SURFACE CHEMISTRY, ADSORPTION ENERGY, AND ADSORPTION EQUILIBRIA

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The Theory of Adsorption Equilibria and Adsorption Energy

FOR a long time adsorption was interpreted mainly by empirical and semi-empirical methods. Thus, Polanyi's theory, by its very nature, does not permit derivation of adsorption potentials, or even of the shapes of adsorption isotherms. The adsorption potential is determined by purely empirical means from the experimental isotherm. From the Langmuir and the B.E.T. theory for localised adsorption on homogeneous surfaces the shape of the adsorption isotherm can be found theoretically, but the equilibrium constants of adsorbate–adsorbent interactions are again determined from the experimental adsorption isotherm. These theories are therefore semi-empirical. The same is true of the modifications to the Langmuir and the B.E.T. theory which take into account adsorbate–adsorbate interactions. The simplest equations of this type are the approximate relationships suggested for unimolecular localised adsorption by the present author:[1]

$$h = \frac{\theta}{K_1(1-\theta)(1+K_n\theta)} \text{ or } \frac{\theta}{h(1-\theta)} = K_1 + K_1K_n\theta \qquad (1)$$

and for multi-molecular adsorption by the author and D. P. Poshkus:[1]

$$\frac{\theta(1-h)^2}{h[1-\theta(1-h)]} = K_1 + K_1K_n\theta(1-h) \qquad (2)$$

where θ is the surface coverage, $h = p/p_s$ is the relative vapour pressure, and K_1 and K_n are the respective equilibrium constants of adsorbate–adsorbent and adsorbate–adsorbate interactions. As in the Langmuir and B.E.T. equations, which are particular cases of equations (1) and (2) when $K_n = 0$, only the shape of the θ–h plot is found theoretically, while the constants K_1 and K_n are determined from the experimental adsorption isotherms.[2] Similarly, Hill's and deBoer's equation[3,4] for non-localised unimolecular adsorption,*

$$h = \frac{\theta}{K_1(1-\theta)} \exp[\theta/(1-\theta) - K_2\theta] \qquad (3)$$

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* Also the appropriate Hill's equation for multimolecular adsorption.

[1] A. V. Kiselev, *Doklady Akad. Nauk S.S.S.R.*, 1957, **117**, 1023; *Kolloid. Zhur.*, 1958, **20**, 338; A. V. Kiselev and D. P. Poshkus, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1958, 1520.

[2] A. V. Kiselev, N. V. Kovaleva, V. A. Sinitsyn, and E. V. Khrapova, *Kolloid. Zhur.*, 1958, **20**, 444.

[3] T. L. Hill, *J. Chem. Phys.*, 1946, **14**, 441.

[4] J. H. de Boer, "The Dynamical Character of Adsorption," Oxford, 1953.

gives only the shape of the adsorption isotherm: eqn. 3 is found by means of the Gibbs equation from the empirical two-dimensional equation of state, while the constants K_1 and K_2 are found from the experimental isotherms.[2,5] Thus, equation (3) is also semi-empirical. The same is true of many attempts to obtain an adsorption-isotherm equation by statistical thermodynamics: in these cases only the general shape of the θ–p curves is usually found, while the equilibrium constants containing the partition function of a given adsorbate on a given adsorbent are not calculated theoretically but are found from the experimental isotherms.

All this renders it impossible to surmount the limits of purely experimental investigation: each time a new adsorbent–adsorbate system has to be studied, new experiments have to be made and the adsorption equilibria found experimentally. This state of affairs is further complicated by the very scanty information on the structure of adsorbents, so that to take their irregularities into account one must again proceed from the experimental adsorption isotherms and adsorption heats. All this makes a rather dismal picture, showing how the theory of adsorption equilibria lags behind the present-day theory of chemical and many bulk-phase equilibria.

However, considerable progress has been made recently; this gives grounds for greater optimism. First, adsorbents have been obtained with surfaces sufficiently homogeneous to enable verification of the simplest theories, and sufficiently large to make possible accurate measurement of adsorption isotherms as well as adsorption heats and specific heats of adsorption systems. We are referring primarily to graphitised carbon blacks,[5–15] especially thermal carbon blacks heated to ~3000°, whose surface consists mainly of basal faces of graphite crystals.[5,9,13–15]

Secondly, a method has been devised for calculating the potential energy of adsorption Φ of molecules on homogeneous crystal faces starting from

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[5] S. Ross and W. Winkler, *J. Colloid Sci.*, 1955, **10**, 319, 330.

[6] R. A. Beebe, J. Biscoe, W. R. Smith, and C. B. Wendell, *J. Amer. Chem. Soc.*, 1947, **69**, 95; R. A. Beebe, M. H. Polley, W. R. Smith, and C. B. Wendell, *ibid.*, p. 2294; R. A. Beebe and D. M. Young, *J. Phys. Chem.*, 1954, **58**, 93.

[7] N. N. Avgul, G. I. Beresin, A. V. Kiselev, and I. A. Lygina, *Zhur. fiz. Khim.*, 1956, **30**, 2106; *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1956, 1304; 1957, 1021; 1959, 787; A. V. Kiselev, N. N. Avgul, G. I. Beresin, I. A. Lygina, and G. G. Muttik, *J. Chim. phys.*, 1958, 197.

[8] A. V. Kiselev, Proc. 2nd Internat. Congress on Surface Activity, Vol. II, London, 1957, p. 168.

[9] M. H. Polley, W. D. Schaeffer, and W. R. Smith, *J. Phys. Chem.*, 1953, **57**, 469; C. H. Amberg, W. B. Spencer, and R. A. Beebe, *Canad. J. Chem.*, 1955, **33**, 305; R. A. Beebe and R. M. Dell, *J. Phys. Chem.*, 1955, **59**, 746, 754; W. B. Spencer, C. H. Amberg, and R. A. Beebe, *ibid.*, 1958, **62**, 719.

[10] J. W. Ross and R. J. Good, *J. Phys. Chem.*, 1956, **60**, 1167.

[11] E. L. Pace, *J. Chem. Phys.*, 1957, **27**, 1341.

[12] N. N. Avgul, G. I. Beresin, A. V. Kiselev, and A. Ya. Korolev, *Kolloid. Zhur.*, 1958, **20**, 298.

[13] A. V. Kiselev and E. V. Khrapova, *Kolloid. Zhur.*, in the press.

[14] N. N. Avgul, A. V. Kiselev, and I. A. Lygina, *Kolloid. Zhur.*, in the press; *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, in the press.

[15] A. A. Isirikyan and A. V. Kiselev, *Kolloid. Zhur.*, in the press.

information on only the structure and physical properties of the adsorbent and adsorbate. It is true that this method encounters two difficulties, even in the simplest cases, when adsorption occurs under the influence of only electrokinetic (dispersion) attractive forces. It is based on using the Kirkwood–Müller formula[16] to calculate the energy constant C_1 of electrokinetic attraction in the term C_1r^{-6} (r is the distance between interacting centres) and similar formulæ[17–19] for the subsequent terms C_2r^{-8} and C_3r^{-10}. However, these quantum-mechanical formulæ are not strictly accurate. Moreover, the exponential repulsion constant ρ in the $b \exp (r/\rho)$ type potential is usually found empirically from compressibility experiments, while the constant b is excluded when the condition of equilibrium (minimum Φ at a certain selected distance from the surface) is introduced. The constant b is then replaced by a different constant related to the equilibrium distance between the closest interacting centres, which is calculated from the constants of the respective lattices taken separately, *i.e.*, under potential-field conditions which differ somewhat from such conditions for the adsorbate–adsorbent system. However, with due regard for these difficulties, which have not as yet been overcome by present-day quantum mechanics, we can obtain the value of the adsorption potential from the physical properties of the adsorbate and the adsorbent. The numerous calculations carried out so far by this method have resulted in $-\Phi$ values satisfactorily close to the most reliable measured heats of adsorption.[7,11,17–26]

Thirdly, definite progress is noticeable also in the statistical-thermodynamic treatment of adsorption equilibria. The simplest cases were examined by Hill,[27] Pace,[11] and Fisher and McMillan.[21,28] Hill made a direct attempt to calculate the equilibrium constant of the B.E.T. equation for certain of the simplest cases, confining himself to an "ideal" adsorbent. In this connection mention should also be made of Kemball's paper[29] which contains attempts to calculate the adsorption entropy by an examination of various models of adsorbate-molecule movement at the adsorbent surface. Proceeding from a theoretical calculation of Φ and

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[16] J. G. Kirkwood, *Phys. Z.*, 1932, **33**, 57; A. Müller, *Proc. Roy. Soc.*, 1937, *A*, **161**, 476.

[17] A. V. Kiselev, *Vestnik Akad. Nauk S.S.S.R.*, 1957, No. 10, p. 43.

[18] N. N. Avgul, A. A. Isirikyan, A. V. Kiselev, I. A. Lygina, and D. P. Poshkus, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1957, 1314.

[19] A. V. Kiselev and D. P. Poshkus, *Zhur. fiz. Khim.*, 1958, **32**, 2824.

[20] R. M. Barrer, *Proc. Roy. Soc.*, 1937, *A*, **161**, 476.

[21] B. B. Fisher and W. G. McMillan, *J. Chem. Phys.*, 1958, **28**, 562.

[22] W. J. C. Orr, *Proc. Roy. Soc.*, 1939, *A*, **173**, 349.

[23] A. D. Crowell and D. M. Young, *Trans. Faraday Soc.*, 1953, **49**, 1080; A. D. Crowell, *J. Chem. Phys.*, 1954, **22**, 1397; 1957, **26**, 1407.

[24] T. Hayakawa, *Bull. Chem. Soc. Japan*, 1957, **30**, 236.

[25] R. A. Pierotti and D. Halsey, *J. Phys. Chem.*, 1959, **63**, 680.

[26] E. L. Pace and A. R. Siebert, *J. Phys. Chem.*, 1959, **63**, 1398.

[27] T. L. Hill, *J. Chem. Phys.*, 1948, **16**, 181; J. W. Drenan and T. L. Hill, *ibid.*, 1949, **17**, 775.

[28] B. B. Fisher and W. G. McMillan, *J. Chem. Phys.*, 1958, **28**, 555.

[29] C. Kemball, *Proc. Roy. Soc.*, 1946, *A*, **187**, 73; 1947, *A*, **190**, 117.

the entropy values obtained by Kemball, the present author and D. P. Poshkus[30] attempted to calculate the equilibrium constant of the B.E.T. equation for the adsorption of benzene on graphite and on magnesium oxide. However, the entropy values used in these calculations were obtained by Kemball[29] for models which were selected rather arbitrarily. Therefore selection of the models of adsorption-complex movement based on independent facts is a very important problem. These facts must be obtained by spectral and magnetic investigations. Only preliminary attempts have been made in this direction as yet.[31,32]

Such, in general terms, is the state of the problem of theoretical calculation of adsorption energies and adsorption equilibria. It shows that at present this question should be posed in all its aspects, to draw it to the attention of both experimentalists and theoreticians. There are grounds for hope that despite inevitable disappointments the properties of adsorption systems will with increasing frequency become theoretically predictable from their nature.

This Review deals with several examples of the effect of the nature of adsorption systems (*i.e.*, the surface chemistry and molecular structure of the adsorbate) on adsorption properties, mainly the adsorption energy but partly the adsorption equilibria.

Adsorption Heats

Heats of Adsorption of Vapours of Non-polar Substances on Graphitised Carbon Blacks. The heats of adsorption of the simple gases and a number of hydrocarbons on graphitised carbon blacks have been determined.[5–12,15]

Preliminary calculations of the adsorption potential of non-polar molecules on graphite reported by the present author[8] at the Second International Congress of Surface Activity in London in 1957 were soon afterwards refined in the works of N. N. Avgul, I. A. Lygina, D. P. Poshkus, and the present author.[18,33] These refinements involved accounting for the later terms in the equation for dispersion energy, introduction of more accurate values for the exponential repulsion constant ρ, and summation over a large number of graphite carbon atoms. The adsorption energy was computed by the formula

$$\Phi = -C_{i1}\sum_j r_{ij}^{-6} - C_{i2}\sum_j r_{ij}^{-8} - C_{i3}\sum_j r_{ij}^{-10} + B'\sum_j \exp(-r_{ij}/\rho) \qquad (4)$$

where i is the force centre of the adsorbate molecule; the constant C_{i1} of electrokinetic interaction of this centre with the carbon atom j of the graphite was calculated by the Kirkwood–Müller formula, and the constants C_{i2} and C_{i3} by similar formulæ.[18,19] The contribution of the term $-C_{i2}\sum_j r_{ij}^{-8}$ was about 10% of Φ, and of the term $C_{i3}\sum_j r_{ij}^{-10}$, about 1%

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[30] A. V. Kiselev and D. P. Poshkus, Proc. 2nd Internat. Congress on Surface Activity, Vol. II, London, 1957, p. 202.

[31] G. L. Kington, "The Structure and Properties of Porous Materials," p. 247, ed. D. H. Everett, F. Stone, London, 1958.

[32] A. V. Kiselev and V. I. Lygin, *Kolloid. Zhur.*, in the press.

[33] N. N. Avgul, A. V. Kiselev, I. A. Lygina, and D. P. Poshkus, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1196.

(therefore, owing to the approximate nature of the calculation, the latter term may be neglected). The constant B' was found from the condition of minimum energy of interaction with the entire lattice Φ at an equilibrium distance from the outer phase. The value $\rho = 0{\cdot}28$ Å resulted in Φ values close to those obtained in calculating[18,19,33] the contribution of the repulsion potential by the Lennard-Jones exponential formula $B'' \sum_j r_{ij}^{-12}$.

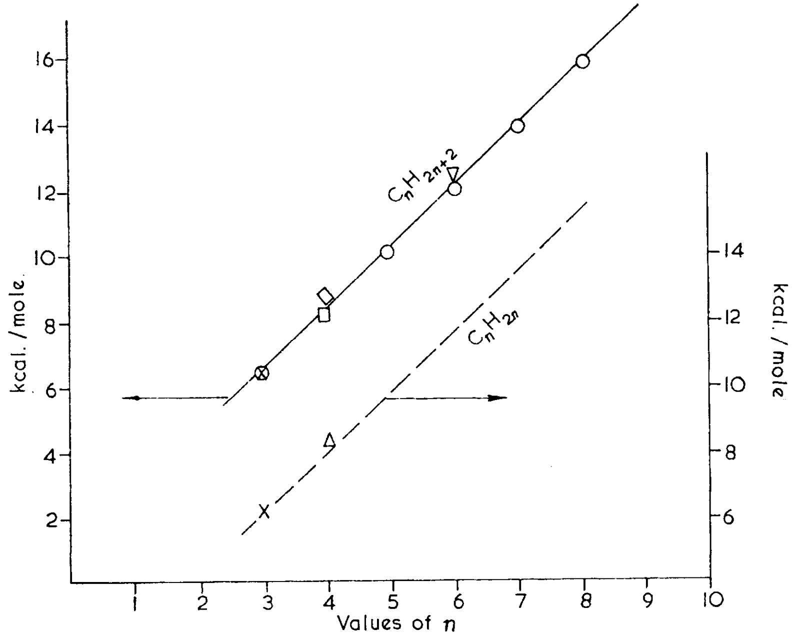

FIG. 1. *Experimental values of standard differential heats of adsorption* Q_a^0 *(points) and theoretical energies* $-\Phi^0$ *calculated by equation* (4) *(lines) for normal alkanes (full line) and olefins (broken line) with n carbon atoms on graphitised carbon black.* References are: ○ 7, 8; □ 10; ◇ 6; △ 6; ⊗ 34; × 34; ▽ 15, 39.

Fig. 1 is a comparison of the refined calculation of Φ according to equation (4) (with approximate allowance for the adsorbate–adsorbate interaction energy for standard surface coverage $\theta = 0{\cdot}5$) with the experimental values of standard differential adsorption heats of a number of n-alkanes and olefins on graphitised carbon black.* Table 1 lists the results

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* Measurements of the differential adsorption heats Q_a of n-hexane vapour on T-1 thermal carbon black graphitised at 3000° showed[15] that the region of initial Q_a drop due to residual heterogeneity of the specimen had greatly narrowed. But the region of increase of Q_a on filling of the monolayer by adsorbate–adsorbate interaction had become wider and the height of the maximum had increased in comparison with Spheron-6 1700° carbon black.[7,8] For adsorption of benzene complete monolayer coverage of the surface involves hardly any increase in the heat of adsorption. This is perhaps due to partial compensation of the weaker electrokinetic adsorbate–adsorbate attraction by electrostatic repulsion of the H–C dipoles in the ring plane and of the quadrupoles formed by the system of π-electrons and residual charges on the carbon atoms of benzene.[35]

for several other adsorbates, particularly isoalkanes, for which the different distances of the separate links of the molecule from the graphite surface were taken into account.[7] These results show that calculation by equation (4) gives, first, the correct sequence of the adsorption energy values (for example, $-\Phi^0$, as $Q_a{}^0$, for benzene are *smaller* than for hexane) and, secondly, satisfactory quantitative agreement.[18] The calculations and experiments of Crowell and Young[23] and of Pace[11] for argon, and those of Pace and Siebert[26] for hydrogen and deuterium suggest the same conclusion.

TABLE 1. *Graphite adsorption energies* $-\Phi^0$ *calculated by us,*[18,34] *and experimental differential adsorption heats* $Q_a{}^0$ *on the surface of graphitised carbon blacks at standard coverage* $\theta = 0{\cdot}5$ (kcal./mole).

Adsorbate	$-\Phi^0$	$Q_a{}^0$	*Ref.*
Hydrogen	0·90*	0·91	26
Deuterium	0·95*	0·95	26
Neon	1·0	1·0	36
Argon	2·6	2·7; 2·6; 2·3	6, 11, 37
Krypton	3·7	3·5; 4·5	5, 9
Nitrogen	2·6	2·8; 2·3	6, 37
Propane	6·8	6·5	34
n-Butane	8·5	8·7; 8·3	6, 10
n-Pentane	10·4	10·2	7, 8
n-Hexane	12·4	12·1; $12{\cdot}5_5$	7, 8, 15
n-Heptane	14·2	14·0	7, 8
n-Octane	16·1	16·0	7, 8
2,2-Dimethylbutane	10·2	10·0	7, 8
3-Methylhexane	13·2	12·7	7, 8
2,2,4-Trimethylpentane	12·6	12·7	7, 8
Cyclopentane	9·6	8·9	7, 8
Methylcyclopentane	10·4	10·2	7, 8
Propene	6·2	6·2	34
Benzene	10·3	10·0; 10·3	7, 8, 38
Toluene	12·0	12·1	7, 8

Heats of Adsorption of Alcohols and Water on Graphitised Carbon Black. The adsorption energy of alcohols differs from that of the corresponding hydrocarbons in that the dispersion interaction of the hydro-

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* After Pace and Siebert,[26] with a 10% correction introduced by us for the contribution of the term $-C_{i2}\sum_j r_{ij}{}^{-8}$.

[34] A. G. Bezus, V. P. Dreving, and A. V. Kiselev, *Kolloid. Zhur.*, in the press.

[35] A. V. Kiselev and D. P. Poshkus, *Doklady Akad. Nauk S.S.S.R.*, 1958, **120**, 834.

[36] J. G. Aston and J. Greyson, Proc. 2nd Internat. Congress on Surface Activity, Vol. II, London 1957, p. 39.

[37] S. Ross and W. W. Pultz, *J. Colloid Sci.*, 1958, **13**, 397.

[38] A. A. Isirikyan and A. V. Kiselev, *J. Phys. Chem.*, in the press.

carbon part of the molecule is supplemented by hydroxyl interaction, namely, the weak electrokinetic interaction of the hydroxyl oxygen atom with graphite and electrostatic polarisation of the graphite carbon atoms by the OH dipole. Besides, in this case a strong adsorbate–adsorbate interaction comes into play, involving formation of a hydrogen bond between the hydroxyl groups of the alcohol molecules.[14]

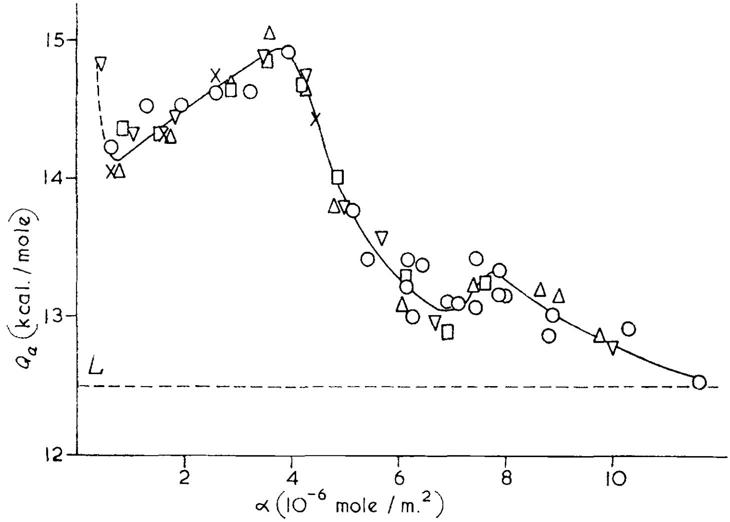

FIG. 2. *Dependence of differential heat of adsorption Q_a of butan-1-ol vapour on the amount adsorbed per unit area α by graphitised thermal carbon blacks. The horizonta broken line here and in other figures represents the heat of condensation.*

Fig. 2 shows the dependence of the differential heat of adsorption Q_a of butan-1-ol on thermal carbon black graphitised at 3000° on α (the amount adsorbed per unit area of surface) as obtained by N. N. Avgul and I. A. Lygina. Residual surface heterogeneity hinders determination of the initial heat of adsorption of isolated alcohol molecules: in the region of coverage of the more homogeneous part of the surface (where the curve begins to rise), the heat of adsorption of butan-1-ol is already considerably higher than that of n-butane. Thus, at $\theta = 0{\cdot}5$, $Q_a{}^0$ for butan-1-ol is 14·4 and for butane is 8·4 kcal./mole; the difference between these values, 6·0 kcal./mole, is close to the energy of the hydrogen bond in alcohols.

In the region of predominant second-layer adsorption, Q_a again passes through a weak maximum.

Fig. 3 presents the Q_a–α curves for adsorption of a number of alcohols on a carbon black, with a less homogeneous surface (Spheron-6 calcined at 2800°).[14] The increment per CH_2 group in the $Q_a{}^0$ values of the lower alcohols (1·5 kcal./mole) is smaller than the corresponding increment for

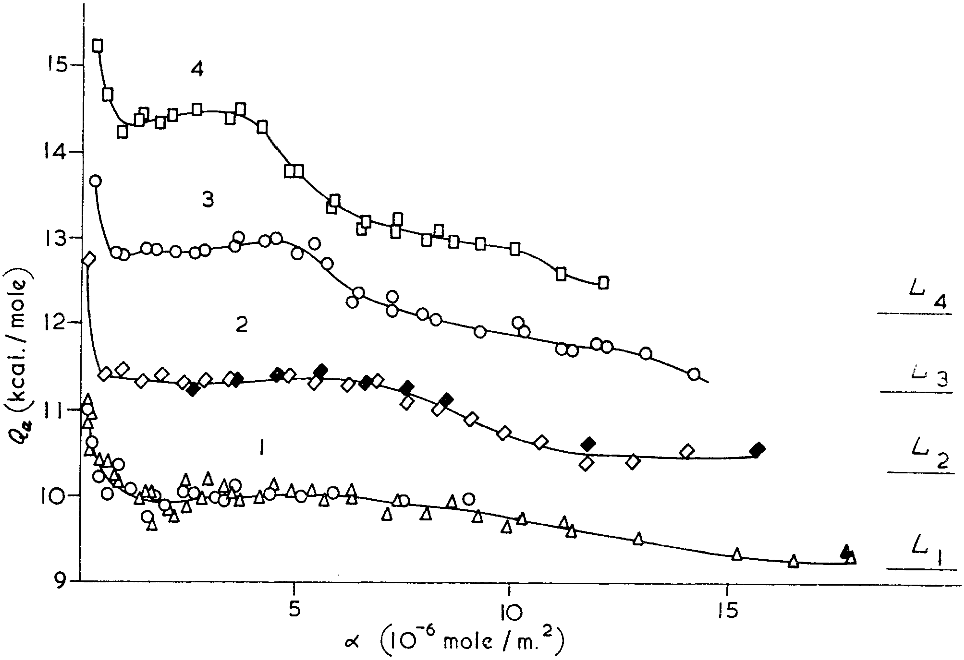

FIG. 3. *Dependence of the differential heat of adsorption* Q_a *on the amount adsorbed per unit area* α *of normal alcohol vapours on Spheron-*6, 2800° *carbon black. L's are the corresponding heats of condensation. Here and below, solid points indicate desorption.* 1, *Methanol*; 2, *ethanol*; 3, *propan-*1-*ol*; 4, *butan-*1-*ol*.

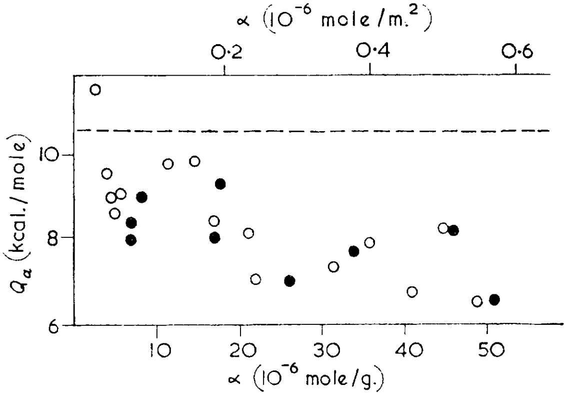

FIG. 4. *Dependence of differential heat of adsorption* Q_a *of water vapour on the amount adsorbed per unit area* α *and a by Spheron-*6, 2800° *carbon black.*

n-alkanes (1·90 kcal./mole); this is because in hydrogen-bonded alcohols the hydrocarbon part of the alcohol molecule closest to the hydroxyl group cannot assume the most favourable orientation.

Fig. 4 shows the Q_a–α relation for adsorption of water on the same carbon black.[14] Measurement of the heat of adsorption at low p/p_s is greatly complicated in this case owing to the exceedingly small adsorption values. Nevertheless, it can be confidently concluded that the heat of adsorption Q_a of water vapour on the surface of the graphitised carbon black is smaller than its heat of condensation L.

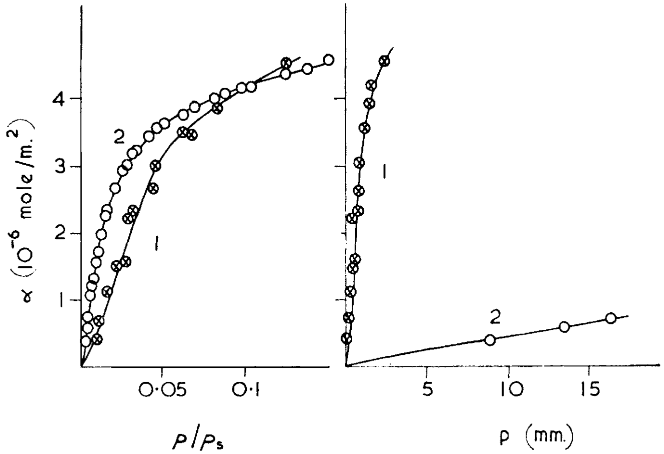

FIG. 5. *Adsorption isotherms of* (1) *butan-*1*-ol and* (2) *n-butane on Spheron-*6, 2800°, *carbon black.*

Fig. 5 shows the adsorption isotherms of butane and butan-1-ol in relation to p and p/p_s. At identical values of p the adsorption of butan-1-ol is greater than of butane, and at equal p/p_s the reverse. This agrees with the fact that the full heat of adsorption Q_a of butanol is larger than that of butane, while the net heat of adsorption $Q_a - L$ of butanol is less than that of butane.[14] Fig. 6 shows the adsorption isotherms of water and of alcohols. These isotherms are described satisfactorily by equations (1) and (2) for localised adsorption in conformity with the fact that in this case the adsorbate–adsorbate interaction cannot be neglected in comparison with the adsorbate–adsorbent interactions.*

Heats of Adsorption of Hydrocarbons on Magnesium Oxide. The dependence of the heats of adsorption of n-hexane and benzene on the surface coverage of magnesium oxide calcined at 1000° is illustrated in

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* At the transition to graphitised thermal carbon blacks with more homogeneous surfaces the isotherms of adsorption of lower alcohols are represented better by the isotherm equations for non-localised adsorption.[14] This is probably connected with the increase in the regions of free migration for these molecules.

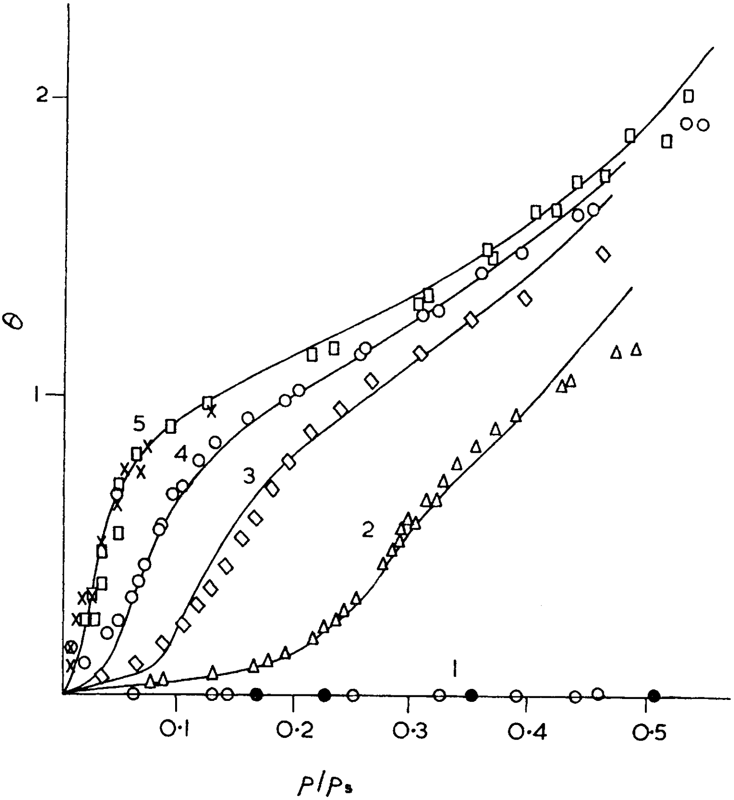

FIG. 6. *Adsorption isotherms of* (1) *water vapour,* (2) *methanol,* (3) *ethanol,* (4) *propan-*1-*ol, and* (5) *butan-*1-*ol on Spheron-*6, 2800° *carbon black. The curves are calculated by means of equation* (2).

Fig. 7.[39] At medium monolayer coverage the heat of adsorption depends little on θ, and therefore the $Q_a{}^0$ values at $\theta = 0{\cdot}5$ can be accepted as the standard values of the differential heat of adsorption. Table 2 lists these values in comparison with the values of $-\Phi^0$ calculated from equation (4) after allowance for polarisation of the adsorbate molecules and correction for the energy of adsorbate–adsorbate interaction at $\theta = 0{\cdot}5$.[18,19] The energy of induction attraction is very small here because ions of opposite signs alternate on the (100) face of the magnesium oxide. It can be seen from the Table that the calculated energies of adsorption agree satisfactorily in this case with the measured heats of adsorption.

The agreement between the calculated and the measured energies of adsorption of nitrogen, krypton, and methane on sodium bromide has been pointed out by Fisher and McMillan.[21]

[39] A. A. Isirikyan and A. V. Kiselev, *Zhur. fiz. Khim.*, 1960, **34**, 2817.

TABLE 2. *Calculated energies of adsorption* — Φ^0 *on the* (100) *face of magnesium oxide, and experimental differential heats of adsorption* $Q_a{}^0$ *on magnesium oxide at* $\theta = 0{\cdot}5$ (*kcal./mole.*)

Absorbate	$-\Phi^0$	$Q_a{}^0$	*Ref.*
n-Hexane	9·7	9·4	39
n-Heptane	11·1	11·3	39
n-Octane	12·6	12·4	39
Benzene	8·6	9·1; 9·2	39, 40
Toluene	10·1	10·3	40

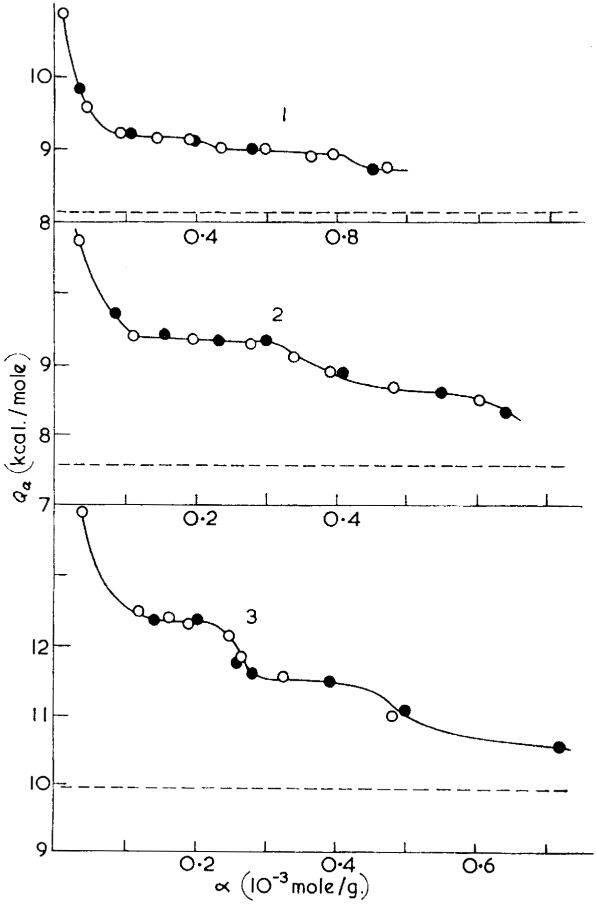

FIG. 7. *Dependence of differential heat of adsorption* Q_a *of* (1) *benzene,* (2) *n-hexane, and* (3) *n-octane vapours on surface coverage of magnesium oxide.*

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[40] S. D. L. Shreiner and C. Kemball, *Trans. Faraday Soc.*, 1953, **49**, 1080.

Heats of Adsorption of Hydrocarbons on Magnesium Hydroxide. Investigation of the energy of adsorption on hydroxides is of major interest, as identical and identically oriented hydroxyl dipoles project from the surface in this case. They create a more homogeneous, though weaker, electrostatic field than does the (100) face of magnesium oxide and similar ionic lattices.[41] This causes an increase in the energy of adsorption of molecules that have markedly non-uniform electron-density distribution. Such distribution occurs when a molecule has either a dipole or a large quadrupole moment, formation of a strong or weak hydrogen bond then being possible if the orientation is favourable. Interaction arises (supplementary to the dispersion energy) more for benzene than for hexane. In the benzene molecule the π-electron clouds increase the electron density on both sides of the hexagon of carbon atoms,[35] causing a weak hydrogen bond with the hydroxyl groups on the outer surface of the magnesium hydroxide. The energy contribution of the electrokinetic interaction with this lattice, as in the case of graphite, is higher for hexane than for benzene.[41] In conformity with this are the experimental $Q_a{}^0$ values:[42] for n-hexane 9·0 and for benzene 9·6 kcal./mole.

Complete calculation of the energy of interaction of the benzene molecule with magnesium hydroxide is difficult owing to the absence of reliable data on the charge distribution in the hydroxyl of $Mg(OH)_2$. Therefore the problem has been solved so far only as functions of the degree of covalency of the bond and of the value of the OH dipole moment.[43]

Heats of Adsorption on Silicas with Hydrated and Dehydrated Surfaces. Adsorption on amorphous hydroxides with large surfaces—silica gels and aerosols—is of great practical importance. By drying silica gels after their formation at not more than 150°, or by hydrothermal treatment of dehydrated silicas, completely hydrated silica surfaces can easily be obtained.[44,45] Sufficiently prolonged evacuation at ordinary temperatures (not above 150°) makes it possible to free these surfaces almost completely from adsorbed water, retaining a dense coating of hydroxyl groups of the silica proper. This is demonstrated by the reversibility of the isotherms and by the heats of adsorption of the water vapour, as well as by a study of the infrared spectrum in the region of valency vibrations of the hydroxyl in Si–OH or Si–OD and in the region of deformation of the water molecules.[46] Fig. 8 shows, first, the infrared spectrum of an evacuated silica gel with a hydrated surface. There is a major absorption by silica-hydroxyl in the region of valency vibrations, with an indication of a weak hydrogen

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[41] D. P. Poshkus and A. V. Kiselev, *Zhur. fiz. Khim.*, 1960, **34**, 2640.
[42] A. V. Kiselev and D. P. Poshkus, *Kolloid. Zhur.*, 1960, 22, 403.
[43] D. P. Poshkus and A. V. Kiselev, *Zhur. fiz. Khim.*, 1960, **34**, 2646.
[44] A. V. Kiselev, *Kolloid, Zhur.*, 1936, **2**, 17.
[45] A. V. Kiselev, "The Structure and Properties of Porous Materials," ed. D. H. Everett, F. Stone, London, 1958, p. 195.
[46] A. V. Kiselev and V. I. Lygin, *Kolloid. Zhur.*, 1959, **21**, 581; 1960, **22**, 403.

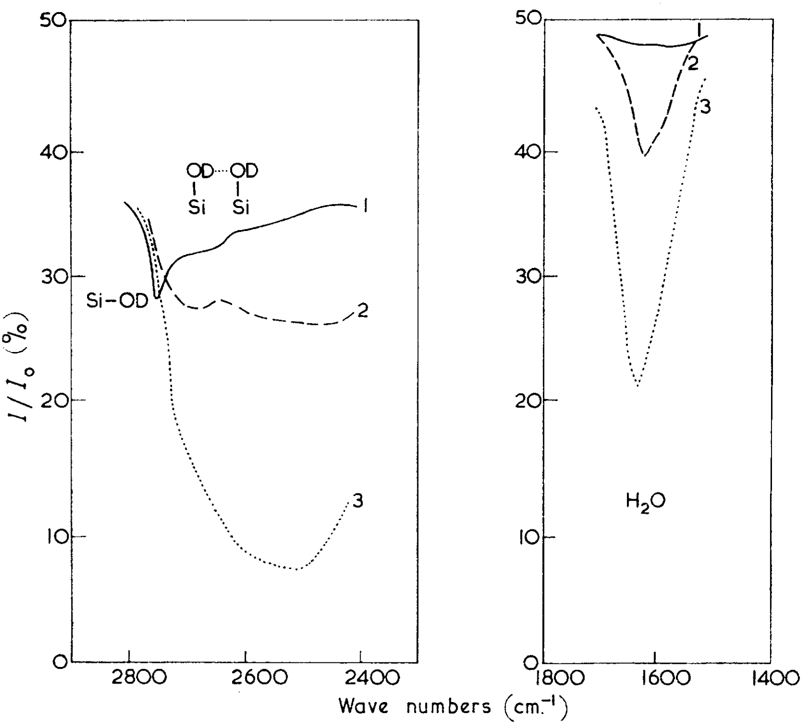

FIG. 8. *Infrared absorption spectra in the system silica gel–water. Left: Region of valency vibrations of silica gel hydroxyl groups. Right: Region of deformation vibrations of water hydroxyl groups.* (1) *After evacuation at* 200°; (2) *after adsorption of monolayer of water;* (3) *after capillary condensation.*

bond between them.[47] In the region of deformation vibrations of the water molecules there is no absorption, and therefore there is practically no water on the surface in the form of adsorbed molecules. Secondly, Fig. 8 shows the corresponding spectrum after adsorption of approximately a monolayer of water. It now displays a hydrogen bond between the water molecules and the silica gel hydroxyls and considerable absorption in the region of deformation vibrations in the water molecules. Finally, after capillary condensation of water, both these effects became stronger, almost reaching the normal effects in ordinary liquid water.[46]

The presence of a hydroxyl coating on the surface of hydrated silica results, not only in strong adsorption of molecules capable of forming hydrogen bonds with the silicic acid hydroxyl groups (water, alcohol,

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[47] A. V. Kiselev and V. I. Lygin, Proc. 2nd Internat. Congress on Surface Activity, Vol. 2, London, 1957, p. 204; V. I. Lygin, *Vestnik Moskovskovo Universiteta*, 1958, No. 1, 223.

etc.[45,48]), but also, as in the case of magnesium hydroxide, in a sharp increase in the adsorption of molecules, non-polar on the whole, but with a very non-uniform electron-density distribution. With favourable orientation of the quadrupole moment (parallel to the hydroxyl axis) these molecules are adsorbed much more strongly than are molecules of similar dimensions having the same or even higher polarisability but a smaller quadrupole moment. D. P. Poshkus and the author demonstrated[35] that calculation of the Coulomb contribution to the energy of electrostatic interaction of the benzene molecule with the surface hydroxyl groups (quadrupole–dipole electrostatic interaction) results in energy values which make it possible to account for the fact[45,49] that the heat of adsorption of benzene on a hydrated silica gel surface is greater than that of hexane (Fig. 9).* This conforms with the shifts of stretching frequency in the infrared absorption spectra of the surface hydroxyl groups observed by A. N. Terenin and V. N. Philimonov[52] in the overtone region during the adsorption of benzene ($\Delta\nu = 236$ cm.$^{-1}$) and n-hexane ($\Delta\nu = 70$ cm.$^{-1}$).† This also accounts for the sharp lowering of the heat of adsorption of benzene (in contrast to hexane) on dehydration of the silica surface[45–49] (see Fig. 9) and the corresponding decrease in the adsorption of nitrogen[54] whose molecules possess a rather large quadrupole moment. The higher adsorption of nitrogen on the hydrated surface is in conformity with the relatively high values of the shift in vibration frequency of the silica hydroxyls.[55,56]

Fig. 10 shows plots of $(Q_a - L)$ against α for n-hexane and benzene,[49] and Table 3 gives the values of their differential adsorption heats at $\theta = 0{\cdot}5$ on a series of adsorbents (both with and without hydroxyl groups) coated on their surface. It can be seen from the Figure and the Table that in passing from the non-polar adsorbent-graphitised carbon black to silica gel which has a highly hydrated surface, the difference of the heats of adsorption of these hydrocarbons changes its sign.

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* For the same reasons the standard heat of adsorption on a hydrated silica gel surface is higher for propene than for propane[50] ($7._4$ and $5._0$ kcal./mole) and higher for but-1-ene than for butane.[51]

† For the main spectral region V. I. Lygin *et al.*[53] recently obtained the values 90 and 26 cm.$^{-1}$ for the stretching frequency shifts of groups OD in a silica gel surface coated by adsorption of benzene and hexane.

[48] A. V. Kiselev, Proc. 2nd Internat. Congress on Surface Activity, Vol. 2, London, 1957, p. 179.

[49] L. D. Belyakova and A. V. Kiselev, in the collection, "Obtaining the Structure and Properties of Sorbents," Leningrad, 1959, p. 180 (in Russian).

[50] A. G. Bezus, V. P. Dreving, and A. L. Klyachko-Gurvich, *Kolloid. Zhur.*, in the press.

[51] W. R. Smith and R. A. Beebe, *Ind. Eng. Chem.*, 1949, **41**, 1431.

[52] A. N. Terenin, in the collection, "Surface Properties of Chemical Compounds and their Role in Adsorption Phenomena." ed. A. V. Kiselev, Moscow State Univ. Press, 1957, p. 206 (in Russian); V. N. Philimonov, *Optika i Spekroskopiya*, 1956, **1**, 490.

[53] A. V. Kiselev and V. I. Lygin, *Kolloid. Zhur.*, in the press.

[54] A. V. Kiselev and E. V. Khrapova, *Kolloid. Zhur.*, 1957, **19**, 572.

[55] R. McDonald, *J. Amer. Chem. Soc.*, 1958, **79**, 850.

[56] G. J. C. Frohnsdorff and G. L. Kington, *Trans. Faraday Soc.*, 1959, **55**, 1173.

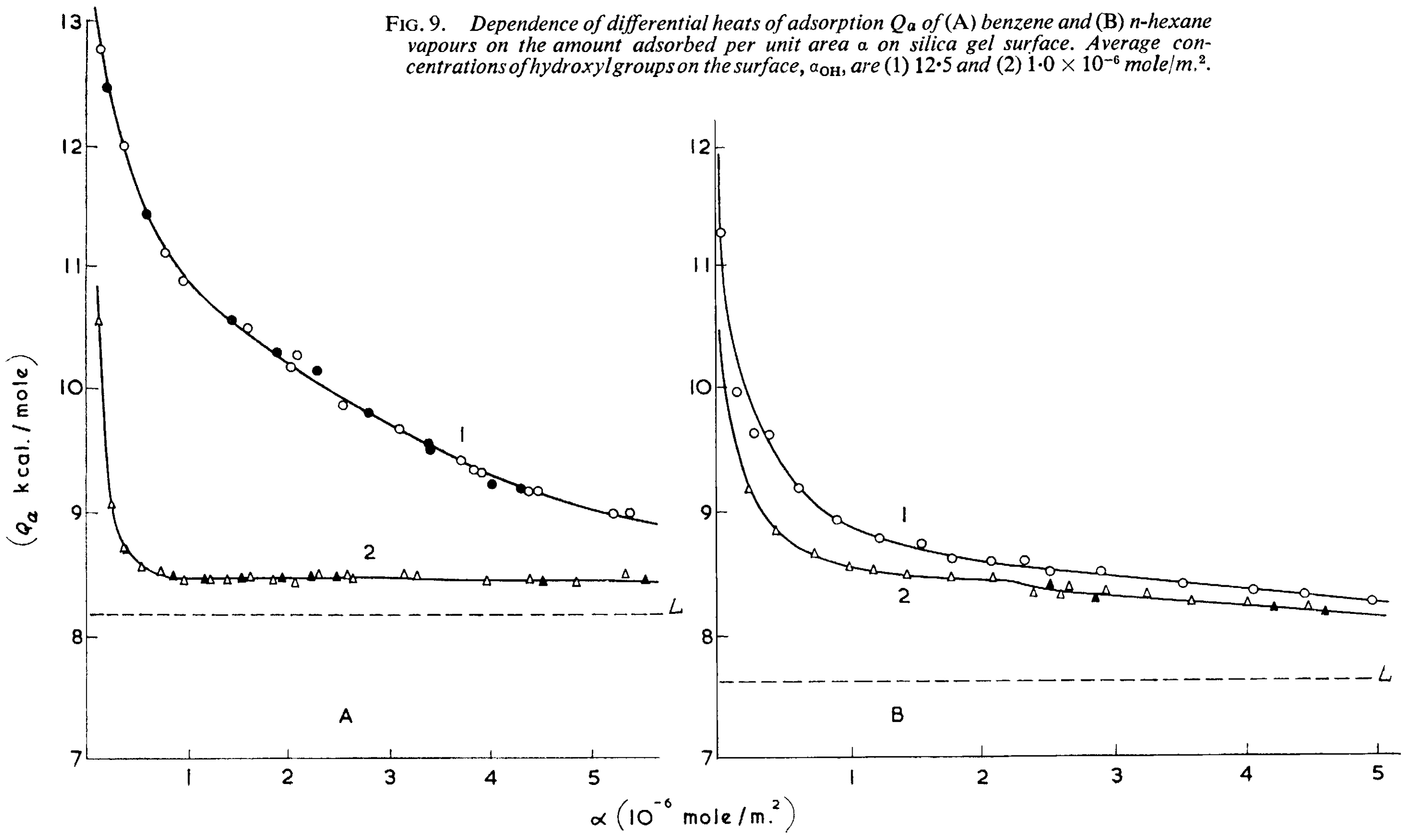

FIG. 9. *Dependence of differential heats of adsorption Q_a of* (A) *benzene and* (B) *n-hexane vapours on the amount adsorbed per unit area* α *on silica gel surface. Average concentrations of hydroxyl groups on the surface,* α_{OH}, *are* (1) 12·5 *and* (2) 1·0 × 10^{-6} *mole/m.*^{2}.

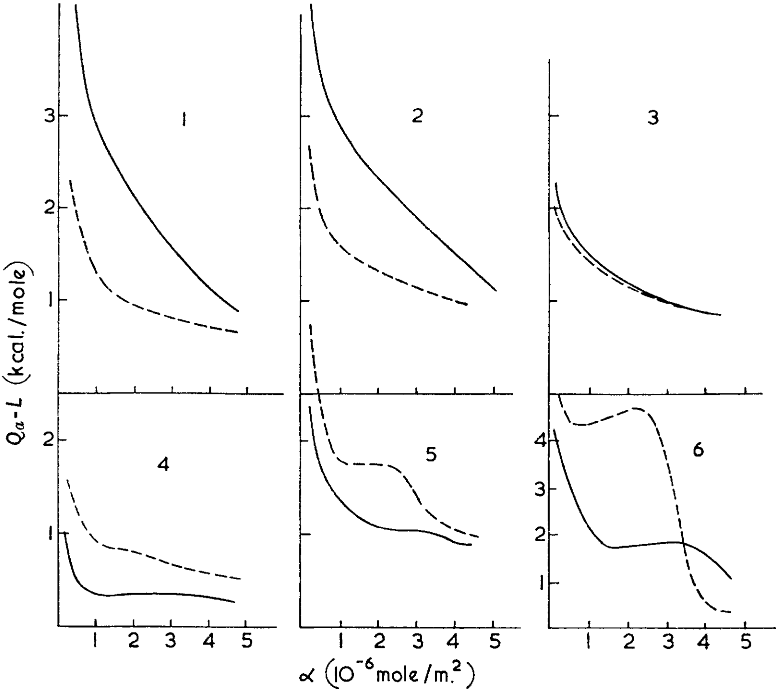

FIG. 10. *Dependence of differential net heat of adsorption* Q_a—*L on adsorption* α *for benzene (solid curves) and n-hexane (broken curves) on surfaces of silica with mean surface concentration of hydroxyl groups* α_{OH} = 12·5 *μ-moles/m.*^{2}; 2—*ditto with* α_{OH} = 10·8; 3—*ditto with* α_{OH} = 3·5; 4—*ditto with* α_{OH} *as follows:* (1) 12·5, (2) 10·8, (3) 3·5 *and* (4) 1·0 × 10^{-6} *mole/m.*^{2}; *and* (5) *on magnesium oxide amd* (6) *on Spheron*-6, 1700° *carbon black.*

TABLE 3. *Standard heats of adsorption* Q_a^0 *of n-hexane and benzene vapours on various adsorbents* (kcal./mole).

Adsorbent	*Hexane*	*Benzene*	*Hexane — Benzene*
Graphitised carbon black	12·5	10·3	+2·2
Magnesium oxide	9·4	9·2	+0·2
Silica gel with strongly dehydrated surface	8·6	8·5	+0·1
Magnesium hydroxide	9·0	9·6	−0·6
Silica gel with strongly hydrated surface	8·8	10·4	−1·6

Heats of Adsorption on Silica with its Surface Chemically Modified by Trimethylsilyl Groups. In this case trimethylsilyl groups are chemically bonded to the silica surface.[57,53] Fig. 11 shows the scheme of this bonding

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[57] H. W. Kohlschütter, P. Best, and G. Wirzing, *Z. anorg. Chem.*, 1950, **285**, 236.

[58] A. V. Kiselev, N. V. Kovaleva, A. Ya. Korolev, and K. D. Shcherbakova, *Doklady. Akad. Nauk* S.S.S.R., 1959, **124**, 617; I. Yu. Babkin, V. S. Vasilyeva, I. V. Drogalyeva, A. Ya. Korolev and K. D. Shcherbakova, *ibid.*, 1959, **129**, 131.

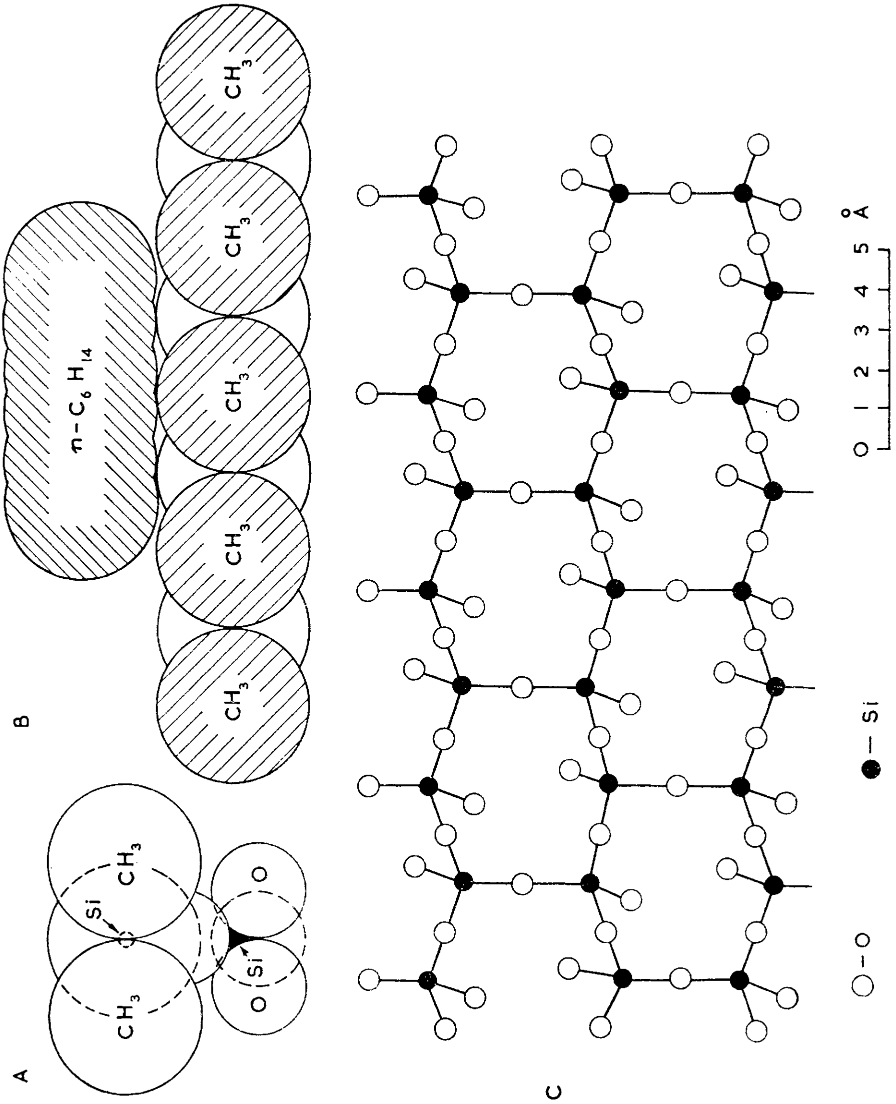

FIG. 11. (*a*) *Possible combination of trimethylsilyl group with silicon–oxygen tetrahedron.* (*b*) *Model of close-packed methyl group layer with* (*above*) *adsorbed n-hexane molecule.* (*c*) *Tridimite structure.*

and a simplified model of the modifying layer.[59] After sufficient modification of the surface the adsorbate moves away from it, causing the adsorption potential to drop sharply, especially in the case of molecules adsorbed

[59] I. Yu. Babkin and A. V. Kiselev, *Doklady. Akad. Nauk S.S.S.R.*, 1959, **129**, 357.

not only by electrokinetic but also by electrostatic interactions (polar, quadrupole) with the hydrated silica surface.

A calculation of the energy of adsorption on such a modified surface, made by I. Yu. Babkin and the author,[59] resulted in values for n-hexane and benzene of about $4{\cdot}_3$ and $4{\cdot}_0$ kcal./mole. *i.e.*, much smaller than the heats of condensation. Measurements of differential heats of adsorption, carried out by us with aerosol specimens modified in A. Ya. Korolev's laboratory,[58] showed that despite the residual surface heterogeneity the net heats of adsorption of hydrocarbons on sufficiently modified specimens were actually negative (Fig. 12).[60] Incipient capillary condensation at the contact points between the aerosol particles results in excessive Q_a values,

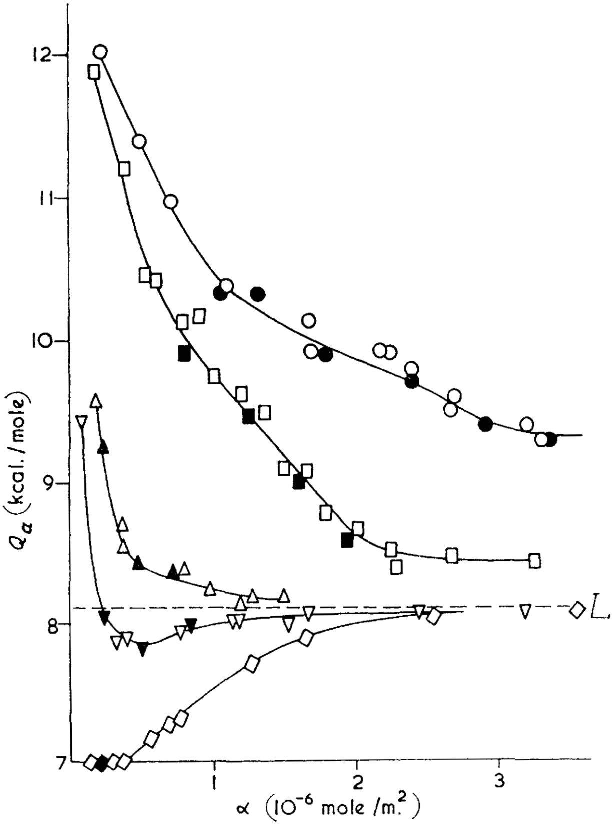

FIG. 12. *Dependence of differential heat of adsorption Q_a of benzene vapour on the amount adsorbed per unit area α by modified aerosols. Surface concentration of* $SiMe_3$: o, 0; □ ~60%; △ ~80%; ▽ ~90%; ◇ 100%.

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[60] I. Yu. Babkin, A. V. Kiselev, and A. Ya. Korolev, *Doklady Akad. Nauk S.S.S.R.* 1961, **136**, 373.

and therefore the true values for the pure adsorption interaction are still smaller, *i.e.*, still closer to those calculated in ref. 59. Fig. 13 presents the corresponding adsorption isotherms. Increasing the degree of modification often lowers the adsorption value by dozens of times.[58,60,61]

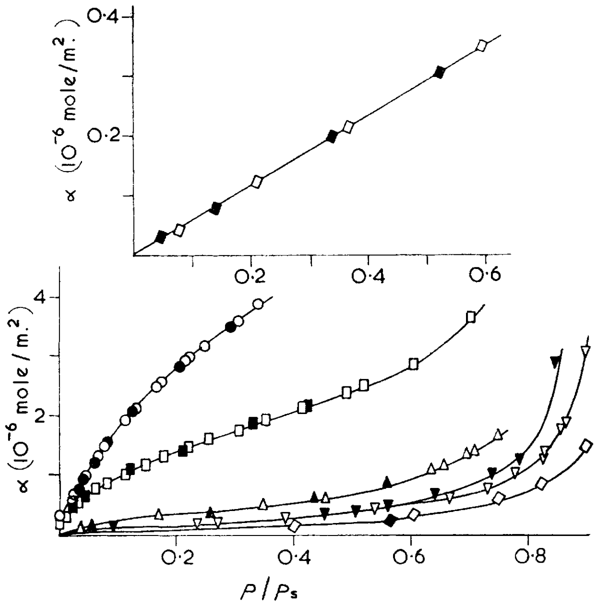

FIG. 13. *Adsorption isotherms of benzene vapour on modified aerosols. Surface concentration of* $SiMe_3$: o, 0; □ ~60%; △ ~80%; ▽ ~90%; ◇ ~ 100%. *The lowest isotherm is on a larger scale.*

The sharp drop in the energy of universal electrokinetic interactions, and the possibility of obtaining very homogeneous surfaces and of bonding a modifying layer (which screens the adsorbent) of new active functional groups to the surface, make chemical modification a good method of controlling the properties of fillers for various media, pigments, and adsorbents for chromatography, particularly for the application of gas chromatography to mixtures of heavy hydrocarbons and their derivatives and associated compounds.[62] For instance, by hydrothermal treatment of silica gel and chemical modification of its surface by trimethylsilyl groups it was possible to separate benzene and hexane vapours, even at room temperature.[63]

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[61] A. V. Kiselev, A. Ya. Korolev, R. S. Petrova, and K. D. Shcherbakova, *Kolloid. Zhur.*, 1960, **22**, 671.

[62] A. V. Kiselev and K. D. Shcherbakova, "Gas-Chromatographie, Material zum 2. Symposium über Gas-Chromatographie in Böhlen," Oktober 1959, ed. R. E. Kaiser, A. G. Struppe, p. 198.

[63] V. S. Vasilyeva, I. V. Drogaleva, A. V. Kiselev, A. Ya. Korolev, and K. D. Shcherbakova, *Doklady Akad. Nauk S.S.S.R.*, in the press.

Adsorption Equilibria

An Attempt at Complete Statistical-thermodynamic Calculation of Adsorption Equilibria. As was pointed out in the first section, the chief problem in this field is to calculate isotherms for adsorption on a homogeneous surface, proceeding only from the structure and physical properties of the adsorbent and the adsorbate. Several papers dealing with this trend were mentioned above. D. P. Poshkus and the present author[64] carried out a statistical-thermodynamic calculation of the change in chemical potential when argon is adsorbed on a graphite basal face for low θ, according to the formula:

$$\Delta\mu = -\boldsymbol{R}T \ln \left(\frac{\boldsymbol{h}^2}{2\pi m\boldsymbol{k}T}\right)^{3/2} \cdot \frac{f_a'\omega_m}{\boldsymbol{k}Tj_r} \cdot \frac{p^0}{\theta} \tag{5}$$

derived on the basis of the expression given by Hill[27] for the equilibrium constant. Here $\boldsymbol{h}$ and $\boldsymbol{k}$ are the Planck and Boltzmann constants, m is the mass of the adsorbate molecule, ω_m is the area it occupies in a dense monolayer, j_r is the partition function for internal degrees of freedom of the adsorbate molecule in the gas; $\theta = N_a\omega_m/s$ and $f_a' = f_a/s$ (f_a is the partition function of the adsorbate molecule over the entire surface s, and N_a is the number of adsorbed molecules).

As Hill[27] did, when calculating f_a we used the approximation[65]

$$f = f_{\text{class}}\nu^{**} \tag{6}$$

Here we have the fully classical partition function

$$f_{\text{class}} = \frac{1}{\boldsymbol{h}^n} \int \ldots \int \exp\left(-\boldsymbol{H}/\boldsymbol{k}T\right) \mathrm{d}p_1 \ldots \mathrm{d}p_n \, \mathrm{d}q_1 \ldots \mathrm{d}q_n \tag{7}$$

(n = number of degrees of freedom of the molecule, $\boldsymbol{H}$ = Hamiltonian for the adsorbate molecule, and

$$\nu^{**} = f\,(\text{harm. oscill. quant.})/f\,(\text{harm. oscill. class.}) \tag{8}$$

where f (harm. oscill. quant.) and f (harm. oscill. class.) are the partition functions of harmonic oscillators in the quantum-mechanical and classical form respectively, calculated from the shape of the potential-energy surface of the adsorbed molecule in the vicinity of the minimum).

The potential energy in the Hamiltonian was calculated for the adsorbed atom by means of equation (4) as a function of the co-ordinates x, y, and z (xy is the plane passing through the carbon atom of the graphite basal

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[64] A. V. Kiselev, and D. P. Poshkus, *Doklady Akad. Nauk S.S.S.R.*, 1960, **132**, 876.

[65] K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, 1942, **10**, 428.

face, and z is the direction normal to this plane). Substitution into equation (7) and integration with respect to the impulse components p gives:[27]

$$f_{\text{class}} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \cdot \frac{2s}{3a^2\sqrt{3}} \iiint \exp\left(\frac{-\Phi\,(x, y, z)}{kT}\right) \operatorname{erf}\left(-\frac{\Phi}{kT}\right)^{1/2} z_0\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \qquad (9)$$

where $(3a^2\sqrt{3})/2$ is the area of the hexagon formed by the carbon atoms of the basal face ($a = 1{\cdot}418$Å is the graphite lattice constant), $\operatorname{erf}\left(-\frac{\Phi}{kT}\right)^{1/2}$ is the probability integral. Integration with respect to x and y in equation (9) is carried out within the limits of a single hexagon. The value of the integral was calculated graphically. Integration was carried out for those values of z for which the potential energy of the adsorbed atom $\Phi(x, y, z) \leqslant 0$.[27] The value of $\exp\,[(-\,\Phi\,(x, y, z)/kT]$ for argon on graphite with z/z_0 deviating from unity (z_0 being the equilibrium distance depending on x, y) falls rapidly. Since, in the limits of z/z_0 within which integration was carried out, the value of the factor $\operatorname{erf}\,(-\,\Phi/kT)^{1/2}$ is substantially equal to unity, we neglected it.

For an argon atom located above a graphite surface the quantum-mechanical factor

$$\nu^{**} = \frac{h\nu_x}{kT}\left[1 - \exp\left(-\frac{h\nu_x}{kT}\right)\right]^{-1} \frac{h\nu_y}{kT}\left[1 - \exp\left(-\frac{h\nu_y}{kT}\right)\right]^{-1} \frac{h\nu_z}{kT}\left[1 - \exp\left(-\frac{h\nu_z}{kT}\right)\right]^{-1} \qquad (10)$$

where ν_x, ν_y, and ν_z are the frequencies of vibration of the adsorbed argon atom parallel to the corresponding axes near the potential minimum (above the centre of the hexagon for $z = z_0$). Calculating the frequencies of oscillation

$$\nu_x = \frac{1}{2\pi}\sqrt{\frac{K_x}{m}}\,, \quad \nu_y = \frac{1}{2\pi}\sqrt{\frac{K_y}{m}}\,, \quad \nu_z = \frac{1}{2\pi}\sqrt{\frac{K_z}{m}} \qquad (11)$$

we estimated the constants K_x, K_y, and K_z analytically according to the formulæ

$$K_x = \left(\frac{\partial^2\Phi}{\partial x^2}\right)_{\substack{x=0\\ y=0\\ z=z_0}}, \qquad K_y = \left(\frac{\partial^2\Phi}{\partial y^2}\right)_{\substack{x=0\\ y=0\\ z=z_0}}, \qquad K_z = \left(\frac{\partial^2\Phi}{\partial z^2}\right)_{\substack{x=0\\ y=0\\ z=z_0}}. \qquad (12)$$

In this case $\nu_x = 3{\cdot}35 \times 10^{11}$, $\nu_y = 5{\cdot}8 \times 10^{11}$, and $\nu_z = 1{\cdot}5 \times 10^{12}$ sec.$^{-1}$, whence $\nu^{**} = 2{\cdot}00$.

The value ω_m depends on the packing of the argon atoms over the surface. The partition functions j_r for the internal degrees of freedom of the argon atom were assumed to be the same in the adsorbed as in the gaseous phase.

Substituting the corresponding expressions and value into expression (5) we obtained the relation between $\Delta\mu$ and θ during the transition of argon from a gas at $p^0 = 760$ mm. Hg on to the surface of the graphite basal face at $T = 77{\cdot}8$°K (this relation being almost independent of ω_m):

$$\Delta\mu = -1{\cdot}25 + 0{\cdot}35 \log_{10} \theta \text{ (kcal./mole)} \qquad (13)$$

Fig. 14 compares the initial regions of the experimental and the calculated plots of $-\Delta\mu$ against θ. The experimental curve was calculated from the adsorption isotherm measured in expression (5) by the thermodynamic formula $\Delta\mu = RT \log_{10} [p(\theta)/760]$. The calculated curve lies fairly close to the experimental one.* Thus on the basis of theoretical calculations of the adsorption energy the change in chemical potential of argon on passing from the gaseous phase to the adsorbed state can be calculated at low graphite surface coverages by a statistical method.

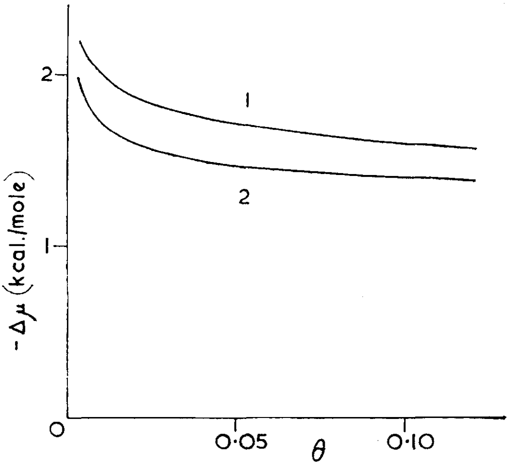

FIG. 14. *Dependence of change in chemical potential — $\Delta\mu$ of argon on coverage θ of graphite surface.* (1) *Calculated.* (2) *Experimental.*

An Attempt to Base the Model of the Adsorbate Molecule Movement on Spectral Data. A proper choice of the model for adsorption complexes is very important because the model affects the calculation of the partition

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* Analysis shows that the difference between the calculated and the experimental curve lies within the limits of error of the calculation.[66] At higher values of θ interaction between the adsorbed molecules has an effect on the experimental curve. We have not taken this into account in the calculated curve (the energy of this interaction was calculated in ref. 11).

[66] D. P. Poshkus and A. V. Kiselev, *Zhur. fiz. Khim.*, in the press.

functions and entropies of the complexes. Very important in this connection are the spectral investigations of chemical compounds and adsorption complexes formed on a surface. To solve these problems systematic and detailed investigations of infrared spectra must be available. V. I. Lygin and the present author[32] tried to estimate the entropy of water adsorbed on a hydrated silica surface with allowance for the frequencies of the valency and deformation vibrations of the hydroxyl groups of the silica and the adsorbed water molecules. The calculation was carried out for two localised models: a water molecule bonded (i) to one surface hydroxyl group by a single hydrogen bond (which allows free rotation around this bond), and (ii) to two surface hydroxyl groups by two hydrogen bonds (retarded rotation, libration). Estimates were made of the values of rotational, vibrational, and configurational entropies. Their sum amounted to about 7·5 e.u. for the first model and 4·5 e.u. for the second. The experimental result[67] indicates higher values. Possibly this is related to the necessity of taking into account the oscillations parallel to the surface, and to non-uniformity of distribution of the hydroxyl cover over the surface.

This estimate of the entropy of water-hydroxyl adsorption complexes on silica is very approximate, because so far the models have been selected on the basis of only average adsorption characteristics[45] and frequencies—on the basis of spectral data obtained only in the main region of the spectrum, where they give information chiefly on the internal vibrations of the atoms in the molecules. In the future a study must be made of the vibrational and rotational spectrum in the far infrared region for the molecule as a whole with respect to its surface. It is essential also that the frequencies of the retarded rotation should make it possible to estimate the height of the potential barriers.

Semiempirical Calculation of Adsorption Equilibrium on a Homogeneous Surface. Formulæ 1—3 show,[1–4] as was pointed out in the first section, the type of functional relation between θ and p or p/p_s, the constants K_1 and K_n in (1), (2), or K_1 and K_2 in (3) being found from the experimental isotherm. Since $\theta = \alpha/\alpha_m$, where α_m is the absolute adsorption at $\theta = 1$, to calculate θ from experimental data we must know the value of the area ω_m occupied by an adsorbate molecule in a dense monolayer ($\alpha_m = 1/\omega_m$). This value of ω_m can be found independently of adsorption from the van der Waals dimensions of the adsorbate molecule, and their probable orientation and packing.[39]

Equation (2) describes three types of isotherms.[1,2] At high K_1 and low K_n, *i.e.*, when the adsorbate–adsorbate interaction can be neglected with respect to the adsorbate–adsorbent interaction, this equation describes an isotherm with a convex* beginning and one inflexion, *i.e.*, approaches the B.E.T. isotherm. When these interactions are commensurate, equation

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* In this context, convex means dy/dx is increasing.

[67] A. G. Foster, *J.*, 1945, 360.

(2) describes an isotherm with a concave beginning and two inflexions (for example, alcohols on graphitised carbon blacks, see Fig. 6). Finally, when the adsorbate–adsorbent interaction is very weak, the isotherm is concave throughout (water on graphitised carbon[14]).

The values of the constants K_1 and K_n, though of but relative importance, are nevertheless interesting because they make it possible to compare conveniently the adsorption isotherms of various substances on the same adsorbent[68] or of the same vapour on different adsorbents.[45] Table 4 lists the rounded values of the ratios of these constants for adsorption of a number of vapours on graphitised carbon blacks at temperatures close to room temperature.

TABLE 4. *Ratio of equilibrium constants of adsorbate–adsorbent K_1 and adsorbate–adsorbate K_n interactions for adsorption of various vapours on graphitised carbon black.*

Adsorbate	K_n/K_1	*Shape of isotherm**
Benzene	0·003	Convex with one inflexion
Cyclopentane	0·12	Concave at first with two inflexions
Sulphur dioxide	7·0	Concave at first with two inflexions
Methylamine	13	Concave at first with two inflexions
Methanol	350	Concave at first with two inflexions
Water	(50,000)	Concave throughout

Of major interest are the wave-shaped isotherms of unimolecular and multimolecular adsorption of vapours. For example, for nitrogen vapour at −195° on graphitised thermal carbon black the isotherm is at first concave and then passes through several inflexion points. Each wave of this isotherm can be described[13] by an equation of the same type, namely, equation (2), with the corresponding (different for different waves) pairs of values of the constants K_1 and K_n. Fig. 15 gives the experimental points and curves calculated with the aid of three pairs of K_1 and K_n constants, found by the three successive waves in co-ordinates of equations (1) and (2).

A complete theoretical calculation of the equilibrium constants in this case requires statistical-thermodynamic treatment of multimolecular adsorption with allowance for adsorbate–adsorbate interactions. Several steps in this direction have been made by Pace.[11]

Empirical Accounting for Geometrical and Chemical Surface Heterogeneity. Discussion of these methods is not the object of this Review and therefore we shall only indicate their possibility. In studies of the dependence of experimental adsorption on the pore size and degree of

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* In this context, convex means dy/dx is increasing.

[68] A. V. Kiselev, "Adsorption, Brief Description of Exhibits on the Stand at Soviet Science, Technology, and Culture Exhibition in New York, 1959," U.S.S.R. Academy of Sciences, Moscow, 1959.

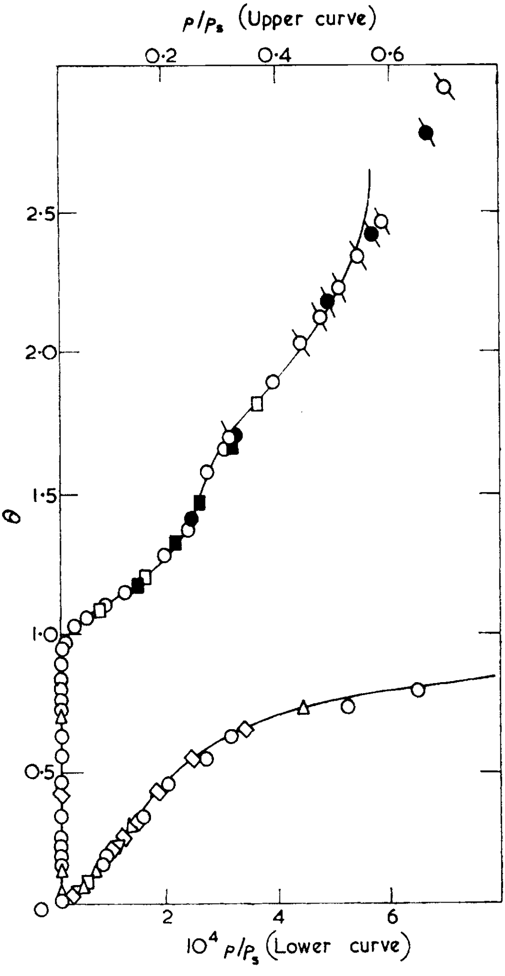

FIG. 15. *Adsorption isotherm of nitrogen vapour on thermal carbon black graphitised at 3000°. The curves are calculated by means of equations* (1) *and* (2).

chemical modification of the surface (for example, the degree of hydration of a silica gel surface) adsorption can be expressed as a function of these factors. Comparing the corresponding graphs for a given adsorbate–adsorbent system at various p/p_S, the adsorption isotherms can be found from them by knowledge of the pore size and the degree of chemical modification of the surface. Examples of the application of this method to the adsorption of benzene vapour on silica gels are given in ref. 45. This group of empirical methods of isotherm calculation includes also the

Polanyi theory as developed by M. M. Dubinin and his co-workers.[69] The equations of the adsorption isotherms are derived in these works, the type and constants being found experimentally. This method is convenient for finding the adsorption isotherms of various substances at different temperatures from a single isotherm for one substance.

Conclusion

The examples discussed above illustrate the value of different methods for describing and interpreting adsorption equilibria and heats of adsorption; these methods should be developed in parallel. However, as methods of calculating adsorption energies and partition functions improve, as the models of the movement of adsorption complexes introduced into the calculations become better founded on spectral and other physical methods, and, finally, as more accurate information on the structure of adsorbents accumulates, so the absolute calculation of heats of adsorption and adsorption equilibria purely from the structure and physical properties of the adsorbent and the adsorbate should acquire greater importance. And, though this method will long remain inferior in accuracy to direct measurement, it has already the notable advantage that it makes it possible to determine, not so much what the adsorption properties of the system in question are, as why they are what they are.

[69] M. M. Dubinin and E. D. Zaverina, *Zhur. fiz. Khim.*, 1949, **23**, 1129; K. M. Nikolayev and M. M. Dubinin, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. Khim. Nauk*, 1958, 1165; M. M. Dubinin, "Industrial Carbon & Graphite," Pergamon Press, London, 1958, p. 219.