THERMAL EXPANSION OF COALS AND CARBONISED COALS.

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The coefficient of thermal expansion of a solid, being determined by the vibrational amplitudes of an orchestra of atomic—and larger—oscillators, should depend on its molecular constitution rather than upon the physical structure on a colloidal scale of magnitude. With the important reservation discussed in the next section, it can be regarded as an intra-micellar property rather than one concerned with micellar surfaces and inter-micellar contacts. Its variation as between different specimens of coal was expected to throw light on a number of obscure questions, as, for example :

1. whether or not the anisotropy of coal—the mechanical properties of which vary markedly with orientation with respect to the " bedding " plane—extends to the atomic (or molecular) dispositions within the micelles;
2. whether or not there is any marked trend in the size or nature of the dynamic unit of structure with increasing " maturity " of the coals;
3. whether the important changes in the technical qualities of coal engendered by preheating below 300° c. (such as the suppression of " caking properties ") are associated with intramicellar chemical change, or confined to the micellar surfaces and contacts. Aside from the other forms of chemical change, any variation in the size or number of the dynamic units—whether brought about by condensation, polymerisation or cross-linking—would be likely to reveal itself in a dependence of the expansion coefficient upon temperature of pre-treatment.

Thermal Coefficient of Adsorption Swelling.—The presence of films at the micellar surfaces introduces a complication which is liable to obscure the issues. Confirming an earlier observation, Bangham, Fakhoury and Mohamed [1] found that for a given quantity (s) of a lower alcohol adsorbed on charcoal, the percentage linear expansion (x_s) was directly proportional to the absolute temperature T. The effect upon the thermal expansion coefficient (α) of the charcoal is considerable.

Degassed charcoal . . . . . . $\alpha = 4 \cdot 5 \times 10^{-6}/° c.$
Charcoal with nearly saturated film of lower alcohol
(constant adsorption) . . . . . $\alpha = 33 \times 10^{-6}/° c.$

The relationship $x_s \propto T$—interesting theoretically since it emphasises the essentially dynamic nature of adsorption swelling—is to be expected only when the equation

$$x = \lambda F$$

(where F is the surface energy lowering) is obeyed and the constant λ is independent of temperature in the range considered. Direct proportionality of x to T is to be expected, also, only when the differential heat of sorption $(\partial H/\partial s)_T$ is independent of the surface concentration (as for methanol adsorbed on charcoal).

[1] *Proc. Roy. Soc. A.*, 1934, **147**, 160.

The relations

$$T(\partial F/\partial T)_s = F \text{ where } (\partial H/\partial s)_T \text{ is constant,}$$
$$T(\partial F/\partial T)_s > F \text{ where } (\partial H/\partial s)_T \text{ increases with } s,$$
$$T(\partial F/\partial T)_s < F \text{ where } (\partial H/\partial s)_T \text{ decreases with } s,$$

are readily derived thermodynamically.[2]

Unlike $(\partial F/\partial T)_s$ and $(\partial x/\partial T)_s$, to which the above generalisations apply, the coefficients $(\partial F/\partial T)_p$ and $(\partial x/\partial T)_p$ (where p is the pressure of vapour in equilibrium with the adsorbed film) are *negative*, on account of the vaporisation of the films.

In practice the conditions for measuring $(\partial x/\partial T)_s$ are difficult of achievement. The dimensional changes undergone by a rod of charcoal (or coal) containing moisture, when heated at a steady rate, are determined by the relative rates of inward heat transfer and of outward mass transfer of moisture. What usually happens is that the thermal expansion is at first markedly greater than for the dried material ; thereafter it falls off and there is shrinkage over a relatively small temperature range followed by renewed expansion when the films have evaporated. On cooling again in a dry atmosphere contraction is continuous.

Method of Experiment.—To avoid the obscuring effects arising from the adsorption expansion the following method of experiment was adopted. The specimen was heated in dry nitrogen and maintained at (say) 100° C. until the shrinkage rate became insignificant. The temperature was then lowered by stages with readings every few degrees and again raised slowly to 100° C. with further readings. It was then raised rapidly to. (say) 150° C., and the whole procedure repeated. The maximum preheat temperature was thus raised by *ca.* 50° C. in successive experiments.

MATERIALS.—Three " bright " coals of different carbon content were used, these being in the form of rod-shaped monoliths or cold-pressed artefacts (without binder) as-ease of preparation dictated. For making the artefacts the coal, ground to pass a 72-mesh B.S. sieve, was pressed at 12,000 lb./in.[2] for 1 minute.

The coals were :

Coal K, a " bituminous " coal of high oxygen content, from which both monolith and artefact rods could be produced.

Coal F, a " bituminous " coal of high carbon content used technically for coke manufacture ; this coal being very friable, only artefacts could be used.

Anthracite C, from which could be obtained monoliths (both parallel and normal to the " bedding plane ") but not artefacts without binder.

The analyses of these coals are set out in Table I.

TABLE I.

	Ash °/$_o$.	Per cent. (Parr's basis).				Heat of wettin in MeOH (cal./g).
		Carbon.	Hydrogen.	Nitrogen.	Oxygen + errors.	
K	1·0	82·4	5·1	1·9	10·6	16·6
F	4·1	89·7	5·0	1·8	3·5	2·0
C	2·1	94·2	2·9	1·2	1·7	7·6

Apparatus.—The samples, 64 mm. in length, were mounted between the jaws AA' of a silica optical-lever extensometer illustrated in Fig. 1. The silica plates DD', lightly ground and accurately parallel, are at such distance apart that when the brass roller R (5 mm. diameter) is placed between them the springs CCC' are slightly strained. The surface of R is lightly ground and at one end there is a mirror the reflecting surface of which is coplanar with the axis of R. The extenso-meter is supported in a Pyrex jacket, one end of which is closed by a sealed-in optically plane window and protrudes from the furnace. Light from a lamp is projected on to the mirror and focussed on a scale at 125 cm. distance. The scale could be read to 0·1 mm., and the overall magnification obtained was × 500.

[2] *Trans. Faraday Soc.*, 1937, **33**, 805.

Inside the furnace, and insulated from the nichrome windings, was a heavy brass block bored to fit closely the jacket of the extensometer. This gave within the jacket a zone 13 cm. long within which the temperature did not differ by more than 0·5° c. from that of the block.

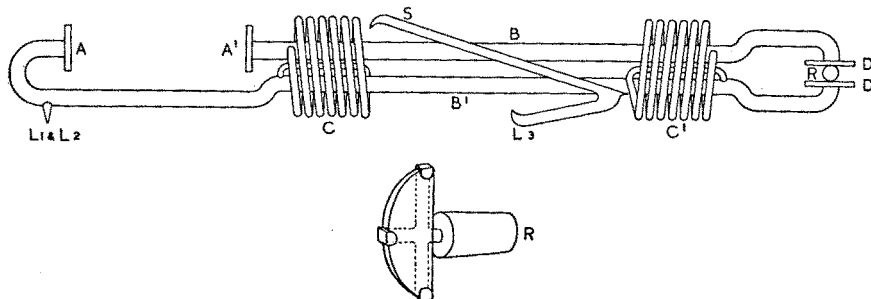Temperature measurements were made with Pt/Pt-Rh thermocouples, one

FIG. 1.

located in a hole in the furnace block and another at the centre of the specimen. Thermocouples were incorporated in the artefacts at the time of pressing.

Throughout each experiment a steady stream of dry oxygen-free nitrogen was passed through the jacket at 18 litres/hr.

Results and Discussion.

Abnormal Expansions Associated with First Heating.—During the initial relatively rapid heating of Coal K to each new maximum temperature the value of α exceeded that observed during the subsequent cooling and reheating over the same temperature range. The data in Table II illustrate this point; the abnormal coefficients are shown in brackets. There can be little doubt that these abnormalities arose from the presence of adsorbed films and are the counterpart of the effects noted with charcoal. As the temperature of the specimen is raised steadily, the period of abnormal expansion is followed rather sharply by one of *shrinkage*. In the lowest temperature range the film which volatilises is readily identifiable as moisture, but this does not necessarily apply to the higher temperatures.

TABLE II.—COAL K.

Range (°c.).	$\alpha \times 10^6/°$ c.
20- 55	= 32(41)
55-100	= 39(45)
100-150	= 43(49)
150-200	= 48(53)

The low thermal conductivity of coal precluded rapid uniform heating and further examination of this phenomenon was not attempted. The abnormal thermal expansion was less conspicuous in the case of Coals F and C which have much smaller adsorbing surfaces than K.
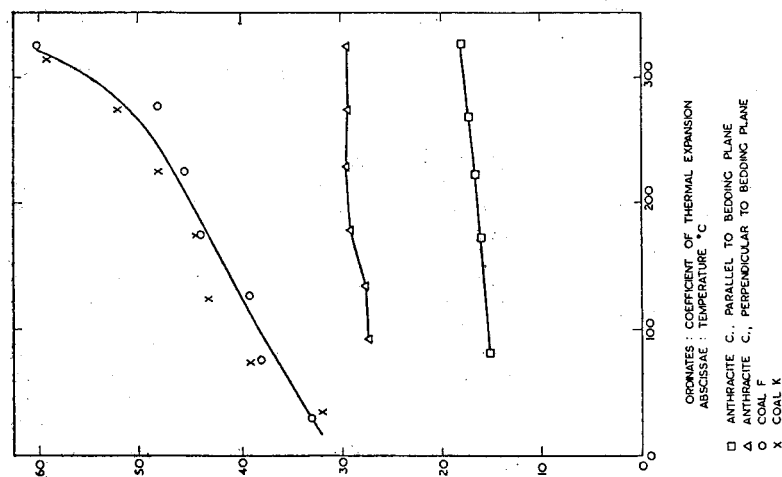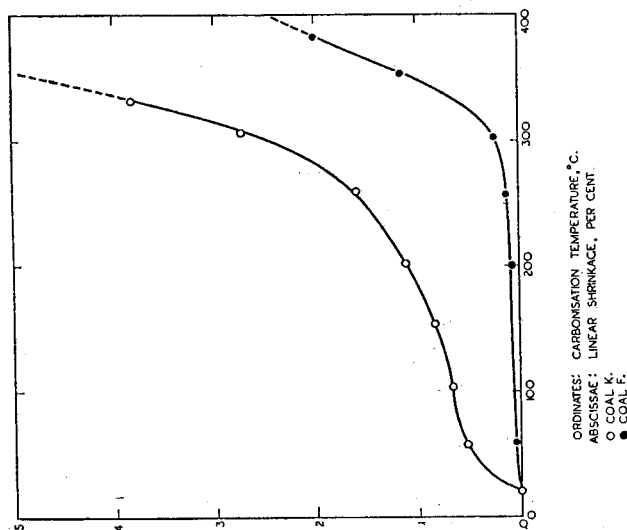
Irreversible Shrinkage.—The isothermal shrinkage of Coals F and K in the range below 400° c. is plotted as a function of temperature in Fig. 2. The results have no absolute significance but depend on the procedure outlined. In the range below 100° c. the shrinkage of the Coal K is much more marked than with the much less hygroscopic Coal F.

We are indebted to J. Sandor for an observation which confirms that the shrinkage of coal K below *ca.* 100° is readily reversed by allowing the sample to take up moisture. This is no longer true of the shrinkage at higher temperatures.

Reproducible Thermal Expansion.—The following generalisations summarise the results obtained with specimens after the effects of abnormal expansion and shrinkage had been eliminated by preheating.

1. The expansion coefficient for each temperature range was practically independent of the preheat temperature below 300° c.

2. Within each temperature range, α for the two bituminous coals was independent of : (a) " rank " ; (b) whether artefact or monolith ; (c) pressure applied during fabrication (of artefacts) ; (d) orientation with respect to the bedding plane (of monoliths).

3. For the bituminous coals F and K, α increases steadily and markedly with temperature (Fig. 3) : $\alpha_{30}{}^\circ = 33 \times 10^{-6}/^\circ$ c. ; $\alpha_{330}{}^\circ = 60 \times 10^{-6}/^\circ$c.

FIG. 2.

ORDINATES: CARBONISATION TEMPERATURE,°C.
ABSCISSAE: LINEAR SHRINKAGE, PER CENT
○ COAL K.
● COAL F.

FIG. 3.

ORDINATES : COEFFICIENT OF THERMAL EXPANSION
ABSCISSAE : TEMPERATURE °C

□ ANTHRACITE C., PARALLEL TO BEDDING PLANE
△ ANTHRACITE C., PERPENDICULAR TO BEDDING PLANE
○ COAL F
× COAL K

4. When the two bituminous coals were preheated above 350° c. (for F) and 325° c. (for K), α at all lower temperatures was greatly diminished by this treatment (Fig. 4 and 5), though it remained temperature-dependent.

5. For carbonisation temperatures above 600° c. for coal F and 550° c. for coal K the volume expansion coefficient 3α falls well below the value recorded by Riley and Nelson [3] for macrocrystalline graphite.

[3] *Proc. Physic Soc.*, 1945, **57**, 477.

(In Fig. 4 and 5 the broken line represents one-third the volume
coefficient calculated from Riley and Nelson's data.)

ORDINATES: COEFFICIENT OF THERMAL EXPANSION, X 10⁴
ABSCISSAE: CARBONISATION TEMPERATURE, °C

X = THERMAL EXPANSION AT 100° C.
⊙ = " " " 200° C.
⊡ = " " " 300° C.
◁ = " " " 400° C.

FIG. 4.

ORDINATES: COEFFICIENT OF THERMAL EXPANSION, X 10⁴
ABSCISSAE: CARBONISATION TEMPERATURE, °C

THERMAL EXPANSION AT 100° C.
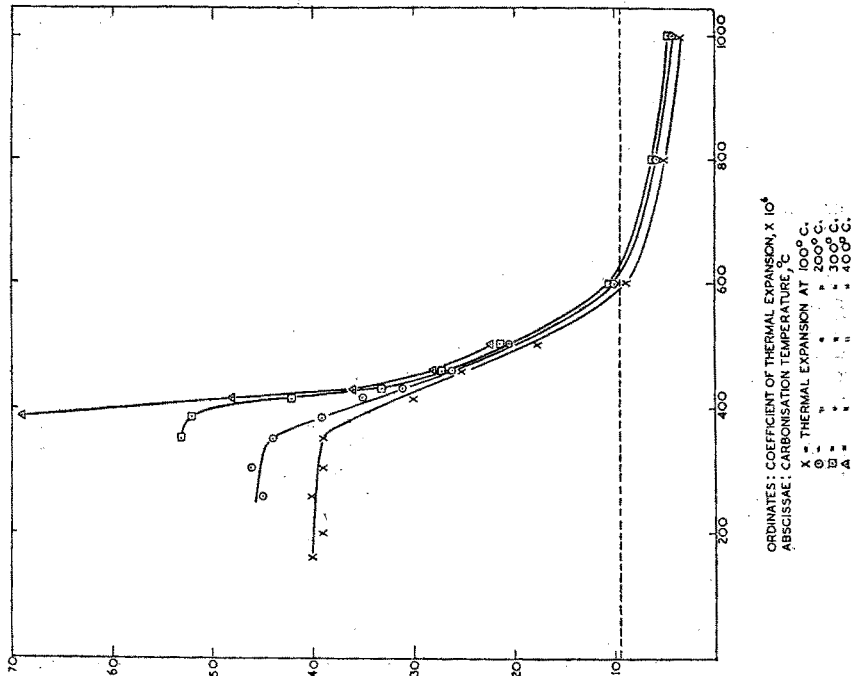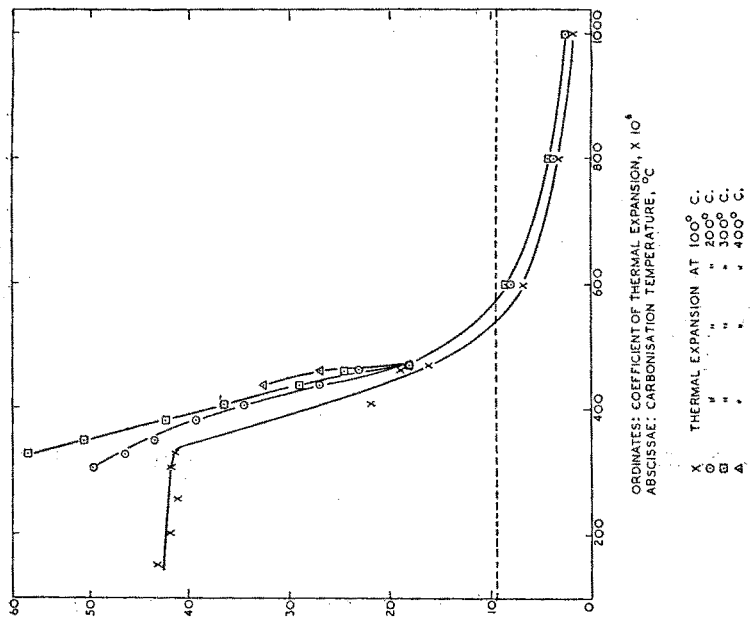" " " 200° C.
" " " 300° C.
" " " 400° C.

X
⊙
⊡
◁

FIG. 5.

6. The high carbon bituminous coal F yields a coke for which α is
significantly greater than that from the high oxygen coal K.

7. For the *anthracite* C, α varies much less with temperature but is markedly dependent on orientation (Fig. 3). Perpendicular to the bedding plane its value is remarkably close to that reported by Riley and Nelson for graphite normal to the layer planes; but whereas graphite between 0° and 400° contracts in directions parallel to layer planes, α for anthracite parallel to the bedding plane is positive and increases with temperature.

Discussion.

The values of α for the coals F and K far exceed those characteristic of materials having a continuous covalent network structure, and this suggests that forces of the van der Waals type play an important part in determining their state of aggregation. These relatively high values are retained when the coals are heated to 385° c. (F) and 350° c. (K) ; below these temperatures there is no evidence of polymerisation, cross-linking, or deep-seated chemical change such as may account for the diminution which sets in sharply at higher preheat temperatures. The two coals behave remarkably alike but this does not apply to their carbonised residues.

At room temperature α for coals F and K has a value $33 \times 10^{-6}/°c$. which is low in comparison with most organic high polymers, but comparable with that for some vulcanised rubbers. Whereas many organic polymers (and some glasses) show evidence of a second-order transition, characterised by a sharp increase in the coefficient from one nearly constant value to another, the coals show a *gradual* increase in α (indicative of an increase of internal mobility) over a wide temperature range.

It is indeed remarkable that the values of α and of $d\alpha/dT$ are so little affected by heating to temperatures such that a substantial fraction of the material is volatilised and the linear shrinkage may range as high as 5 % (coal K). The most probable explanation would appear to be that the source of the material volatilised is the surface layers of the micelles, which then shrink in together under the mutual action of their surface forces. The abnormally large expansion coefficients recorded on heating (rapidly) to each new temperature level seem to indicate that, prior to evaporation, this material probably forms a mobile adsorbed layer which may also be the seat of chemical changes leading to the formation of distillation products not present in the original material.

Unlike the bituminous coals F and K, the anthracite C was markedly anisotropic. Too much weight should not be attached to the perhaps fortuitous agreement between one of the coefficients and that of graphite normal to the layer planes. It is clear that the regions of continuous covalent network are considerably more extensive in anthracite than in bituminous coal, especially in the direction parallel to the bedding plane.

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GENERAL DISCUSSION*

Dr. W. W. Barkas (*Princes Risborough*) said : The modulus E_A is given by

$$E_A = 100\, F\Sigma/x$$

but by Magg's equation (1) this is identical with

$$E_A = -\, 100\Delta G/x$$

so that this modulus can be derived directly from the free energy decrement and the linear extension, independently of the theory of *surface* free energy

* On two preceding papers.

changes. In this form attention is drawn to the fact that E_A is actually the ratio of a hydrostatic stress to a directional strain, and it is for this reason that it cannot be identified with Young's modulus where the stress and strain are both directional. The connection between E_A and E_M is through the Poisson's ratios which would require independent measurement.

These observations are not intended to diminish the importance attached to the modulus E_A. The elastic moduli commonly accepted are purely arbitrary choices based on convenience, and any other form of modulus has a right to recognition if its usefulness can be established, but it is an advantage to have the connection between the usual and special moduli clearly set up.

Prof. G.-M. Schwab (*Athens*) (*communicated*) : I want to direct attention to an interesting consequence of the adsorption swelling of charcoal, discovered in 1941 in our laboratory, and, because of war conditions only published in a German periodical.[1] A sample of charcoal grains, enclosed in a constant volume, or put under a constant mechanical pressure, on adsorption of vapours shows an enormous increase of electrical conductivity, increasing with mechanical pressure and proportional to the adsorbed amount. The reason obviously is an increase of contact areas between the swelling grains (microphone effect), and thus swelling is most sensitively indicated by the conductivity. The phenomenon may be of practical use for automatic vapour detection devices.

Mr. F. A. P. Maggs (*London*) (*communicated*) : The derivation of E_A for the simple cases of thin cylinders or laminæ does not involve quite such an arbitrary definition of the modulus as Dr. Barkas suggests. For such models the surface pressure acts in the direction of the resulting extension, and E_A is the quotient of the directed stress divided by the corresponding strain. The non-identity with Young's modulus arises from the fact that whereas the cross-section of a thin cylinder strained in mechanically applied tension will decrease to an extent depending upon Poisson's ratio, there would be a superimposed radial expansion in the case where the increase in length is due to film formation. (In this connection I am asked by Dr. Bangham to correct a mis-statement appearing in a footnote on p. 29 of the Proc. of the B.C.U.R.A. Conference on the Ultra-fine Structure of Coals and Cokes (1943), with which Dr. Barkas's name is incorrectly associated.)

With such a material as charcoal, the measurement even of Young's modulus is not without its difficulties, and that of Poisson's ratio was for this reason not attempted. Had the underlying theory been incorrect there is no reason why E_A and E_M should agree even to an order of magnitude, but with charcoal the agreement is very much better than this.

[1] Schwab and Karkalos, *Z. Elektrochem.*, 1941, **47**₁ 345.