bond distances C—C = 1.54 kX, C—O = 1.43 kX and all angles tetrahedral except the ring angle C—O—C, which was taken as 90°, the projection of six maximally extended residues is computed to be 22.4 kX. A chain of maximally extended residues in this configuration does not possess the required twofold screw symmetry, and rotation of the residues to give the required symmetry decreases the fiber repeat period. Bond angles or lengths must be changed, therefore, to obtain agreement with the observed fiber repeat period of 22.6 kX. If the symmetrical chair configuration of minimum steric repulsion is retained, the most reasonable change is to increase the oxygen angle in the ring. Increasing this angle to 109° and using the same values as above for all other angles and distances, the projection of six maximally extended residues is computed to be 26.1 kX. It is evident that models can be constructed having the symmetrical chair configuration and satisfying the requirements of twofold screw symmetry and the observed fiber repeat period by selecting a value for the ring oxygen angle between 90 and 109°. Such agreement, of course, does not eliminate from consideration models of the amylose chain based on other configurations of the glucose ring.

In the structure proposed, the effective thickness of the glucose residue is 4.5 Å., which is consistent with the value found in cellulose and alkali cellulose.[9] The width of the glucose residues plus the contribution of alkali and water (position undetermined) is 12.7 Å., again consistent with the corresponding value found in sodium cellulose III.[8]

Summary

Amylose forms crystalline addition compounds with lithium, sodium, potassium, ammonium, cesium and guanidinium hydroxide. Diffraction patterns indicate these compounds constitute an isomorphous series based on the orthorhombic space group $P2_12_12_1$. Analyses of lithium, potassium and cesium hydroxide amylose shows their composition to be $3C_6H_{10}O_5 \cdot MOH \cdot 3H_2O$, and it is probable that this formula represents the composition of the entire series.

All compounds have the same fiber repeat period, 22.6 kX, corresponding to the extension of six glucose residues. Positions of the alkali ions and the lateral packing of the amylose chains have been determined with the aid of Patterson projections.

[9] K. H. Meyer, L. Misch and N. P. Badenhuizen, *Helv. Chim. Acta*, **22**, 59 (1939).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, AND PHYSICAL CHEMICAL RESEARCH, ENGINEERING DIVISION, CHRYSLER CORPORATION]

Surfaces of Solids. XVIII. The Heats of Emersion and Desorption of Water from Graphite at 25°

BY PAUL R. BASFORD, GEORGE JURA AND WILLIAM D. HARKINS

I. Introduction

A recent paper,[1] gives the adsorption isotherms of water and *n*-heptane on a sample of graphite with a content of less than 0.004% ash and presumably free from oxygen. In that paper some of the problems associated with the graphite–water system were indicated, but their discussion was deferred until after the completion of the calorimetric study of the system as presented here.

II. Experimental

The graphite, furnished through the courtesy of Dr. Lester L. Winter of the National Carbon Company, is described elsewhere. The calorimeter and technique of the measurements was that of Harkins and Jura.[2] Because of the low area of the sample, 4.22 sq. m. g.$^{-1}$, the limited supply of the powder and the small amount of water adsorbed per gram, the technique of Harkins and Jura[2] for determining the amount of water adsorbed could not be used. Instead, the equilibrium pressure of the adsorbed vapor was determined. The amount of adsorbed water was then obtained from the data of the isotherm. For high values of p/p_0 this leads to a considerable uncertainty in the exact amount adsorbed. However the actual results in this region are such that this error is insignificant.

III. Experimental Results

The heat of emersion of graphite as a function of the amount of water adsorbed (molecules per sq. cm.) is exhibited in Fig. 1. Each value listed in Table I is the average of either two or three determinations, usually three. The table gives also the number of determinations and the average deviation of each determination. From this table it is possible to calculate all the heat values given.

Unfortunately, the results are not very precise, due to (1) low area coupled with small heat effects per unit area, and (2) difficulty of dispersion. The absolute error in a single determination is about twice that of Harkins and Jura[2] in their cor-

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[1] W. D. Harkins, G. Jura and E. H. Loeser, THIS JOURNAL, **68**, 554 (1946).

[2] W. D. Harkins and G. Jura, *ibid.*, **66**, 919 (1944).

TABLE I

THE HEAT OF EMERSION OF GRAPHITE FROM WATER AT 25°, AND THE INTEGRAL HEAT OF DESORPTION OF WATER FROM GRAPHITE AT 25°, AS A FUNCTION OF THE AMOUNT OF ADSORBED WATER

Cc. H_2O (S. T. P.) adsorbed per g.	No. molecules per sq. cm. ($\times 10^{14}$)	$h_{E(S_fL)}$ ergs cm.$^{-2}$	$h_{D(VS)}$ ergs cm.$^{-2}$	Number of detns.
0.0000	0	167 ± 3	0	5
.00728	0.046	82 ± 16	89.4	2
.0332	.211	65 ± 7	118.6	2
.0625	.398	58 ± 11	138.7	3
.1450	.923	− 62 ± 54	297.2	2
.2192	1.396	− 73 ± 12	342.0	2
.2820	1.796	−132 ± 29	430.1	3
.3882	2.472	− 32 ± 45	379.8	3
.4970	3.165	− 15 ± 20	413.3	3
1.111	7.076	8 ± 14	675.4	3
1.471	9.369	− 9 ± 23	858.6	3
1.754	11.171	32 ± 11	949.0	2
1.978	12.598	49 ± 11	1035.7	2
2.134	13.591	− 88 ± 47	1245.0	3
2.288	14.572	− 37 ± 47	1265.3	3
2.325	14.807	− 99 ± 42	1345.0	3
2.484	15.820	− 95 ± 52	1414.2	3
2.741	17.457	− 89 ± 56	1527.9	3
3.260	20.762	− 94 ± 44	1773.4	3
4.220	26.876	−124 ± 55	2249.0	3
4.652	29.628	− 62 ± 62	2386.9	3

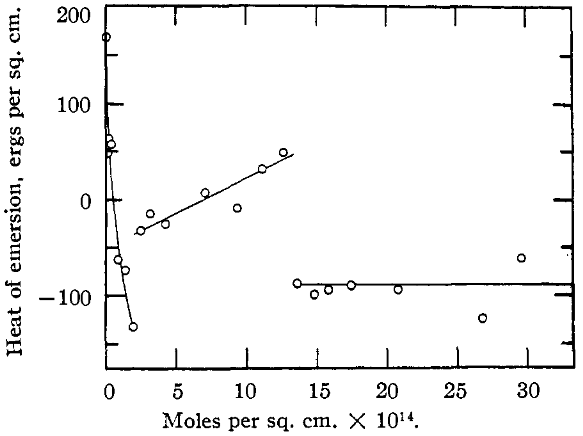

Fig. 1.—The heat of emersion of graphite, with various amounts of water adsorbed in its surface from water at 25°.

responding determinations with titanium dioxide of area 13.8 sq. m. g.$^{-1}$. In order to obtain much more precise values, a calorimeter with an increased sensitivity by a factor of 10 would be essential. The present results, however, are the best that can be obtained with our present equipment. Fortunately, many of the changes in energy are so large that certain conclusions can be drawn.

Figure 1 exhibits two points of interest: (1) the heats of emersion are negative when the amount of water adsorbed per gram is between 0.5 $\times$ 10^{14} and 7.0 $\times$ 10^{14} molecules per sq. cm. and also for all values above 13.5 $\times$ 10^{14} molecules per sq. cm.; and (2) there are two discontinuities in the values of the heat of emersion, the first between 1.8 $\times$ 10^{14} and 2.5 $\times^{14}$ and the second between 12.6 $\times$ 10^{14} and 13.6 $\times$ 10^{14} molecules per sq. cm. The first of these is important, since, insofar as is known to the writers, this is the first case in which heat has been found to be absorbed in the process of immersion of a solid. In other later work it was found also that when a sample of clean silver sulfide is immersed in *n*-heptane at 25° heat is absorbed. The detailed set of data for this and other systems will be presented in a later paper.

The general position of the two discontinuities in the heat of emersion corresponds to those in the derivative of the volume with respect to the pressure in the adsorption isotherm. Jura, Loeser, Basford and Harkins[3] have shown that if a second order phase transition occurs there is finite discontinuity in $(\partial v/\partial p)_{T,\Sigma}$. If there is a finite discontinuity in this derivative, it can be shown that there should also be a finite discontinuity in the heat of emersion. Similarly, for a first-order change, the heat of emersion is independent of the amount adsorbed for those values of the amount adsorbed over which the transition occurs. For a third order change there is a finite discontinuity in the derivative of the heat of emersion with respect to the amount adsorbed. Thus, the behavior of the heat of emersion can be used as a criterion for a phase change of the second or third order. The effect of temperature on isotherms in the region of a first order change is so striking that there can be no reasonable doubt of the phenomenon. In the vicinity of second order changes the experimental problem is more exacting, since it is necessary to prove the existence of a discontinuity in the derivative.

However, for the water–graphite system discussed in this paper, the discontinuities in the derivative are supported by a directly measured discontinuity in the heat functions. For the adsorption of water on graphite the discontinuities in the adsorption isotherm are so small that their existence was not entirely certain until the discontinuities in the heats were found. The isotherm is shown in Fig. 2. In this respect the discontinuities found here differ from those previously reported by the writers. Those discontinuities reported earlier were so large that the isotherm was sufficient to establish their existence without doubt.

One of these discontinuities occurs in the monomolecular film at *ca.* 56 Å.^{2} per molecule, but the second does not appear until the film becomes polymolecular at *ca.* 7.5 Å.^{2} per molecule. (The area occupied by a water molecule at 25° is at least 10.6 Å.^{2} in a monolayer.) The regions of the discontinuities in this isotherm are shown on an expanded scale in Fig. 3. The chord-area method

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[3] G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *J. Chem. Phys.*, **14**, 117 (1946).

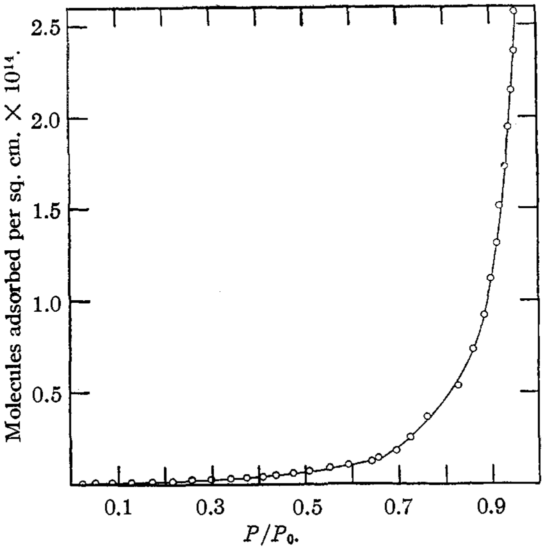

Fig. 2.—Isotherm of adsorption of water on graphite at 25°.

was used to obtain the derivative, $(\partial v/\partial p)_{T,\Sigma}$. This is shown in Fig. 4.

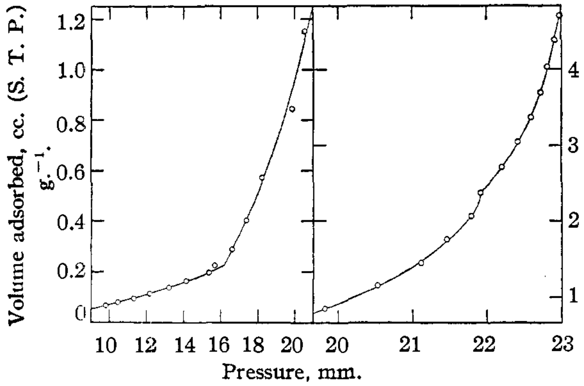

Fig. 3.—Discontinuities in the adsorption isotherm of water on graphite at 25°.

The values of the derivative, $(\partial v/\partial p)_{T,\Sigma}$, and of the heat of emersion, $h_{E(SfL)}$, are shown plotted against the number of molecules per sq. cm. in Fig. 5. Both quantities show discontinuities at substantially the same points.

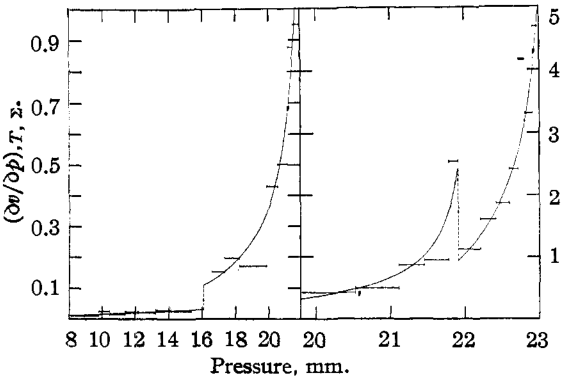

Fig. 4.—Chord area plot for determination of $(\partial v/\partial p)_{T,\Sigma}$, in the region of the discontinuities.

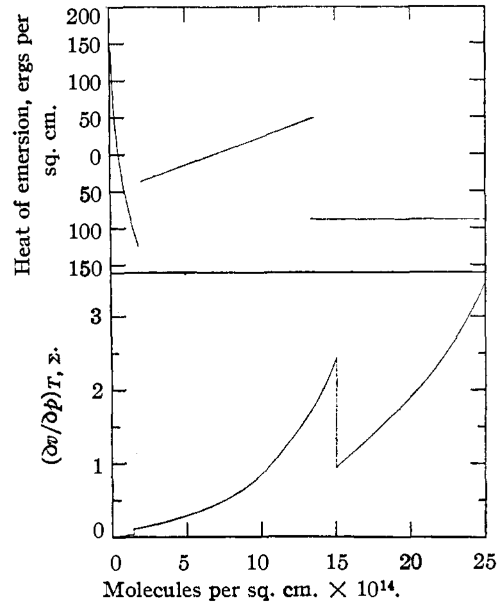

Fig. 5.—The discontinuities in the heat of emersion and in $(\partial v/\partial p)_{T,\Sigma}$.

In addition to the work on water, the heats of emersion from benzene and *n*-heptane of the graphites of 0.004 and 0.46% of ash were determined. These values and those of Harkins and Boyd[4] for a sample of graphite containing 10% ash are listed in Table II.

TABLE II

THE HEATS OF EMERSION OF GRAPHITE FROM LIQUIDS (ERGS CM.$^{-2}$ AT 25°)

Graphite	Water	Benzene	*n*-Heptane
10% ash	265	225	......
0.46% ash	225 ± 8	147 ± 10	167 ± 10
Less than 0.004% ash	167 ± 3	163 ± 2	146 ± 10

The values indicate that the heat of emersion is highly dependent on the ash content of the graphite. These differences do not seem to be explained by the assumption that a certain fraction of the surface is ash and the remainder is graphite.

In the case of the graphite with 0.46% ash the heat of emersion was determined also in undried benzene. The value found was 219 ± 16 ergs cm.$^{-2}$, while with thoroughly dried benzene it was 147 ± 10 ergs cm.$^{-2}$ (*cf.* 225 ± 8 for water). This indicates that when working with non-polar solids, it is essential to dry even hydrocarbons if correct results are to be obtained.

The absolute method for the determination of area[5] was applied to the graphite of less than 0.004% ash by saturating the powder with *n*-hep-

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[4] W. D. Harkins and G. E. Boyd, THIS JOURNAL, **64**, 1195 (1942).

[5] W. D. Harkins and G. Jura, *ibid.*, **66**, 1362 (1944).

tane. The area of the particles covered with the film was found to be 4.6 ± 0.6 sq. m. g.$^{-1}$. For graphite the geometry of the individual particles is not well enough known to correct this figure exactly for the additional area due to the film. If the graphite particles were cubes, the area of the sample would be 4.1 sq. m. g.$^{-1}$, while if they were rectangular parallelopipeds whose dimensions are in the ratio of 10–10–1 the area would be 4.4 sq. m. per gram, and if these dimensions are 100–100–1 the correction is negligibly small. Actually, the particles are thin flakes, so a ratio of 10-10-1 (*i. e.*, Σ = 4.4 ± 0.6 sq. m. g.$^{-1}$) is the best that can be estimated. The areas determined by the adsorption of nitrogen, *n*-heptane, and *n*-hexane vary from 4.06 to 4.42 sq. m. g.$^{-1}$, depending on the gas and on whether the relative method of Harkins and Jura[6] or the theory of Brunauer, Emmett and Teller[7] is used. From the available data it is not possible to decide which of the areas determined by adsorption is the correct one, so the weighted average, 4.22 sq. m. g.$^{-1}$ was used. The good agreement between the area as determined by the absolute method and those obtained by adsorption indicates that the sample is non-porous and that capillary condensation need not be considered. If an appreciable fraction of the area were in small pores, the area determined by the absolute method would be less than those by adsorption. Since this is not the case, the solid may be considered to be non-porous.

Figure 6 exhibits the integral heat of desorption of water vapor at 25° from the low ash content graphite. The values were calculated from the data for the heat of emersion by the relationship

$$h_{\mathrm{D(VS)}} = h_{\mathrm{E(SL)}} - h_{\mathrm{E(S_fL)}} + n\lambda \tag{1}$$

where $h_{\mathrm{E(SL)}}$ is the heat of emersion of the clean solid from water, $h_{\mathrm{E(S_fL)}}$, is equal to $-h_{\mathrm{I(S_fL)}}$ when n moles is adsorbed per sq. cm., and λ is the heat of condensation, 10,480 cal. mole^{-1}. Table I includes the values of $h_{\mathrm{D(VS)}}$ so calculated. The two discontinuities correspond to those in the heat of emersion. The data on adsorption available to the writers indicate that these discontinuities are quite common when a sufficiently detailed investigation is made of the heat of adsorption.

The differential heat of adsorption in calories per mole of water is equal to 1.463 × 10^{16} times the slope of the curve in Fig. 6. It decreases from approximately 100,000 cal. mole^{-1} when 4.65 × 10^{12} molecules are adsorbed per sq. cm. to 30,000 cal. mole^{-1} at 1.80 × 10^{14} molecules per sq. cm. When the amount of water adsorbed is between 2.47 and 12.60 × 10^{14} molecules per sq. cm., the heat is constant, within the limits of the large experimental error, at 9,100 cal. mole^{-1}. Above 13.59 × 10^{14} molecules adsorbed per sq. cm. the heat is again constant and equal to 10,500 cal. mole^{-1}, which is equal to the heat of condensation. Of these results the high values exhibited by the differential heat of adsorption below 1.80 × 10^{14} molecules per sq. cm. are not understood at the present time.

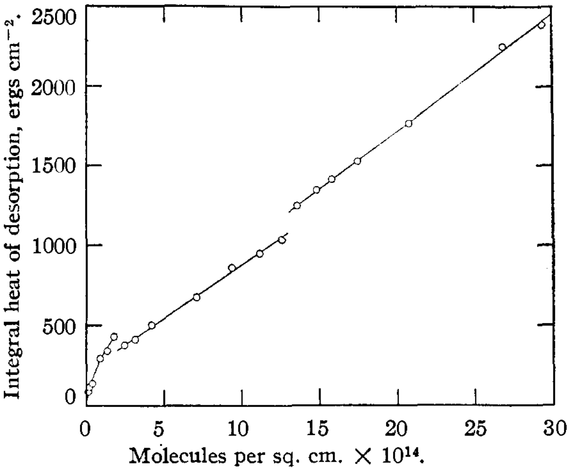

Fig. 6.—The integral heat of desorption of water from graphite in ergs per sq. cm.

There is no precedent in the literature for such high values for the heat of adsorption when physical adsorption is involved. However, to the knowledge of the writers, no data are available in the literature when so few molecules are present on the surface. Analogous results in the very low pressure region have been obtained with water and titanium dioxide. Until more data are available, it is not possible to give any explanation of the seemingly unreasonably high values. The amount of ash is too small to be responsible. The remainder of the values are in complete accord with results which have been obtained when water is adsorbed on charcoal.

Figure 7 shows the change in total surface energy, free surface energy, and the product of the temperature and entropy as a function of the amount of water adsorbed. In this system, in that of water–titanium dioxide, as well as in previously reported systems, the greatest contribution to the heat evolved arises from the entropy rather than from the free energy. The discontinuities in the derivative of the free energy do not show on the scale of Fig. 7.

IV. Discussion

The film of water on graphite exhibits certain relations which are difficult to understand. The results of the calorimetric and adsorption determinations in this and the preceding paper are not sufficient for this purpose. It is probable, before a more complete understanding is possible, that (1) other graphites and other solids which exhibit a similar behavior must be investigated, (2) the precision of the measurements, especially those of the heat involved, must be increased, and (3) experimental procedures other than those used thus far must be used.

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[6] W. D. Harkins and G. Jura, THIS JOURNAL, **66**, 1366 (1944).

[7] S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

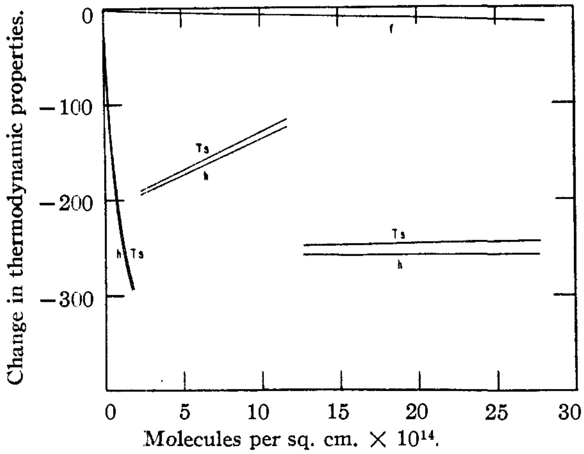

Fig. 7.—The decrease of free surface energy (*f*), of total surface energy (*h*), and of the product, temperature times surface entropy (*Ts*), as a function of the amount of water adsorbed. The uppermost curve is the decrease of free surface energy; this accounts for relatively little of the total surface energy. The two curves to the left below (*h* below *Ts* above) very nearly coincide. In the remaining two sets of curves, *h* is in both cases below and *Ts* above. All curves are drawn to the same scale.

The two experimental facts which lead to the greatest difficulty are (1) the film is polymolecular at high vapor pressures, and (2) the contact angle is not zero. Unfortunately, the thickness of the film cannot be determined with any certainty. This difficulty arises on account of the fact that there is no reliable estimate of the number of molecules required to form a monomolecular layer. The only method for obtaining this quantity lies in the theory of Brunauer, Emmett and Teller,[7] which, as indicated below, does not seem to be applicable to this case.

Although the simple two-constant equation of this theory apparently reproduces well the experimental data from $p/p_0 = 0.1$ to $p/p_0 = 0.35$, the value of v_m (0.3 cc. g.$^{-1}$) is such that the effective area of the water molecule obtained is 52 Å.^{2} per molecule, or five times that which would be expected for a closely packed monolayer. Though a loosely packed film would not be unexpected, the actual number of molecules required to form a monolayer would seem to be greater than corresponds to this value. Thus, the BET theory does not seem to be applicable. Second, the value of c is less than unity, which means that $E_1 - E_L < 0$. Actually, as is shown later, $E_1 - E_L > 0$, and is over 2300 cal. mole^{-1}. Thus, it appears that *in this particular case* the theory fails. The failure is probably due to the fact that the agreement between theory and experiment in the region $p/p_0 =$ 0.1 to 0.35 is fortuitous, since, at relative pressures above 0.4, $p/v(p_0 - p)$ actually decreases with an increase in p/p_0. This behavior is unusual.

If it is assumed that the water molecules form a tightly packed film, v_m must equal 1.49 cc. g.$^{-1}$ and the average thickness of the film at a relative pressure of 0.985 would be 3 v_m, or about 10 Å. The extrapolation of the observed isotherm to $p/p_0 =$ 1 gives as the thickness about 5 v_m, or 17 Å. Thus, the minimum estimated thickness of the film is 10 Å., but it is more probable that it is 16 Å. On the basis of the theory of Brunauer, Emmett and Teller (v_m = 0.3 cc.) the calculated minimum thickness of the film would be about 50 Å., and probably 83 Å. The value of the contact angle for water–graphite is discussed in an earlier paper.[1]

The fact that the contact angle is not zero indicates that the film is non-duplex, which in turn signifies that in the outermost layer of the film the water molecules do not assume the packing and orientation that exists in the surface of liquid water. If the film were only monomolecular, this state would be understandable and expected. It is difficult to conceive, however, how the effect of the surface can be sufficiently marked at a distance of at least three molecular diameters, and probably more, to affect seriously the packing and orientation of the water molecules.

The available evidence indicates the existence of a polymolecular non-duplex film, a type of film postulated by Harkins.[8] If future work should show that this class of film exists, then this film of water on graphite is the first member of this class to be found.

Thermodynamically, there is no question as to the self-consistency of the available data. This can be shown in the following manner. For the formation of a duplex film it is necessary that

$$\gamma_S - \gamma_{SL} \geqq \gamma_L \tag{2}$$

while the condition that a duplex film cannot be stable is[9]

$$\gamma_S - \gamma_{SL} < \gamma_L \tag{3}$$

If the inequalities are combined with the relation

$$\gamma_{S_e} = \gamma_{SL} + \gamma_L \cos \vartheta \tag{4}$$

it is found, if inequality (2) holds for the system under discussion, that

$$\pi_e \geqq \gamma_L (1 - \cos \vartheta) \tag{5}$$

while if a duplex film cannot be formed

$$\pi_e < \gamma_L (1 - \cos \vartheta) \tag{6}$$

It is inequality (6) which is of interest. The question is, can π_e have a value less than a pre-assigned positive value for a film of a given thickness. It is possible for the following reasons. π_e is given by the integration of the Gibbs adsorption equation, as suggested by Bangham.[10,11,12] The equation is

$$\pi_e = \frac{RT}{V_M \Sigma} \int_0^{p_0} \frac{v}{p}\, dp \tag{7}$$

$$\pi_e = \frac{RTp_0}{V_M \Sigma} \left(\frac{v}{p}\right)_{\text{Average}} \tag{8}$$

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[8] W. D. Harkins, in J. Alexander, "Colloid Chemistry," Reinhold Publishing Corp., New York, N. Y., 1945, p. 12.

[9] W. D. Harkins, *J. Chem. Phys.*, **9**, 552 (1941).

[10] D. H. Bangham, *Trans. Faraday Soc.*, **33**, 805 (1937).

[11] D. H. Bangham and R. I. Razouk, *ibid.*, **33**, 1463 (1937).

[12] D. H. Bangham and R. I. Razouk, *Proc. Roy. Soc.* (*London*), **A166**, 572 (1938).

From eq. (8) it is apparent that, even if the values of π_e and the volume of gas adsorbed at saturation are fixed, then, mathematically it is possible to construct an infinite number of isotherms so that eq. (8) is satisfied. The only general statement is that for a given π_e, the larger the value of the volume adsorbed at saturation, the smaller must be the volume adsorbed at low pressures. Whether or not any of these mathematically possible isotherms exist physically can be determined only by experiment. The results of the adsorption of water on graphite indicate that such a case actually occurs.

The preceding paragraphs show also that, from the thermodynamic standpoint, the thickness of the adsorbed film does not determine whether or not the contact angle is zero or greater than zero. The physical evidence also indicates that the film thickness of itself does not determine the contact angle.

The only point upon which there might be a reasonable doubt is the value of the contact angle of water against graphite, but even here all the evidence is that the angle is not zero. The actual determinations of this quantity are discussed in the earlier paper.[1] The present calorimetric data also indicate a contact angle greater than zero. If the contact angle were zero over a small temperature region within which the measurements are made, the heat of emersion at $p/p_0 = 1.0$ would be 119 ergs cm.$^{-2}$. At $p/p_0 = 0.985$ this quantity is -86 ergs cm.$^{-2}$ and is apparently not increasing with p/p_0. To judge from the behavior of the heat of emersion up to a relative pressure of 0.985, another phase transition would be essential if the heat of emersion is to become that characteristic of a zero contact angle. Experimental difficulties encountered in this region preclude any definite statement as to this possibility.

It would be of interest to estimate the decrease of the energy of interaction of the solid as the film thickness increases, but the observed data are not sufficiently accurate to do this quantitatively. The uncertainty in the amount of gas adsorbed in a single layer is even more serious. If it is assumed, as a rough approximation, that the water molecules have an effective cross-sectional area of 10.6 Å.^{2}, *i. e.*, that the film is tightly packed, the energy of interaction between the solid and the first V_m adsorbed is a maximum. If it is also assumed that the second and third layers have the same packing, then the average energy in excess of condensation for the adsorption of the first v_m is 2300 cal. mole^{-1}; for the second, 1500 cal. mole^{-1}; and for the third, zero cal. mole^{-1}. These figures are obtained from Fig. 6 by dividing the appropriate value of $h_{D(VS)}$ by the number of molecules per sq. cm., multiplying by 1.423×10^{16} and subtracting λ (*i. e.*, 10,480 cal. mole^{-1}). Since none of these is very large compared with RT ($RT = 600$ cal. per mole) it is evident that even the first layer is not nearly complete before an appreciable number of molecules are adsorbed in the second and higher layers. Under these conditions, the 2300 cal. per mole calculated for the first layer must be too low, since many of the molecules included are in the second and higher layers, with lower interaction energies. The figures for the second and third layers must be similarly revised.

Neither the data nor the assumptions about the number of molecules in a monolayer are good enough to attempt to determine $E_1 - E_L$ to any degree of accuracy. The values of 2700, 1300 and -150 cal. mole^{-1} for $E_1 - E_L$, $E_2 - E_L$ and $E_3 - E_L$ approximate the observed values moderately well if the usual assumption is made of a Boltzmann distribution between the layers. Another difficulty with this simple treatment is that the heat must be a continuous function of the amount adsorbed. This is contrary to the experimental results. Even in this respect any simple approach is precluded. It is evident that no analysis based on the simplified theories now available is capable of explaining the observed facts.

Summary

1. The heat of emersion (h_e) from water of a graphite of specific area = 4.22 sq. m. g.$^{-1}$ and of ash content less than 0.004%, presumably free from any oxygen complex, was determined as a function of the amount of water adsorbed on the surface. For the clean graphite (h_e) is 167 ergs cm.$^{-2}$, decreasing to -132 ergs cm.$^{-2}$ when 1.80×10^{14} molecules of water are adsorbed per sq. cm. From 2.47×10^{14} to 12.60×10^{14} molecules per sq. cm. the heat of emersion increases from -32 to $+49$ ergs cm.$^{-2}$. From 13.59 to 29.63×10^{14} molecules adsorbed per sq. cm. the value, within a large experimental error, is constant at -84 erg cm.$^{-2}$.

2. There are two finite discontinuities in the heat of emersion. These discontinuities coincide with two discontinuities in the derivative of the volume with respect to the pressure in the isotherm. Either of the above is sufficient to show that a second order phase change occurs in the film formed by adsorption. The actual determination of both discontinuities is the best evidence which can be obtained for this type of phase change.

3. For the first time negative heats of emersion have been obtained.

4. The area of the solid was determined by the use of the *absolute* method of Harkins and Jura, using *n*-heptane at 25°. The area obtained was 4.4 ± 0.6 sq. m. g.$^{-1}$. This agrees with the area determined by adsorption (4.06 to 4.42 sq. m. g.$^{-1}$). Since the absolute method gives the value at saturation, and adsorption at low relative pressures, it is evident that capillary condensation is negligibly small.

5. From the amount of water adsorbed as determined from the isotherm, the area of the solid,

and the fact that capillary condensation is negligible, it is shown that the film of water on graphite attains a minimum thickness of 10 Å. at a relative pressure very close to saturation. The extrapolation of the isotherm to unit relative pressure indicates a minimum thickness of 16 Å. These figures are obtained on the postulate that the density of the adsorbed material is that of the liquid at the same temperature. The physical relations indicate that the packing must be looser than in the liquid. Consequently, the figures quoted are to be considered minima and not a reliable estimate of the true thickness.

6. It is shown thermodynamically that the film can be polymolecular with a contact angle not equal to zero. It is also pointed out that this situation leads to a difficult problem in the construction of a model compatible with both conditions.

7. It is shown that $E_1 - E_L > 0$, $E_2 - E_L > 0$ and $E_3 - E_L < 0$.

8. The integral and differential heats of adsorption of water on graphite are determined from the heats of emersion.

9. The heats of emersion are used to determine the change in total surface energy caused by the adsorption of water. These values combined with the free surface energy changes as determined from the adsorption isotherm permit the calculation of the change in surface entropy.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK AND CO., INC.]

Synthesis of DL-Methionine

BY EARL PIERSON, MARIO GIELLA[1] AND MAX TISHLER

Consideration of the various syntheses of methionine indicates that the first recorded synthesis, that of Barger and Coyne,[2] using β-methylmercaptopropionaldehyde, is the most direct in approach. The over-all yield of about six per cent. by the modified Strecker reaction and the difficulty in obtaining the required aldehyde discouraged the use and the further development of this synthesis.

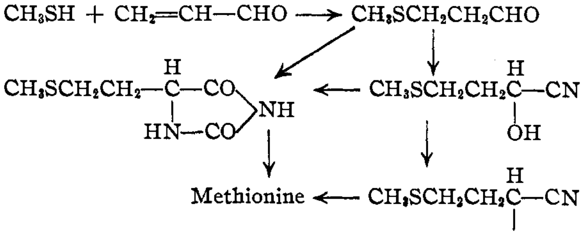
With the recent availability of commercial acrolein, and the reports that β-methylmercaptopropionaldehyde has been prepared from acrolein and methylmercaptan,[3] the development of a practical synthesis of methionine became of interest.

Catch and his collaborators[4] recently prepared methionine from acrolein and methyl mercaptan in 29% yield by a modified Strecker reaction employing liquid hydrogen cyanide. We have also prepared methionine in about the same over-all yield (25%) by the Strecker reaction without resorting to the use of liquid hydrogen cyanide. Further improvement was observed using the well-known Bücherer hydantoin synthesis, whereby an over-all yield of 50% was obtained.

It was found that methyl mercaptan adds smoothly to acrolein at atmospheric pressure when the reaction is catalyzed by a small amount of copper methyl mercaptide.[5]

The conversion of β-methylmercaptopropionaldehyde into 5-(β-methylmercaptoethyl)-hydantoin was accomplished by the usual Bücherer procedure and also by transformation into the cyanohydrin followed by treatment with ammonium carbonate.

The hydrolysis of the hydantoin to methionine was effected by concentrated hydrochloric acid at 135°, by ammonium sulfide solution at 135°, and by aqueous sodium hydroxide at 100°. The routes investigated are indicated.



Experimental

1. **β-Methylmercaptopropionaldehyde.**—Gaseous methyl mercaptan, 48 g., 1.0 mole, was bubbled during the course of thirty minutes under the surface of a cooled, stirred mixture of 56 g. (1.0 mole) of acrolein and 0.5 g. of cupric acetate, while the internal temperature was maintained at 35–40°. The mixture was agitated for an hour and distilled under reduced pressure giving β-methylmercaptopropionaldehyde, 87 g., 84%; boiling 52–54° (11 mm.), $n^{20}D$ 1.4850, d_{20} 1.036; *MR*D (calcd.) 28.4, found 28.7. The undistilled aldehyde is sufficiently pure for use in the reactions described below.

The 2,4-dinitrophenylhydrazone was prepared in the conventional manner, m. p. 116–119°.

Anal. Calcd. for $C_{10}H_{12}O_4N_4S$: C, 42.45; H, 4.26; N, 19.70. Found: C, 42.23; H, 4.20; N, 19.61.

2. **α-Hydroxy-β-methylmercaptobutyronitrile.**—β-Methylmercaptopropionaldehyde, 10.4 g., 0.10 mole, was shaken for ten minutes with a solution of 10.4 g., 0.10 mole, of sodium bisulfite in 35 ml. of water. A substantial amount of the adduct crystallized upon cooling to room temperature. A solution of 4.9 g., 0.10 mole, of sodium cyanide in 15 ml. of water was added in three portions, without permitting the temperature to exceed 35°. The oil that separated immediately was extracted

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[1] Present address: A. C. Lawrence Leather Company, Peabody, Mass.

[2] Barger and Coyne, *Biochem. J.*, **22**, 1417 (1928).

[3] Kaneko and Mii, *J. Chem. Soc. Japan*, **59**, 1382 (1938); Rothstein, *J. Chem. Soc.*, 1560 (1940).

[4] Catch, Cook, Graham and Heilbron, *Nature*, **159**, 578 (1947).

[5] The English investigators[4] used a tertiary amine as a catalyst.