theory assuming a_1b_2/a_2b_1 to be unity (this assumption is undoubtedly not valid).
5. The fraction of polar groups associated with one water molecule at saturation is shown to be equal to the fraction of amorphous polymer in unstretched and stretched nylon. The significance of this observation is not clear.
6. As the initial differential heats vary widely for sorption on chemically similar polar groups, the structural configuration of the groups must be considered.
7. Differential and integral free energies and heats of hydration are graphed or tabulated for five polymers, cellophane, cellulose acetate, polyvinyl alcohol, polyvinyl butyral and vinylidene chloride–acrylonitrile co-polymer.

Cuprous Chloride Derivatives of C₅ Diolefins

BY A. L. WARD AND E. C. MAKIN, JR.[1]

Studies on the formation of cuprous chloride compounds with butadiene and isoprene have been reported by Gilliland and his co-workers.[2] The butadiene–cuprous chloride was found to have the formula, $C_4H_6 \cdot 2CuCl$, and that reported for the compound with isoprene was $C_5H_8 \cdot 3CuCl$. However, the authors expressed considerable doubt as to the latter formula, suggesting that the reaction may not have been complete in their experiments.

In addition a cuprous chloride complex of piperylene, formed by reaction with $CuNH_4Cl_2$ solution, has been reported by Lur'ye and co-workers,[3] and a similar solution was used by Craig[4] to separate the geometrical isomers of piperylene from contaminating olefins by formation and subsequent dissociation of the cuprous chloride compounds. The complex salts were formed at room temperature and decomposed at 60 to 100°. In this study by Craig it was observed that the *cis* isomer formed a more stable derivative than the *trans* isomer.

In the present research, vapor pressure curves for the cuprous chloride complexes of isoprene and a mixture of the piperylene isomers have been

(1) Present address: Copolymer Corporation, Baton Rouge, Louisiana.
(2) Gilliland, Bliss and Kip, THIS JOURNAL, **63**, 2088 (1941).

(3) Lur'ye, Marushkin, Chistov and Shlossberg, *C. A.*, **32**, 6099 (1938); *Sintet. Kauchuk*, **3**, No. 6, 13 (1934).
(4) Craig, Geometric Isomers of Piperylene, Abstract of Papers for American Chemical Society Meeting, September, 1942, Buffalo, N. Y.