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FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

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TECHNICAL MEMORANDUM NO. 51 OF 1965



ADSORPTION SWELLING.

A SURVEY OF THE LITERATURE.

by:

A.A. MEINTJES.

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INTRODUCTION:

The purpose of this study is to gain an insight into one possible aspect of the problem of scaling of coal, that is the part which is played by the swelling and shrinkage of coal and coal minerals which accompany the adsorption and desorption of moisture and various atmospheric gases. The degradation (or "weathering" as it is generally termed) of coal pillars or of coal or rock left in the roof and floor of mine workings, is of particular significance in South Africa where bord and pillar mining is widely practised. Pillars must retain their strength to support the overlying strata for long periods of time. In this context the term weathering means the physical degradation of coal which occurs under various environmental conditions (oxidation, adsorption of water, etc.)

The coal in some fields or in particular seams is more prone to weathering than that from other coal-fields or seams. The relative liability to degradation does not depend on the inherent friability of the coal. Coal types which are hard and compact when freshly mined, can suffer more on exposure to the atmosphere than other relatively friable and soft coal types.

The cause of coal weathering can unfortunately not be pinpointed with certainty, as there is most probably an interplay of various processes. This makes it all the more desirable to elucidate the overall process and determine which are the more important causative factors.

The swelling of substances like agar-agar or rubber when exposed to saturated vapours of water and benzene, is

a well known phenomenon. In this case where the adsorbents are clearly non-rigid, their component molecules are obviously pushed apart by the adsorbate and in extreme cases can become entirely separated to form an ordinary solution. Adsorption-swelling is, however, not restricted to non-rigid adsorbents. It also occurs in rigid adsorbents like charcoal and silica gel, though the extent of swelling is much less.

The swelling of all solids is, however, similar in nature: the forces holding the solid together are weakened by the adsorption of foreign molecules which results in expansion. It is difficult to consider the expansion of non-rigid and rigid adsorbents on the same basis and only the latter will be dealt with in detail. Rigid solids with a graphite type of structure where the adsorbate penetrates between layers will not be considered here. The moisture-induced expansion of certain clay minerals with laminated structures falls into this category.

CHANGES IN SURFACE ENERGY AND TENSION DUE TO ADSORPTION:

An explanation of the expansion of rigid porous solids during the adsorption of gases can be sought in the resultant changes in the surface tension of the solid. In view of the confusion as to the equivalence or otherwise of the concepts of surface tension and surface free energy, as applied to solids, the distinction¹ is discussed below.

The surface energy is the work necessary to form unit area of surface by a process of division. Surface tension is the tangential stress (force/unit length) in the surface layer; this stress must be balanced either by external forces or by volume stresses in the body.

The surface tension γ is related to surface free energy by:-

$$\gamma = F' + A (dF'/dA) \dots\dots\dots (1)$$

where F' is the surface free energy per unit area and A is the area of the surface.

For solids the surface tension is not equal to the surface free energy.

The processes occurring at a liquid-gas interface have been interpreted theoretically² with success using the Gibbs adsorption isotherm. The surface tension of liquids is easily measured and changes in this property can be

determined/

determined accurately. The surface tension of a liquid is numerically equal to its surface energy. (This also applies to changes in these two quantities.)

Unfortunately no such simplicity exists for solids. Methods for measuring their surface tension do not exist, and neither do methods for measuring changes in this quantity. Bangham and co-workers^{3, 4} were able to show by direct analogy with liquids that the Gibbs adsorption isotherm could be applied to solids. If F_0' is the surface energy (in erg/cm²) of the solid in vacuum and F' that of the solid with adsorbed material on it, then

$$\pi = -\Delta F' = F' - F_0' = RT \tau \ln p \dots\dots\dots (2)$$

The decrease in free energy is equal to π , the spreading pressure. As the free energy is reduced, the spreading pressure becomes larger. The pressure of the gas above the solid is p , and τ is the concentration of the adsorbed material. Equation 2 is converted into the experimental variables usually measured to give

$$\pi = \frac{RT}{M\Sigma} \int_0^p \frac{q}{p} dp \dots\dots\dots (3)$$

where M is the molar volume at S.T.P., Σ the surface area in cm²/g and q the volume of gas adsorbed (at S.T.P.). This equation is not applicable to the capillary condensation region where equilibrium is not obtained.

In general π cannot be obtained from a theoretical adsorption isotherm equation, since such equations are not accurate enough over wide ranges of pressure. Graphical integration of an experimental isotherm is necessary, and procedures to do this and the precautions that have to be taken have been discussed by Harkins and Jura⁵. In particular, these authors stress the need for accurate data in the very low pressure region of the isotherm, since at low pressures very high values for the quotient q/p are found.

While there is an obvious physical meaning to the π values obtained for liquid surfaces, the significance of values obtained at the gas-solid interface is doubtful. Pierce and Smith⁶ consider that the non-uniformity of the surface and possible localization of adsorption sites of high energy lead to erroneous conclusions as to the meaning of the π values obtained. The majority of adsorbents used

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in physical adsorption studies have a very heterogeneous surface.

The nature of the migration of the adsorbed surface phase is a possible key to the difference between adsorption on liquid and solid surfaces. For liquid surfaces, it is to a good approximation possible to assume that the heat of adsorption ΔH is the same at all points on the surface. For such a surface the adsorbed molecules behave as an ideal two-dimensional gas, moving about in all directions parallel to the surface of the liquid. This is analogous to the random three-dimensional motion of the molecules of an ideal gas.

In contrast, the free movement of the molecules adsorbed by a solid is restricted to an extent dependent on the periodic nature of the force fields at the surface of the solid. In such cases the activation energy required by an adsorbed molecule to move from one adsorption site to another ($\Delta H'$) becomes important. There is little theoretical or experimental knowledge of the magnitude of $\Delta H'$ but it is generally considered⁷⁻⁹ that $\Delta H' \leq \Delta H/2$.

Little consideration has been given to the equality or otherwise of the surface energy and π values, calculated by the above methods and the surface energy changes. For liquids the two changes are equal. Bangham³ has shown that for solids, when the adsorbed phase can be considered to behave as a two-dimensional gas, the surface tension lowering and surface energy lowering are equal and also equal to the spreading pressure. In the case of chemisorption where the adsorbed molecules are fixed (for lengthy times relative to the duration of the experiment), π will be zero, since no surface migration can take place. Nevertheless, the surface free energy will still be decreased.

Crawford and Thompson¹⁰ believe that there should be a relation between π and $\Delta H'$ for solids, such that when $\Delta H'$ is large enough, π will be zero.

When adsorption takes place on solids with H' small relative to ΔH , the following relation is considered valid:

$$\pi = \gamma_0 - \gamma_1 = \Delta\gamma = F' - F_0' = \Delta F' \dots\dots (4)$$

where the surface tension of the solid in vacuum is γ_0 , and γ_1 with an adsorbed gas phase, and F_0' and F' are the corresponding surface free energies.

THE EXPANSION OF SOLIDS DURING ADSORPTION.

HISTORICAL:

In the development of the work on the adsorption expansion of rigid adsorbents, the first experiments were unfortunately ten years or so in advance of any theoretical explanation of the facts.

The study of the swelling of rigid solids following adsorption was mainly confined to the use of charcoal and coal as adsorbents. Changes in the size of a cube of charcoal during adsorption were first observed by Meehan¹¹. Carbon dioxide was adsorbed at room temperature, and it was shown that the expansion was isotropic, even though the original wood prior to charring was markedly anisotropic. Following this, Bangham and his co-workers¹²⁻¹⁹ made a thorough study of the phenomenon of adsorption swelling during the years 1928 to 1946. Most of the work was done with charcoal, but some experiments on coal were also reported.^{18, 19} A wide range of adsorbents was used, including water, ammonia, sulphur dioxide, carbon dioxide, benzene, pyridine and several of the lower alcohols. These gases or vapours were nearly all adsorbed at room temperatures. The length changes were measured with a mechanical-lever extensometer. Values of the linear expansion varied from 1-2% with pyridine to 0.16% with carbon dioxide.

Other early workers in this field include Briggs and Sinha²⁰ who measured the effect of carbon dioxide on coal and McBain et al²¹ who measured the adsorption of water, heptane and benzene on sugar charcoal.

Following the classical work of Brunauer, Emmett and Teller²² later workers were able to put their results on a quantitative basis, which Bangham was unable to do. The B.E.T. theory provided for the first time an accurate method for determining the surface area of any porous substance.

Haines and McIntosh²³ developed a capacitance type extensometer and using rods of zinc chloride activated charcoal, adsorbed dimethyl ether, butane and ethyl chloride. Wiig and Juhola²⁴ used a charcoal with a very high surface area and measured by means of a cathetometer the expansion due to water adsorption of a long rod of the material. Razouk and El Gobeily²⁵ determined the expansion of willow-wood

charcoal during the adsorption of methyl alcohol, carbon dioxide, oxygen, ammonia and sulphur dioxide, using a mechanical-lever extensometer.

Since 1950 the scope and nature of the adsorption-expansion process has been studied in greater detail. Amberg and McIntosh²⁵ were the first to use porous glass as adsorbent and studied water adsorption. In later work^{27, 28} butane, ethyl chloride, and ammonia were adsorbed. Flood and Heyding²⁹ worked with zinc chloride activated charcoal rods and adsorbed water and nitrogen at room temperatures. Further work with helium, argon, krypton and hydrogen has been reported,²⁹ and more recently with ethane, propane, butane, methanol and carbon tetrachloride.^{31, 32}

Apart from the work of McIntosh and co-workers^{26, 27, 28} with porous glass, all the above experiments were conducted with charcoals and carbons of varying degrees of surface complexity. Heats of adsorption were reported in only one case²⁶ on the adsorbent used in an adsorption-expansion experiment. Consequently, it is uncertain whether the process whereby expansion was produced was solely due to physical adsorption, or whether a small amount of chemi-sorption dominated the whole process. For any theoretical understanding of the effect, this knowledge is essential since only physical adsorption is completely reversible and lends itself to satisfactory thermodynamic interpretation.

The above reasoning led Yates³³ to choose porous glass as adsorbent in his studies of the expansion produced by the adsorption of the non-polar gases argon, krypton, nitrogen, oxygen and hydrogen. The same apparatus and sample were used by Yates^{34, 35, 36} to investigate the adsorption of polar gases.

THEORY OF EXPANSION:

Under suitable conditions physical adsorption can take place beyond the stage of monolayer formation to form multiple layers of adsorbed molecules.³⁷ In the multilayer region the process is formally defined as physical adsorption, but it has more in common with the condensation which occurs in the transition from a vapour to a liquid. Zsigmondy³⁸ postulated that the adsorbed molecules condense to form an ordinary liquid in the pores of the adsorbent when multilayer adsorption takes place (capillary condensation). This is

associated with hysteresis in the isotherms and as they are therefore not reversible, the application of thermodynamics to such isotherms is difficult.

Apart from the few cases where entropy changes predominate,³⁹ the process of adsorption occurs spontaneously because of a decrease in the free energy which takes place.⁴⁰ This free energy is that of the surface on which adsorption takes place. An atom on the surface of the solid is subject to unbalanced forces, the inward pull being larger than the outward. Physically, this is the reason for the finite surface tension that occurs in all surfaces. Any gas molecules adsorbed on such a surface saturate some of the unbalanced surface forces, decreasing the surface tension and energy. Bangham and Fakhoury^{13, 14} suggested that the phenomenon of adsorption expansion was related to this change in free energy and proposed the equation:

$$x = -edF' \dots\dots\dots (5)$$

where x is the percentage linear expansion, dF' the surface free energy lowering, and e a constant, dependent probably on the particular solid and the gas being adsorbed. The relation between dF' and the spreading pressure π was discussed above and also the determination of dF' from accurate isotherms on a solid of known surface area. Further work by Bangham and Maggs¹⁸ related the constant e to the elastic properties of the charcoal. The solid was considered to be made up of one long thin non-porous rod such that its specific surface is equal to that of the porous solid. The spreading pressure was assumed to act as a tangential stress tending to increase the length of the rod. Then it was found by simple calculation that

$$E = 100 \frac{\Sigma \rho}{e} \dots\dots\dots (6)$$

where E is the Young's modulus of the solid, Σ the specific surface area in cm²/g., and ρ the density of the non-porous rod. This equation was also shown by Bangham to be valid if the solid is considered as a plane-continuous lamina.

Meehan¹¹ showed in the first experiments on this subject that the expansion was isotropic. This was later confirmed more accurately by Flood and Heyding.²⁹ Yates³³ considered that a better model of the process would be obtained by relating the expansion constant e to the bulk

modulus/

modulus of the solid rather than the Young's modulus. In the measurement of Young's modulus, an expansion along one axis is accompanied by contraction along the other two, while in measurements of bulk modulus the size change is isotropic. Yates took as a model a system composed of lightly sintered spheres, the reasonable assumption being made that such an aggregate will have the elastic properties of the isolated spheres. Other more sophisticated models of porous solids have been suggested,²⁹ but until more is known of the porous solids used in adsorption-expansion experiments, the simplest possible model is to be preferred.

Yates derived an equation relating the expansion produced by the adsorption of gases to the bulk modulus of the porous solid as follows:

The surface tension of an isolated solid must be balanced by elastic strains induced in the solid. For a solid sphere Shuttleworth⁷ has shown that

$$P_1 - P_2 = \frac{2\gamma_0}{r_0} \dots\dots\dots (7)$$

If γ_0 and r_0 are the surface tension and radius in vacuo respectively, P_2 , the external pressure, is zero and P_1 is the internal pressure resulting from the action of surface tension forces - differentiation yields

$$dP = \frac{2(r_0 d\gamma - \gamma_0 dr)}{r_0^2} \dots\dots\dots (8)$$

Substituting the isothermal bulk modulus,

$K = -V \left(\frac{\delta p}{\delta V}\right)_T$ and integrating between the limits r_0 and r_1 , where r_1 is the increased radius due to a decrease in surface tension $\Delta\gamma$ from γ_0 to γ_1 , if both Δr and $\Delta\gamma$ are small, the relation:

$$\frac{3Kx}{200} = \frac{-\Delta\gamma}{r_0} \dots\dots\dots (9)$$

is obtained.

The product of the specific surface area Σ and the density ρ , of the sphere is $3/r_0$

$$\therefore \frac{9Kx}{200} = -\Delta\gamma\Sigma\rho \dots\dots\dots (10)$$

Assuming, according to Bangham, that in the case of physical

adsorption/

adsorption the change in surface tension can be approximated to the change in surface free energy, and using equation 5 one obtains

$$K = \frac{200}{9} \frac{\Sigma \rho}{e} \dots\dots\dots (11)$$

From equation 5 if the solid is isotropic

$$-e dF' = 100 \frac{dl}{l} = \frac{100}{3} \frac{dV}{V}, \text{ where}$$

V is the volume of the solid and l its length,

$$\therefore -e = \frac{100}{3V} \left(\frac{\delta V}{\delta F'} \right)_T \dots\dots\dots (12)$$

as equation 5 is valid only for isothermal conditions.

The total surface free energy change is given by

$$dF = dF'A = dF'\Sigma \rho V, \text{ where } A \text{ is the area of the}$$

solid. Thus, substituting, Yates obtained the relation

$$\left(\frac{\delta F}{\delta V} \right)_T = \frac{-3}{2} K \dots\dots\dots (13)$$

The validity of equation 13 was tested by means of an interferometric technique, using monochromatic light of wavelength λ , in which the linear expansion of porous glass was measured in terms of N, the fringe movement.

The two-dimensional pressure π was calculated from the adsorption isotherm and is related to the surface tension lowering, assumed equal to the surface free energy lowering, by

$$\pi = -\Delta F' = \Delta \gamma = \gamma_0 - \gamma_1 \dots\dots\dots (14)$$

since a decrease in surface free energy corresponds to an increase in two-dimensional pressure.

Equation 13 can be written, at constant temperature.

$$K = \frac{-2}{3} \frac{dF}{dV} = \frac{4}{9} \frac{\Sigma \rho l}{\lambda} \frac{d\pi}{dN} \dots\dots\dots (15)$$

since $dV = \frac{3\lambda V}{2l} dN$

Similarly, from equation 6 it can be calculated that

$$E = 2 \frac{\Sigma \rho l}{\lambda} \frac{d\pi}{dN} \dots\dots\dots (16)$$

Yates calculated the values of E and K from the above two equations and compared his results with the values supplied by the makers of the glass. The bulk modulus K calculated from the adsorption-expansion data was half as large again as that from direct experimental measurement, whereas the Young's modulus E calculated according to Bangham's theory was about

three and a half times as large. Thus Yates came to the conclusion that the expansion of porous glass during physical adsorption was more closely related to the bulk modulus of the glass than Young's modulus.

An alternative approach to the problem of adsorption-expansion is that of Flood and Heyding²⁹ who derived a simple thermodynamic equation to correlate the change in length δl of a rigid porous adsorbent with its elastic and adsorptive properties. They obtained the equation:

$$\delta l/l = -\frac{1}{3}\beta (1 + \phi k - \phi k \alpha) \delta p \dots \dots \dots (17)$$

where $\delta l/l$ is the length change per unit length, β is the co-efficient of cubic compressibility of the solid adsorbent, ϕ is the ratio of void volume to solid volume, K is the ratio of linear average stress to volumetric average stress, α is the mean number of volumes adsorbed averaged over the pressure interval δp and p is the hydrostatic pressure surrounding the adsorbate-adsorbent system. The assumptions made in this derivation are (a) both adsorbate and adsorbent can exist separately in equilibrium with externally applied forces in states that are thermodynamically identical with their states in the adsorbent-adsorbate system; and (b) adsorption isotherms represent paths of thermodynamic reversibility. Reasonable agreement was obtained between calculated and observed results for systems reported in the literature viz.: water vapour on carbon, methanol on carbon, ethyl chloride on carbon and water vapour on glass. Experimental data were obtained for the systems nitrogen on activated carbon rods and water vapour on activated carbon rods.

More recently Dacey and Cadenhead⁴¹ investigated the swelling and shrinkage of a rod of "Saran" charcoal on the adsorption and desorption of six different adsorbates, water, HCN, H₂S, NH₃, C₂H₆ and hexane. No initial shrinkage of the specimen or desorption hysteresis was observed. They found that the theoretical treatment of Flood and Heyding predicts the behaviour of their specific adsorbent remarkably well for all cases where adsorption saturation was not reached.

SUMMARY OF PUBLISHED EXPERIMENTAL WORK:

This section is restricted to results obtained when the surface coverages were less than about 1.5 monolayers. All work where the surface area of the solid is uncertain¹¹⁻²¹

is/

is excluded.

Haines and McIntosh²³ used zinc chloride activated rods of length between 8 and 13 cm, the length changes being measured with a capacitance extensometer. The ratio of the smallest length change detectable to the original length, $\Delta l/l$ was about 2×10^{-4} for their system, butane, dimethyl ether, and ethyl chloride were used as adsorbates, at room temperature. Results for rod No. 13 (average surface area $960 \text{ m}^2/\text{g}$) are given in Figure 1, taken from Table 1²³ of their paper. For two of the gases used contraction took place. This was not the case when dimethyl ether was adsorbed on rod No. 11 at 20°C , only expansions were observed. Values of π at V_m (monolayer coverage) and $V_m/2$ are given for ethyl chloride (e.c.) and dimethyl ether (d.e.) on Figure 1. Beyond the minimum of the curve, the relation $x = -edF'$ is quite well obeyed.

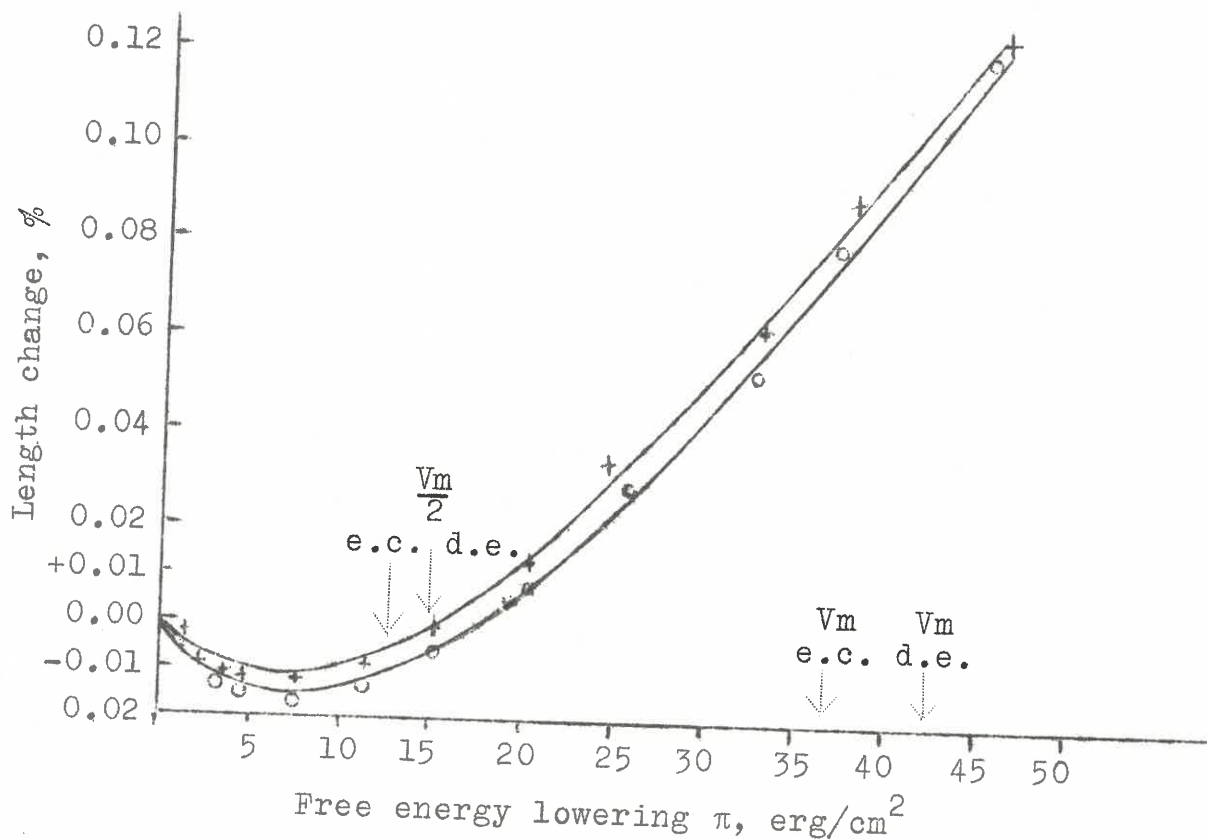


Figure 1. Expansions of an activated charcoal rod produced by the adsorption of ethyl chloride (e.c.) (O) at 10°C and dimethyl ether (d.e.) (+) at 6.5°C .²³

The possible cause of the contraction was considered in some detail but no unique mechanism was suggested. Values of the Young's modulus E were calculated from equation 6. Water was also adsorbed at 20°C , and only small length changes took place at low relative humidities. Large

hysteresis/

hysteresis affects were found in the capillary condensation region.

In the next publication,²⁶ the same extensometer was used with a rod of porous glass 11 cm. long. The surface area was 117 cm²/g calculated from water isotherms. Length changes were measured with a sensitivity $\Delta l/l$ of 2×10^{-6} for water vapour adsorbed at 11.8, 18.7 and 25.8°C. The main interest was in the capillary condensation region, and for each of the three isotherms, only the first three points of each one were in the region below $\epsilon = 1.5$. Probably for this reason, their plots of π vs. $\Delta l/l$ (Figure 2) were quite good at coverages greater than unity but showed quite large deviations at lower coverages. The Young's modulus E obtained from the initial expansion region was 3.8×10^{11} dynes/cm². Heats of adsorption were calculated for the three water isotherms, and were about 15.5 k.cal/mole at monolayer coverage. All effects were found to be reversible.

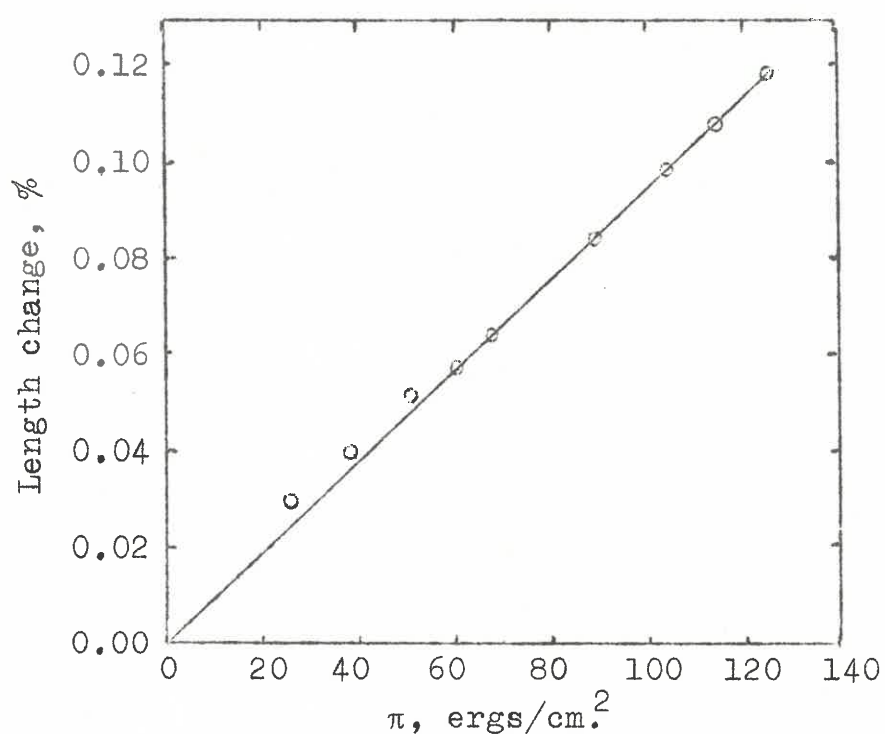


Figure 2. Length changes of porous glass produced by H₂O adsorption as a function of free energy lowering π .²⁶

Later experiments were performed using a similar extensometer with a different porous glass rod. Butane (at -6.2°C) ammonia (-39.2°C) and ethyl chloride (6.0°C) were adsorbed. As the capillary condensation region was again that of main interest, no details were given of the

expansion/

expansion below monolayer coverage, although isotherms down to fairly low pressures were given.²⁷ Graphs were presented of length changes due to butane, detailed in the capillary condensation region, and discussed.²⁸ No details were given of the ethyl chloride length changes except that Bangham's equation was tested for butane and ethyl chloride. Length change data were not obtained with ammonia or with ethyl chloride at low coverages. Some irreversibility was found in the adsorption isotherms for all the gases used, especially the polar ones, since the hysteresis loop did not close on desorption. Earlier work showed similar anomalous effects with oxygen⁴³⁻⁴⁵ which were attributed⁴⁵ to small amounts of chemisorption on the grease sometimes present on the surface of the porous glass.

Flood and Heyding²⁹ compared results obtained by earlier workers^{23, 24, 26} from the standpoint of volume average stresses in the solid created by the adsorbate in the adsorptive force field. In addition, length changes were measured for a zinc-activated carbon rod. The rod was 8.8 cm long and the traveling microscope used measured the length changes to $\pm 2 \times 10^{-4}$ cm. The sensitivity $\Delta l/l$ is thus about 2.5×10^{-5} . In addition to length-change measurements, radial changes were also measured. No surface area values were reported although the isotherm was given for water. Considerable attention was paid to effects in the capillary condensation region. Later work³⁰ was carried out with another carbon rod of similar properties using improved optical equipment which enabled length changes of $\pm 2 \times 10^{-5}$ cm. to be measured.

An extremely sensitive vacuum interferometer was developed by Yates³³ which was capable of use over the range of temperature normally used in adsorption work, namely, from +450 to -196°C. This makes pretreatment of the sample possible under conditions usually used in physical adsorption studies, with an ultimate vacuum of 10^{-5} mm.

Easy removal of surface grease on the porous glass was possible by burning it off with oxygen in situ. This pretreatment with oxygen was found to be important in obtaining completely reproducible results.⁴⁰ A tube of porous glass 5.1 cm. long was used, the minimum length change that could be detected was 3×10^{-6} cm., so that the sensitivity $\Delta l/l$ of the interferometer in this particular

case was 5.4×10^{-7} . Heats of adsorption were determined from isotherms at 90 and 79°K for argon, nitrogen, oxygen, and hydrogen. Earlier work⁴³⁻⁴⁵ with porous glass did not include any direct determination of heats of adsorption.

In all the work reported earlier for charcoals, and even with water on porous glass,²⁶ it is possible that small amounts of chemisorption might have been the interfering factor. Yates studied the adsorption of the rare gases argon and krypton in order to eliminate the possibility of chemisorption. The expansions for argon together with those for nitrogen and oxygen are shown in Figure 3 as a function of the volume of gas adsorbed.³³ The length changes are given in fringes, a change of 1 fringe corresponds to a percentage length change of 5.4×10^{-4} .

The average monolayer capacities were 41.0 for A, 41.8 for N₂ and 46.3 for O₂ in cm³/g - giving an average surface area of 173.3 m²/g. In addition the equation relating the bulk modulus to the expansion (equation 13) was tested. The relation found by Bangham between the expansion Δl and the free energy lowering π was demonstrated (Figure 4) to be valid for this system with some deviation at low coverage. These deviations are probably due to difficulty in obtaining accurate π values in this region.

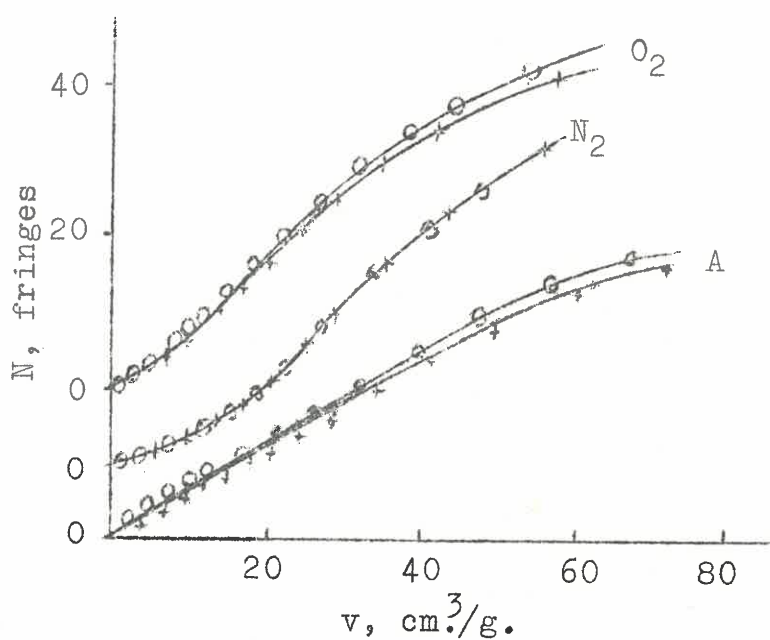


Figure 3. Expansion of porous glass during the adsorption of A, O₂, N₂, O, 90°K, x 79°K³³.

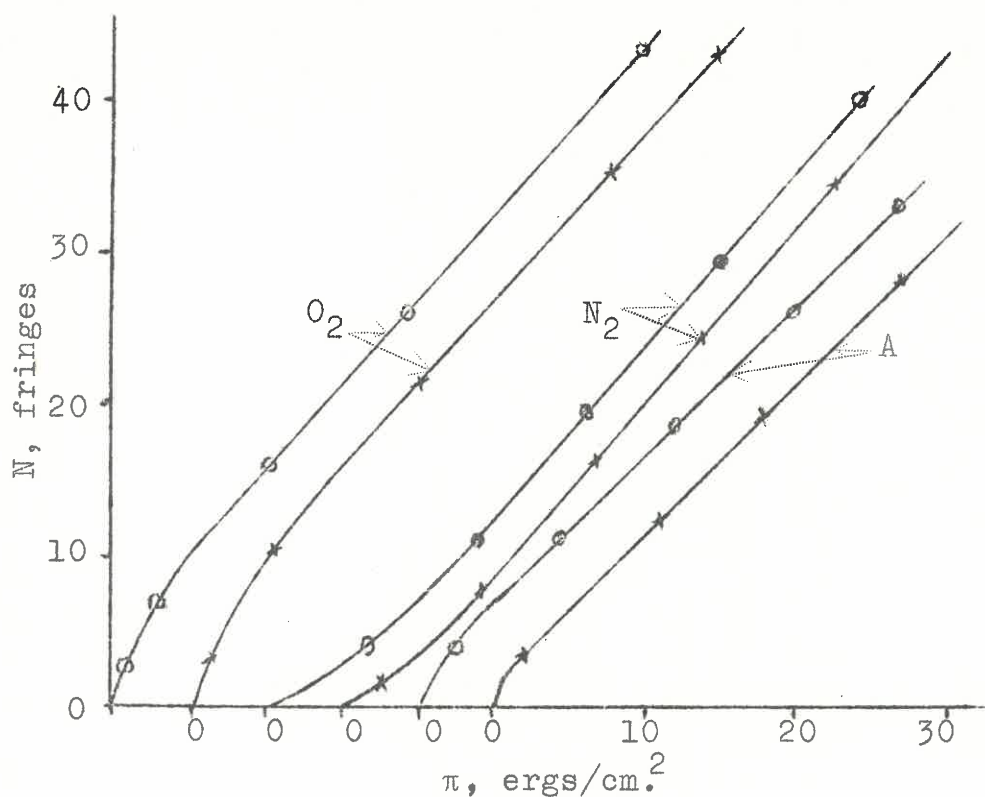


Figure 4. Length changes of porous glass as a function of free energy lowering π 0 90°K, x 79°K³³.

Since the expansions were measured as a function of fringe shifts (N), the gradient of the expansion - π curves are given by $dN/d\pi$. Average values are: argon, 1.01; nitrogen, 1.12; oxygen, 1.16; krypton, 0.76; and hydrogen, 1.83. The difference between the first three gases, of similar boiling points, is small, but Yates considered that the accuracy of his results was sufficient to make these differences significant.

The bulk modulus theory was compared with the Young's modulus theory for values obtained for argon only. The bulk modulus obtained from the expansion results is about half as large again as the value determined by direct experimental methods, but the Young's modulus is about three and one-half times as large.

Later work was reported with the same sample³⁴ which enabled accurate comparisons to be made with the earlier results. The first polar gas that was used was carbon monoxide, and contraction took place before expansion, in a manner similar to that reported earlier for certain charcoals.²³ It is likely that the contraction is related to the polar nature of the carbon monoxide molecule,⁴⁶ and the anomalous behaviour of nitrogen to its quadrupole moment.^{47, 48} The quadrupole moments of argon and krypton

are zero, and those of hydrogen and oxygen are small. The finite quadrupole moment of nitrogen and its effects on adsorption have been discussed by Drain.⁴⁹

Carbon dioxide was also adsorbed and this molecule is of interest, since it is similar to nitrogen, having a quadrupole moment and no dipole moment. Yates³⁴ found that the expansion curves with carbon dioxide were very similar to those of nitrogen, especially if plotted as a function of coverage rather than volume of gas adsorbed. More accurate results were given for hydrogen, and neon was also studied.

The adsorption of gases with larger dipole moments showed very much greater contractions than did carbon monoxide.³⁵ Sulphur dioxide gave a contraction about three times as large, and ammonia thirty times as large. These results were later extended by a detailed investigation of the effect over a wide range of temperatures.³⁶ In addition to sulphur dioxide and ammonia, methyl chloride and dichlorodifluoromethane were adsorbed. In keeping with its rather inert nature, CCl_2F_2 produced results similar to carbon monoxide. Except for carbon monoxide, detailed results showed that for all adsorbates a small expansion preceded the contraction. As the temperature of adsorption is increased, the contractions become smaller and finally disappear. The reversibility of these changes was investigated and also the time effects near the minimum in the contraction curves.

In recent years, the emphasis in the study of physical adsorption has shifted towards the thermodynamic properties of the adsorbed phase, particularly its entropy. Answers have been sought as to the nature of the adsorbed phase and whether the adsorbed molecules behave as a two-dimensional gas, a liquid, or a solid, and also what effect adsorption has on the critical and melting temperatures of the adsorbates.

Various new experimental techniques have been applied to this problem. The electrical properties (polarizability) of the adsorbate have been studied and nuclear magnetic resonance and spectroscopic methods (infra-red) applied. Further details of these methods will not be discussed in detail as investigation in this direction is outside the scope of the Institute's present interests.

CONCLUSION:

The adsorption swelling of coal (especially low-rank coals) is almost certainly a link in the problem of coal pillar "scaling". Localised stresses created in surface layers can contribute to the coal degradation. Fundamental work will have to be carried out in order to obtain results which can be applied to the practical solution of this problem. Coal is unfortunately an extremely heterogeneous substance and this fact coupled with the relatively high ash content of South African coals will complicate matters.

As pointed out above (page 3) accurate adsorption isotherms are required in the low partial-pressure region before the theory relating adsorption to expansion can be applied. Accurate values of the elastic moduli of our coals are also necessary. In addition the determination of the stresses created in coal or shale as a result of adsorption would be of practical interest.

A.A. MEINTJES
SENIOR TECHNICAL OFFICER.

PRETORIA.
20th December, 1965.

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