

## THE FREE AND TOTAL ENERGIES OF INTERACTION OF COALS WITH METHYL ALCOHOL.

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*Received 18th February, 1948.*

It is possible, in principle, to calculate the heat of immersion of a solid in a liquid from adsorption data. Thus, for reversible adsorption of an insoluble vapour, the free-energy lowering  $\Delta G$  of the adsorbent is given by the integrated form of the Gibbs-Duhem equation,<sup>1</sup>

$$\Delta G = \frac{RT}{M} \int_{p_1}^{p_2} m \, d \log_e f, \quad . \quad . \quad . \quad . \quad (1)$$

where  $p_1$ ,  $p_2$  are the initial and final pressures of the vapour,  $m$  is the quantity in grams of vapour adsorbed at a pressure  $p$  (or fugacity  $f$ ), and  $M$  is the molecular weight of the adsorbate. This equation holds whatever the mechanism of interaction: e.g. whether the adsorbed phase

<sup>1</sup> Bangham, *Nature*, 1944, **154**, 837.

is mobile or static, and whether the solid is rigid or expands during the adsorption. If  $p_1$  is zero and  $p_2$  is the saturation vapour pressure  $p_0$ , it is convenient to denote the value of  $\Delta G$  by  $\Delta G_v$ . The free-energy lowering  $\Delta G_L$ , when the pure solid is wetted by liquid, is not in general identical with  $\Delta G_v$ ; if, for example, the process of immersion represents merely the wetting of an area  $\mathcal{E}$  of an adsorbed film,

$$\Delta G_L = \Delta G_v + \mathcal{E}\gamma_{LV} \cos \theta, \quad . \quad . \quad . \quad (2)$$

where  $\gamma_{LV}$  is the surface tension of the liquid when in contact with its saturated vapour and  $\theta$  the contact angle.\*<sup>2</sup> The change in total energy  $\Delta H$  associated with a free-energy lowering  $\Delta G$  is given by the Gibbs-Helmholtz equation, so that the heats of saturation and of wetting of the adsorbent are :

$$\Delta H_v = \Delta G_v - T \frac{\partial(\Delta G_v)}{\partial T}, \quad . \quad . \quad . \quad (3)$$

$$\Delta H_L = \Delta G_L - T \frac{\partial(\Delta G_L)}{\partial T}. \quad . \quad . \quad . \quad (4)$$

The heat evolved when the pure solid is exposed to saturated vapour can, therefore, be evaluated directly from a pair of adsorption isotherms at different temperatures (eqn. (1) and (3)); to calculate the heat of wetting,  $\Delta H_L$ , information must be available concerning the processes which take place when, after exposure to saturated vapour, the solid is immersed in the liquid.

The adsorption method sometimes has advantages over the direct calorimetric measurement. For example, when some of the heat is liberated slowly it may be hidden by the cooling losses of the calorimeter, and the apparent heat of wetting may be far lower than the real value. The isotherms, however, can be determined under such conditions that each point represents an equilibrium measurement; the calculated heat changes,  $\Delta H_v$ , are therefore correct. Since the difference between  $\Delta H_v$  and  $\Delta H_L$  is usually fairly small,† the method is useful when there is a suspicion of large errors in the calorimetric results.

In an earlier investigation,<sup>3</sup> it was concluded from calorimetric evidence that the greater part of the heat of wetting of coals by methyl alcohol is liberated rapidly. Subsequent measurements<sup>4</sup> of the densities of coals in a number of liquids showed that the pores in coals are not uniform in diameter along their length but contain constrictions no more than a few Ångström units in diameter. Furthermore, the apparent densities sometimes drifted slowly with time towards higher values suggesting that several hours were required to achieve complete penetration. This result reopened the question whether some part of the heat of wetting might be liberated too slowly to be detected in the calorimeters which were available, and it was decided to use the adsorption method as a check.

Certain difficulties have to be overcome. King and Wilkins<sup>5</sup> have found that the adsorption isotherms of water on coals show hysteresis, and Maggs<sup>6</sup> also found hysteresis when using methyl alcohol as adsorbate. The isotherms therefore do not satisfy the thermodynamic condition of

\* If the adsorbent saturated with vapour expands on immersion, the expression for  $\Delta G_L$  is more complicated and includes a term to represent the work of expansion. On the other hand, when there is capillary condensation  $\Delta G_v = \Delta G_L$ . For further details, see ref. <sup>13</sup>.

† For the adsorbent used here (coal), there is insufficient knowledge to enable the difference between  $\Delta H_v$  and  $\Delta H_L$  to be calculated as suggested in the preceding paragraph.

<sup>2</sup> Bangham and Razouk, *Trans. Faraday Soc.*, 1937, **33**, 1459.

<sup>3</sup> Griffith and Hirst, *Proc. Conf., Ultrafine Structure of Coals and Cokes, B.C.U.R.A.* (London, 1944), p. 80.

<sup>4</sup> Franklin, *Trans. Faraday Soc.* (in press).

<sup>5</sup> King and Wilkins, ref. 3, p. 46.

<sup>6</sup> Maggs, *ibid.*, p. 95.

reversibility assumed in eqn. (1) above, and the appropriate method of calculating the free-energy lowering has to be found. The second difficulty arises from the peculiar mechanical properties of coals. King and Wilkins,<sup>6</sup> and Dunningham<sup>7</sup> have shown that when freshly mined coal is dried and subsequently exposed to water vapour, the amount of water adsorbed is less than the original moisture content of the coal; the effect has been attributed to an irreversible shrinkage of the coal material when it is first dried. In addition, Dunningham<sup>7</sup> attributed the hysteresis in the adsorption isotherms to irreversibility of the mechanical properties, and Maggs<sup>8</sup> has shown for several coals that the stress-strain relationships are only partly reversible. Lawall and Holland<sup>9</sup> also observed hysteresis in the stress-strain curves of West Virginia coals.

The mechanical instability makes it difficult to determine the temperature dependence of the sorption isotherm in order to derive the quantity  $\frac{\partial(\Delta G_v)}{\partial T}$  (eqn. (3)). The difficulty arises in the following way. Bangham

and Maggs<sup>10</sup> have found evidence showing that the swelling of coal which accompanies adsorption is primarily due to the pressure of the adsorbed film. If the temperature is raised, the film pressure increases and the solid swells further. On lowering the temperature, the solid may not then revert to its original condition. Thus, if the vapour pressure is measured at  $T_1$ , then at a higher temperature  $T_2$ , and finally at  $T_1$  once more, the two measured pressures at  $T_1$  may be different. It is therefore necessary to ensure that the experimental observations used to calculate the temperature dependence are properly chosen.

In the presentation which follows, the results of preliminary experiments are described to illustrate the characteristic features of the sorption isotherms of methanol on coal and the phenomena associated with the measurement of the temperature dependence. These experiments are discussed in the light of existing knowledge of the structure and physical properties of coals. The method, which then emerges, for obtaining the heat changes from the sorption isotherms is used to derive the numerical values of the heats of wetting of three coals.

### Experimental.

**Apparatus.**—The volumetric method was used for determining the sorption isotherms. A diagram of the glass apparatus is shown in Fig. 1. The mercury cut-offs also served as pressure gauges which were read by a vernier cathetometer. The quantities adsorbed on the coal were calculated assuming that the vapour obeyed Boyle's law. The whole system was connected to a mercury-vapour diffusion pump backed by a rotary oil pump. Prior to adsorption measurements, coal samples were evacuated first in the cold and then, for several hours, at 110° C. to a final pressure of  $10^{-5}$  mm. Hg.

**Materials.**—**METHYL ALCOHOL.** Pure methyl alcohol, as supplied by James Burrough Ltd., was freed from dissolved gases and submitted to vacuum distillation in the adsorption line. The middle fraction was used for measurements.

**COALS.** Three bituminous coals were investigated: a Northumberland coal K, a Yorkshire coal H, and a South Wales coal F. The analyses are given in Table I. For the heat of wetting and sorption measurements the samples were ground to pass a 240 B.S. sieve.

**Description of the Sorption Isotherms.**—The main features of the methanol sorption isotherms are summarised below.

- (1) The isotherms on coals K and H are sigmoid in shape, whereas that on coal F is similar to the Langmuir isotherm showing no point of inflexion (Fig. 2).
- (2) The area of the hysteresis loop increases with the sorption capacity of the coal. Thus coal F, which at saturation adsorbs 5 % of methanol by weight,

<sup>7</sup> Dunningham, *ibid.*, p. 57.

<sup>8</sup> Maggs, *Trans. Faraday Soc.*, 1946, **42B**, 284.

<sup>9</sup> Lawall and Holland, *Eng. Exp. Station, Res. Bull. No. 17* (West Virginia University).

<sup>10</sup> Bangham and Maggs, *ref. 3*, p. 118.

shows only a small hysteresis loop confined to a limited pressure range ; whereas with coals  $\kappa$  and  $\eta$ , which adsorb 26 % and 18 % respectively, the hysteresis loops cover the whole pressure range, and the adsorption and desorption curves are further apart (Fig. 2).

(3) The desorption curves can be traced back to the origin, i.e. the adsorbed vapour can be removed completely. This is true no matter whether the coal has previously been exposed to methanol vapour or not.

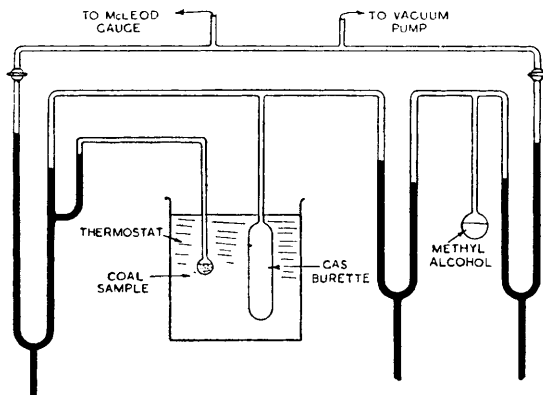


FIG. 1.

(4) If successive isotherms are determined on a fresh sample of coal, the amount adsorbed at a particular pressure on the second adsorption may exceed the corresponding quantity on the first.

(5) If the coal is flushed with methanol vapour prior to the determination of the isotherm, the *adsorption* curve may be reproduced.

(6) When there is hysteresis, the *desorption* curve has no unique position but depends on how far the adsorption has been taken (Fig. 3).

**Phenomena Associated with the Determination of the Temperature Dependence.**—The first attempts to determine the temperature dependence of the

TABLE I.

	Coal $\kappa$ .	Coal $\eta$ .	Coal $\epsilon$ .
<i>Ultimate Analysis</i>			
% D.m.f. (Parr's basis)			
Carbon . . . .	82.5	83.1	90.0
Hydrogen . . . .	5.3	5.3	5.0
Nitrogen . . . .	2.1	2.0	1.7
Oxygen . . . .	10.1	9.6	3.3
Volatile matter, d.m.f..	38.2	35.5	24.3
B.S. Swelling number .	1½	2½	9

isotherms were made on the desorption part of the cycle. When the equilibrium pressure obtained after desorbing a quantity of vapour at a temperature  $T_1$  had been determined, the temperature was raised to  $T_2$  and the new pressure was measured after allowing about 16 hr. to attain equilibrium. On returning to the original temperature the pressure was higher than before, the difference between the two pressures at  $T_1$  being about 50 % of the difference between the later pressure at  $T_1$  and the pressure at  $T_2$ .

Subsidiary experiments were carried out to investigate the effect in more detail and the following general observations were made.

(1) When the temperature dependence was observed on the *adsorption* part of the cycle, the pressure changes were reversible.

(2) After *desorption* at  $T_1$ , attaining equilibrium, and raising the temperature to  $T_2$ , the pressure drifted to higher values. The drift at  $T_2$  was observed even when the pressure at  $T_1$  had been steady for two days.

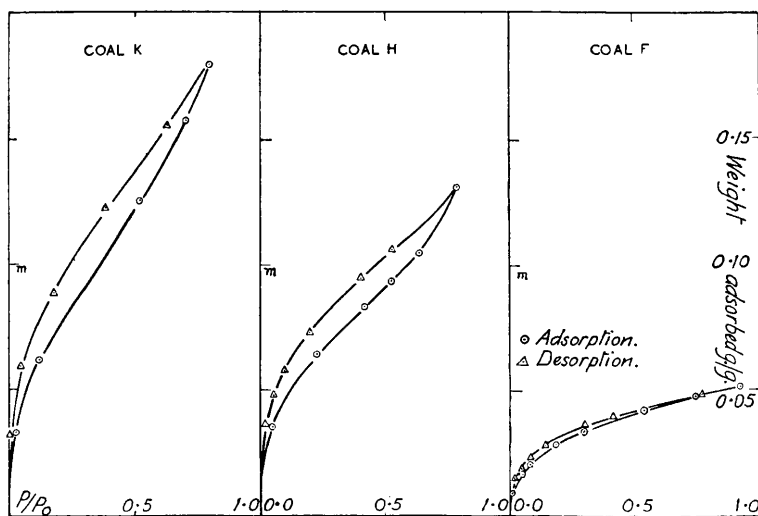


FIG. 2.—Equilibrium relative pressure.

(3) If the temperature was then lowered to the original value  $T_1$  a steady pressure was reached in about 15 min. and no change in pressure was observed during the subsequent 24 hr.

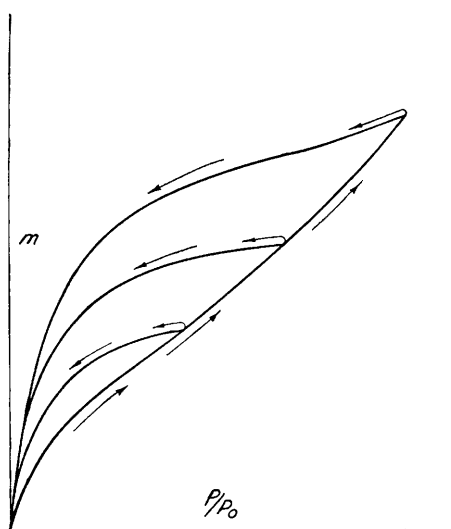


FIG. 3.

(4) If the temperature was raised temporarily above  $T_2$ , the drift at  $T_2$  was accelerated.

(5) On the logarithmic scale, the difference between the original and final pressures at the lower temperatures was equal (within experimental error) to the drift which occurred at the higher temperature.

- (6) The drifts were greatest in the region of greatest hysteresis.  
 (7) If desorption was effected at  $T_2$  (the higher temperature) instead of at  $T_1$ , the pressure change on going to  $T_1$  was reversible.

These observations strongly suggest that the peculiar behaviour of the system is due to the superposition of two effects, one which is reversible to within experimental error, the other an irreversible effect which sets in when the temperature is raised. The irreversible effect causes a gradual drift of the vapour pressure to higher values. In general, the magnitude of the reversible effect may be obtained from the pressure at the higher temperature and the value of the pressure *subsequently* observed at the lower temperature.

## Discussion.

### I. Sorption Isotherms on Coals.

The main features of the isotherms are consistent with, and lend support to, a model for the structure of lower rank coals proposed by Bangham, Franklin, Hirst and Maggs.<sup>11</sup> The model was put forward as being the simplest representation of the structure of coal in accord with the essential features of the known experimental facts. The model is, of course, idealised. It is supposed that in an early stage of coalification, micelles of preferred size are formed and that throughout the subsequent history these tend to retain their individuality. A low rank coal is likened to an assembly of close-packed spherical micelles of equal size (about 200 Å diam.). From the physical standpoint, coalification is regarded as a process whereby the contact regions of the micelles flatten so that the contact areas increase and the whole assembly consolidates. The coals used in the present investigation are three of those on which the experimental measurements leading to the model were made, and it may be stated that the Northumberland coal K would be represented as a close-packed spherical aggregate with little flattening in the contact regions, the Yorkshire coal H would have rather larger contacts and the Welsh coal F would have very large contact regions between the micelles (Fig. 4).

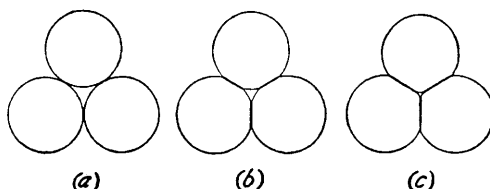


FIG. 4.

Assemblies of this kind owe their cohesion in part to the strength of the actual contacts and in part to the surface forces which act across the narrow gaps around the contacts. As the contacts increase in size one would expect the relative contribution of the surface forces to diminish. This contribution should therefore be greatest for the Northumberland coal, less for the Yorkshire coal and least for the Welsh coal.

The swelling of solids which occurs on adsorption of vapours has been discussed by Bangham,<sup>12</sup> and one of the present authors<sup>13</sup> has extended Bangham's theory to cover the case when surface forces contribute appreciably to the cohesion. In this extension of the theory, it is supposed that in the course of adsorption the constituent units of the solid tend to

<sup>11</sup> Bangham, Franklin, Hirst and Maggs (in preparation).

<sup>12</sup> Bangham, Fakhoury and Mohamed, *Proc. Roy. Soc. A*, 1934, **147**, 152.  
 Bangham, ref. 3, p. 26.

<sup>13</sup> Hirst, *Faraday Soc. Discussion*, 1948, **3**.

be forced apart \* by the spreading force of the adsorbed film. Since surface forces fall off as an inverse power of the distance over which they act, the forces tending to cause the swollen solid to revert to its original condition are weaker than those which initially opposed swelling. It follows that on lowering the vapour pressure the solid does not revert to its original condition and the isotherms exhibit hysteresis. It may be noted that the observed sizes of the hysteresis loops are in the order which this theory would predict from the coal models. It should further be noted that according to the theory the following primary meaning is attached to the hysteresis loops: the large initial resistance to swelling prevents the solid from expanding sufficiently to adsorb the quantity of vapour consistent with the minimum free energy of the adsorbent for the vapour pressure. It follows that the free-energy lowering of the adsorbent must be calculated by using eqn. (1) in conjunction with the *desorption* curve.†

The above ideas on the structure of coals and the mechanism of swelling suggest an explanation of the phenomena encountered when attempting to measure the temperature dependence of the isotherms. The pore system in an assembly of spheres contains constrictions whenever neighbouring spheres are in contact, and during swelling and shrinking these small holes will expand and contract. During desorption, the narrowing constrictions may trap some of the adsorbate. Helped by the increase in film pressure when the temperature is raised, the trapped adsorbate might force its way out, thus increasing the vapour pressure. This would explain very simply why the pressure changes should be reversible when desorption is carried out at the higher temperature. It is perhaps significant that, when the sorption isotherms were retraced to the origin, the adsorbate could not be removed by pumping only. It was always necessary to raise the temperature to remove the last traces.

To sum up, it appears from the preliminary experiments that the heat of saturation of coal by methyl alcohol may be calculated from the isotherms as follows:

- (1) by using the *desorption* isotherm to derive the free-energy lowering;
- (2) by assessing the temperature dependence from the vapour pressures at two temperatures, when the temperature is changed from a higher to a lower value.

## II. Numerical Results.

**The Heat of Saturation and the Heat of Wetting.**—The sorption isotherms were extrapolated to saturation pressure  $p_0$ , and the numerical values for the free-energy lowerings per gram of solid when exposed to saturated vapour, were derived by applying eqn. (1) to (a) the desorption curve and (b) the adsorption curve. From the reversible temperature dependence of the isotherms determined on desorption, the temperature derivatives of the free-energy lowerings were evaluated and hence the heats of saturation,  $\Delta H_v$ , by applying eqn. (3). The results obtained for the three coals investigated are shown in Table II. Table II also

\* There is experimental evidence that on adsorption of vapours the constituent units of coal do, in fact, tend to separate. First, the volume of methyl alcohol adsorbed at saturation pressure exceeds the original pore volume by the order of 100 %, even when allowance is made for the compression of the liquid in the adsorbed phase. (It is assumed throughout that methyl alcohol is adsorbed on coal as an insoluble surface film.) Second, Maggs<sup>14</sup> has demonstrated for one coal that the material is more deformable in the swollen condition.

† It is shown elsewhere<sup>13</sup> that if the work of expansion is appreciable the free-energy lowerings calculated from the desorption isotherms may be too great. No reliable measurements of the work of expansion are yet available, but it is believed that the corrections would not be large.

<sup>14</sup> Maggs (unpublished).



gives the heats of wetting measured directly, on identical samples, in a calorimeter (the "routine" calorimeter described in an earlier paper<sup>3</sup>).

**Discussion.**—From Table II it appears that the heats of wetting determined experimentally are *higher* than the values calculated from the isotherms.\* The measured calorimetric values could exceed the heat of wetting if the physical process were accompanied by a chemical reaction. It is, however, found experimentally that the calorimetric heat liberations are not lowered by repeated measurements on the same sample, so that the possibility of irreversible chemisorption may be ruled out. It is therefore concluded that the experimental values are not greater than the real heats of wetting, and hence that the calculated heats of saturation,  $\Delta H_v$ , are less than the heats of wetting.

TABLE II.

Coal.	$-\frac{\partial(\Delta G_v)}{\partial T}$ (cal./degree)	Desorption.		Adsorption.		Calorimetric. $\Delta H_L$ (cal./g.).
		$\Delta G_v$	$\Delta H_v$	$\Delta G_v$	$\Delta H_v$	
		(cal./g.).		(cal./g.).		
K . . .	0.19	8.4	13.2	7.1	11.1	17.6
H . . .	0.17	6.3	9.5	5.4	8.1	12.2
F . . .	0.24	2.5	4.2	2.1	3.8	4.7

Two possible explanations of this result suggest themselves.

1. As mentioned above,  $\Delta H_v$  and  $\Delta H_L$  are not necessarily identical. For example, Bangham and Razouk<sup>15</sup> have shown experimentally that there is a real difference between the free-energy lowerings accompanying the saturation and wetting of charcoal by methanol. If the assumption is made that the ratio  $\Delta H_L/\Delta H_v$  ( $= 1.25$ ) calculated from their data<sup>15</sup> for the charcoal-methanol systems holds also for the coal-methanol system, one obtains the values for  $\Delta H_L$  shown in columns (4) and (5) of Table III. It will be seen that for coals K and H there still remains an

TABLE III.

Coal.	$\Delta H_v$ (cal./g.).			$\Delta H_L$ (cal./g.).		
	Calculated from Isotherms—			Calculated from Isotherms using $\Delta H_L/\Delta H_v$ for Charcoal.		Experimental (calorimetric).
	as Observed.		Corrected.			
	Adsorption (1).	Desorption (2).	Desorption (3).	Adsorption (4).	Desorption (5).	(6).
K . . .	11.1	13.2	15.8	13.9	16.5	17.6
H . . .	8.1	9.5	11.5	10.1	11.9	12.2
F . . .	3.8	4.2	4.7	4.7	5.3	4.7

appreciable difference between  $\Delta H_L$  calculated from the *adsorption* data (4) and the experimental values (6). The observation supports the hypothesis that the free-energy change should be calculated from the *desorption*

\* The reverse might have been expected, had the calorimetric results been subject to errors due to slow heat evolution (cp. p. 2).

<sup>15</sup> Bangham and Razouk, *Proc. Roy. Soc. A*, 1938, **166**, 572.



isotherm and the good agreement between columns (5) and (6) will be noted.

2. The free-energy lowerings,  $\Delta G_v$ , calculated from the desorption isotherms of coals K and H (which show marked hysteresis) may be too low. This is because the position of the desorption curve depends on how far the adsorption is taken (Fig. 3) and the true curve can only be obtained after allowing the solid to reach adsorption equilibrium at saturation vapour pressure. Unfortunately,\* with the apparatus used, it was difficult, without loss of experimental accuracy, to take the isotherm further than 0.85 saturation pressure. The observed desorption curves may therefore lie below the true curves. An attempt has been made to set a limit to the resulting error † in the calculated values  $\Delta H_v$  column (2), and the corrected values so obtained are shown in column (3) of Table III. These are in much closer agreement with the experimental heats of wetting. It should be noted that there is no corresponding correction which would raise the experimental *adsorption* curve so that the discrepancy between the values in columns (1) and (6) still remains.

When the desorption isotherms are used as the basis for calculation, the two suggested methods of correction (perhaps taken together) are adequate to account for the discrepancy between the calculated and experimental heats: i.e. there is no evidence to show that a significant difference exists between these values. It is concluded, therefore, that the experimental heats of wetting are approximately correct, and that no large part of the heat is liberated too slowly to be detected by the calorimeter. It should be emphasised, however, that this result was obtained using samples of coal of a particular size grading (–240 B.S.S.). The effect of particle size on the apparent heat of wetting and the structural changes which occur when coals are ground, form the subject-matter of a later paper.

**Note on the Differential Heats of Adsorption.**—From the measured temperature dependence of the equilibrium vapour pressure,† the differential heats of adsorption of methyl alcohol on the three coals have been calculated using the Clapeyron-Clausius equation. The net heats (i.e. the difference between the total energy of adsorption and the latent heat of condensation—9,200 cal./mole—of methanol) derived at various points on the isotherms are shown in Table IV. (The estimated accuracy is  $\pm 200$  cal./mole.) The results may be summarised as follows.

- (1) All the net heat values exceed zero by an appreciable amount.
- (2) Over the course of the isotherm the net heat of adsorption drops from 3,500–4,000 cal./mole to about 1,000 cal./mole for coals K and H, and from 3,000 cal./mole to about 1,500 cal./mole for coal F. The larger drop suggests that in the case of the first two coals the adsorbed films are thicker. This is also suggested by the difference in the shape of the isotherms and would be in accord with the predictions of the theory underlying the model concerning the relative pore sizes of the coals.

\* The theoretical argument (see p. 997 and ref. <sup>13</sup>), that the desorption isotherm should be used for calculating the free-energy lowering, developed from consideration of the experimental results given in the present paper. These were sufficient to show that there was no *large* error in the calorimetric heats of wetting and the primary object of the investigation had thus been achieved. To determine the exact position of the desorption isotherm further experimental work, using more suitably designed apparatus, will clearly be necessary. For the present purpose the magnitude of the correction was estimated roughly as follows. The extrapolation of the desorption isotherm to saturation pressure gives a smaller saturation capacity than is obtained by extrapolating the adsorption curve. If we assume that, at any pressure, the ratio of sorption capacities corresponding to the true and observed desorption curves, respectively, is equal to the ratio of the saturation capacities obtained by the two methods of extrapolation, then the true and apparent free-energy lowerings would show the same relative difference. For coals K and H this difference is of the order of 20 %.

† The reversible temperature dependence determined as suggested on p. 997.

(3) The low-pressure values for the net heats are about 4,000 cal./mole. for coals K and H, and 3,000 cal./mole for coal F. A small increase in the methanol heat of adsorption with the oxygen content of the coal is therefore indicated.

TABLE IV.—DIFFERENTIAL HEATS OF ADSORPTION.

	Coal K				
$p/p_0$ . . . . .	0.02	0.15	0.41	0.52	0.69
$m \times 10^2$ (g./g.) . . . .	4.1	7.6	11.5	12.5	14.9
Net diff. heat (cal./mole) .	3,600	2,500	1,600	1,200	900
	Coal H				
$p/p_0$ . . . . .	0.02	0.10	0.20	0.51	0.79
$m \times 10^2$ (g./g.) . . . .	3.6	5.8	7.2	10.3	12.9
Net diff. heat (cal./mole) .	4,300	3,000	2,300	1,500	900
	Coal F				
$p/p_0$ . . . . .	0.02	0.14	0.42	0.70	0.87
$m \times 10^2$ (g./g.) . . . .	1.2	2.6	3.9	4.7	5.0
Net diff. heat (cal./mole) .	3,100	2,500	2,000	1,700	1,500

(4) The low-pressure value for the methanol heat of adsorption on coal F is in good agreement with the value obtained by Razouk<sup>18</sup> for methanol on charcoal (3,200 cal./mole). The latter figure was found to remain constant up to saturation pressure.

The authors wish to record their gratitude to Dr. D. H. Bangham, Director of B.C.U.R.A. Research Laboratories, for his interest and advice in connection with this work.

Summary.

Pairs of sorption isotherms at different temperatures enable the free and total energies at saturation to be calculated by the method of integration. Sorption hysteresis, where present, introduces an element of uncertainty into the calculation, but an attempt is made to overcome this difficulty and to explain the cause of the hysteresis effects encountered. The calculated values of the heats of saturation are compared with the heats of immersionsal wetting in the liquid as determined calorimetrically.

Values for the differential heats of adsorption are deduced at several points of the isotherm.

B.C.U.R.A.,  
13 Grosvenor Gardens, S.W.1.

<sup>18</sup> Razouk, *J. Physic. Chem.*, 1941, **45**, 190.