

the reversed air/ethylene flame are available. These establish the presence of carbonyl and associated hydroxyl groups. There is also strong absorption in the regions 700–900 cm^{-1} and 2,800–3,100 cm^{-1} . Similar absorption is also exhibited by the soluble material from the various flames burning at reduced pressure. The ultra-violet absorption spectra from the deposits collected from normal flames of methane, ethylene and propane burning under reduced pressure all show very similar characteristics. Decreasing absorption between 2200 Å. and 4000 Å. was exhibited with small, variably spaced maxima, some of which occurred at 2875, 3000, 3350 and 3750 Å.

A more detailed account of these investigations is to be published elsewhere.

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¹ Parker, W. G., and Wolfhard, H. G., *J. Chem. Soc.*, 2038 (1950).

² Arthur, J. R., *Nature*, 165, 567 (1950).

³ As measured by the Kurlbaum method, see Lewis, B., and Von Elbe, G., "Combustion Flame and Explosion of Gases", Chapter 19 (Cambridge, 1938).

Calculation of Surface Areas from Room-Temperature Adsorption Isotherms

ADSORPTION studies currently in progress in these laboratories are providing evidence that the application of the Brunauer–Emmett–Teller method to room-temperature isotherms is in certain instances liable to lead to substantial errors. The adsorption of methanol on lignites at 25° C. presents a case in point.

The isotherms are here generally of the type recently described by Jura and Powell¹, that is, the rate of adsorption falls rapidly to a negligible value as monolayer capacity is approached, and subsequent adsorption (probably largely governed by swelling of the adsorbent) proceeds at a relatively fast and constant rate. Monolayer capacities can therefore be calculated directly either from the point of intersection of the two (slightly extrapolated) isotherm branches², or alternatively, as Jura and Powell have done, from the point at which the initial rate of adsorption has fallen to zero. The two methods are formally identical. In either case, however, it turns out that whereas the value of s_0 thus obtained is in very good agreement with that derived from, for example, Gregg's $FA-F\Sigma$ plot³, it is up to 50 per cent higher than the figure computed from the Brunauer–Emmett–Teller graph. The results set out in the accompanying table, in which Σ_1 refers to the Brunauer–Emmett–Teller values and Σ_2 to surface areas calculated from the point of intersection of the isotherm branches, illustrate this; in all cases, the cross-sectional area per methanol admolecule has been taken as 12 Å.².

The fact that Σ_2 agrees well with values obtained by Gregg's method whereas $\Sigma_1 < \Sigma_2$ affords, in

SURFACE AREA OF DRY, ASH-FREE COAL ($\text{m}^2/\text{gm}.$)

Adsorbent	Σ_1	Σ_2	Σ_3	Σ_4
Bacchus Marsh lignite, Victoria	269	357	385	270
Yallourn lignite, Victoria	250	348	388	235
Koeflach lignite, Austria	273	332	334	270
Salt Range lignite, Pakistan	146	197	198	130

itself, a tacit indication of a deficiency in the Brunauer–Emmett–Teller treatment. The point can, however, be checked by resorting to measurements of the heats of wetting of the lignites in methanol and converting heat releases to surface areas by means of Maggs's equivalent⁴, $1 \text{ m}^2 \equiv 0.1 \text{ calorie}$. The resultant values, reproduced in the table as Σ_3 , are in excellent agreement with those of Σ_2 .

At the present stage of the investigations, one cannot be certain about the nature of the deficiency in the Brunauer–Emmett–Teller method; it may arise from the fact that the method was originally worked out in a narrow (and very low) temperature region. In any event, this view is supported by the observation that the tangent to the point of intersection of the two isotherm branches leads to a value of Σ that is virtually identical with the Brunauer–Emmett–Teller estimate (cf. Σ_4 in the table). In other words, the intercept of the tangent on the s -co-ordinate (equivalent to the intercept on this co-ordinate of the projected linear portion of a normal sigmoid isotherm) appears to provide the numerical solution to the Brunauer–Emmett–Teller monolayer equation. It follows, therefore, that in those instances in which the slope of the linear portion of a sigmoid isotherm increases with temperature, the Brunauer–Emmett–Teller method will only yield reliable results at very low temperatures (where the tangent to the point of intersection of the isotherm branches or the linear portion of a sigmoid isotherm would both run approximately parallel to the pressure axis).

It is hoped to present a fuller discussion of these considerations, and a more rigid analysis of the problem, elsewhere in due course.

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¹ Jura, G., and Powell, R. E., *J. Chem. Phys.*, 19, 251 (1951).

² Berkowitz, N., and Schein, H. G., *Fuel* [31, 19 (1952)].

³ Gregg, S. J., BCURA Conf. Ultrafine Struct. Coals and Cokes, 110 (London, 1944).

⁴ Maggs, F. A. P., BCURA Conf. Ultrafine Struct. Coals and Cokes, 95 (London, 1944).

Rearrangement of Hexamethyl Acetone

DURING the course of recent studies concerned with the alkylation of isoparaffins, in which hexamethyl acetone was used as one of the reagents, an interesting rearrangement of this ketone was observed. Hexamethyl acetone, benzene, and sulphuric acid (s.g. 1.84) were stirred together at room temperature for 24 hr.; the resulting material was purified by distillation and recrystallization. The product of the reaction was shown to be a mixture of the original ketone and 3:3:4:4-pentan-2-one.

The following mechanism is suggested: