642. *Statistical Thermodynamic Interpretation of the Sorption of Water and Methanol by Carbon.*

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When the statistical thermodynamic treatment of localised sorption with interaction is applied to the characteristic sigmoid isotherms of water and of methanol on carbon below the monolayer value, it is found to describe the isotherms (*i.e.*, the free energy of sorption) reasonably for all save, in some cases, small values of θ. The analysis shows that exothermic lateral interaction, though present, is so small as to rule out normal intermolecular hydrogen bonds. On the other hand, the energy of binding to the sorbent surface is adequate for two hydrogen bonds between a sorbate molecule and the surface in the case of water, and for one such bond for methanol together with a more substantial contribution of dispersion forces.

It has been shown [1] that water isotherms in charcoal, which are well known to be of Type V in Brunauer's classification,[2] give the strong upward inflexions in the region well *before* a monolayer is completed, and that in the vicinity of the monolayer value the isotherm flattens to some extent before capillary condensation begins. The first part of the isotherm therefore recalls the behaviour of the hydrogen–palladium or hydrogen–zirconium system, at temperatures a little above the critical temperature for the appearance of the well-known two-phase invariant-pressure region. These hydrogen alloys have been successfully interpreted in terms of an energy release when two hydrogen atoms occupy adjacent sites.[3,4] For the water–carbon isotherms also Dubinin and his co-workers [1] postulate a strong lateral interaction between water molecules, due to hydrogen-bond formation, so that islands of a condensed monolayer appear and grow, until a saturated monolayer is completed.

Although the two kinds of system—hydrogen-alloy and water–charcoal—are physically very distinct, from the viewpoint of statistical thermodynamics the formulation of the respective sorption isotherms may be similar. One postulates a set of localised homogeneous sorption sites, whether inside the sorbent or on its surface, and an interaction energy $2w/Z$ per pair of atoms or molecules adsorbed on adjacent sites. Z denotes the co-ordination number of a site. Then an isotherm for sorption without dissociation is obtained: [5]

$$K = \frac{\theta}{p(1-\theta)}\left(\frac{2(1-\theta)}{\beta+1-2\theta}\right)^{Z} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here p denotes the equilibrium pressure. and θ is the fraction of all the available sites which are occupied. The quantity $\beta = \left\{1 - 4\theta(1-\theta)[1 - \exp - (2w/Zkt)]\right\}^{\frac{1}{2}}$, and K is a constant which can be explicitly evaluated for the various possible degrees of freedom of the sorbed molecules and the same for all values of w, including zero.* We have used the model for localised sorption with interaction to investigate water–carbon isotherms,

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* For example, for an oscillator vibrating with mean frequency $\bar{\nu}$ and of mass m,

$$K = \frac{1}{kT}\left(\frac{kT}{2\pi m}\right)^{3/2}\frac{1}{\bar{\nu}^3}\exp \chi/RT$$

where k is the Boltzmann constant and χ is the least energy required to remove an Avogadro number of oscillators into the gas phase from the sorbent, in absence of lateral interaction (see also eqn. 5). If one defines a sorption heat by $\partial \ln K/\partial T = \Delta H_1/RT^2$, then $\Delta H_1 = \chi + \frac{1}{2}RT$.

[1] Dubinin, Zaverina, and Serpinksky, *J.*, 1955, 1760.

[2] Brunauer, "The Adsorption of Gases and Vapours," Oxford Univ. Press, 1944, Chapter 6.

[3] Lacher, *Proc. Roy. Soc.*, 1937, *A*, **161**, 525.

[4] Martin and Rees, *Trans. Faraday Soc.*, 1954, **50**, 343.

[5] Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge Univ. Press, 1939, p. 441.

and to examine further the hypothesis that the water molecules are interlinked, and condense, by hydrogen bonding.[1] It is known that the strength of the hydrogen bond between water molecules is about 5·5 kcals.[6] The methanol–carbon isotherm [7] also behaves similarly to the water–carbon one, and will likewise be examined in terms of the above model.

Free-energy Relations.—In the Figure are shown experimental isotherms, and isotherms calculated according to eqn. 1, by the following procedure. The v_m, or monolayer, value was chosen (Table 1, column 2). Then if $p(\frac{1}{2})$, $\beta(\frac{1}{2})$ denote the values of p and of β when $\theta = \frac{1}{2}$, we have

$$p(\tfrac{1}{2}) = \frac{1}{K}\left(\frac{1}{\beta(\frac{1}{2})}\right)^Z = \frac{1}{K}\exp\left(+\frac{w}{kT}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that

$$\frac{p}{p_0} = \frac{p(\frac{1}{2})}{p_0}\,\frac{\theta}{(1-\theta)}\left(\frac{2-2\theta}{\beta+1-2\theta}\right)^Z \exp\left(-\frac{w}{kT}\right) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where p_0 denotes the saturation pressure of the liquid sorbate. Then, from the experimental isotherm and v_m, $p(\frac{1}{2})/p_0$ was read off. For example, for one particular water–carbon [1] isotherm $p(\frac{1}{2})/p_0$ was 0·43. Values of w/kT were then selected, and used, together with likely values of Z, to give the best agreement of the experimental and the calculated isotherm.

Although v_m might have been determined by some traditional method, such as the B.E.T. plot, it is clear that this procedure is basically wrong for adsorption in a monolayer obeying eqn. 1. We have therefore chosen v_m by inspection and refined its value by trial, in association with the similarly selected and refined values of w/kT, so that the best result was obtained. All relevant numerical data for the best agreement are summarised in Table 1.

TABLE 1. *Analysis of sorption of water and methanol on carbon in terms of equation* 1.

System	Mono-layer value (moles/g.)	Temp.	Z	$-2w/Z$ (cal./Avogadro no. of mol. pairs)	$-w/kT$	10^5K from exptl. curves	$10^{13}K_0$ from exptl. curves	$-\Delta H$ or $-\Delta H_1$ (kcal./mole)	$\bar{\nu}$ (10^{13} sec.$^{-1}$) * (*A*)	$\bar{\nu}$ (10^{13} sec.$^{-1}$) * (*B*)
H_2O–channel black [1]	1·5	20°	6	400	2·0	1·35	—	10·7 (ΔH)	—	—
	1·5	20	4	640	2·2	1·12		,,		
	1·5	20	3	930	2·7	0·91		,,		
	1·5	20	2	1750	3·0	0·50		,,		
H_2O–sugar charcoal [8]	10·3	0	6	410	2·28	3·49	1·37	10·5 (ΔH_1)	0·73	0·98
	10·3	100	6	550	2·23	0·0190	1·33	,,	0·81	1·25
	10·3	0	4	700	2·60	2·53	0·99	,,	0·77	1·09
	10·3	100	4	760	2·40	0·0134	0·75	,,	0·88	1·50
$CH_3{\cdot}OH$–graphite [7]	0·06	0	6	325	1·80	1·45	—	9·0 (ΔH)	—	—
	0·06	0	4	540	2·0	1·18		,,		

* (*A*) Non-rotating vibrator; (*B*) freely rotating vibrator.

The Figure shows that localised adsorption with interaction gives a satisfactory description of the isotherms of water and of methanol, for values of θ corresponding to the upward inflexion of the isotherm to values approaching 1. However, eqn. 1 is sometimes unable to express the experimental contour of the isotherm for water when θ is small. The isotherms shown in the Figure have been calculated by taking $Z = 6$ (close packed monolayer) and $Z = 4$ (square array). In addition, the interaction energy $2w/Z$ has been evaluated for water for $Z = 3$ (triangular array such as might be expected for lateral hydrogen bonding) and even $Z = 2$ (linear array). Interaction energies are of appreciable magnitudes, but are much less than that of normal hydrogen-bond formation in water.

Energy Considerations.—From the temperature coefficients of K in eqn. 1 a heat ΔH_1 may be obtained, defined by $\partial \ln K/\partial T = \Delta H_1/RT^2$. This heat measures the interaction

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[6] Stuart, " Die Struktur des freien Molekuls," Springer, Berlin, 1952, p. 49.

[7] Pierce and Smith, *J. Phys. Chem.*, 1950, **54**, 356.

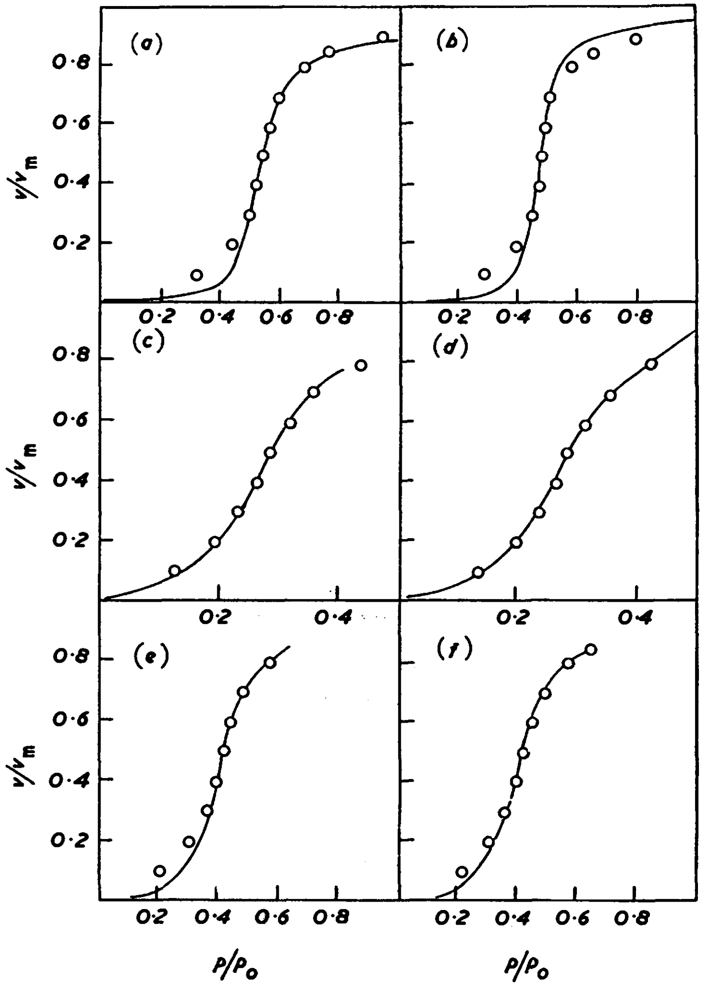
[8] Coolidge, *J. Amer. Chem. Soc.*, 1927, **49**, 715.

between sorbate molecules and the sorbing surface without including the contribution of lateral interaction. ΔH_1 is not identical with the isosteric heat ΔH [$(\partial \ln p/\partial T)_a = \Delta H/\boldsymbol{R}T^2$] which does include lateral interaction. From eqn. 1 we have :

$$(\partial \ln p/\partial T)_a = -(\partial \ln K/\partial T)_a - Z[\partial \ln (\beta + 1 - 2\theta)/\partial T]_a \quad . \quad . \quad . \quad (3)$$

or, since $\partial \ln K/\partial T$ is independent of the amount sorbed,

$$\Delta H = \Delta H_1 - Z\boldsymbol{R}T^2[\partial \ln (\beta + 1 - 2\theta)/\partial T]_a \quad . \quad . \quad . \quad . \quad . \quad (4)$$



Adsorption isotherms for : (*a*) *water on sugar charcoal at* 100°, $Z = 6$; (*b*) *water on sugar charcoal at* 0°, $Z = 4$; (*c*) *methanol on graphite at* 0°, $Z = 6$; (*d*) *methanol on graphite at* 0°, $Z = 4$; (*e*) *water on channel black at* 20°, $Z = 6$; *and* (*f*) *water on channel black at* 20°, $Z = 4$.

The subscript a denotes that differentiation is carried out while keeping constant the amount sorbed, and so also for the model used, θ. The second term on the right-hand side of eqn. 4 represents the contribution of lateral interaction (Table 2).

Values of K (Table 1, column 7) were obtained from eqn. 2, for the appropriate value of $w/\boldsymbol{k}T$ (column 6). For the water–sugar charcoal system the results at 0° and at 100° serve to determine $\Delta H_1 = -10{\cdot}5$ kcal./mole. To obtain calculated isosteric heats lateral contributions must be added. These are similar on sugar charcoal and on channel black, according to the values of $w/\boldsymbol{k}T$ of Table 1, and are given for channel black in Table 2.

The isosteric heat of —10·7 kcal./mole for channel black [1] depends little upon θ for intermediate and larger values of θ, and does not show the required rise due to interaction, either because of a compensating fall due to some heterogeneity of sites or because the data are not accurate enough to disclose the rise. The isosteric heat for the methanol–graphite system is also nearly independent [7] of film density for larger values of θ.

TABLE 2. *Calculated lateral-interaction energies (cal./mole).*

	Energy for $CH_3 \cdot OH$–graphite [7] at 0°		Energy for H_2O–channel black [1] at 20°	
θ	$Z = 6$	$Z = 4$	$Z = 6$	$Z = 4$
0·1	290	400	370	490
0·2	500	640	620	780
0·3	680	800	840	970
0·4	830	950	1000	1130
0·5	1000	1150	1180	1280
0·6	1150	1220	1340	1430
0·7	1280	1360	1520	1590
0·8	1450	1530	1720	1790
0·85	1560	1680	1810	1910
0·9	1660	1750	1970	2060

The values recorded in Table 1, whether of ΔH or ΔH_1, show that the heats of interaction of sorbate with the surface, ΔH_1, are large. They are, however, for a range of values of θ only slightly more exothermal than are the heats of condensation of the liquid sorbates. An extreme example of this trend is found in the sorption of mercury on carbon [9] or in chabazite,[10] where the transfer from liquid mercury to the sorbent is an endothermal process and the liquid does not wet the sorbent.

Equilibrium Constants.—We may ascribe appropriate modes to the adsorbed molecules, and then evaluate statistically the equilibrium constant K of eqn. 1. If, for instance, we regard the water molecules adsorbed on sugar charcoal as non-rotating vibrators, then the result is :

$$K = \frac{\sigma}{\sqrt{\pi}}\frac{1}{kT}\left(\frac{kT}{2\pi m}\right)^{3/2}\left(\frac{kT}{8\pi^2}\right)^{3/2}\frac{1}{\bar{\nu}^6}\frac{1}{(I_1 I_2 I_3)^{\frac{1}{2}}}\exp\left[-\frac{(\Delta H_1 - 2RT)}{RT}\right] . \quad . \quad (5)$$

where σ is the symmetry number (2 for water), m the molecular mass, $\bar{\nu}$ the mean vibration frequency, and I_1, I_2, and I_3 the principal moments of inertia. When we write $K = K_0 \exp[-(\Delta H_1/RT)]$ and evaluate K_0 we obtain the values given in column 8 of Table 1. The statistical thermodynamic significance of K_0 is then apparent from eqn. 5, and since for water,[11] $I_1 I_2 I_3 = 5{\cdot}67 \times 10^{-120}$ g. cm.^{2} we may determine $\bar{\nu}$ (column 10 of Table 1). These values of $\bar{\nu}$ are considerable, although perhaps compatible with the rather high bonding energy of water to the surface. Alternatively to eqn. 5 it may be supposed that the water is a freely rotating oscillator on the surface. The appropriate value of K was again obtained by the statistical thermodynamic method, and the value of $\bar{\nu}$ determined from it (column 11, Table 1). This time the values of $\bar{\nu}$ appear too high to be associated with a bonding energy of only 10·5 kcal./mole. It therefore is most likely that the water molecules lose rotational freedom when adsorbed on the sugar charcoal.

Discussion.—The energy relations of the water sorption and the equilibrium constants are such that the molecules may well be thought to have at least two-point attachment to the surface through hydrogen bonds and mirror-image forces. Attachment may be to chemisorbed oxygen atoms or to carbon atoms of graphite-like layers. The total heat of attachment, ΔH_1, happens to be rather near to that of two $-O-H \cdots O{=}C{<}$ bonds. Methanol can form only one hydrogen bond with the surface, but the dispersion-force interaction with the sorbent should be substantially larger than for water.

The analysis shows that if true hydrogen bonds occur in the first layer they arise between sorbate and sorbent and not between the sorbate molecules themselves. Interaction energies, while exothermal and reasonably able to account for the upward inflexion

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[9] Coolidge, *J. Amer. Chem. Soc.*, 1927, **49**, 1949.

[10] Barrer and Woodhead, *Trans. Faraday Soc.*, 1948, **44**, 1001.

[11] Eucken, *Z. Elektrochem.*, 1920, **26**, 377.

of the isotherms, are much too small to represent lateral interaction by normal hydrogen-bond formation. Evidently, in favourable cases, the statistical-thermodynamic analysis can give considerable insight into the mechanism of the sorption process and can modify some earlier views.

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