WU4/B/114

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

TECHNICAL MEMORANDUM NO. 2 OF 1964.

ADSORPTION OF WATER VAPOUR BY COAL.

BY.

P. G. SEVENSTER

AND

L. BODENSTEIN.

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

TECHNICAL MEMORANDUM NO. 2 OF 1964.

ADSORPTION OF WATER VAPOUR BY COAL.

The study of the behaviour of moisture on
coal is a rather complex one. The moisture holding
capacity of coal and the ability to adsorb water affects
many characteristics of the material.

The equilibrium moisture capacity may serve as
a criterion of certain physical properties such as surface
area and porosity, while the moisture adsorbed itself may
affect such properties as grindability, combustion, spon-
taneous ignition and weathering.

Furthermore, the process of adsorbing water is
related to heat generation and expansion phenomena. It is
clear that moisture is an important part of coal; this may
be the reason for the extensive investigations carried out
on the subject, both experimentally and theoretically.
In the present investigation the adsorption of water vapour
on coals of varying moisture content was studied.

When a thoroughly evacuated adsorbent is brought
into contact with a gas or vapour, its molecules distribute
themselves between the gas phase and the adsorbed phase.
After a while the process stops and a state of stable
equilbrium is reached. The amount of gas adsorbed per gram
of adsorbent at equilibrium is a function of the temper-
ature, the pressure and the nature of the adsorbent and the
adsorbate.

Usually, either pressure or temperature alone are
varied while the other variable is kept constant. When the
pressure of the gas is varied at constant temperature, the
plot of the amount adsorbed against the pressure is called
the adsorption isotherm. This is the most frequently de-
termined relation. With varying temperature and constant
pressure one obtains the adsorption isobar.

The .../

The method used in this study for the determination of the adsorption isotherms and other information was that of McBain and Bakr[1] using quartz spring balances. These balances are useful for determining the weight of adsorbed gases or vapours under various conditions. The springs do not corrode easily, have a small negative temperature coefficient and a low thermal coefficient of volumetric expansion. Fused silica can be drawn out to a thin fibre and still be strong enough to carry quite a load. Spirals made of this fibre show no deformation even after being loaded for long periods, as long as care is taken not to overload them. Variation in the thickness of the fibre permits a wide variety of sensitivities; when properly calibrated and treated these springs are accurate. The main source of error in the determination of the weight of adsorbed material using quartz springs is in the buoyancy correction, but as long as the experiments are carried out at low pressures the correction is small.

Three samples of varying air dried moisture content were used: Sigma: 7.8%, Klippoortje: 3.0% and Enyati: 1.8%; the moisture contents were determined by the routine method used for the proximate analyses of coals (B.S.1016, part 3, 1957).

Five fractions of each sample were prepared. Each fraction was ground separately, and carefully so as to reduce the losses due to fines production to a minimum, and attempting to obtain uniform samples over the whole size range.

EXPERIMENTAL PROCEDURE:

The apparatus used is shown in Figure 1.

The main parts of the apparatus are the quartz balances C, enclosed in glass tubes B. The samples were weighed into crucibles D, made of aluminium foil, and hung from the balances. The temperature of the samples in each experiment was kept constant by means of thermostat E, filled with a mixture of glycerine and water. The flask F, contains a sulphuric acid solution for regulating vapour pressure in the apparatus. The water bath G, was used to vary the temperature of F.
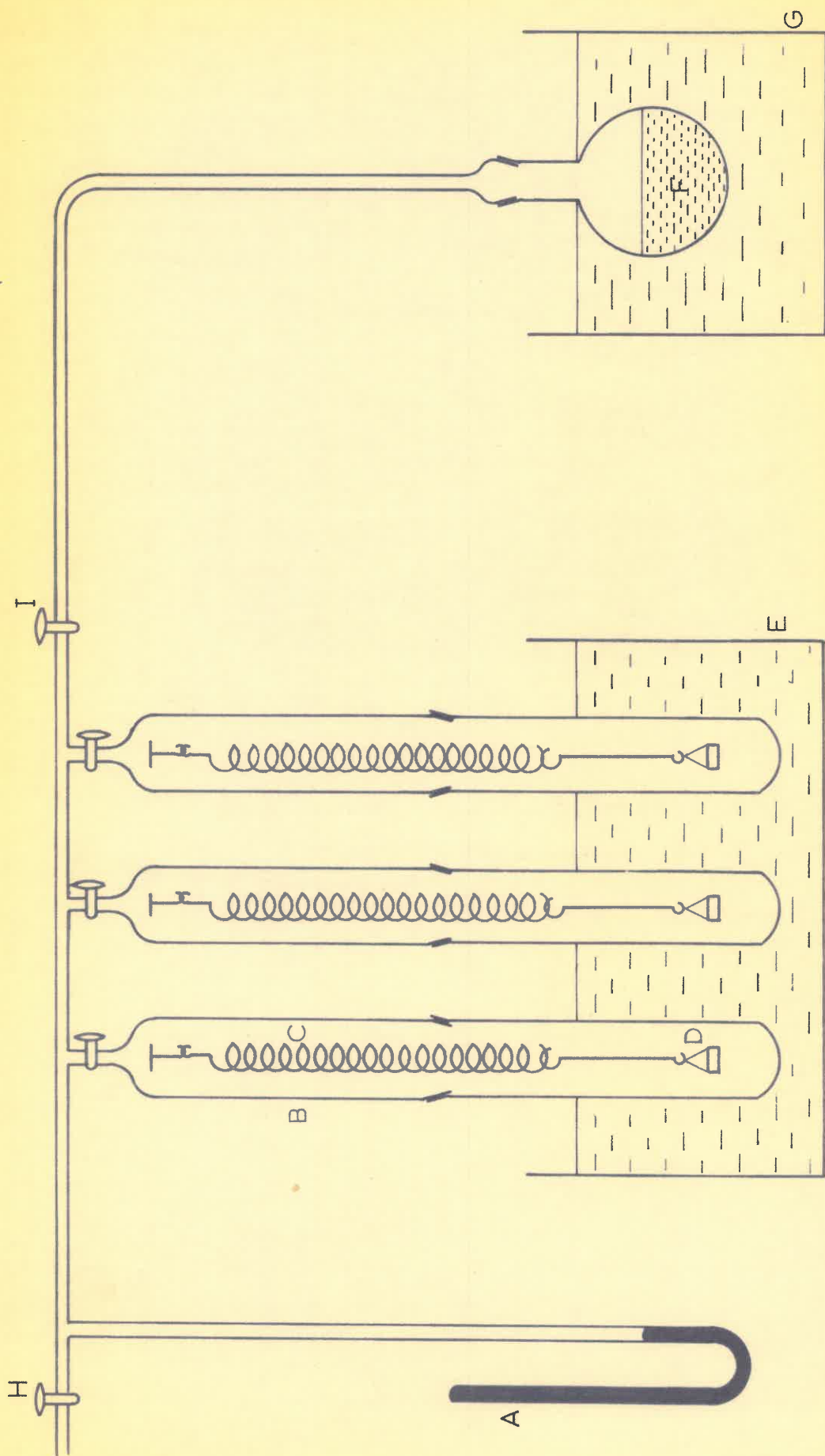
The .../

FIG. I.   Apparatus used to obtain adsorption data of Coals.

The vacuum manometer A, was used to check the vapour pressure values and the vacuum.

The variation of vapour pressure with temperature and concentration of the sulphuric acid solutions was obtained from International Critical Tables.

The adsorption was observed by measuring the extension of the springs with a cathetometer.

· The procedure followed was to weigh into the crucibles a sufficient amount of air dried coal to obtain 0.8 g of dry coal after the samples had been evacuated (0.8 g plus moisture). — The crucibles were then suspended from the springs, enclosed in the glass tubes, the thermostat E placed in position and heated. Evacuation with a speedivac pump continued for at least two hours at a temperature of $90^{\circ}C$. The mixture in E was then cooled to the temperature desired for the experiment and zero values were determined with the cathetometer. Then tap H was closed and I opened, connecting the apparatus to F, heated beforehand to a specific temperature. The adsorption was followed until equilibrium was reached which was assumed to be established when no change in weight occurred for two hours. The extension of the springs in millimeters was then converted to increase in weight due to water vapour adsorbed, using the sensitivity factors of the springs.

RESULTS:

The adsorption isotherms for three fractions of each sample were drawn. This was done at $25^{\circ}C$ for relative humidities up to $\pm92\%$ of the maximum vapour pressure of water at $25^{\circ}C$.

The curves obtained were of the S-shaped type, which according to Brunauer[2] signifies multimolecular adsorption.

Some of the isotherms are shown in Figure 2.

Another ..../

Another relationship investigated, is that between the weight of vapour adsorbed at equilibrium and the vapour pressure. It was established that the amount of vapour adsorbed increased consistently with an increase in vapour pressure while the temperature was kept constant at $25^{\circ}C$. The results are summarised in Table 1.

TABLE 1.

Effect of vapour pressure on H_2O adsorbed at $25^{\circ}C$.

Pressure	4.7mm	10.2mm	12.2mm	21.0mm
Sigma	.0282g	.0444g	.0372g	.0635g
Klippoortje	.0084g	-	.0152g	.0238g
Enyati	.0061g	.0106g	.0118g	.0256g

The adsorption process is always exothermic. Therefore, according to the principle of le Chatelier, the amount adsorbed at equilibrium must decrease with increasing temperature. The results given in Table 2, are concordant with this statement. (See Figure 3).

TABLE 2.

Effect of temperature on H_2O adsorbed.

Temperature	$60^{\circ}C$	$38^{\circ}C$	$25^{\circ}C$
Sigma	.0196g	.0575g	.0637g
Klippoortje	.0078g	.0197g	.0238g

Table 3 gives the weight of water vapour adsorbed by the different fractions of the three samples at $25^{\circ}C$. Klippoortje shows a decrease of adsorption with increase in particle size, but there is no consistent variation with varying particle size for the other two samples.

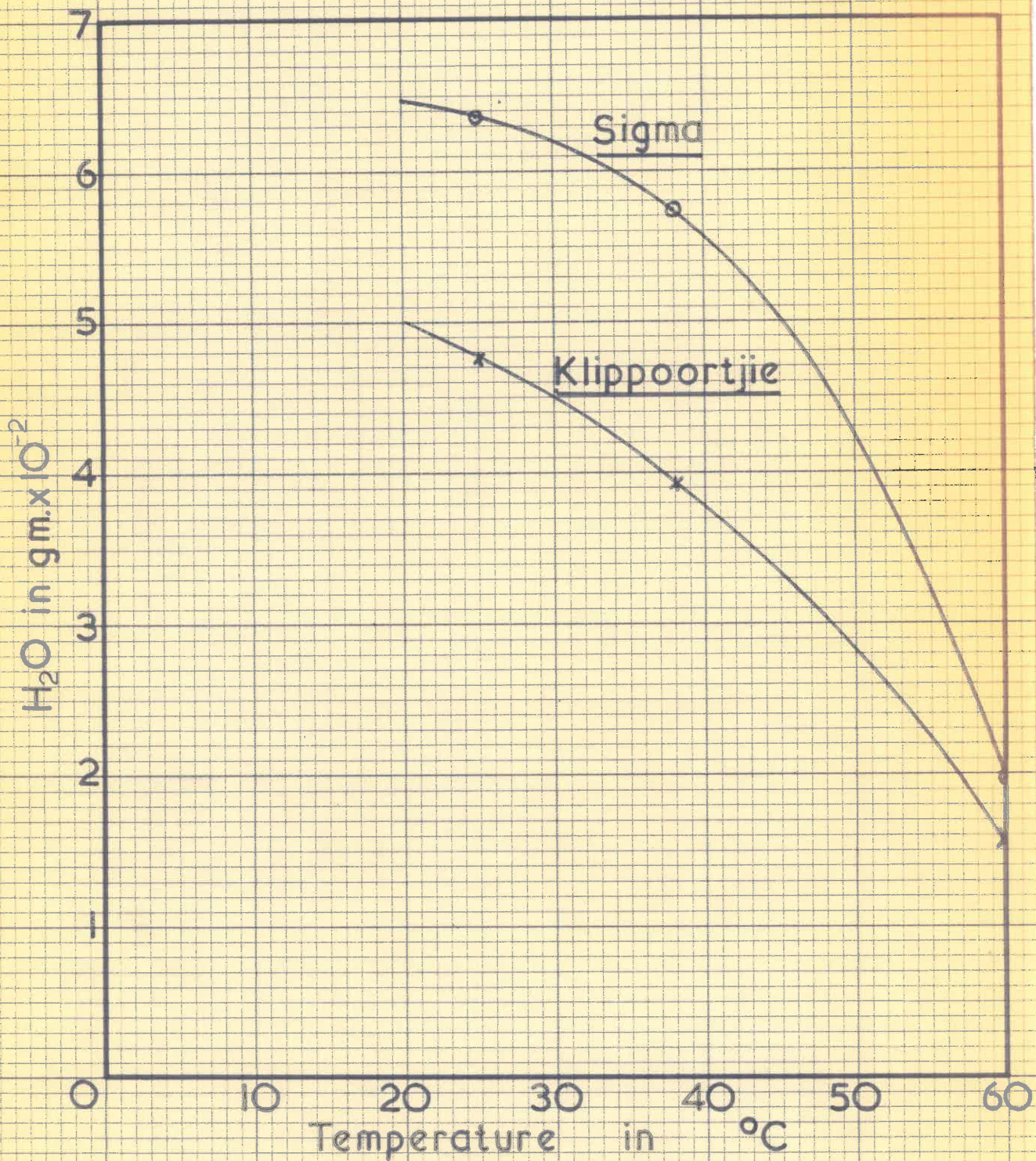FIG.3   EFFECT OF TEMPERATURE ON AMOUNT OF H_2O ADSORBED

TABLE 3.

Weight of Water Vapour Adsorbed at 25°C (grams).

Fraction	-200	-150	-60+150	-20 +60	-8 +10
Sigma	.0703	.0795	.0642	.0628	.0755
Klippoortje	.0362	.0360	.0330	.0288	.0240
Enyati	.0208	.0205	.0220	.0194	.0235

THE RATE OF ADSORPTION.

The rate of adsorption was very high initially. In most cases 70 - 80% of the equilibrium amount was adsorbed within the first 40 minutes. After this the adsorption rate dropped considerably and equilibrium was reached after 150 - 200 min. Figure 4, typically illustrates this trend.

Increase in temperature caused an increase in rate of adsorption as can be seen from Table 4. This table gives the percentage of the equilibrium amount of vapour adsorbed after 60 minutes by the -20 +60 fractions of Klippoortje and Sigma coals.

TABLE 4.

Percentage of Equal Amount of Water Vapour Adsorbed after 60 minutes at Varying Temperatures.

Temperature	25°C	38°C	60°C
Sigma	92.8	97.2	99.0
Klippoortje	81.5	87.3	89.8

Table 5 gives the adsorption percentages after 60 minutes of the -60 +150 fractions of the three samples at 25°C. These figures do not show any relation between pressure variation and adsorption rate.

TABLE 5 ..../

TABLE 5.

Percentage of the Equilibrium Amount of Water
Vapour Adsorbed after 60 Minutes at 25°C and
Varying Pressures.

Pressure	5.7mm	9.1mm	9.7mm	17.2mm	20.3mm
Sigma	90.5	89.0	88.4	94.1	87.4
Klippoortje	92.0	100.0	92.6	100.0	98.2
Enyati	93.3	100.0	100.0	100.0	100.0

The particle size seems to have a varying influence on the rate of adsorption of the different coals. From Table 6 can be seen that after 60 minutes the -20 +60 and -60 +150 fractions of Sigma adsorbed the highest percentage, while the finer and coarser fractions of this coal adsorbed at a lower rate.

The -150 fraction of Klippoortje adsorbed 100% after 60 minutes, while all the other fractions adsorbed less.

In the case of Enyati, however, the -200, -150 and -8 +10 fractions adsorbed 100% after 60 minutes, while the other two fractions (-60 +150 and -20 +60) adsorbed less. This is the opposite of what was found with Sigma.

TABLE 6.

Percentage of Equilibrium Amount of Water Vapour
Adsorbed After 60 Minutes (Effect of Particle Size).

Fraction	-200	-150	-60+150	-20 +60	-8+10
Sigma	88.1	89.1	95.7	96.8	78.3
Klippoortje	86.1	100.0	90.2	76.1	41.1
Enyati	100.0	100.0	94.4	95.1	100.0

It is therefore clear that the rate of adsorption must be influenced by factors not taken into account in this experiment. An improvement may be made by determining the adsorption rate of the 5 fractions simultaneously. The practice of determining the adsorption separately, 3 fractions at a time, with one used as a reference is not satisfactory.

THE ADSORPTION OF WATER VAPOUR IN THE PRESENCE OF AIR.

Measurements of the rate of adsorption and the equilibrium amount of water vapour adsorbed in the presence of air were also undertaken.

Samples of coal were evacuated at $90^{o}C$. While the temperature of the samples was maintained at $25^{o}C$, the amount of water vapour adsorbed by the coal was noted.

After equilibrium was attained between the coal and air, water vapour was admitted and the gain in weight observed. Measurements of water vapour adsorption were made at $25^{o}C$ and 4.2, 6.0 and 15 mm. mercury.

The results obtained are tabulated in Table 7.

TABLE 7.

Amount of Water Vapour Adsorbed in the Presence of Air by Completely Dry Coal.

Sample:	Amount Adsorbed in gm/gm.		
	4.2 mm.	6.0 mm.	15 mm.
Sigma	.0006	.0019	.0019 (0.05)
Klippoortje	.0006	.0008	.0013 (0.30)
Enyati	.0008	.0012	.0018 (0.35)

The figures given in brackets (Table 7) are the values of water vapour adsorbed when the coal has not been exposed to air after the initial evacuation.

It is, therefore, obvious that air has a considerable inhibitive effect on water vapour adsorption,

but ..../

but only when the coal is initially dried out completely. (In the case where there is water initially present, air does not inhibit the adsorption as demonstrated by the fact that coal normally may lose or gain moisture when changes in the atmospheric humidity conditions occur.)

In order to ascertain whether structural changes, due to complete drying or oxidation of the coal surface were responsible for this behaviour, the same samples were again evacuated and exposed to water vapour alone. It was found that all the samples adsorbed amounts of water very nearly equal to their normal moisture contents.

It appears, therefore that this behaviour may be related to diffusion effects. This view is supported by the fact that equilibrium in these measurements was reached only after $1\frac{1}{2}$ days as compared to about 2 hours in the experiments where air was absent.

This interesting observation requires further investigation because of the implication it has on studies in the expansion of coal in changing humidity conditions and in the spontaneous heating of coal.

(SIGNED) P. G. SEVENSTER.
PRINCIPAL RESEARCH OFFICER.

L. BODENSTEIN
ASSISTENT TECHNICAL OFFICER.

PRETORIA.
13/8/64

R E F E R E N C E S.

1. McBain, J.W. and Bakr, A.M.; J. Am. Chem Soc., 48(1926)
                                      Brunauer, p. 37.
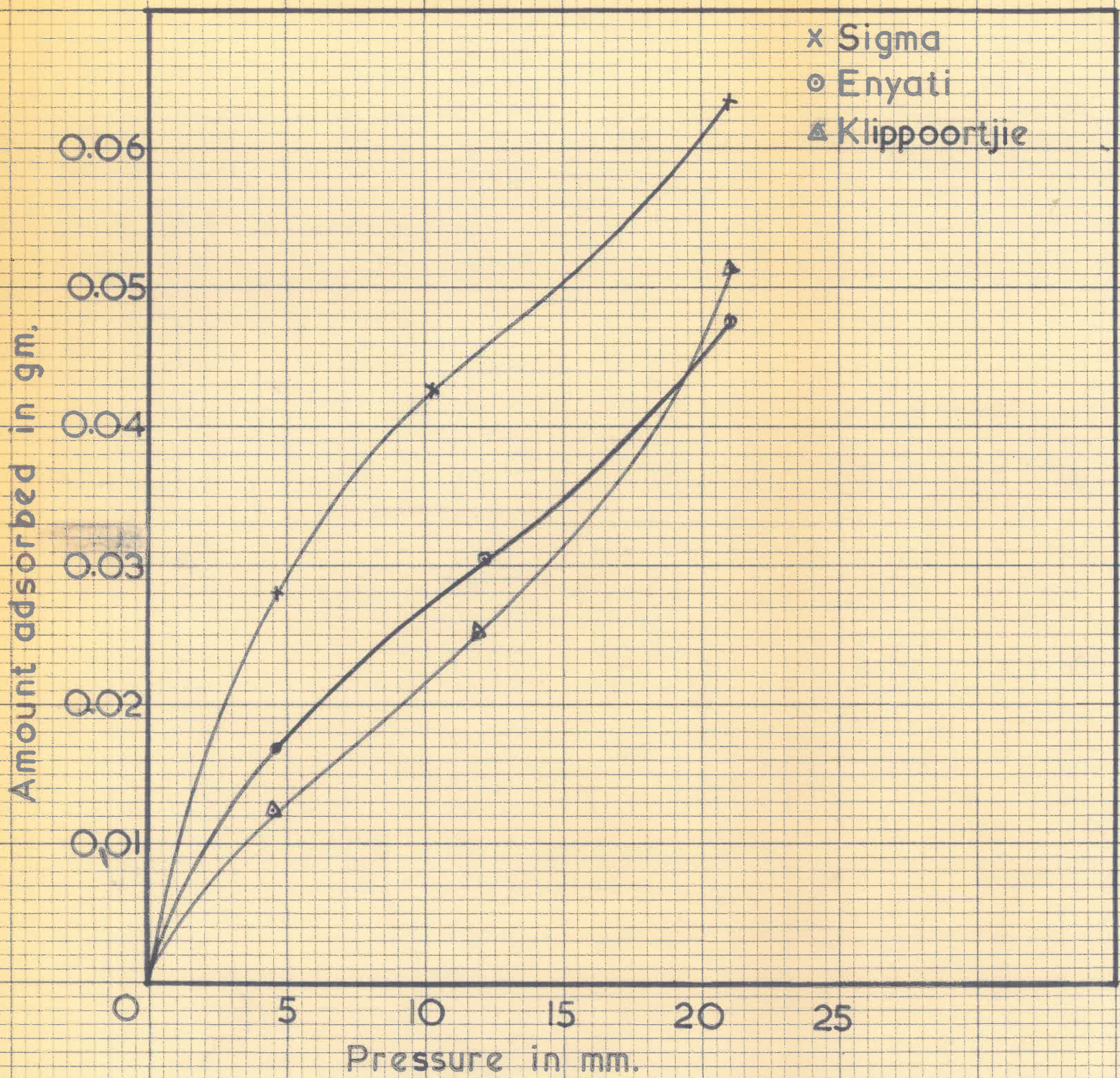
2. Brunauer: The Adsorption of Gases and Vapours. p. 142.

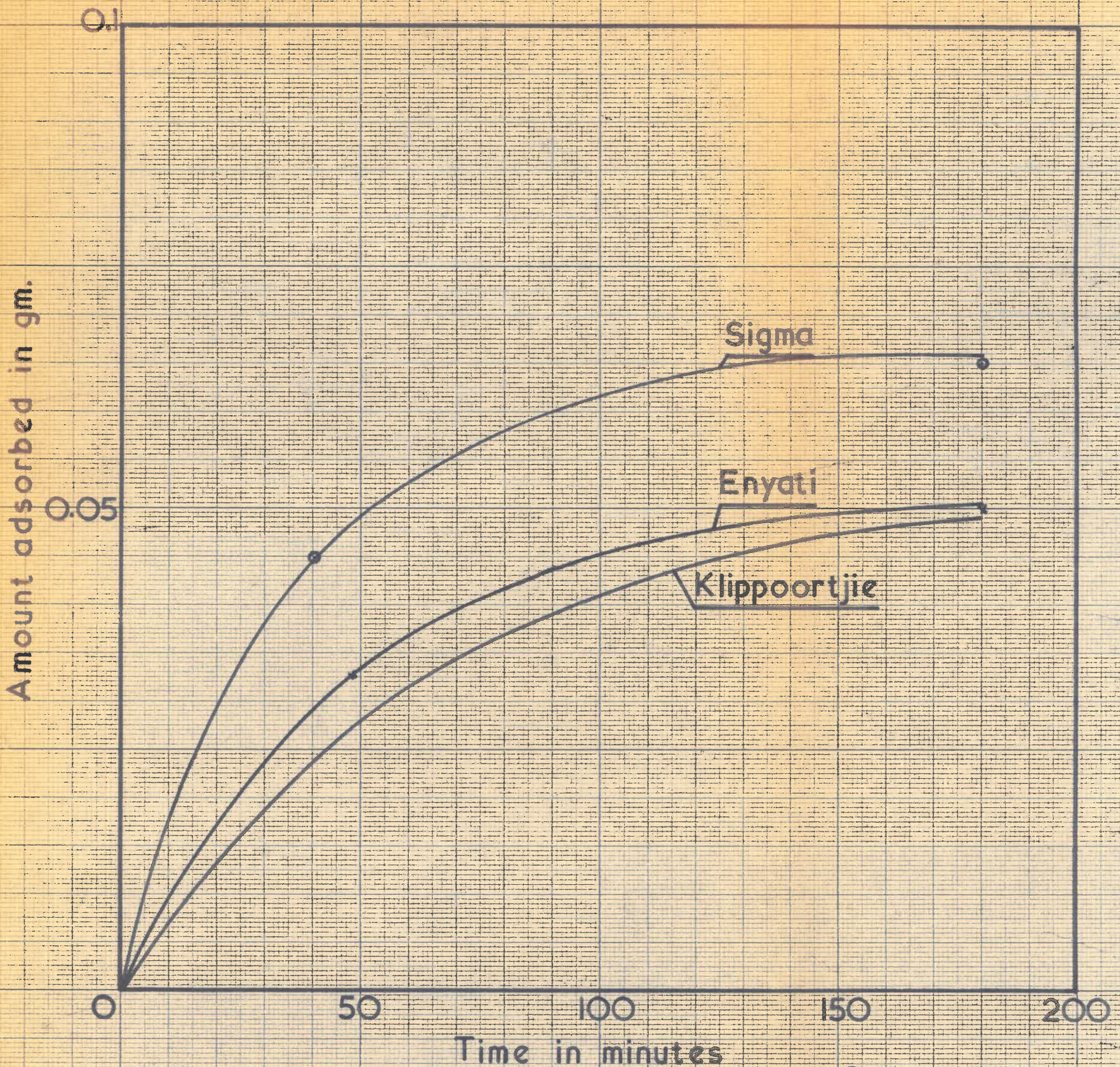-------------

FIG.2   ADSORPTION ISOTHERMS AT 25°C

FIG.4 RATE OF H_2O ADSORPTION AT 25°C AND 2·5cm. Hg VAPOUR PRESSURE