

DIFFUSION AND SORPTION
IN POLYMER-ZEOLITE COMPOSITES.

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Abstract

The sorption of fourteen polymerizable organic substances by a variety of zeolites and other solid catalysts has been studied with a view to establishing which types of substance undergo polymerization within the zeolitic structure.

The techniques used in the study included chemical analysis, thermogravimetric analysis, sorption of argon and sorption and permeation of water.

Ethyl and n-butyl vinyl ethers and α -methyl styrene formed large quantities of polymeric substances over the catalysts HY, H mordenite and kaolinite although the monomers, which normally polymerize by a cationic mechanism, did form significant amounts of polymer within the cavities of other zeolites.

In every case, the organic substances tested formed residues within the zeolites which were difficult to remove.

Investigation showed that, in those zeolite-monomer systems which were most thoroughly studied, adhesion between the phases did not survive exposure to water. It is significant that organic groups remained within the zeolitic cavities even after treatment with water and evacuation.

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CHAPTER 1

INTRODUCTION

1.1 Statement of objectives

One object of this work was to study some of the properties of various molecular sieve zeolites and other crystalline alumino-silicates with particular reference to their ability to catalyse certain polymerization reactions. If polymerization could be effected within the zeolitic micropores and polymer chains could continue into external bulk polymer, then a means would have been found of bonding filler and polymer-very strongly in a composite material.

Good adhesion between a continuous phase polymer and its dispersed filler could in turn enhance such properties of the composite as rigidity, hardness, tensile strength, thermal conductivity and the ability to resist sudden stress. Whether or not these properties remain unchanged over prolonged periods would depend upon the strength and permanence of the adhesion between the phases of the composite. The ability of adhesion between polymer and a hydrophilic filler to withstand adverse conditions such as contact with a high concentration of water would be one useful measure of the stability of the composite.

Zeolites seem to be particularly suitable for the work since they contain uniform networks of pores and cavities^(1,2) in which polymer chains could be anchored. They also possess considerable catalytic activity⁽³⁻⁶⁾ and may be modified where necessary for particular types of reaction by exchange or by removal of their cations.

The preparation of compression moulded composites of zeolites with inert thermoplastic resins for use as cation permselective membranes has led to the conclusion that the electrical properties of such composite membranes are largely determined and rendered less satisfactory by the presence of salt solution imbibed from the external solution into pores between crystals and the inert resin⁽⁷⁾. This difficulty may be removed if the adhesion between the two phases was unaltered in the presence of salt solutions.

The permanence and stability of polymer-filler bonding has been investigated in this work by sorption and permeation studies. Sorption isotherms of certain monomers on zeolites gives some information about the nature of the sorbed monomer, while subsequent sorption of an inert gas would enable an estimation of the presence of gaps between sorbent and the sorbed and possibly polymerized phase to be made. Complementary permeation measurements have been made to determine the differences in diffusion behaviour caused by the inclusion of a filler in homopolymer membranes.

1.2 The nature of zeolites with particular reference to their catalytic activity.

1.2.1 The structure of the zeolites used in this work.

Molecular sieve zeolites are crystalline aluminosilicates which contain narrow, uniform channel systems which, under atmospheric conditions, would be completely full of water. Certain of the zeolites have structures which are sufficiently rigid to remain stable after the removal of this zeolitic water

and can then selectively adsorb a variety of sorbates or guest molecules.

Some forty naturally occurring zeolite minerals, together with several purely synthetic varieties are known. All are composed of SiO_4 and AlO_4 tetrahedra arranged in three-dimensional patterns to give large internal surfaces accessible by external surface entry pores⁽¹⁾.

The simplest group of zeolites, the sodalite hydrates, have cubic symmetry and are based on the regular truncated octahedral sodalite unit. This 14-hedron with its six square faces and eight hexagonal faces is itself composed of twelve aluminium and twelve silicon ions at vertices of the solid in positions adjacent to three silicon-ion-occupied vertices. Thirty-six oxygen ions midway along each edge complete the cage. Sodalite-hydrate consists of these 14-hedra stacked in 8-fold co-ordination by sharing both square and hexagonal faces. Each unit encloses a cavity of $6.6\text{\AA}^*$ internal diameter which is accessible to small polar molecules such as water and ammonia by diffusion through the six-ring apertures⁽⁸⁾.

Another zeolite in which sodalite cages occur is Linde Sieve type A. The sodalite units are linked together through their square faces by four bridging oxygen ions⁽⁹⁾. This arrangement provides a large internal cavity, the 26-hedral α -cage, with a diameter of about $11\text{\AA}$. Each α -cage gives access, through six eight-ring apertures of about $4\text{\AA}$ diameter,

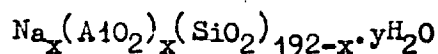
* See Appendix B

to six identical 26-hedra so that the framework contains three mutually perpendicular sets of intersecting channels. The sodalite cavities, or β -cages, are accessible from the α -cages through distorted, $2\text{\AA}$ diameter six-rings of oxygen. The unit cell of sodium A has the composition $\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$, charge neutrality being maintained by the sodium ions.

Exchange of sodium ions by calcium ions in the type A zeolite increases the effective pore diameter to near $5\text{\AA}$ and this allows n-paraffins but not branched paraffins to be adsorbed.

The mineral faujasite has a framework which can be constructed from sodalite cages linked tetrahedrally through each of four hexagonal faces by six bridging oxygen ions^(10,11) per linkage. Wide 26-hedral cavities, called super-cages, are thereby produced in the structure which are accessible through four 12-ring windows of 8 to $9\text{\AA}$ diameter from adjacent identical cavities. These voids are sufficiently large and accessible to accommodate about five benzene molecules in each⁽¹¹⁾, but the smaller β -cages are available only to small polar molecules.

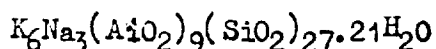
Synthetic near-faujasites are available commercially with a number of different cations and with various silica to alumina mole ratios. The unit cell composition of the sodium form of these materials is



where y has a value close to 250 and where the mole ratio $\frac{\text{SiO}_2}{\text{AlO}_2}$ describes the type of zeolite. Generally, a type X zeolite has a mole ratio of less than 1.5 while a type Y has a higher mole ratio, up to about 3. A higher silica to

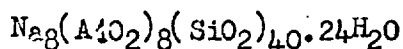
alumina ratio is normally associated with better acid stability but slightly reduces the unit cell parameter and the absolute sorptive capacity of the zeolite.

The synthetic type L zeolite has no naturally occurring relative. It has the approximate unit cell formula of



and a hexagonal structure based on ~~an~~ aluminosilicate ^{similar to the one} framework ~~is~~ found in the chabazite zeolites cancrinite, erionite and offretite⁽¹²⁾. This contains a polyhedral cage formed by five six-membered and six four-membered rings, and each cavity is linked through the planes of its upper and lower six-membered rings to similar cavities thus forming columns in which hexagonal prisms and polyhedra alternate. These columns run parallel to the c-axis and are crosslinked to each of three others by oxygen bridges which form part of twelve-membered rings. These rings, which lie in planes normal to the c-axis and have free diameters of between 7 and 8Å, circumscribe channels parallel to the c axis which have a maximum free diameter of 13Å.

The silica rich, naturally occurring zeolite mordenite has a sodium exchanged form of unit cell formula



The aluminosilicate network consists of characteristic chains formed by configurations of linked tetrahedra. Each chain is linked laterally to other chains so as to produce a system of large channels parallel to the c-axis and interconnected by smaller channels. These channels are circumscribed by rings of

12 tetrahedra. The rings have major and minor free diameters of 6.95 and 5.84 Å. These large channels are lined by smaller side pockets each of which, halfway towards the neighbouring large channels, branches through two distorted 8-membered rings of 2.8 Å minimum free diameter into two smaller side pockets opening into the next main channel. The inclusion of cations within these side pockets means that each main channel is effectively isolated from its neighbours.

Although the main channels of mordenite are of 6.6 Å free diameter it has been found that the natural mineral does not readily sorb molecules whose critical dimensions exceed 4 Å⁽¹⁴⁾. This is probably due to the presence of foreign material or to the location of cations in the main channels^(15,16). Mordenite which exhibits sorptive properties of a zeolite possessing 12-membered ring channels has been synthesized and has been called large-port mordenite to distinguish it from the conventional small-port variety⁽¹⁷⁾.

1.2.2 Catalytic activity of zeolites

If catalysis is assumed to occur within the high surface area intracrystalline volumes then clearly both the zeolitic entry pores and the channel-cavity system must be sufficiently open to allow transport of reactant molecules from the bulk phase to the active sites. Certain polymerization and isomerization reactions, however, are thought to take place at the external surface of the zeolite. Such reactions include the polymerization over a calcium A zeolite of propylene⁽¹⁸⁾, isobutene⁽¹⁹⁾, vinyl chloride⁽²⁰⁾ and styrene⁽²¹⁾. The molecular

dimensions of these monomers are too great to allow them entry into the small pores of a type A zeolite.

The type of polymerization reaction which it was desired to explore in this work is one in which polymer chains extend from within the internal volume of a zeolite to the external polymer matrix. Systems of monomers and zeolites have therefore been examined in which the monomer is readily sorbed within the zeolite so has some likelihood of polymerizing inside as well as outside the porous crystals.

Catalysis within the near faujasite zeolites is influenced by cation type^(5,6,8), cation location in the lattice⁽⁸⁾, zeolitic silica to alumina ratio⁽⁸⁾, and the presence of proton donors^(8,21). A variety of energy terms contribute to the physical bond in zeolitic structures and these, together with the pore geometry, determine selectivity in adsorption⁽²²⁾. These interactions are

1	dispersion energy	ϕ_D
2	close range repulsion energy	ϕ_R
3	polarization energy	ϕ_P
4	field-dipole energy	$\phi_{F\mu}$
5	field gradient-quadrupole energy	ϕ_{Fq}
6	dipole-dipole energy	$\phi_{\mu\mu}$
7	dipole-quadrupole energy	$\phi_{\mu q}$
8	quadrupole-quadrupole energy	ϕ_{qq}

It is of interest, therefore, to discuss not only those factors which affect catalytic activity but also those which determine adsorption selectivity. $\phi_D, \phi_R, \phi_P, \phi_{F\mu}$ and ϕ_{Fq} are the most

important contributions and will be described briefly.

Dispersion forces arise from the interaction of instantaneous dipoles, quadrupoles etc. in adjacent molecules and their energy of interaction may be described by⁽²³⁾,

$$\phi_D = - \sum \left(\frac{A_1}{r^6} + \frac{A_2 + A_3}{r^8} + \frac{A_4}{r^{10}} \right)$$

(i) (ii) (iii)

where the terms (i) (ii) and (iii) are in the order of decreasing magnitude and the summation is over all pairs of interacting centres, one of which is the sorbed molecule and r is the centre to centre distance of a pair. These terms can be assigned to the following:

- (i) is due to fluctuation giving dipole-dipole coupling
- (ii) is due to fluctuation giving dipole-quadrupole coupling
- (iii) is due to fluctuation giving quadrupole-quadrupole coupling.

Terms (ii) and (iii) can contribute as much as 10% and ~~10~~ respectively to the dispersion energy⁽²⁴⁾.

Repulsion forces arise from the overlapping of electron clouds of neighbouring molecules. In terms of Pauli's exculsion principle, electrons become excited to higher energy levels to avoid overlapping with other molecular orbitals having the same quantum numbers. This energy increase accounts for the repulsion. It is usually described empirically by

$$\phi_R = \sum \frac{B}{r^{12}}$$

If it is assumed that dispersion and repulsion energies are

approximately additive and temperature independent, then

$$\phi_D + \phi_R \approx -\sum \frac{A}{r^6} + \sum \frac{B}{r^{12}}$$

where the summation as before is over all possible pairs of interacting centres of which one is the sorbed molecule. At the equilibrium distance, $r = r_0$, $B = \frac{1}{2}Ar_0^6$, and this sum becomes the Lennard-Jones 6, 12 potential

$$\phi_D + \phi_R = -\sum A \left(\frac{1}{r^6} - \frac{r_0^6}{2r^{12}} \right)$$

The value of A can also be determined from the theory of dispersion forces⁽²⁵⁾.

When an atom or molecule is placed in a uniform external electro-static field, F, the electrons and molecules experience a relative displacement, and a dipole is induced of magnitude $\mu_{ind} = \alpha F$ where α is the mean polarisability of the molecule. The energy of the induced dipole in the electric field is

$$\phi_p = \int_0^F \mu_{ind} dF = -\frac{1}{2} \alpha F^2.$$

The potential energy of a dipolar molecule in an electric field may be expressed as

$$\phi_{F\mu} = -\mu F \cos \theta$$

where μ is the dipole moment and θ is the angle which the dipole makes with the direction of the field, F.

The interaction between a linear quadrupole and the field gradient is given by

$$\phi_{FQ} = -\frac{1}{8}Q(3 \cos^2 \theta - 1) \frac{dF}{dX}$$

where Q is the quadrupole moment and $\frac{dF}{dX}$ is the field gradient, and where θ is the angle between the quadrupole axis and the field.

Energetic heterogeneity in the water-sodium faujasite system at low coverage has been attributed to field-dipole interaction⁽²⁶⁾, while the energetic heterogeneity of chabazite towards carbon dioxide, carbon monoxide, nitrogen, oxygen and hydrogen has been explained in terms of field gradient-quadrupole interactions⁽²⁷⁾.

The total interaction of a polarisable molecule, possessing a dipole and a quadrupole moment, with a sorbent which generates a local electric field is given by

$$\phi = \phi_D + \phi_R + \phi_P + \phi_{F\mu} + \phi_{FQ} + \phi_{SP}$$

where ϕ_{SP} is the self potential of the sorbate molecules and represents the molecule-molecule interaction energies in the sorbed phase. Several calculations of these components have been made for gases in zeolites⁽²⁸⁻³⁰⁾.

The variety and proportions of sorbates admitted to the intracrystalline cavity system are controlled by the free dimensions of the entry windows. Zeolites incorporating 4-, 5-, 6-, 8-, 10- and 12-membered oxygen rings into the lattice structure are known⁽¹⁾ but even small molecules cannot diffuse through 4- and 5- rings and an appreciable activation energy is involved in the passage of water or ammonia through the 6-rings of sodalite⁽³¹⁾. Ease of penetration increases rapidly thereafter with ring size.

Not all rings containing the same number of atoms are equivalent in size. Type A zeolite, chabazite, erlonite and some other members of the chabazite group all have 8-windows, but the free dimensions of these rings vary with the degree of

nonplanarity⁽¹⁾. Linde A possesses nearly planar 8-rings and can freely admit n-paraffins, but in general structures with 8-rings can exert a wide range of molecular sieving behaviour based only on ring distortion.

Number, valency, size and location of cations in the zeolitic lattice have important effects on the accessibility of intracrystalline cavities through the entry pores. This is dramatically demonstrated in zeolite A where replacement of about 40% of the sodium ions by calcium results in an increase in the effective pore diameter from about 4Å to about 5Å^(2,9). Marked effects of cation upon diffusion coefficients of various gases in chabazite, mordenite and levynite have also been reported⁽³²⁾, and for low molecular weight hydrocarbons diffusion coefficients about 50% lower in hydrogen mordenite than in sodium mordenite have been observed⁽³³⁾. Since cations may partially obstruct intracrystalline channels it has been suggested that sorption rates might normally be expected to decrease with increasing cation density⁽³⁴⁾.

Silicon-oxygen bonds are slightly shorter than aluminium-oxygen bonds and so a given ring size may decrease slightly with higher silicon content⁽³⁵⁾. Another influence of silica to alumina ratio is that since each lattice AlO_4 unit has a unit negative charge and an associated cationic positive charge, an increase in charge density will result from any decrease in the ratio $SiO_2 : Al_2O_3$.

One other factor of critical importance to adsorption selectivity is the effect of solvation. Zeolite lattices are

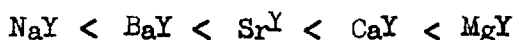
not totally rigid⁽¹⁾ and lattice distortions as well as changes in cation position accompany hydration-dehydration processes^(36,37). Time and temperature of activation will therefore be variables influencing the sorption rates of certain sorbates⁽³⁸⁾. The controlled additions of polar modifiers that are strongly adsorbed and relatively immobile at the temperature of subsequent sorption can act as additional barriers in pore systems⁽¹⁾. The addition of small amounts of water, ammonia or methylamine to zeolites such as chabazite or mordenite results in the variation of diffusion coefficients of ethane or permanent gases by three to four orders of magnitude^(39,40).

As was mentioned earlier, the location of cations in the zeolitic lattice can influence catalytic activity⁽⁸⁾. For example, 48 of the sodium ions in the sodium X unit cell all occupy positions near the centre of the 6-rings at the mouths of the sodalite cages.⁽¹⁰⁾ A more detailed picture has emerged from single crystal X-ray studies on a dehydrated calcium exchanged Y type natural faujasite^(41,42), and three cation sites were described. The S_I sites, of which there are 16 per unit cell, are located in the interior of the hexagonal prisms, positioned between two puckered 6-rings in 12-fold co-ordination to oxygen, here ions are effectively shielded from the surface of the supercage systems. The S_I sites are preferred by calcium ions over the other two sites. The 32 S_{II} sites of each unit cell are found next to the 6-rings in the hexagonal windows between the supercages and sodalite cages. Here each cation has three nearest oxygens because of ring puckering. S_{III} sites are situated

next to the 4-rings in the square faces between super cages and sodalite cages, and are probably populated only in the univalent cation form of the zeolite.

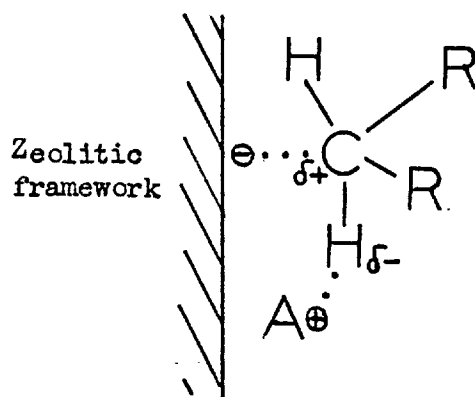
Calculations of the electrostatic field strengths of surface cations near S_{II} and S_{III} sites in an X-type zeolite of $Si_{/Al}$ molar ratio = 1 and in a Y-type zeolite of $Si_{/Al}$ molar ratio = 2 have shown that in both cases, fields were significantly larger nearer S_{III} and S_{II} at a distance of $2\text{\AA}$ from the univalent cation centre provided both sites were occupied^(41,42). The catalytic activity induced near the two sites could therefore be appreciably different.

Fields associated with bivalent cations have been calculated to be greater than those arising with univalent cations^(41,42), and it seems likely that for a given cationic charge the Coulombic fields would become greater as cationic radius decreases. Experimental results consistent with these expectations have been found for the n-hexane isomerization activity of a series of catalysts⁽⁴¹⁾, where the order of reactivity was



Catalytic activity of zeolites may well involve the cations themselves acting as carbonicogenic centres^(41,42). Calculations of the electrostatic fields in zeolitic cavities at distances up to several Angstroms from bivalent cations show that, where these fields are accessible to reactant molecules, the fields are strong enough to induce substantial shifts of bonding electrons of the reactant. As the field increases, polarization of the adsorbate would become more pronounced and

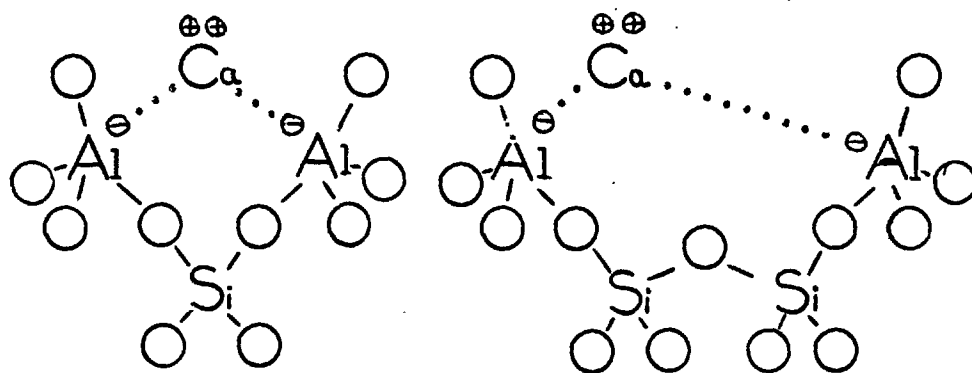
shifts approaching $\overset{\oplus}{C} \overset{\ominus}{H}$ are envisaged.



A carbon atom which is polarized to this degree could then serve as the active centre for carbonium ion reactions. Reactant is serving as the cocatalyst, in effect.

A cation lying on the surface of a super-cage in a faujasite zeolite, such as the one near an S_{II} site, is in relatively low co-ordination with lattice oxygen. In such a position, the field associated with the cation would not be well shielded and would be accessible to guest molecules in the super-cage. The effects of these fields would vary greatly with the Si/Al molar ratio of the zeolite⁽⁶⁾, however, and may be visualized structurally for a divalent cation exchanged zeolite. An increase in the molar ratio from 1 to 2 in the sodium form decreases the cation density and therefore increases the distance between cation sites. It does not, however, significantly alter the

bonding or location of the cation with respect to the AlO_4 tetrahedra. In the case of a divalent cation exchanged zeolite, such an increase on the Si/Al molar ratio would move the cation position from a site essentially equidistant between two AlO_4 tetrahedra to an asymmetric position close to one of the tetrahedra.



Si/Al molar ratio = 1

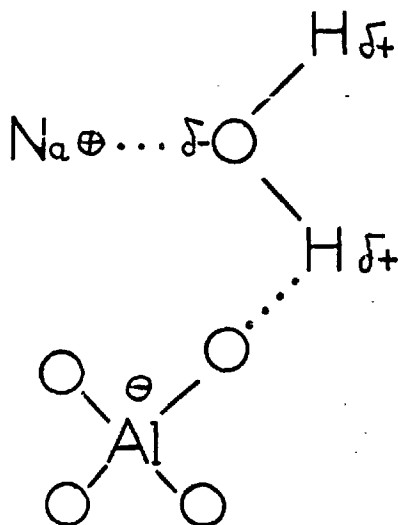
Si/Al molar ratio = 2

A polarization would exist, in the case of the asymmetrically positioned cation ion, between the unscreened cationic charge and the unsatisfied, more distant lattice AlO_4 negative charge. Calculations of the difference in the electrostatic field magnitude at points $2\text{\AA}$ toward the centre of a $10\text{\AA}$ pore from a calcium ion occupying an S_{II} site in calcium X and Y have revealed a value of $0.7 \text{ volt/\AA}$ between the stronger Y zeolite ($\text{Si}/\text{Al} = 2$) and the weaker X zeolite ($\text{Si}/\text{Al} = 1$). Experimentally, the n-hexane isomerization activity of MgX was found to be less than the activity of $\text{MgY}^{(41)}$.

Water plays an important role in the catalytic behaviour of both group 1⁽⁴³⁾ and group 2^(44,45) ion exchanged faujasites. Maximum activity of a calcium X catalyst in the dehydration of tert-butanol was observed when the number of water molecules was equal to the number of zeolitic calcium ions^(44,45). Water would accumulate during the dehydration of an alcohol⁽⁴⁴⁻⁴⁶⁾, and because of its high dielectric constant can effectively screen the cation fields and thus modify the magnitudes of the fields accessible to reactants. A fully hydrated zeolite would be catalytically inactive.

It was mentioned earlier that reactant diffusivities and cation positions are, in some zeolites, dependent on the degree of hydration.

The very high isosteric heat of water adsorption in zeolites, approaching 130 kJ mole^{-1} at low coverage⁽²⁶⁾, reflects the magnitudes of the electrostatic fields available for interaction with sorbates within the zeolites. Infra-red spectroscopic studies have demonstrated that faujasites containing alkali and alkaline earth cations retain hydroxyl groups on their surface even after evacuation at 450°C ^(47,48). O-H stretching vibrations in sodium X-water systems suggest that isolated water molecules are adsorbed simultaneously by an ion-dipole interaction with the exchangeable cation and by hydrogen bonding of one of the water hydrogen atoms to a lattice oxygen⁽⁴⁷⁾.

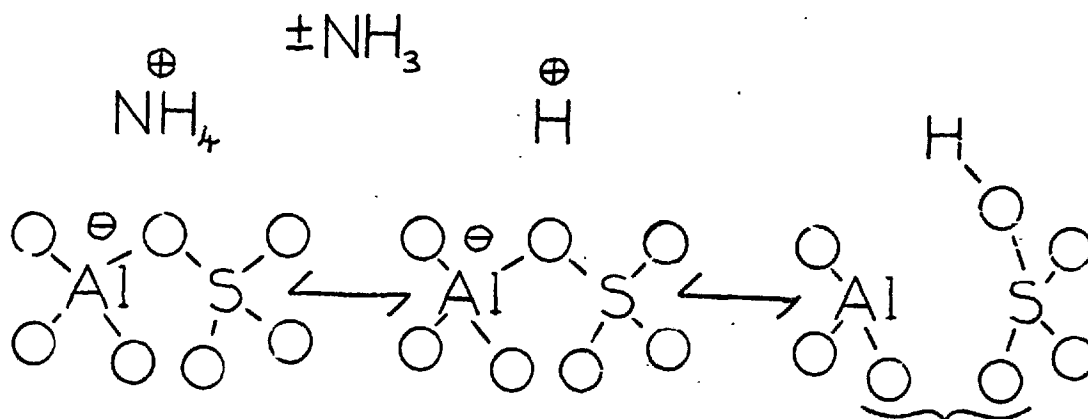


The polarizing action of the cationic fields in either sodium or calcium X zeolites might render a water hydrogen atom or a lattice hydroxyl group hydrogen atom protonic. Certainly, if the cationic fields are powerful enough to polarize hydrocarbon C-H bonds then the creation of protons from either of the sources mentioned above is a reasonable possibility.

Several protonic forms of zeolites have broad catalytic application and they can, in general, be formed either by direct ion exchange with mineral acids or by thermal decomposition of ammonium exchanged zeolites. Hydrogen mordenite was prepared by contact with dilute mineral acids⁽¹⁷⁾, was acid stable and had high catalytic cracking activity^(49,50), but hydrogen forms of less silicon rich zeolites, prepared in this manner, tend not to be stable upon dehydration at higher temperatures^(6,28). This breakdown was believed to be a consequence of close proximity

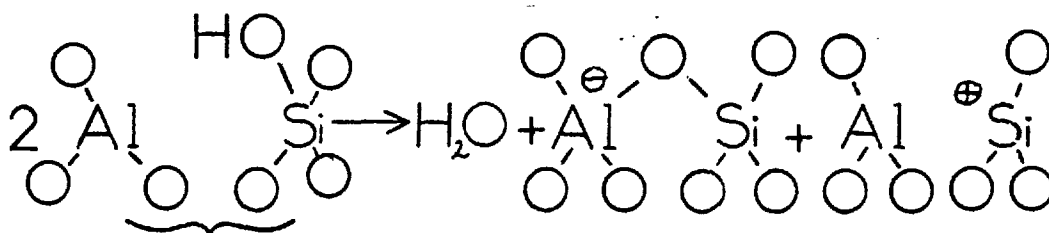
of aluminium atoms which facilitated the rearrangement of the framework.

Decationated mordenite and Y-type faujasites can be formed after replacing sodium ions with ammonium and with subsequent thermal decomposition of the ammonium ions^(51,52). Infra-red studies have contributed significantly to an understanding of these zeolites⁽⁵³⁻⁵⁵⁾, and it has been proposed that protons remaining after the release of ammonia are able to react with lattice oxygen in Si-O-Al bonds to form a 3-coordinate aluminium adjacent to a silanol group:



Thus, a classical Bronsted acid form is proposed as being in equilibrium with the silanol form, and it is probable that proton donation can occur upon the approach of a strong base. Ammonia is the obvious example of this.

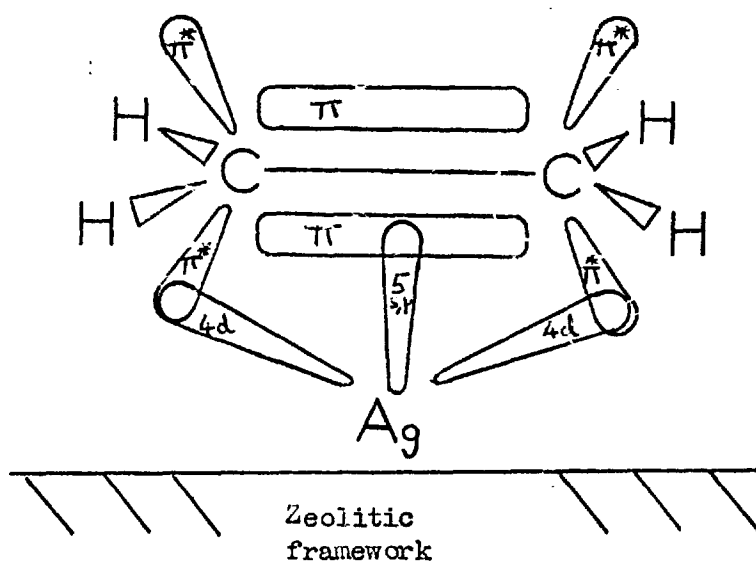
At higher temperatures, the protonic faujasites decompose in a process involving the loss of one mole of water per pair of AlO_4 tetrahedra to form a defect structure^(6,53-57).



Transition metal exchanged and rare-earth exchanged faujasites also exhibit catalytic activity⁽⁸⁾. The trivalent rare-earth cations possess a high charge density⁽⁵⁸⁾, high enough to cause considerable electrostatic fields in the intracrystalline volumes occupied by guest molecules. The effect of such polarizations on adsorbates could be the formation of carbonium ion reaction centres in the manner described for the divalent alkaline earth zeolites, but in the case of the rare-earth zeolites this activity would be more pronounced.

Infra-red studies of ethylene adsorbed by silver X zeolite have shown that specific orbital interactions occur between the sorbent and guest molecules⁽⁴⁸⁾.

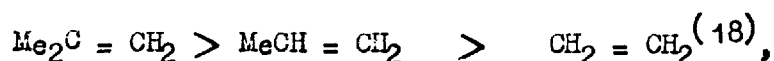
These may be represented as:



1.2.3 Polymerization and related reactions catalysed by zeolites.

At temperatures of around 300°C, nickel exchanged sodium X catalyses the polymerization of ethylene and propylene to predominantly dimeric products in continuous flow systems⁽²¹⁾. After initially high activity, conversion was found to decrease markedly after longer times, deactivation probably resulting from the intracrystalline formation of a viscous oily polymer. This could be removed by solvent extraction or by heating under vacuum at 370°C and catalytic activity restored. After one experiment, aliphatic polymers with major carbon numbers at C₂₁, C₂₂ were found.

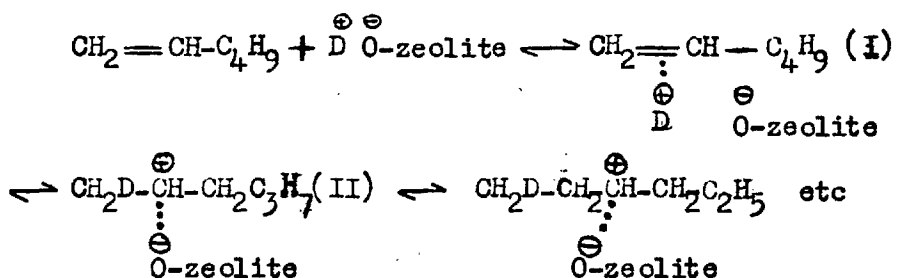
Generally, olefinic polymerization over zeolites has been found to follow the order of activity:



and reactions over hydrogen Y, dehydroxylated Y and rare-earth X zeolites occurred at lower temperatures than over other zeolites⁽⁵⁴⁾. The structure of the branched polymers obtained from polypropylene polymerization over calcium X have been found to be similar to the type reported for conventional acid catalysts such as ortho-phosphoric acid supported on Kieselguhr⁽¹⁸⁾. A carbonium ion mechanism would certainly be consistent with the order of substrate reactivity as well as the preferred zeolite catalysts since an olefinic carbon atom would be more able to support a positive charge if it has a higher electron density such as would be caused by adjacent alkyl group. Clearly the protonic nature of hydrogen zeolites and the high charge density of the cations in rare-earth zeolites would provide

powerful acid catalysts.

A carbonium ion isomerization-polymerization of 1-hexene over a deuterated rare-earth X zeolite has been suggested⁽⁵⁹⁾, and a mechanism consistent with the experimental data is:

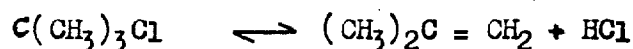


Electrophiles I and II would be closely associated as ion pairs with anionic sites in the zeolite lattice, and the elimination of protons from them would provide 2- and 3-hexene isomers respectively. The zeolite catalyst was dissolved after one 1-hexene isomerization run, and the oily organic extract was found to contain a C_{60} polymer.

The room temperature isomerization and polymerization of 2,3-dimethyl-1-butene and 1-hexene over partially deuterated hydrogen Y zeolites have confirmed that these are carbonium ion type reactions⁽⁶⁰⁾. Infra-red spectra have indicated that pyridine adsorbed on a decationated zeolite preheated to 300°C was present essentially as pyridinium ions⁽²⁰⁾, while if the zeolite was preheated at 560°C, then pyridine bound to Lewis acid sites was present.

The polymerization product formed after the sorption of tert-butyl chloride on alkaline-earth type A zeolites and on mordenite probably results from the formation of butene⁽⁶¹⁾, which subsequently polymerizes. Equilibrium probably exists both in the gas phase as well as in the sorbed phase, between the alkyl halide

and olefin,



A zeolite would rapidly remove hydrogen chloride molecules and shift the equilibrium across to the right. Once olefin had been formed it could extract protons from the zeolite lattice, probably from the sorbed hydrogen chloride, and a monomeric carbonium ion would be formed. A large variety of polymers could result from such a cationic reaction, and indeed several dimers, trimers and tetramers were detected.

Various patents exist for preparing specific butene polymers by room temperature reactions of isobutene over zeolite catalysts⁽⁶²⁻⁶⁴⁾. These polymers would be formed by a carbonium ion mechanism. The ability of dehydrated zeolites to act as proton donors to adsorbed molecules thus yielding carbonium ions has been conclusively demonstrated by their reactions with triphenyl carbinol and other Hammett indicators to give the corresponding coloured carbonium ions^(65,66).

Zeolites are used to catalyse reactions which, on current evidence, do not take place by carbonium ion mechanisms. For example, the acidic catalysis of toluene to benzene and methane promotes undesired transalkylation conversions whereas alkali metal zeolites act to produce good yields of these hydrocarbons⁽⁶⁷⁾. It is supposed that this reaction over the zeolites is primarily a radical-type, and requires a catalyst of high surface area but low acidity. Support is lent to this theory by the results of electron spin resonance investigations of various sorbed zeolites. 2-Pentene and 1-octene, for example, yield radicals

over rare-earth Y zeolites⁽⁶⁴⁾ and N_2F_4 yields NF_2 radicals over calcium A and sodium X zeolites⁽⁶⁹⁾. Aromatic radical cations are formed when various compounds are sorbed by dehydrated Y⁽⁵⁷⁾, and by calcium and rare-earth faujasites⁽⁶⁸⁾. Zeolites have been found to be useful as a convenient storage and isolation medium of free radical species such as NF_2 ⁽⁶⁹⁾ and NO_2 ⁽⁷⁰⁾.

The loading of zeolites with alkali metals has provided catalysts that have double bond isomerization activity but very little accompanying skeletal isomerization⁽⁸⁾. Sodium X loaded with 10.4% by weight of sodium has showed a 94% conversion of 1-pentene to 2-pentene at room temperature and also a 38% conversion of 1,3-cyclohexadiene at 100°C to a mixture of 1, 4-cyclohexadiene and benzene. However, only a rather narrow range of sodium loadings was found to be effective.

1.3 The nature of polymerization reactions.

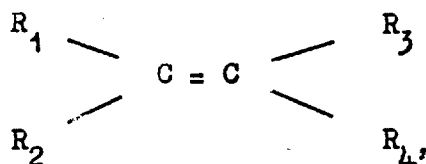
Although the name polymer could be applied to low molecular weight products containing more than two identical repeat units, perhaps a more general definition should refer to substances of sufficiently high molecular weight to ensure that their properties have become reproducible. Deviations from this principle should allow the name to be used to describe products formed by novel reactions or for unconventional purposes where these products may be of any molecular weight and may contain any number of repeat units.

The study of polymerization reactions in the internal surfaces of zeolites gives limited opportunity for the determination either of molecular weight or for the characterization of physical and

chemical properties. The words polymer and polymerization are therefore used here with a less rigorous definition in mind.

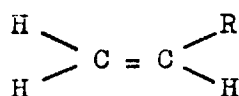
Of the many different polymerization reactions which have been investigated, it is possible to group at least some by type. Examples of polymerization reactions by polycondensation, hydrogen transfer, addition of unsaturated monomers, ring opening, crosslinking of resins and several other types of mechanism have recently been extensively reviewed⁽⁷¹⁾. This study has, in general, involved only polymerization by the addition of unsaturated monomers.

The simplest examples of unsaturated monomer addition reactions are those involving ethylenic monomers,



where R is hydrogen or some other group. There are, however, very few tetra substituted monomers which give high polymers, but tetrafluoroethylene and chlorotrifluoroethylene are important exceptions to this rule. In general, the largest group of polymerizable ethylenic compounds are the monosubstituted ones in which $R_1 = R_2 = R_3 = \text{hydrogen}$. Several monomers in which $R_1 = R_2 = H$ polymerize readily and a few in which $R_1 = R_3 = H$ are also reactive.

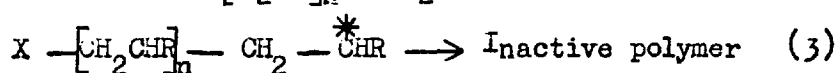
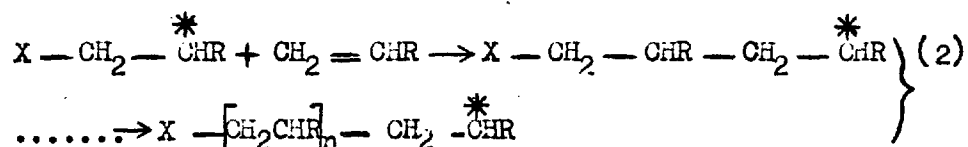
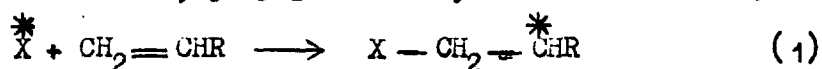
Vinyl compounds,



undergo polymerization by a number of postulated mechanisms

depending on such factors as the nature of group R, the conditions of the reaction (such as whether it is in the vapour phase or in solution and so on), and very importantly the means by which polymerization is induced. More will be said later about these considerations, but at this stage a little should be mentioned about the basic steps of general vinyl polymerization reactions.

Three basic steps are common to any ethylenic polymerization, initiation (1), propagation (2), and termination (3).



The nature of the active centre $*$ is determined by the method of initiation and may be a free-radical^(72,73), a cation^(74,75), an anion⁽⁷⁶⁾ or it may be a centre for co-ordination with the catalyst⁽⁷⁷⁻⁷⁹⁾.

Initiators are compounds which join particular monomer molecules and the growth of the polymer is then independent of the initiating species, while a catalyst often starts the growth of many chains and takes part in the addition of each monomer. Practically, however, the terms have been used interchangeably, although generally free-radical and anionic processes are said to use initiators while cationic and co-ordination reactions involve the use of catalysts. More will be said on this subject in the next section.

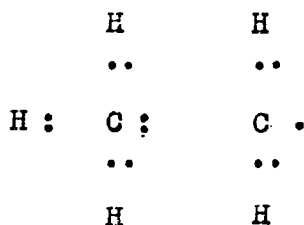
1.3.1 Survey of literature concerning the polymerization of unsaturated monomers.

The considerable number of polymerizable unsaturated monomers is bound to restrict any investigation of such compounds. For this reason, only those substances which seemed to offer scope in this study of polymerization reactions in zeolites are mentioned here.

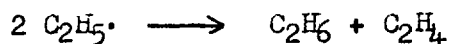
Reactions will be dealt with in order of the type of mechanism presumed to be involved.

1.3.2 Free-radical polymerization

A free-radical is an organic fragment which possesses an odd or unshared electron. An ethyl radical could be represented as

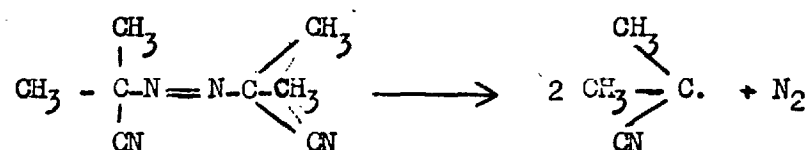


and whereas the usual tetrahedral configuration of bond angles is maintained in the first carbon atom, the second carbon, containing the unpaired electron, has all its substituents in a coplanar configuration. These fragments are highly reactive with most organic molecules, and in the absence of substrates the radicals destroy themselves by disproportionation and to a much lesser extent by combination⁽⁷²⁾:

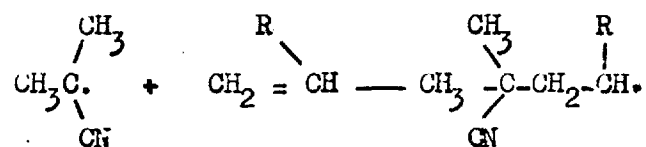


Other radicals, such as the triphenyl methyl radical, are sufficiently resonance stabilized to exist in equilibrium with their combination product, in this case hexaphenylethane⁽⁸⁰⁾. Nitro group stabilized radicals exist almost entirely in the radical form. Such stable radicals as these are poor initiators of vinyl polymerization, whereas unstabilized radicals such as the ethyl radical, are very effective initiators. The stable radicals do have an important use, however, as they are effective scavengers of radicals and have been used for counting radicals by observation of the disappearance of characteristic colours caused by their unpaired electrons⁽⁸¹⁾.

Self-initiation of certain monomers is thought possible⁽⁷²⁾, but generally the addition of free-radical producing compounds is more practical. A commonly used catalyst of this kind is azodiisobutyronitrile which yields reactive dimethylcyan-carbinyl radicals,



Fragments such as this are able to assist a variety of monomers to form a new radical with a net gain in resonance stabilization,



The polymerization continues until the supply of monomer ceases when chain termination occurs by either disproportionation or coupling.

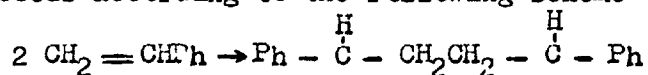
Most commercial polymers have to be of controlled molecular

weight and require the inclusion of various agents such as stabilizers, plasticizers, slip and antiblock additives. Accordingly, extensive use is made of the ability of polymer radicals to undergo chain transfer processes.

Polymer radicals may transfer intermolecularly or intramolecularly with existing chains at active sites to yield long-chain or short-chain branching respectively.

Thermal polymerization of vinyl monomers occurs by radical mechanism and such reactions are inhibited by the presence of known radical scavengers. Benzoquinone, for example, effectively prolongs the induction period in the thermal polymerization of styrene but once this induction period is over, the polymerization as measured by rise in relative viscosity, is the same in cases where the scavenger was absent as in cases where it was present in various concentrations⁽⁸²⁾.

Methyl methacrylate may also be thermally polymerized in a reproducible manner if scrupulous care is taken in the removal of any inhibitor⁽⁸³⁾, but it polymerizes at an observed rate of only about 1% of that of styrene under similar conditions. The rate of thermal polymerization of styrene itself is quite low, about 0.1% per hour at 60°C, and it is thought that the reaction proceeds according to the following scheme^(72,84):



At room temperature, thermal polymerization of styrene may require months or years. The temperature for thermal polymerization has to be chosen with care since, although lower

temperature reactions require much time, they produce a product of far higher molecular weight. One method employs a temperature of 125°C ⁽⁸⁵⁾ for the reaction under which conditions a 90% yield of polymer is obtained after approximately 24 hours, the molecular weight of which is about 150,000.

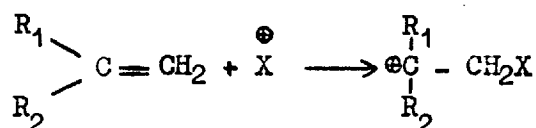
Acrylonitrile polymerization is too exothermic to make bulk polymerization satisfactory, and consequently a means of dispersing the reaction heat has to be employed. Solution, suspension and emulsion techniques have been successfully employed⁽⁷¹⁾.

Of the 1, 1-disubstituted ethylenes, perhaps the most important is methyl methacrylate and since it will polymerize readily to a very clear, colourless polymer it has been used extensively in the work under discussion. It may be safely bulk polymerized in situ at 40°C and in the presence of about 0.1% or less of benzoyl peroxide will yield the clear product in about 24 hours.

1.3.3 Cationic polymerization.

The ability of many zeolites to catalyse carbonium ion reactions suggests that these catalysts may be equally suited to promoting polymerization reactions via a cationic mechanism.

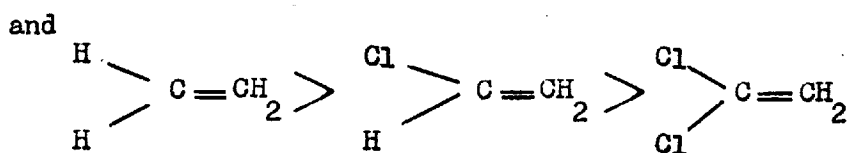
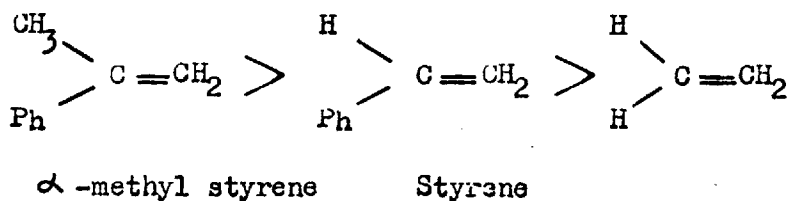
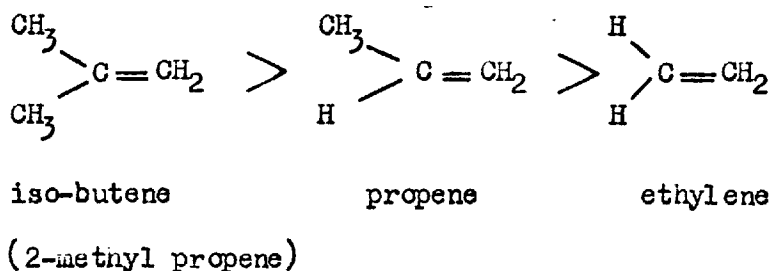
Polar or heterolytic splitting of the double bond of a vinyl derivative by the action of electron accepting catalyst species is the necessary process of cationic polymerization. The olefin molecule acts as an electron donor, or base, and after interaction with the catalyst it becomes the carrier of the positive charge.



The formation of the carbonium ion is followed by a series of additions of the monomer leading to the formation of a macro-ion, which can be stabilized by a complicated process of splitting off a positive charge. This results in the formation of a new active centre which can produce another initiating carbonium ion⁽⁸⁶⁾. The regeneration of active species, together with the impossibility of the mutual recombination of two growing chains of identical charge, makes this type of reaction very different from the radical polymerization discussed earlier.

Among other differences between cationic and radical polymerizations, the former generally proceed rapidly even at low temperatures⁽⁸⁷⁾, have a lower activation energy, and are not slowed down by the usual radical inhibitors. They are often sensitive, however, even to trace quantities of polar substances of basic character which markedly affect the reaction rate and the molecular weight of the polymer produced⁽⁷⁴⁾.

Monomer molecules act as electron donors throughout the course of cationic reactions and so a higher polymerization activity is displayed by those vinyl derivatives which have a greater electron density at the double bond. Such monomers are those having electropositive, or electron repelling, substituents. Conversely, ethylene monomers with electro-negative substituents have a reduced electron density at the double bond and a lessened cationic reactivity.

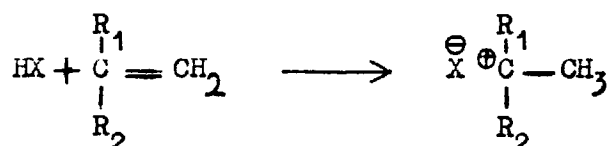


There are, at the moment, about a hundred vinyl monomers which have been found to polymerize by cationic catalysis⁽⁸⁸⁾. Typical of these are isobutene⁽⁸⁹⁾, styrene⁽⁹⁰⁾, α -methylstyrene⁽⁹¹⁾, vinyl ethers⁽⁹²⁾ and N-vinyl carbazole⁽⁹³⁾. Other compounds containing double-bonds which polymerize by similar means are acenaphthylene⁽⁹⁴⁾, benzofuran⁽⁹⁵⁾ and phenyl vinylene carbonate⁽⁹⁶⁾. Certain other types of compound which also undergo cationic polymerization reactions will be considered later.

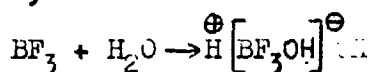
Ethylene itself has very low cationic reactivity. For this reason it is used as an inert solvent for the powerfully exothermic cationic polymerization of isobutene at -103°C ⁽⁹⁷⁾. At higher temperatures ethylene can undergo polymerization but it is no longer a case of the simple addition of monomer to caronium ion but a more complex process⁽⁹⁸⁾. In fact ethylene

polymerizes over zeolites of the following types : hydrogen Y⁽⁵⁴⁾, dehydroxylated Y⁽⁹⁹⁾, rare earth X⁽⁵⁹⁾, and nickel X⁽²¹⁾. All these reactions were, however, at temperatures near to or in excess of 100°C.

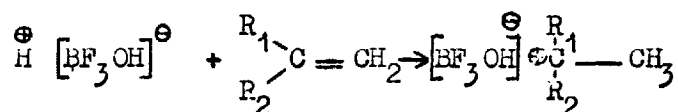
In the relatively simple case monomer protonization involves Bronsted acids,



The aprotic Lewis acids so characteristic of this type of polymerization are unable, however, to transfer protons and their activity depends upon the presence of an ionizable third component, called the cocatalyst. A typical catalyst-cocatalyst system is boron trifluoride together with a trace quantity of water,



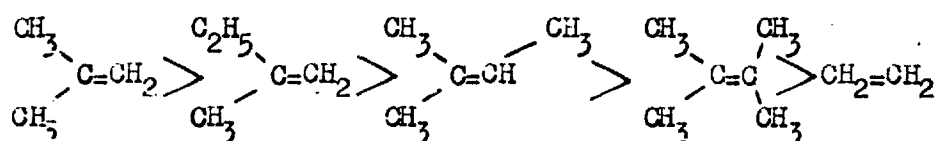
which may then take part in the polymerization reaction,



These carbonium ions are far less stable than the corresponding radicals⁽¹⁰⁰⁾ and can recombine readily with their counterion, isomerize easily and undergo rearrangements to form more stable structures. A result of this last ability is that a polymer can possess a structure independent of the monomeric unit from which it was formed⁽¹⁰¹⁾.

The difficult formation and easy disappearance of carbonium ions results in the failure of stationary states to establish themselves in a number of reactions. For this reason it has not been possible to set up a generally valid reaction scheme comprising a sequence of elementary reactions.

Steric effects, as well as monomer polarity and basicity, influence the mechanism of cationic polymerization reactions. Two trends describe the reactivity of alkyl-substituted olefins. Firstly reactivity decreases with increasing monomer molecular weight and secondly olefins which are unsymmetrically substituted about the double bond are more effective than unsubstituted or symmetrically substituted olefins. For example, the following substituted ethylenes are placed in order of decreasing cationic polymerization reactivity

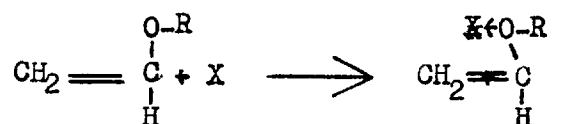


Steric hindrance is probably responsible for the measured heat of reaction, 50.4 KJ/mole, being well below the calculated value, 89.9 KJ/mole, for isobutene⁽¹⁰²⁾. It is interesting to note that the steric hindrance of the benzene ring in styrene or α -methylstyrene is of the same order as that caused by a methyl group which is far less bulky. This is accounted for by the fact that the aromatic ring, itself planar, lies in the same plane as the substituents of the ethylenic carbon atom. Interference is reduced because of this two-dimensional configuration

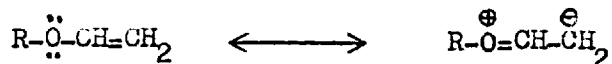
of atoms. The presence of two aromatic rings on the same carbon atom is, however, sufficient to render polymerization beyond the dimer impossible.

The basicity of styrene derivatives is determined by the aromatic substituent, not by a higher electron density at the olefinic double bond⁽¹⁰³⁾. Lewis acids are able to form weak complexes with the benzene nucleus and even benzene itself forms similar complexes. In the absence of any cocatalyst species polymerization is not, however, induced.

Vinyl ethers, or alkoxy-substituted olefins, can form complexes with aprotic acids through a dative bond⁽¹⁰⁴⁾,



The basicity of these compounds is due to the considerable electron pressure on the double bond exerted by the alkoxy group,

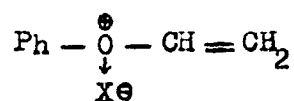


This terminal $\overset{\ominus}{\text{CH}}_2$ group is rendered increasingly nucleophilic as the mesomeric effect of the alkyl group R is raised. Isopropyl vinyl ether would therefore make the terminal group powerfully nucleophilic with the result that reaction with an electrophile yields the structure



which is not capable of initiating a polymer reaction⁽¹⁰⁵⁾. On the other hand, a phenyl group or even a methyl group in the R

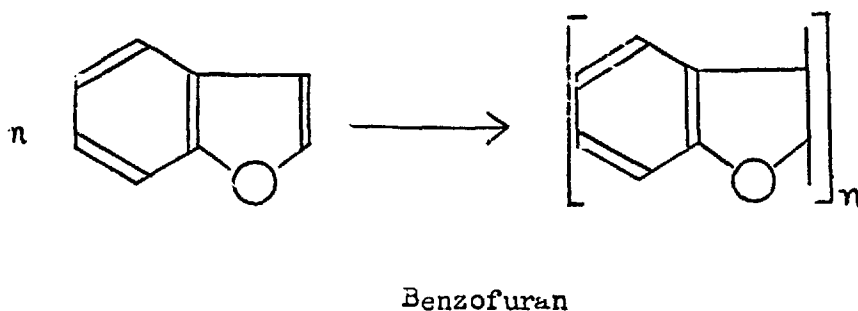
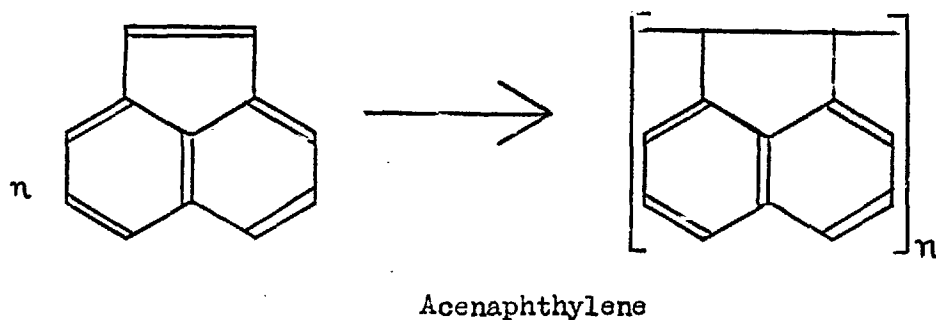
position would have the effect of allowing the complex



to be formed which would permit polymerization to occur.

In the presence of some sort of cocatalyst, vinyl ethers are extremely reactive and at low temperatures yield polymers of high molecular weight, which are, with few exceptions such as in very quick reactions, linear⁽¹⁰⁶⁾.

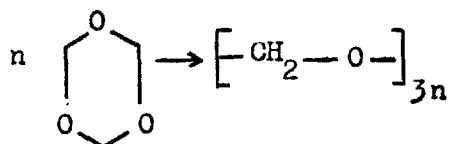
Two compounds which undergo cationically induced polymerizations by head-to-tail linking somewhat similar to vinyl polymerizations are acenaphthylene⁽¹⁰⁷⁾ and benzofuran^(108,109). The latter is closely related to the vinyl ethers.



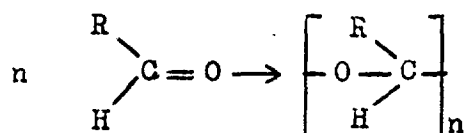
Compounds containing carbon-carbon double bonds are not the only unsaturated monomers able to polymerize by carbonium ion

mechanisms. An important group of monomers are those containing a polymerizable carbonyl group.

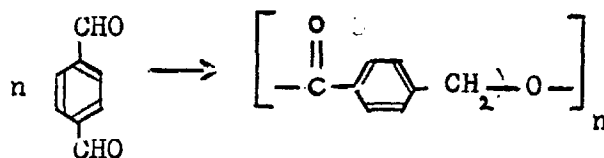
Trioxane will polymerize over a variety of Friedel-Craft type catalysts to a high molecular weight polyacetal⁽¹¹⁰⁾.



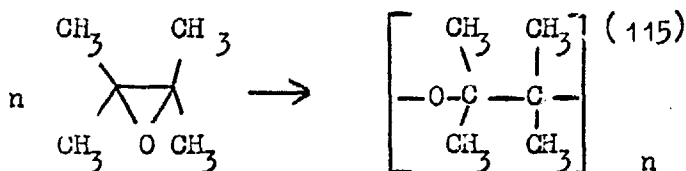
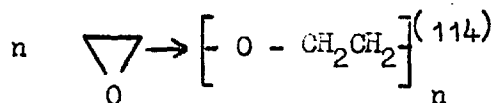
Formaldehyde yields a similar product after cation polymerization⁽¹¹⁰⁾, as indeed can several other aliphatic aldehydes^(111,112),



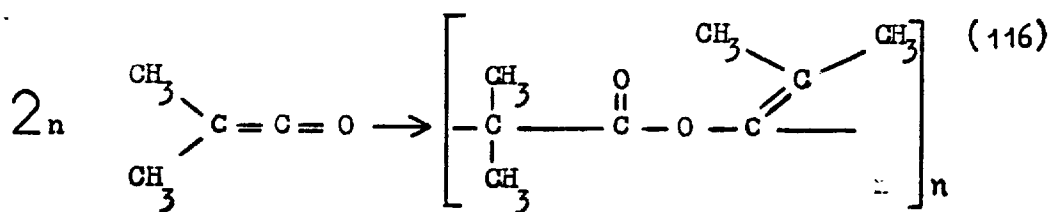
All of these reactions occur at low temperatures. Certain aromatic dialdehydes, such as terephthalaldehyde, can also be converted to high molecular weight polyesters⁽¹¹³⁾,



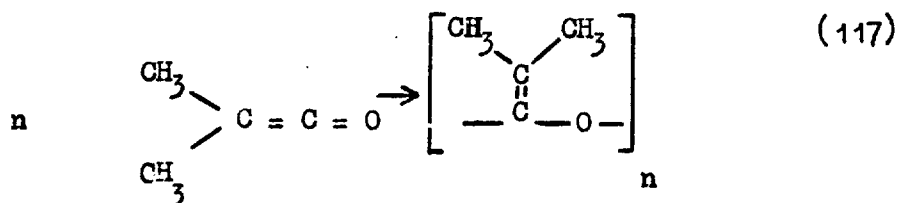
Related monomers which can undergo cationic polymerization reactions include ethylene oxide⁽¹¹⁴⁾, substituted ethylene oxides⁽¹¹⁵⁾ and ketenes^(116,117).



and

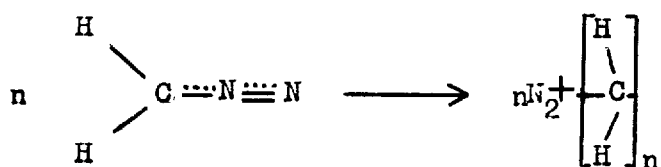


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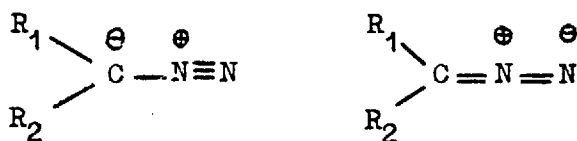


One particularly interesting group of compounds which undergo polymerization to high molecular weight hydrocarbons are the aliphatic diazo compounds.

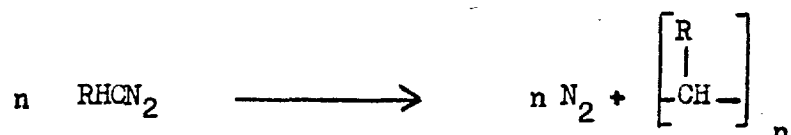
Many years ago it was found that the storage of ethereal solutions of diazomethane for a long period gave a white precipitate of polymethylene⁽¹¹⁸⁾, presumably according to the simplified equation,



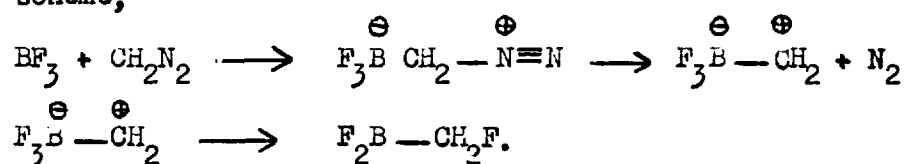
It is, however, better to represent these diazoalkanes by the two canonical forms,



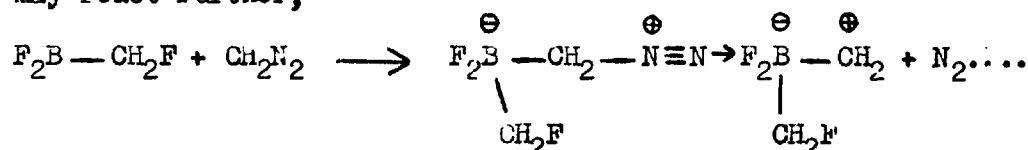
Clearly, the diazoalkanes are able to react as nucleophilic reagents and are thought to be catalysed by a co-ordination mechanism over several boron compounds to yield polyalkanes with a quantitative splitting of nitrogen from the monomer⁽¹¹⁹⁾.



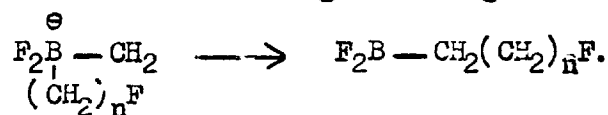
The initiation of the polymerization of diazomethane in the presence of boron trifluoride at low temperature possibly follows the scheme,



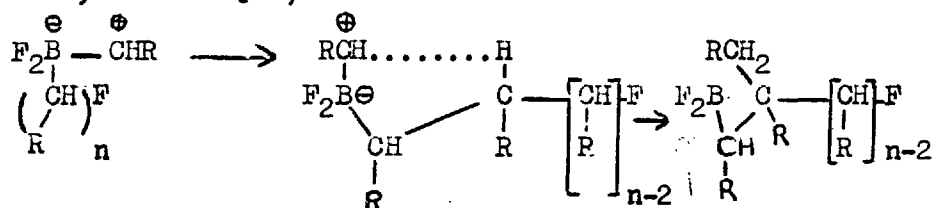
This product has been isolated nearly quantitatively⁽¹²⁰⁾, and may react further,



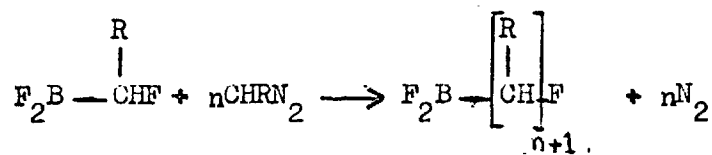
This proposed mechanism assumes that alkyl ions $-(\text{CH}_2)_n^{\oplus}$ will migrate at each rearrangement stage in the reaction⁽¹²¹⁾,



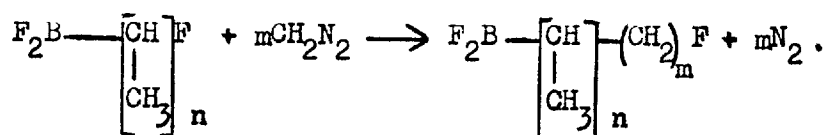
The process can continue until either all the diazomethane has been used up or until chain termination occurs by hydride-ion transfer, for example,



In the absence of this stage, the final polymer molecule will be a compound of similar structure to the initiating molecule,

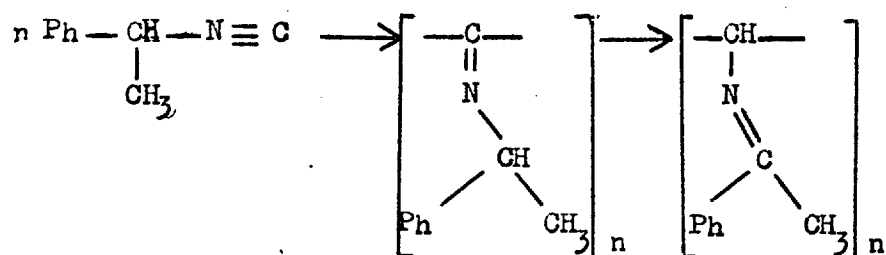


and would behave as an active catalyst towards fresh diazoalkanes. This has been experimentally verified⁽¹²¹⁾. The activity of these polymers is not reduced by either washing or precipitation and provides a convenient method of preparing block co-polymers, for example



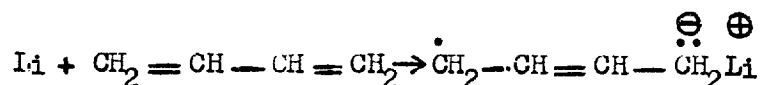
Copper⁽¹²²⁾ and copper salt⁽¹²³⁾ catalysed polymerizations of diazoalkanes are also known.

The polymerization of α -phenylethyl isonitrile over an acidic powdered glass catalyst to give a high polymer may also be of particular interest in a study of polymerization reactions in zeolites⁽¹²⁴⁾.

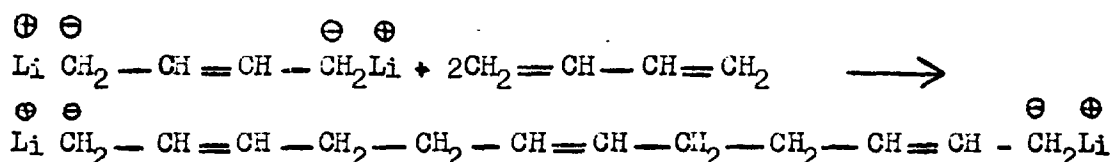


1.3.4 Anionic polymerization

Only quite recently in the history of polymerization studies was the process of an anionic mechanism realised⁽¹²⁵⁾. Among the first reactions to use this type of catalyst was the alkali metal polymerization of 1,3-dienes^(126,127), which involves an electron transfer from metal to the monomer



These radical anions could then combine or, alternatively, a second electron transfer could take place at the other end of the macroion and in either case a dianionic species is formed which is capable of initiating a polymerization reaction



Other monomers which form polymers in the presence of alkali metals are methyl methacrylate, styrene, methyl styrene, acrylonitrile and methacrylonitrile⁽⁷¹⁾. Alternative catalysts to alkali metals may include many ordinary salts of very weak bases, such as Grignard reagents, triphenyl methyl sodium⁽¹²⁸⁾, or even sodium cyanide⁽¹²⁹⁾.

The mechanism of anionic polymerization is not yet understood and nothing will be said on this subject here.

1.4 Summary of Chapter 1.

In this chapter an attempt has been made to cover some of the polymerization reactions which could possibly occur in certain of the considerable variety of molecular sieve zeolites now known.

Hydrogen exchanged zeolites, as well as alkali cation zeolites, and to a great extent rare-earth exchanged zeolites, could well promote polymerization by cationic mechanism.

The radical and anionic mechanisms do not have such obvious parallels in the known reactions of zeolites. However certain possibilities do exist such as radical type reactions in the sodium near faujasites⁽⁶⁷⁾.

CHAPTER 2

An outline to some of the theoretical considerations encountered in this work.

This work has involved the use of a number of different techniques. Consequently only a general introduction to the interpretation of measurements is made here. More details will, where necessary, be included in the discussion of results.

2.1 Zeolite sorbents

When a mole of sorbate is transferred isothermally and reversibly from a gas phase of standard pressure, p_0 , into an infinite amount of sorbate-sorbent mixture the change in chemical potential, $\Delta\mu$, is

$$-\Delta\mu = RT \ln \frac{p_0}{p}$$

where p is the sorbate-sorbent equilibrium pressure. Values of $-\Delta\mu$ are a measure of the affinity of adsorption and can be directly calculated from adsorption isotherms. Such estimates of the affinity of adsorption are of practical importance as they enable the selectivity of a sorbent towards different sorbates to be determined.

If isotherms are determined for the sorbate-sorbent systems at a number of temperatures, it is possible to evaluate another very important thermodynamic characteristic, namely the isosteric heat, $q_{st}^{(130)}$, from the Clausius-Clapeyron equation. For a vapour which obeys the perfect gas laws, this equation has the form:

$$\left(\frac{\partial \ln p}{\partial T} \right)_a = \frac{\tilde{H}_g - \bar{H}_{as}}{RT^2} = \frac{-\Delta \bar{H}_{as}}{RT^2} = \frac{q_{st}}{RT^2}$$

where p is the equilibrium pressure at temperature T K, $\tilde{H}_g$ is the integral enthalpy of sorbate in the gas phase and $\bar{H}_{as}$ is the differential enthalpy of the sorbate in the adsorbed phase. The subscript "a" denotes the amount sorbed, a , is kept constant.

Isosteric heats may therefore be obtained from plots of $\ln p$ against $\frac{1}{T}$ at constant uptakes, a .

Models which give a physical description of the sorbed phase can be tested by comparing measured thermodynamic quantities with values predicted from the models. In this context, two types of model are most often examined namely localised and non-localised sorption.

The ideal localised model describes sorption in terms of sorbate molecules adsorbed on immobile and indistinguishable sites⁽¹³¹⁾. These molecules vibrate about mean positions on their sites and do not interact with each other. Langmuir's isotherm equation which was deduced from this model is

$$\theta = \frac{bp}{1 + bp}$$

where θ is the degree of coverage of the surface, p is the pressure of the gas in equilibrium with the sorbed phase and b is a function described by:

$$b = K_0 \exp \left(-q/kT \right) \quad (132)$$

where K_0 is a term dependent on the thermal entropy of adsorption and q is the heat involved when one molecule is adsorbed from the gas phase.

The mobile model assumes that all adsorbed molecules have sufficient thermal energy to overcome the potential energy

barriers between sites so that they will possess transitional freedom. An isotherm equation for this model is the Volmer equation⁽¹³³⁾:

$$p = K_v \frac{\theta}{1-\theta} \exp \left[\frac{\theta}{1-\theta} \right].$$

If the effect of interactions between sorbed molecules is considered, the equation becomes⁽¹³⁴⁾:

$$p = K_{vw} \frac{\theta}{1-\theta} \exp \left[\frac{\theta}{1-\theta} - \alpha \theta \right]$$

where α is a function of temperature such that

$$\alpha = \frac{2a}{bkT},$$

a and b being the relevant constants of the van der Waals' equation.

Both the localised and mobile models, including variations such as the BET equation^(135,136), are often quantitatively inadequate. Discrepancies arise which may be due to either surface heterogeneity⁽¹³⁰⁾ or, in the case of microporous sorbents such as zeolites, the nature of the sorption phenomena.

Adsorption upon interior surfaces is unlikely to be even qualitatively described in terms of a stepwise surface covering if the internal voids are so small that adsorption forces are felt within the whole void volume. In such microporous systems adsorption is likely to be a process of volume filling and the volume of the pores would be a more appropriate characteristic of the sorbent than its surface area⁽¹³⁷⁾. The term "monolayer equivalent area" has been introduced as an alternative to the conventional specific surface for describing sorption within zeolites⁽¹³⁸⁾, and other microporous sorbents.

General adsorption theories which do not specify a model

for the sorbed phase may offer a satisfactory alternative to the localised and mobile models for cases where the sorbent is microporous. One theory assumes that all space in the vicinity of a solid surface is characterised by a series of equipotential surfaces each of which has an adsorption potential, ϵ distinct from all others in the series⁽¹³⁹⁾. ϵ is given by the expression

$$\epsilon = RT \ln p_0/p$$

and the adsorbate is considered to be a liquid-like phase of volume W such that

$$W = \frac{x}{\rho}$$

x being the weight of gas adsorbed in grammes at the equilibrium pressure and ρ the density of the liquid at the equilibrium temperature T . A characteristic curve for a given sorbate-sorbent system can be produced at a particular temperature by plotting ϵ against W and from this it is possible to predict adsorption isotherms at different temperature⁽¹³⁹⁾.

An application of this theory to the case of microporous sorbents has been attempted by assuming a Gaussian distribution of the adsorption potential in the internal voids of the sorbent⁽¹³⁷⁾. From this theory an adsorption isotherm equation was derived,

$$x = W_0 \rho \left\{ - \exp \left[\frac{K(RT \ln(p_0/p))^2}{\beta^2} \right] \right\}$$

where W_0 is the total volume of all the micropores, K is a constant characterising the pore size distribution and β is the

affinity coefficient for the vapour, defined as the ratio of the temperature independent parachor of a given substance $\underline{p}$ and a standard one $\underline{p}_0$,

$$\beta = \underline{p}/\underline{p}_0.$$

Plots of $\log x$ against $(\log p_0/p)^2$ can be used to estimate W_0 .

Adsorption phenomena may also be described empirically in terms of an equation of state for the adsorbed phase. The free energy change for reversible and isothermal transfer of a mole of gas from an infinite amount of gas to an infinite amount of the sorbed phase is given by the Van't Hoff equation:

$$\Delta G = -RT \ln \left(\frac{a_s}{a_g} \right)_{\text{equilibrium state}} + RT \ln \left(\frac{a_s}{a_g} \right)_{\text{arbitrary state}}$$

where ΔG is the free-energy change, and a_s and a_g are the activities of adsorbed gas and gas in the external phase respectively. If the sorbate is in its standard state both in the gas phase and when sorbed, then

$$\begin{aligned} a_s &= a_g = 1, & \text{and} \\ \Delta G &= \Delta G^\circ = -RT \ln \left(\frac{a_s}{a_g} \right)_{\text{equilibrium state}} = -RT \ln K \end{aligned}$$

In the gas phase one may usually assume $a_g = p$ so that the gaseous standard state is unity when $p = 1$, while in the sorbed phase $a_s = C_s Y_s$ where C_s denotes the concentration and Y_s the activity coefficient of the sorbate. In consequence,

$$\left(\frac{a_s}{a_g} \right)_{\text{equilibrium state}} = K = \frac{C_s Y_s}{p}$$

C_s can be expressed as the number of moles per litre of sorbent-sorbate solution.

The change in chemical potential, $\Delta\mu_2$ of the zeolite lattice as sorbate is imbibed is represented by the equation,

$$\Delta\mu_2 = \int_0^P V dp - \frac{RTM}{m} \int_0^P \frac{x}{p} dp.$$

The first term on the right hand side is negligible under normal pressure conditions. V is the volume of the chosen lattice forming unit, M is the molecular weight of the lattice unit, x is the weight of sorbate in grammes per gramme of sorbent and m is the molecular weight of the sorbate. $\Delta\mu_2$ is also described by

$$\Delta\mu_2 = \int_0^{-\pi} V dp$$

$$\text{or } \Delta\mu_2 = -\pi V,$$

where $-\pi$ is the tension that would have to be applied to the sorbate-free sorbent to reduce its chemical potential to that of the host lattice after sorption had taken place. π may alternatively be described as the hydrostatic pressure which would have to be applied to the sorbate-sorbent solution to raise the chemical potential of the sorbent to that of the sorbate-free sorbent. π is therefore equivalent to osmotic pressure.

$\Delta\mu_2$ can now be equated with the terms in both V and x :

$$-\Delta\mu_2 = \pi V = \frac{RTM}{m} \int_0^P \frac{x}{p} dp.$$

Now since

$$C_s = \frac{Mx}{V_m},$$

$$\int_0^P \frac{x}{p} dp = \frac{V_m}{M} \int_0^P \frac{C_s dp}{p}$$

and therefore

$$\pi V = RTV \int_0^P \frac{C_s}{p} dp$$

or

$$\frac{\pi}{C_s RT} = \frac{1}{C_s} \int_0^p \frac{C_s}{p} dp$$

$\frac{\pi}{C_s RT}$ can itself be represented formally by a virial-type equation

$$\frac{\pi}{C_s RT} = 1 + \alpha C_s + \beta C_s^2 + \gamma C_s^3 + \dots$$

and so

$$\frac{1}{C_s} \int_0^p \frac{C_s}{p} dp = 1 + \alpha C_s + \beta C_s^2 + \gamma C_s^3 + \delta C_s^4 + \dots$$

or

$$\frac{dp}{p} = \left(\frac{1}{C_s} + 2\alpha + 3\beta C_s + 4\gamma C_s^2 + \dots \right) dC_s$$

Integration then yields

$$K = \frac{C_s}{p} \exp \left[2\alpha C_s + \frac{3}{2}\beta C_s^2 + \frac{4}{3}\gamma C_s^3 + \dots \right]$$

and since

$$K = \frac{C_s \gamma_s}{p}$$

$$\gamma_s = \exp \left[2\alpha C_s + \dots \right]$$

When C_s is small, $\gamma_s \rightarrow 1$ and $K \rightarrow \frac{C_s}{p}$, the Henry's law constant.

Since any isotherm may be expressed by an equation similar to the above expression for K , this equilibrium constant may be obtained as $\ln K$ from the extrapolated value of $\ln \frac{C_s}{p}$ as $C_s \rightarrow 0$ in a plot of $\ln \frac{C_s}{p}$ against C_s , because $C_s \rightarrow 0$, $\gamma_s \rightarrow 1$.

2.2 Polymer sorbents : Introduction

For polymers of varying relative polar group content the uptake of benzene has been found to increase with the relative hydrophobic or hydrocarbon group content⁽¹⁴⁰⁾, while the largest uptakes of water are exhibited by polymers containing high proportions of hydrophilic groups⁽¹⁴¹⁾. The relatively small size and ability of water molecules to associate through hydrogen bond formation distinguish this sorbate from most organic substances, consequently not only may strong localised interactions develop between water molecules and suitable polar groups of a polymer but also in relatively non-polar materials the association of the sorbed water is encouraged.

Opacity which develops in several polymer films at high relative pressure, and dielectric measurements on the water-polystyrene system, indicate some degree of association of water in the polymer⁽¹⁴²⁻¹⁴⁵⁾. For several systems, substantial clustering occurs at high relative pressures⁽¹⁴⁶⁾. Although mean cluster sizes of water and methanol in relatively hydrophobic polymers have been calculated and are generally in the range from 1, indicating no association, to 2 or 3 at relative humidities between 0.8 and 0.9⁽¹⁴⁶⁻¹⁴⁸⁾, there is little information on the distribution of cluster sizes.

The ultimate size of cluster is controlled by the amount of free space in the polymer⁽¹⁴⁴⁾, the formation of clusters in glassy polymers would therefore occur preferentially in voids since less disturbance of the polymer matrix as a whole would be required.

The formation of water molecule clusters would be expected

to have a significant effect upon the mobility of water molecules within a polymer because additional energy would be required to break free prior to diffusion. Transport of complete molecular clusters would be unlikely⁽¹⁴⁹⁾. Experimental evidence for clustering has in fact come mainly from observed diffusion coefficients and their dependence upon diffusant concentration^(144, 147, 150-153).

One method of determining diffusion coefficients involves the study of gas or vapour permeation through a membrane of polymer. Permeation may be regarded as a three stage process, penetrant is first sorbed by the ingoing face of the membrane and this is followed by the diffusion of penetrant within the polymer. If a concentration gradient exists across the membrane, this diffusion leads to a net flux of penetrant through the membrane. The final process is penetrant desorption at the outgoing face.

Transport studies such as this are of interest because they yield information on the mechanism of the diffusion process and its dependence on variables such as temperature, pressure and the concentration of penetrant within the polymer. Permeation can also be used, as in the present investigation, to study the physical composition of the polymer, especially in those materials where fillers have been included in the polymer matrix. The penetrant molecule can, in this case, be used as a probe to investigate the nature of the adhesion between the two phases of a composite material. Several reviews are available of the work carried out on the subject of using penetrants to invest-

igate the microstructure of polymer materials^(149, 154-157).

The terms diffusion coefficient, solubility coefficient and permeability coefficient can be defined respectively as follows:

D is the amount of penetrant passing across a plane of unit area in unit time under a unit concentration gradient and normally has the units cm^2s^{-1} ; σ is the concentration C of penetrant sorbed per unit volume of polymer at unit gas phase pressure and has the units $\text{cm}^3(\text{S.T.P.})\text{cm}^{-3}(\text{cmHg})^{-1}$; and P is the amount of penetrant passing through a polymer of unit area and unit thickness in unit time and with a unit pressure differential applied across it and has the units $\text{cm}^3(\text{S.T.P.})\text{cm cm}^{-2}\text{s}^{-1}(\text{cmHg})^{-1}$.

If P , D , and the solubility are concentration independent then $P = D\sigma$. If these quantities depend on C , the relation still applies as $C \rightarrow 0$.

D generally increases with increasing C for organic vapours in polymers⁽¹⁵⁸⁾, a behaviour which is interpreted in terms of the plasticisation or loosening of the polymer matrix by sorbed penetrant. Organic vapours are generally fairly soluble in polymers and polymer-penetrant interactions are significant. On the other hand permanent gas penetrants have low solubilities and give constant D and P at moderate pressures for particular temperatures⁽¹⁵⁹⁾.

In the case of water permeation through polymers, the dependence of D and of solubility on concentration is more complicated⁽¹⁶⁰⁾. For some of the more hydrophobic polymers D decreases with increasing C , presumably as a consequence of the clustering phenomena mentioned above.

2.2.1 Preliminary examination of diffusion equations

For an isotropic medium the rate of transfer of material, i.e. the flux J' , across an area A_c of a section normal to the direction of flow x is related to the concentration gradient

$\frac{\partial C}{\partial x}$ by Fick's first equation

$$J = \frac{J'}{A_c} = -D \frac{\partial C}{\partial x}$$

where J is the flux per unit area and D is the diffusion coefficient which may be a constant, a function of concentration, a function of co-ordinates or of the time or any combination thereof.

The fundamental differential equation for unidirectional diffusion in a slab or sheet membrane can be derived from Fick's first equation by considering the rate of accumulation of material in a volume element having faces of unit area normal to the direction of diffusion at x and $x + \delta x$. Diffusing material enters and leaves the element at rates given by

$$J_{in} = -D \frac{\partial C}{\partial x}$$

$$\text{and } J_{out} = D \frac{\partial C}{\partial x} + \frac{\partial}{\partial x} \left[-D \frac{\partial C}{\partial x} \right] \delta x.$$

The rate of accumulation inside the element is then given by

$$J_{in} - J_{out} = \frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right] \delta x = \delta x \frac{\partial C}{\partial t}$$

$$\text{or } \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right].$$

At the steady state ,

$$\frac{\partial C}{\partial t} = 0$$

and hence

$$\frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right] = 0$$

where no assumptions have been made about the functional dependence of D . For the situation encountered in this work, where C is x dependent and is maintained at C_0 in the ingoing face and at C_1 in the outgoing face, where $x = 0$ and $x = 1$ respectively, the solution of

$$\frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right] = 0$$

will for constant D be

$$C_x = Ax + B$$

$$C_0 = B$$

$$C_1 = A_1 + B$$

$$C_1 = A_1 + C_0 \quad \text{or} \quad A = \frac{C_1 - C_0}{1}$$

and so

$$C_x = \left[\frac{C_1 - C_0}{1} \right] x + C_0$$

This indicates that a linear concentration gradient exists across the membrane and from this relation and the equation

$$J = - D \frac{\partial C}{\partial x}$$

one obtains for constant D

$$J = D \left[\frac{C_0 - C_1}{1} \right]$$

Steady-state solubility measurements can be used to determine the values of C at various ambient pressures of penetrant, in the work under discussion the pressure p_1 at $x = 1$ was maintained close to zero and, since at this pressure penetrant concentration is also zero, both C_1 and p_1 can be neglected. The flux per unit area per unit thickness of membrane J_1 is thus described by

$$J_1 = D C_0$$

The factor P which relates the flux to the pressure differential across a membrane is called the permeability coefficient and is defined by

$$P = \frac{J_1}{(p_0 - p_1)}$$

which reduces to

$$P = \frac{J_1}{p_0}$$

under the above mentioned conditions.

If in addition to the $Q_1 = 0$ condition the membrane also contains no penetrant at zero time, the boundary conditions of the system will become

$$C = C_0 \quad x = 0 \quad t \geq 0$$

$$C = 0 \quad 0 < x < 1 \quad t = 0$$

$$C = 0 \quad x = 1 \quad t \geq 0$$

and the solution of

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right]$$

for constant D can be used to evaluate the amount, Q_t , which has passed through unit area of the membrane in time t . This amount at larger times approaches asymptotically the line

$$Q_t = \frac{DC_0}{1} \left(t - \frac{1^2}{6D} \right)$$

A graph of Q_t against t will thus give this line for large enough times, and if this line is extrapolated to cut the time axis the intercept L (the time-lag) is given by $L = \frac{1^2}{6D}$. The value of D may thus be determined.

When D is a function of concentration only then the time-lag is related to D_C by the equation⁽¹⁶⁴⁾

$$L = \frac{\int_0^1 x C_x dx}{\int_0^C D_C dC}$$

where the subscript C denotes that D is concentration dependent and C_x is the steady state concentration distribution of penetrant in the sheet. Since the flux of penetrant will, at the steady state, be the same for all x,

$$\int_{C_x}^{C_0} D_C dC = \frac{x}{1} \int_0^C D_C dC$$

This equation may be rewritten in terms of fluxes at differing ingoing concentrations as

$$(J_{C_0} - J_{C_x}) = \frac{x}{1} J_{C_0}$$

and serves to eliminate x from the expression in L, to give⁽¹⁶²⁾

$$L = \frac{\int_0^{J_{C_0}} C_x (J_{C_0} - J_{C_x}) dJ_{C_x}}{(J_{C_0})^3}$$

The term $\int_0^{J_{C_0}} J_{C_0} dJ_{C_x}$ may be evaluated from the plot of C_0 against J_{C_0} over the range 0 to C_0 , and this plot also provides the information needed to graph the product $C_{J_{C_x}} J_{C_x}$ against J_{C_x} and so to obtain the second part of the integral. If the above expression of L is adequate then measurements of L and J as functions of C_0 can be interpreted in these terms.

2.2.2 Factors affecting diffusion, permeability and solubility coefficients.

Several factors affect D, P and σ in homopolymer membranes

and these will briefly be discussed here. The effect of incorporated fillers will be included in the next section. Great care has to be taken in both sample preparation and experimental technique, and it is important that conditions should where possible be standardized in order to derive reproducible experimental results.

Permeability, diffusion and solubility coefficients are exponentially related to temperature:

$$P = P_0 \exp(-E_p/RT)$$

$$D = D_0 \exp(-E_D/RT)$$

$$\sigma = \sigma_0 \exp(-\Delta H/RT)$$

where E_D and ΔH are the energy of activation for diffusion and the enthalpy of solution, respectively, and where

$$E_p = E_D + \Delta H$$

E_D and D_0 are, in general, constant over limited temperature ranges for many polymer-penetrant systems. The relative values of E_D and ΔH clearly determine the magnitude and sign of E_p and therefore whether P increases or decreases with rising temperature. Generally, however, P does increase with temperature but for some silicone rubbers E_D values are especially low and decreases in P with increasing temperature have been observed(163).

The size and shape of penetrant molecules are important factors in determining the diffusion within a polymer, and, since more polymer segments are disturbed by them, the larger penetrant molecules generally exhibit smaller D and larger E_D (159). For a similar reason, branched hydrocarbon penetrants often have lower D values compared with their straight-chain isomers which may well diffuse preferentially with their long axes in the direction

of flow⁽¹⁶⁴⁾. Above certain penetrant sizes diffusion is solely controlled by polymer segmental motion and further increases in penetrant sizes have little effect on either D or E_D ⁽¹⁶⁵⁾.

Because diffusion involves the displacement of polymer chain segments, D values are generally decreased as the segmental mobility is reduced. The addition to a main chain of rigid or bulky side groups, or the increase in interchain cohesive forces caused by either changes in chain symmetry or inclusion of polar side groups reduces segmental mobility. Although such polymers offer most resistance to diffusion they are also readily plasticised by penetrants and exhibit marked concentration dependence of penetrant diffusion, an effect illustrated by benzene diffusion in a number of polymers⁽¹⁶⁶⁾.

Below a certain temperature, characteristic of a given polymer, segmental motion is very slow and the polymer may be considered to be a hard glass. Above this glass-transition temperature the material is usually soft and rubbery. Penetrant permeation in glassy polymers is dependent on segmental relaxation processes, especially for organic vapour penetrants. Water transport in the more hydrophobic polymers is not, however, so dependent on T_g ⁽¹⁵⁹⁾, although both E_p and E_D are lower below T_g for water transport through poly(ethylmethacrylate) than above T_g ⁽¹⁵¹⁾. The thermal history of a glassy polymer can also affect values of the three coefficients D , P and σ and any comparisons of these values below T_g should be treated with caution^(149,167).

Generally, sorption and diffusion take place to a very limited extent in the crystalline regions of a polymer. For gases σ is reduced in proportion to reductions in the amorphous

fraction of polymer, but D is further reduced because of the increased tortuosity of diffusion paths⁽¹⁶⁸⁾.

The presence of permanent gases in a polymer has little effect on the transport of other penetrants, but vapours generally interact appreciably with other penetrants. For example, some polymers with large sorptive capacities for water, such as cellophane, allow a more rapid flow of penetrants through them when some water is also present⁽¹⁶⁰⁾.

2.2.3 The effect of fillers in polymer membranes.

If sorption and diffusion through the filler can be considered negligible then filled polymers behave similarly to polymers containing regions of crystallinity. If, however, the surfaces of the filler are not completely wetted by surrounding polymer appreciable sorption of penetrant by the filler is possible. Weak adhesion between the two phases of a filled polymer may result in the formation of voids and there is evidence for this from density measurements⁽¹⁶⁸⁾. The formation of such gaps is facilitated if penetrant-filler surface interactions are significant and in this event an interfacial diffusive flow of penetrant is encouraged.

If sorption on or in a filler is negligible then the overall solubility σ of a gas will be proportional to the volume fraction of polymer in the composite, ϕ_p

$$\sigma = \sigma_p \phi_p \quad (1)$$

The other extreme of overall solubility would be the summation of the solubilities of the constituents which in the absence of gas

gaps would be given by

$$\sigma = \sigma_p \phi_p + \sigma_f \phi_f \quad (2)$$

where $\phi_f + \phi_p = 1$.

If, however, gas gaps are present then the equation may become

$$\sigma = \sigma_p \phi_p + \sigma_f \phi_f + \sigma_g \phi_g \quad (3)$$

It must be remembered that these equations represent only extreme situations and measured values of solubility coefficients may not correspond to them. Measurement of the solubility on n-butane at 30°C in Santocel CS filled silicone rubber has shown, for example, that for filler concentrations in the range $0 < \phi_f < 0.2$ equation (1) closely described the sorption⁽¹⁶³⁾ whereas for the solubility of propane at 40°C in zinc oxide filled natural rubber equation (1) describes those measurements in the range $\phi_f \leq 0.4$ but for higher volume fractions of filler solubilities move across towards the limit expressed by equation (2)⁽¹⁶⁹⁾. Complications arise in the interpretation of solubilities if gas gaps are present, but density measurements can at least be used to determine whether or not these are present.

Many difficulties have arisen in the development of a mathematical treatment of flow in a medium comprising a disperse phase in a continuum. One result of a study of the diffusion of certain permanent gases in filled natural rubbers was the realisation that not only volume fractions of filler but also particle geometry have to be taken into account^(156,170). Flow paths around

obstructions have to be considered as well as the areas of filler particles normal to the direction of penetrant flow, although an estimate of this last factor for the cases of equal volume fractions of randomly dispersed discs, cylinders and spheres can readily be made⁽¹⁶⁸⁾.

If a random array of discs in a continuum is assumed to be equivalent to $\frac{1}{3}$ of the total number being in each of the planes xy , xz , and yz then those in the xy and xz planes would present edges only to the direction of flow. If the discs are of thickness t and radius r_D then the ratio R of projected areas of discs to spheres normal to the direction of flow is

$$R = \frac{r_s}{9} \left[\frac{4t + \pi r_D}{\pi r_D t} \right]$$

where r_s is the radius of the sphere. Therefore for $R > 1$, one must have

$$r_s > \frac{9\pi r_D t}{4t + \pi r_D}$$

which reduces, for thin discs where $\pi r_D \gg 4t$, to $r_s > 9t$.

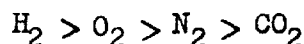
For narrow cylinders of length t and radius r_D and where

$4t \gg \pi r_D$ then the condition for $R < 1$ corresponds to $r_s < \frac{9\pi r_D}{4}$.

Thus, conditions are envisaged where discs hinder flow more than spheres and cylinders less.

Natural rubber containing lamellar fillers has been found to have a lower permeability than rubber containing particles of other shapes. The blocking power was however also dependent on the penetrant and for a series of experiments the ratio of the permeability coefficient of filled and unfilled rubber is in the

sequence(156,170).



As the volume fraction of filler in elastomers was raised above 0.5 then a sharp increase in permeability coefficients was encountered⁽¹⁷¹⁾, a result thought to be due to extensive gaps present between the two phases of the mixture. If the volume fractions of polymer, filler and gas gaps are ϕ_p , ϕ_f and ϕ_g respectively and if the distribution of gas in each obeys Henry's law then, as before,

$$\sigma = \sigma_p \phi_p + \sigma_f \phi_f + \sigma_g \phi_g$$

or alternatively, if

$$K_p = \frac{C'_p}{C_e}, K_f = \frac{C'_f}{C_e}, K_g = \frac{C'_g}{C_e}$$

Where C'_p , C'_f and C'_g are the penetrant concentrations in molecules per cm^3 of the three phases, and C_e is the number of molecules per cm^3 of the external gas phase, then

$$K = K_p \phi_p + K_f \phi_f + K_g \phi_g$$

Here K is the overall solubility constant and if $K_g = 1$ then this simplifies to

$$K = K_p \phi_p + K_f \phi_f + \phi_g$$

The equation of flow in the x-direction is⁽¹⁷²⁾

$$\frac{\partial C_p}{\partial t} + \frac{\partial C_f}{\partial t} + \frac{\partial C_g}{\partial t} = \mathcal{K} D_p \frac{\partial^2 C_p}{\partial x^2} + D_f \frac{\partial^2 C_f}{\partial x^2} + D_g \frac{\partial^2 C_g}{\partial x^2}$$

where $\mathcal{K} D_p$ is the diffusion coefficient in the polymer phase qualified by a structure factor to allow among other factors for increased tortuosity of diffusion paths caused by the

presence of other phases. D_f and D_g are the diffusion coefficients in the filler and gas-gaps phases respectively. The C values represent numbers of molecules in each phase per cm^3 of the composite, and are related to the C' values described above by

$$C_p = \phi_p C'_p$$

$$C_f = \phi_f C'_f$$

$$C_g = \phi_g C'_g$$

$$\text{thus } \frac{C_g}{C_p} = \frac{\phi_g}{\phi_p} \times \frac{1}{K_p}$$

$$\text{and } \frac{C_f}{C_p} = \frac{\phi_f}{\phi_p} \times \frac{K_f}{K_p}$$

The total concentration of penetrant molecules per cm^3 of composite, C , is related to the concentrations of the constituent phases,

$$C = C_p + C_f + C_g$$

and so the one-dimensional form of Fick's second equation is

$$\begin{aligned} \frac{\partial C}{\partial t} &= \frac{\partial C_p}{\partial t} + \frac{\partial C_f}{\partial t} + \frac{\partial C_g}{\partial t} = \left[\frac{K D_p \phi_p K_p + D_f \phi_f K_f + D_g \phi_g}{\phi_g + \phi_p K_p + \phi_f K_f} \right] \frac{\partial^2 C}{\partial x^2} \\ &= D \frac{\partial^2 C}{\partial x^2} \end{aligned}$$

so that D can be related to the volume fractions, and diffusion coefficients in the separate phases by

$$D = \left[\frac{K D_p \phi_p K_p + D_f \phi_f K_f + D_g \phi_g}{\phi_g + \phi_p K_p + \phi_f K_f} \right]$$

If, as is often the case at lower filler concentrations, $\phi_g = 0$, then D reduces to,

$$D = \frac{K D_p \phi_p K_p + D_f \phi_f K_f}{\phi_p K_p + \phi_f K_f}$$

and if negligible diffusion through the filler occurs then

$$\begin{aligned}
 D &= \frac{K D_p \phi_p K_p}{\phi_p K_p + \phi_f K_f} \\
 &= K D_p \left[\frac{\phi_p}{\phi_p + \frac{\phi_f C'_f}{C_p}} \right] \\
 &= K D_p \left[\frac{\phi_p}{\phi_p + \frac{\phi_f \sigma_f}{\sigma_p}} \right]
 \end{aligned}$$

When the penetrant is water vapour, a situation where the affinity of the penetrant for the filler is much greater than for the polymer itself may be encountered. The sorptive capacity of the filler will be greatly influenced by the degree of wetting of the filler by the polymer and in such cases the solubility coefficient σ of the composite may differ from the equation mentioned earlier, namely

$$\sigma = \sigma_p \phi_p + \sigma_f \phi_f,$$

where gas-gaps are not present. The equation may be rewritten, assuming Henry's law, as

$$\sigma = \sigma_p \phi_p + \sigma'_f (1-w) \phi_f$$

where σ'_f refers to the solubility coefficient of the filler when it is in bulk and w is a factor representing the degree of wetting of the filler.

If water sorption by filled polymers does not follow Henry's law, then the expression for the diffusion coefficient will be more complicated.

The simplification that negligible flow occurs through the filler would not be justified in those cases where the individual filler particles are porous and the above treatment of diffusion and permeation in such systems would be more difficult to apply.

The situation would, however, become simpler if polymer was able to fill any pores with filler particles and consequently the degree of divergence from the limiting form of the above model ($D_f = 0$) for membranes composed of polymers containing the highly porous zeolites could give some information on the nature of these otherwise porous fillers when incorporated in membranes.

CHAPTER 3

Materials, apparatus and experimental techniques.

In sections 3.1 to 3.3, the preparation of certain zeolites, organic monomers and polymers will be discussed together with details of the construction of filled and homogeneous polymer membranes. Section 3.4 and 3.5 are concerned with the apparatus.

3.1.1 Zeolites used in this work

Commercial samples of the synthetic zeolites NaA, NaX, NaY, (KNaL and H Mordenite have been used, the first four having been obtained from Union Carbide and the mordenite from the Norton Company. The structures of these materials were briefly described in Chapter 1.

Two ion exchanged zeolites have also been prepared, cupric X as a potential diazoalkane polymerization catalyst and hydrogen Y as a proton-rich catalyst.

Preparation of $\text{Cu}^{\text{II}}\text{X}$ from NaX.

NaX (10g) was shaken overnight in a solution (100cm³) 1 molar in CuCl_2 and 5 molar in NH_4OH . The zeolite was then filtered and the treatment repeated. The resulting cuprammonium exchanged zeolite was then washed with distilled water until the washings contained no chloride ions (silver nitrate test). Drying was limited to the extent of storing the zeolite in a dessicator at room temperature, although activation by degassing at temperatures up to 250°C to remove ammonia preceded catalysis reactions.

Preparation of HY from NaY⁽⁵²⁾

Several methods of preparing hydrogen zeolites by heating ammonium exchanged zeolites have been described, the preparation used in this work being the one which is thought to yield a product of exceptional thermal stability.

NaY(10g) was treated with a solution containing ammonium sulphate (30g) in water (150 cm³) at 100°C for 15 minutes with continuous stirring. The solid was separated from the solution by filtration and treated with a second solution containing ammonium sulphate (10g) in water (150 cm³) under similar conditions. The zeolite was washed free of sulphate ions and heated in air to 540°C for 3 hours. A further solution of ammonium sulphate (30g) in water (600 cm³) was prepared, and the zeolite stirred with this for a further hour at 100°C. After filtration this last step was repeated but this time for a period of two hours. After being washed free of sulphate ions the zeolite was heated without delay to a temperature of 845°C for three hours in air.

The zeolite was contained in a porcelain boat for the heating stages of the preparation, and a silica-tube muffle furnace was used. Temperature was recorded using a calibrated chromel-alumel thermocouple buried within the zeolite.

Other, non-zeolitic sorbents.

The clay mineral kaolinite obtained from English China Clays Ltd. and chromatographic grade silica-gel from British Drug Houses, were also used in this work to a limited extent.

3.1.2 Organic monomers used in this work.

Most of the monomers used are commercially available and no mention need be made of them in this section. It is important to note, however, that those monomers which are able to polymerize by a free-radical mechanism, especially any whose polymerization may be thermally initiated, require a radical-scavenger or inhibitor if they are to be stored. Consequently many monomers used in this work contained such compounds whose removal was necessary before use could be made of the monomers.

Methods of removing radical-scavengers include distillation, washing and chromatographic separation. The first method has the advantage that it enables a purer specimen of monomer to be obtained, but the last method, which is quick and convenient, has been found to be quite satisfactory. Samples of styrene, acrylonitrile, methyl methacrylate and n-butyl methacrylate which may polymerize by a free-radical mechanism have therefore been activated by passing them through a silica-gel column.

Monomers which generally undergo ionically induced polymerization reactions need no reaction inhibitor and unless some contaminant is present may be used directly. Those compounds which can polymerize by an anionic mechanism and which were investigated here include methyl methacrylate, styrene, acrylonitrile (all of which do contain inhibitors since they also undergo radical reactions) and α -methyl styrene.

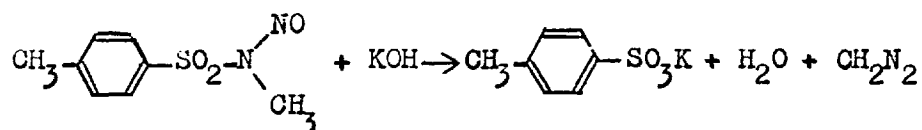
The group of monomers which are most likely to undergo polymerizations catalysed by zeolites by a carbonium ion mechanism are

also mainly available commercially and those chosen for study in this work included isobutene, α -methyl styrene, vinyl ethers, acenaphthylene, benzofuran and acetaldehyde. Diazoalkanes, which undergo cationically induced polymerizations, are much too unstable to be stored for any period and had to be prepared when required, For convenience, however, certain relatively stable precursors can be made which allow the corresponding diazoalkane to be prepared fairly quickly.

The first member of the diazo alkanes, diazo methane, can be prepared in small quantities in almost half an hour according to the following procedure⁽¹⁷³⁾. The precursor is N-methyl-N-nitroso-p-toluenesulphonamide which is available commercially under the trade name 'Diazald'.

2-(2-ethoxy ethoxy)-ethanol (35 cm³) and diethyl ether (10cm³) were added to a solution of potassium hydroxide (6g) in water (10 cm³). The whole was contained in a long-necked distilling flask fitted with a dropping funnel and an efficient condenser. The flask with contents was placed on a hot-plate and maintained at a temperature of 70°C. The dropwise addition of a solution of 'Diazald' (24.5g) in diethyl ether (140 cm³) was commenced as soon as the ether in the flask began to distil. The addition was continued over a period of 20 minutes and an ethereal solution of diazo methane collected in more diethyl ether (20 cm³) in a receiving flask. The outlet tube of the condenser dipped below the surface of the receiving liquid which was cooled to a temperature of 0°C. When the dropping funnel was empty, a further quantity of

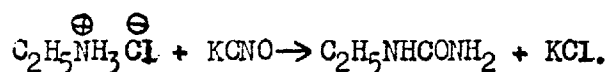
diethyl ether (40 cm³) was added slowly and distillation was continued until the distilling ether had become colourless.



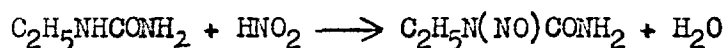
The ethereal solution was dried over metallic sodium, above which it was stored at 0°C, and its concentration was estimated by back titration of a portion against a standard methanolic potassium hydroxide solution after the addition of a measured excess of standard ethanolic benzoic acid solution.

Higher homologues of diazo methane may be prepared from either a 4-methyl-4-alkyl nitrosamino-2-pentanone⁽¹⁷⁴⁾ or a nitrosoalkyl urea⁽¹⁷⁵⁾ precursor. Both methods were employed quite satisfactorily in earlier work⁽¹⁷⁶⁾, indeed using the former precursor an ethereal solution of diazo n-octadecane was prepared. This long-chain diazoalkane is particularly unstable and readily decomposes on standing to, among other products, an ether insoluble solid polymer. Because of the greater ease of handling solids, for making diazo ethane a nitrosoethyl urea was prepared in this work rather than liquid 4-methyl-4-ethyl nitrosamino-2-pentanone. The procedure for this is given.

Ethylamine (45 g) was diluted with water to 500 cm³ and concentrated hydrochloric acid was added until the solution was acid to methyl red paper. Granular potassium cyanate (100 g) was added and the mixture was boiled, gently for 5 minutes and then vigorously for 10 minutes.



The hot solution was filtered into a solution of sodium nitrite (70g) in water (100 cm³), and cooled to about 0°C. A mixture of concentrated sulphuric acid (60 cm³) and ice (400 g) was prepared in a 3 litre beaker which was placed in a bucket containing an ice-salt bath. The ethyl urea solution was added slowly with constant stirring to the acid solution over a period of half-an-hour and gave a frothy precipitate of nitrosoethyl urea.



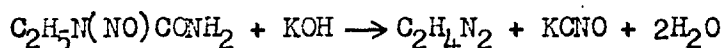
The precipitate was immediately filtered and washed with water until a sample of the crystals could be dissolved completely in methanol with no turbidity. This step is particularly important because both rate of reaction and yield of polymer in the catalytic decomposition of diazo alkanes has been found to be reduced if the nitroso precursor was not properly washed⁽¹⁷⁷⁾.

If the nitrosoethyl urea was not to be used immediately, the crystals had to be dried by pressing between filter papers and stored in a vacuum dessicator. Under these storage conditions and provided the temperature does not rise much above 20°C, the compound is quite stable.

Diazo ethane was prepared by cooling a mixture of diethyl ether (150 cm³) and 50% aqueous potassium hydroxide solution (150 cm³) in a conical flask to below 0°C, and adding to this mixture nitrosoethyl urea (100 g) in small portions with occasional swirling, keeping the flask and its contents below 0°C. The ether layer

became yellow with the formation of diazoethane and could be decanted into a separate flask. A further quantity of ether (150 cm³) was added in portions to the mixture, decanting off the ethereal layer to the other flask.

The ethereal diazo ethane was dried over sodium at 0°C for several hours and filtered before use.



Diazo alkanes are coloured compounds, the two whose preparations have just been described being yellow gases at room temperature. They have reputations as explosives and are extremely poisonous⁽¹⁷⁸⁾, although their toxic and explosive effects are minimised when they are kept in solution. Continued exposure to the gases leads to an allergic oversensitivity with symptoms similar to asthma. All work with these compounds should therefore be carried out in an efficient fume-cupboard and the worker should wear a suitable gas-mask.

3.2 Polymerization reactions.

Since most known polymerization reactions may be put broadly into the four categories of free-radical, carbonium-ion, carbanion and the co-ordination catalysed reactions, the polymerization reactions attempted in this work have been carried out with the relevant properties of available zeolites in mind.

The possible free-radical inducing properties of the X and Y type zeolites may enable these catalysts to be used for the polymerization of methyl methacrylate, styrene and acrylonitrile. Consequently attempts have been made to prepare the polymeric materials from these monomers by contact with synthetic near-faujasites. Both monomer sorption by zeolites and the bulk

preparation of composites containing polymer and zeolite have been carried out. An attempt has been made to correlate the sorption and permeation properties of the composites with the corresponding properties of its constituent phases.

Hydrogen exchanged forms of both type Y and mordenite zeolites have been used to study their behaviour in contact with these monomers which may undergo cationically induced polymerization reactions. Generally only monomer sorption by these hydrogen zeolites was studied.

3.2.1 Monomer sorption by zeolites.

Gravimetric and volumetric methods were employed in the study of monomer vapour sorption by zeolites. The apparatus used is described later in this chapter, and details are given here only of the activation of sorbents.

Prior to sorption, all zeolites were thoroughly outgassed to remove water. This involved slowly reducing the pressure above the sample by pumping with the air-inlet tap to the vacuum pump open, and by gradually closing the tap over a period of about ten minutes. As soon as the zeolite was under a pressure of less than 1 mm ^{*}Hg, the cold-tap was surrounded by liquid nitrogen and the mercury-diffusion pump turned on. The zeolite was kept under the pump for about twelve hours, after which time a furnace was placed around the zeolite, and the temperature slowly raised to 400°C at which temperature pumping was continued for a further 24 hours.

Sorption could take place as soon as the zeolite had cooled to the temperature required for the experiment.

* See Appendix B.

Table 1 shows details of some of the monomer sorption experiments which have been attempted.

Table 1Sorption of monomers by zeolites (and some other sorbents).

<u>Monomer</u>	<u>Sorbents</u>
Methyl methacrylate (MMA)	Sodium Y, Hydrogen Y, copper ^{II} X, potassium L, sodium A, silica gel.
n-Butyl methacrylate (n-BMA)	Sodium Y, potassium L.
Acrylonitrile (AN)	Sodium Y, hydrogen Y
Styrene (S)	Sodium Y, hydrogen Y, copper ^{II} X.
α -Methyl styrene (α -MS)	Sodium Y, hydrogen Y, hydrogen mordenite.
Ethyl vinyl ether (EVE)	Sodium Y, hydrogen Y, kaolinite, sodium A, silica gel.
n-Butyl vinyl ether (n-BVE)	Sodium Y, hydrogen Y, hydrogen mordenite.
Acetaldehyde (AA)	Sodium Y, hydrogen Y, silica gel
iso-Butylene (i-B)	Hydrogen Y, hydrogen mordenite
Benzofuran (BF)	Hydrogen mordenite
Ethylene (E)	Hydrogen mordenite

3.2.2 Other reactions involving monomers and zeolite catalysts.

Those monomers whose vapour pressures are insufficiently high near room temperature for the convenient measurement of sorption isotherms, or whose vapours are unstable, were diluted in inert solvents and the solutions added to zeolite catalysts. The zeolite could then be removed and a comparison of sorption properties before and after addition of the solution could be made in order to determine whether any reaction has occurred within the pores of the catalysts. Systems which were examined in this way are shown in table 2.

Table 2Addition of monomers to zeolites.

<u>Monomer</u>	<u>Solvent</u>	<u>Catalyst</u>
diazo methane (d M)	Diethyl ether	Hydrogen mordenite
diazo ethane (d E)	Petroleum ether	Copper ^{II} X
Acenaphthylene (ANP).	Diethyl ether	Hydrogen mordenite

3.3 Preparation of membranes

It had been the intention of this work to determine the diffusion properties of several composite systems, the monomer sorption experiments giving some guidance to the choice of which polymer-zeolite systems was of most interest. Difficulties not only in the preparation of membranes but also in other parts of the experimental work have reduced the programme considerably and only composites with poly(methyl methacrylate) matrices have been dealt with in any detail. Several polymers have been made, however, together with certain other polymer matrix composites and some of the procedures involved in these preparations are described here.

3.3.1 Homopolymer membranes

Membranes of poly(methyl methacrylate) (PMMA), poly(n-butyl methacrylate) (Pn-BMA), polystyrene (PS), poly(acrylonitrile) (PAN) and poly(ethyl vinyl ether) (PEVE) have been made. The first three were prepared by similar procedures, while the other two involved the use of special techniques.

Membranes of PMMA, PnBMA and PS.

Membranes of these materials were cast between square glass slides, separated by a cardboard spacer of suitable thickness (between 0.040 cm and 0.090 cm) and held in place with 'Bulldog' clips. The procedure was as follows.

A sufficient quantity of monomer for the size and number of membranes to be made was warmed in a test tube to 40°C over an electric heater. Benzoyl peroxide (1% by weight) was added and

the solution gently shaken mechanically until, upon cooling, it was still just sufficiently fluid to be poured. In order to reach this state of viscosity, it was necessary to warm and cool the solution repeatedly, although once it had reached this state the reaction rapidly went out of control.

Viscous monomer was poured onto a carefully washed and dried glass slide, the spacer was placed in position and a second clean slide placed so that one edge made contact with an edge of the spacer. Then, as the top slide was gently lowered, monomer was squeezed towards the opposite side of the mould. In this way the formation of air bubbles in the polymer was prevented.

Four 'Bulldog' clips along the edges of the slides held the mould together, and it was stored for 24 hours at 40°C in a horizontal plane to ensure that no material was lost and no air was allowed in. The moulds were then placed in an oven for a further day at 60°C followed by a period of at least a week at a higher temperature. These higher temperatures were:

95°C for poly(methyl methacrylate) membranes;

150°C for polystyrene membranes;

and 60°C for poly(n-butylmethacrylate) membranes.

This stage allowed polymerization to reach completion. After this treatment and upon removal of the clips, the slides, spacer and membrane could be easily separated.

Membranes of PAN

The usual methods of polymerizing acrylonitrile were not employed since if only small quantities of monomer are used the reaction can reasonably proceed in bulk. The yield after warming about 3 cm^3 of monomer to 40°C with about 0.1% of benzoyl peroxide

consisted of a white powder which was soluble in dimethyl formamide. A concentrated solution of the polymer in this solvent was poured into a flat-bottomed tray with a loose-fitting cover and held at 60°C in an oven. After about a day the solvent had evaporated leaving an opaque membrane of polyacrylonitrile. If this was left for a further few days in the oven, it could be readily removed from its former.

Membranes of PEVE

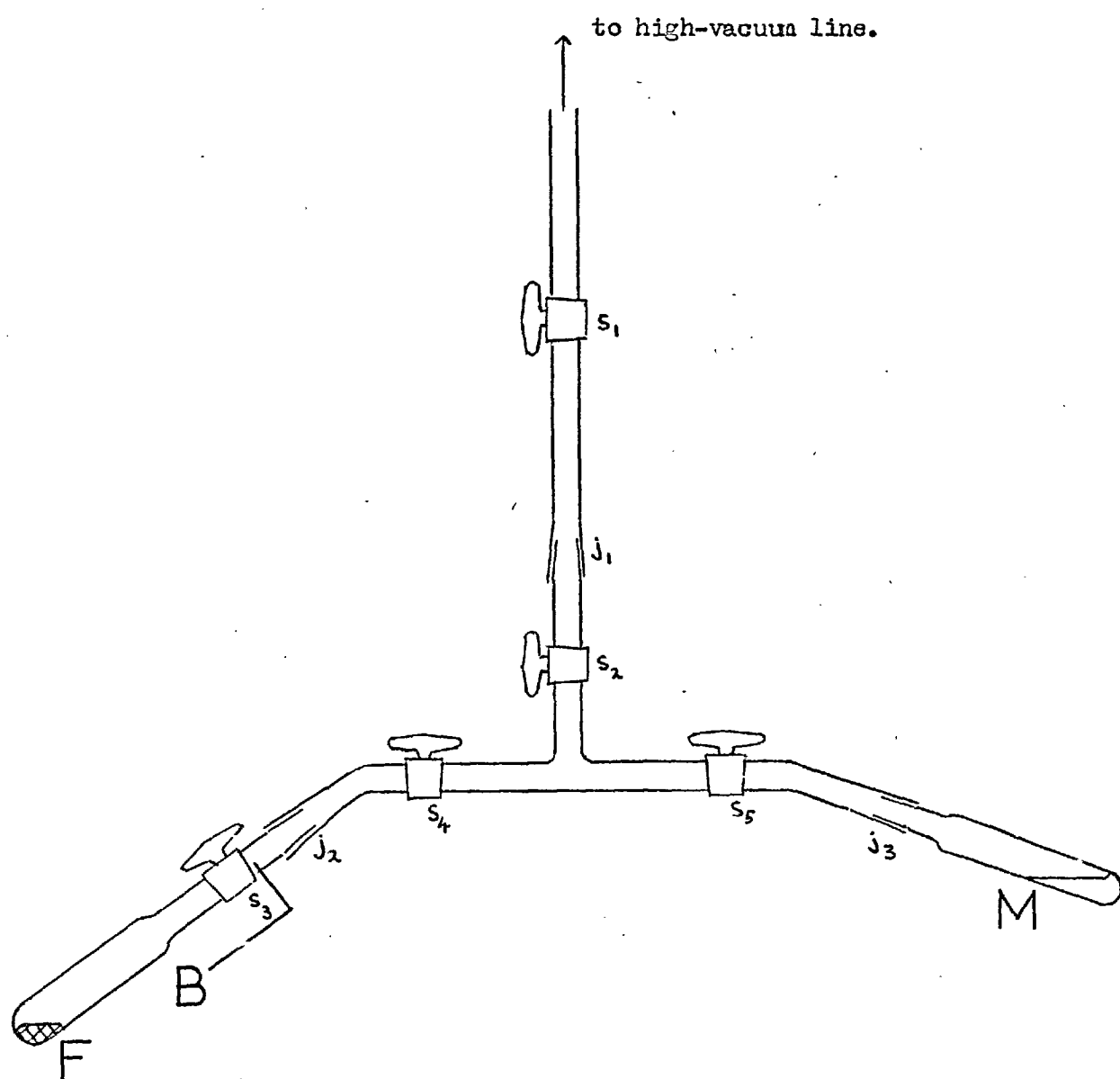
Unpolymerized ethyl vinyl ether was removed from the product of the reaction between this monomer and pellets of Linde 4 A sieve by washing with diethyl ether. The polymer-zeolite mixture was then put in an oven at 40°C for a day to remove unevaporated ether. PEVE was extracted from the mixture in benzene and a membrane made from this solution in the manner described for the PAN membrane.

3.3.2 Filled membranes

The preparation of the filled PMMA and PS membranes was complicated by the desirability of keeping water away from both the constituents of the composite and the resulting membrane. In order to keep the materials anhydrous most of the preparations involved operating under vacuum or under monomer vapour only.

The first step in composite membrane preparation was outgassing of the filler and this took place in the apparatus shown in figure 1. The stopcocks, marked in the figure as s_1 to s_5 , were all of 8 mm bore and the cone and socket joints, marked as j_1 to j_3 , were B49. Tubing was of between 8 mm and 10 mm internal bore.

Apparatus used in the preparation of filled membranes.



The filler was contained in the tube, F, and was outgassed at elevated temperature with s_5 closed. After outgassing the filler, s_4 was closed and the monomer to be polymerized as part of the composite was poured into the tube, M. This liquid monomer was then frozen by surrounding the tube with a Dewar flask containing liquid nitrogen and pumped through s_5 . When both filler and monomer had been outgassed s_1 and s_2 were closed, the apparatus detached from the vacuum-line at j_1 and monomer vapour allowed to pass over to the filler. In the case of zeolite fillers some time was allowed in order that sorption could reach a steady-state, usually 24 hours. More monomer was then distilled over into F by cooling this tube in a liquid nitrogen bath. The final volumes of distillate and filler in F determined the composition of the filled membrane in preparation. When the required amount of monomer had passed into F, s_3 and s_4 were closed and the tube detached at j_2 . This tube was then transferred to a mechanical shaker to disperse the filler uniformly in monomer. The process was facilitated if two or three 3 mm diameter glass balls had been added to the filler.

Before polymerization of the monomer could take place a reaction initiator had also to be added. Benzoyl peroxide was used to initiate the free-radical polymerization of methyl methacrylate and styrene and although several methods of admitting this substance in the absence of air or moisture were attempted, the following simple procedure proved to be the least troublesome.

With s_3 still closed, and having removed surplus grease from the position marked B on the diagram, a few milligrams of benzoyl

peroxide powder were placed at B. The cone of j_2 was then united with the socket of j_1 and, taking care that there was no sudden lowering of pressure around the benzoyl peroxide, s_1 was slowly opened. When the pressure above the initiator had been reduced to about 1 Nm^{-2} , s_1 was closed and s_3 opened. In this way, and with practice, just the right amount of initiator (about 1% by weight) could be admitted. Stopcocks s_1 and s_3 were again closed, the tube detached from the vacuum line and the mixture again shaken. This time, however, shaking took place over a heating-mantle maintained at near to 40°C . The mantle was hemispherical in shape and the tube, protruding through a piece of asbestos paper was shaken within the volume enclosed by the mantle and its asbestos paper cover. Shaking was continued until the mixture became viscous, following the procedure described for the preparation of homopolymer membranes.

The tube and viscous mixture was transferred to a dry-bag where the composite membranes were cast. Moulds were left in the dry-bag at room temperature for three or four days before being transferred to an oven at 100°C for at least another week. Separation of the plates, measurement of membrane thickness and fitting the membrane to its cell for permeation studies were then carried out in the dry-bag.

Several membranes were made, and nine samples of varying volume fraction of filler sodium Y in PMMA were among them. A list of the constituents of filled membranes is shown in table 3.

Table 3Filled polymer membranes

<u>Polymer phase</u>	<u>Filler</u>	<u>Approximate volume fraction of filler.</u>
PMMA	NaY	Between 0.05 and 0.75
PMMA	HY	0.25
PMMA	NaY	0.25
PMMA	(Na,K)L	0.25
PMMA	Silica-gel	0.25
PS	NaY	0.25

3.4 Apparatus

Much of the apparatus used in this work has been built twice, but apart from the differences in details which are described, both versions were of similar design. The original apparatus set up in the old building of the Chemistry Department consisted of two separate vacuum lines, one for permeation experiments and the other for sorption studies. This arrangement was followed for the rebuilt apparatus in the new building.

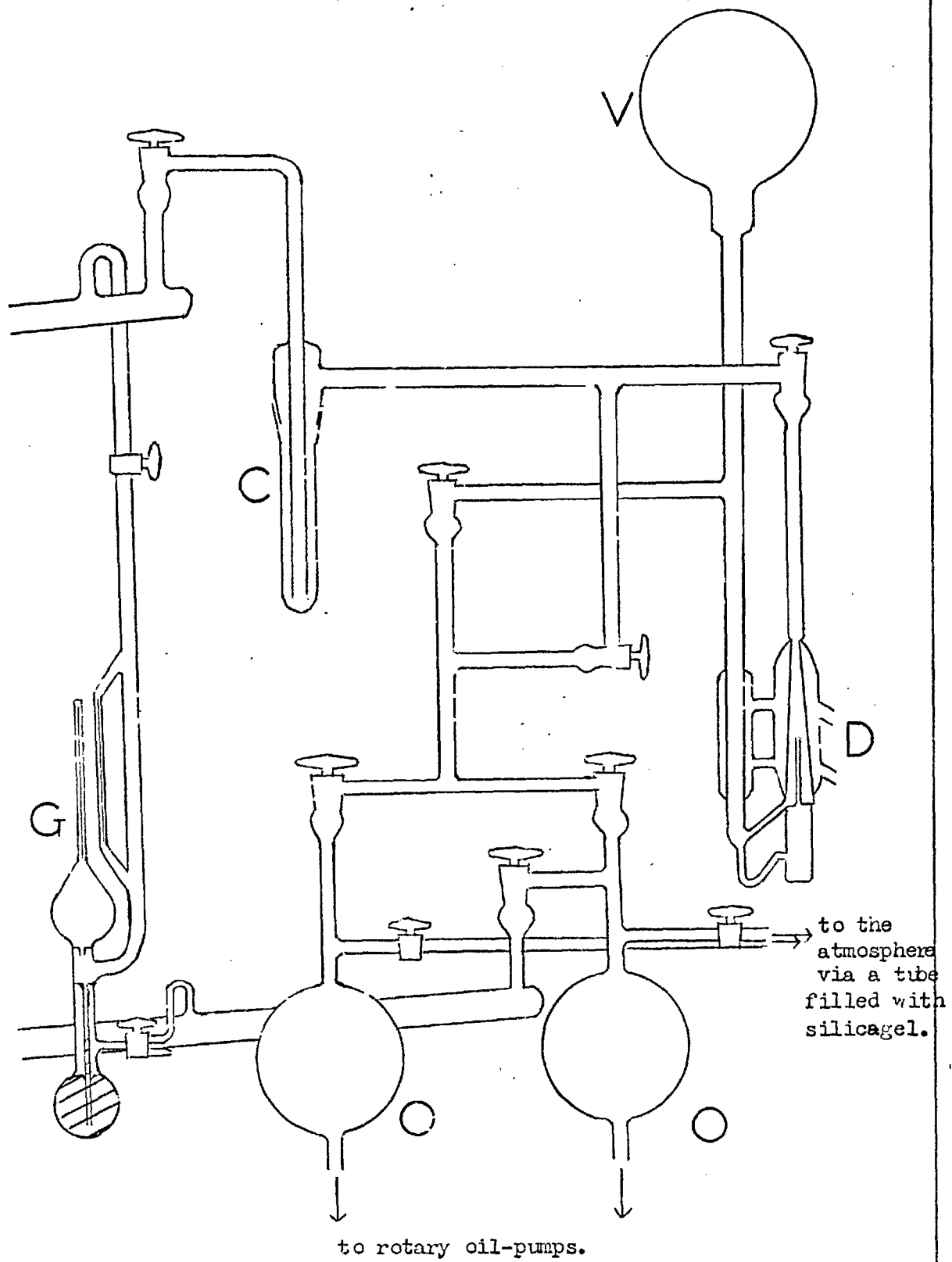
3.4.1 Pumping system

In both sorption and permeation systems, a similar set-up for pumping was used and this will be described first. Figure 2 illustrates the pumping system in which a three-stage mercury diffusion pump (D) was backed by a rotary oil-pump with a 5-litre buffer volume (V) and oil-trap (O) between the pumps. The oil-trap prevented oil entering the apparatus in the event of the oil-pump breaking down, an added precaution here was the inclusion of a one-way valve at the pump inlet tube. The buffer volume backed the diffusion pump on the occasions when the oil-pump was temporarily out of use. A liquid nitrogen trap (C) prevented any condensable vapours passing into the pumps. A McLeod gauge (G) was used to measure the pressure in the apparatus which could be reduced to less than 10^{-3} Nm^{-2} . All tubing and stopcocks, which were, unless otherwise stated, greased with Apiezon N, were of large bore to ensure a good pumping rate.

3.4.2 Sorption apparatus

A volumetric system was employed for low-temperature and

The Pumping System



permanent gas sorption studies while vapour sorption data were obtained using a gravimetric system.

3.4.3 Volumetric sorption system

A volumetric sorption apparatus was connected to the high vacuum line and consisted of a gas burette (B), mercury manometer (M), a sorption cell (S) and gas line (L). Some of the letters marked on figure 3 indicate the extent to which each part of the system was calibrated. The volume between marks t_1 , t_2 , t_3 , M_1 and B_5 comprised the closer volume, and its capacity, V_D , was determined as follows. The volumes of the four bulbs in the gas burette were calculated before other apparatus was built on to the burette by filling with mercury, whose density is well established, and weighing the latter as it was displaced, bulb by bulb. Since the manometer limbs were constructed from 10 mm Veridia precision bore tubing, the volume of the left-hand limb down to an etched mark could be established. A dose of argon was admitted to the outgassed closer volume and the gas pressure noted as the mercury level in the burette stood at each mark from B_1 to B_5 . If the mercury level is at B_n , the corresponding pressure of the gas P_n cmHg and the level of the meniscus in the argon filled side of the manometer (average value of the top and bottom of the meniscus) is x_n cm above M_1 , then the equation of state may be written

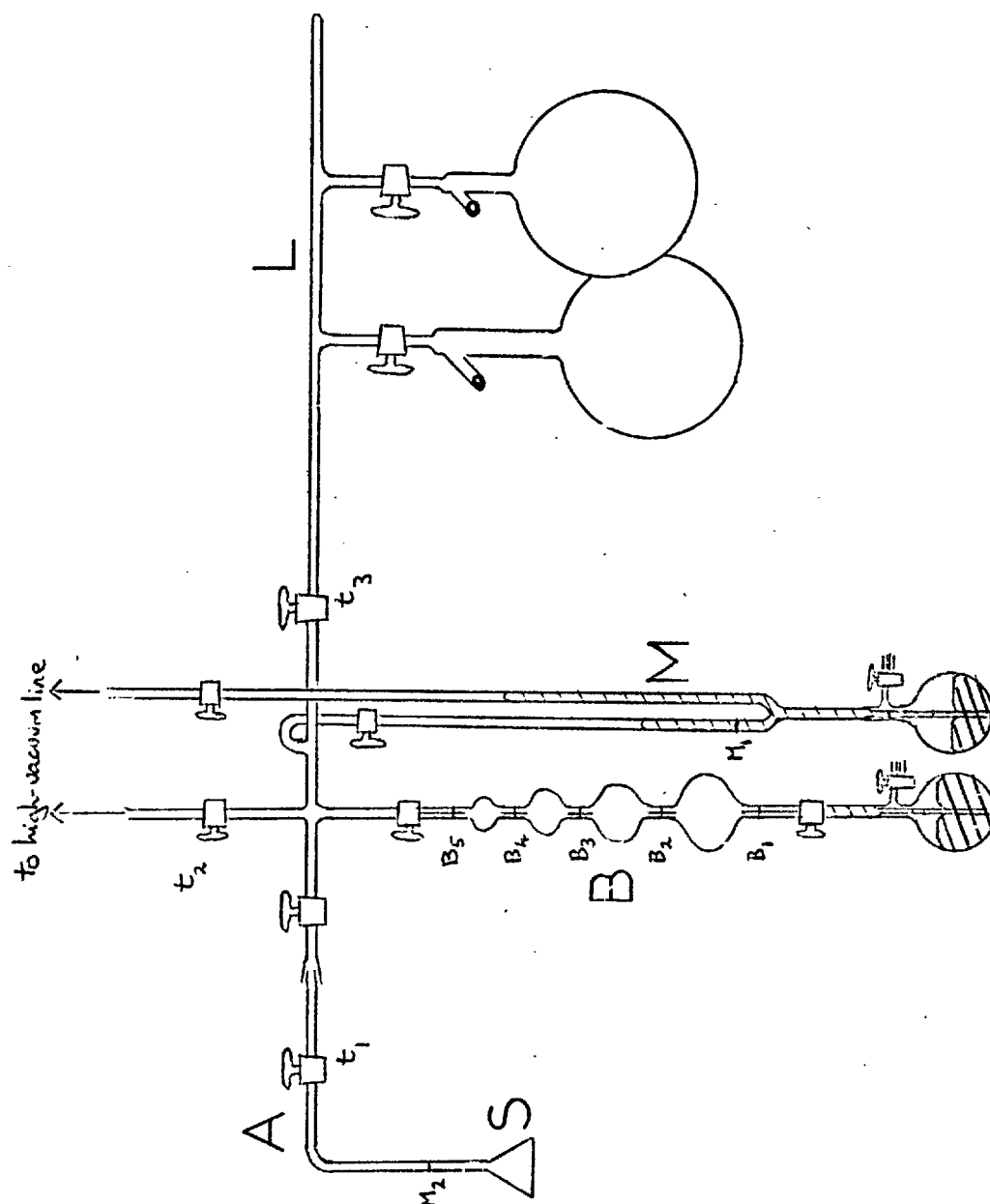
$$P_n (V_D + V_n - \pi(0.5)^2 x_n) = \text{constant} \times T_R$$

where V_n is the gas volume enclosed within the burette,

T_R is the ambient absolute temperature

and V_D , V_n and $(0.5)^2 x_n$ are in cm^3 .

Volumetric sorption apparatus.



V_D may be evaluated to within an error of 0.3% by elimination of the variables in such equations, as the mercury level in the burette is changed from B_1 to B_5 .

All pressures were calculated from observation of the meniscus positions through a 1 m cathetometer, supplied by Precision Industries Ltd., allowances having been made for capillary depression. This depression was determined from the height of the meniscus using tables⁽¹⁷⁹⁾. Pressure, measured experimentally in cmHg, was expressed in the S.I. units Nm^{-2} .

The sorption cell (S) was calibrated by weighing the amount of mercury it could contain. It was loaded with sorbent before being joined, at M_2 , to the tube, tap and cone assembly (A). The volume of the tube section between M_2 and t_1 , referred to as V_d , was also calibrated using mercury. The adjusted volume V_c of the cell (S) after being loaded with sorbent was then calculated from the outgassed weight of the sorbent and its density. The choice of the outgassing conditions depended on the nature of the sorbent.

3.4.4 Measurement of isotherms

The cell, containing outgassed sorbent, was surrounded with a Dewar flask containing either liquid oxygen or liquid nitrogen and allowed to reach thermal equilibrium. Measurements of liquid nitrogen temperature, T_N , were carried out with an oxygen vapour pressure thermometer. Gas was admitted to the doser volume with stopcocks t_1 , t_2 and t_3 closed and with the mercury level in the burette at B_1 , and its pressure measured at ambient temperature, T_R . The volume of gas in the doser volume and burette

was then calculated in cm^3 at S.T.P. according to the perfect gas law. This volume, V_o , is given by the equation

$$P_1^o \left[\frac{V_D - \pi(0.5)^2 x_1^o + V_1}{T_R^o} \right] = \frac{P^\ominus V_o}{T^\ominus}$$

The superscript o refers to measurements of the gas dose before opening of the stopcock t_1 , and $P^\ominus$, $T^\ominus$ refer to standard pressure and standard temperature respectively.

When t_1 was opened, the new steady-state gas pressure P_1^1 was measured and the volume of gas remaining in the gas-phase, V^D , is given by

$$P_1^1 \left[\frac{V_D - \pi(0.5)^2 x_1^1 + \frac{V_1}{T_R^1} + \frac{V_c}{T_N}}{T_R^1} \right] = \frac{P^\ominus V^D}{T^\ominus}$$

The difference between the volume of the dose, V_o and the volume at a pressure P_1^1 above the sample at T_N represents the volume of gas at S.T.P. taken up by the sorbent at that pressure and temperature.

Isotherms of the volume of gas adsorbed per unit volume of outgassed sorbent could be plotted from the results obtained as the mercury level in the burette was moved up to B_2 , B_3 and so on. When the pressure of gas enclosed above B_5 had been measured, t_1 was closed and a new dose admitted through t_3 , the mercury level having been lowered to B_1 . In subsequent calculations account had to be taken of the volume of gas enclosed in the sorption cell and adsorbed by the sorbent.

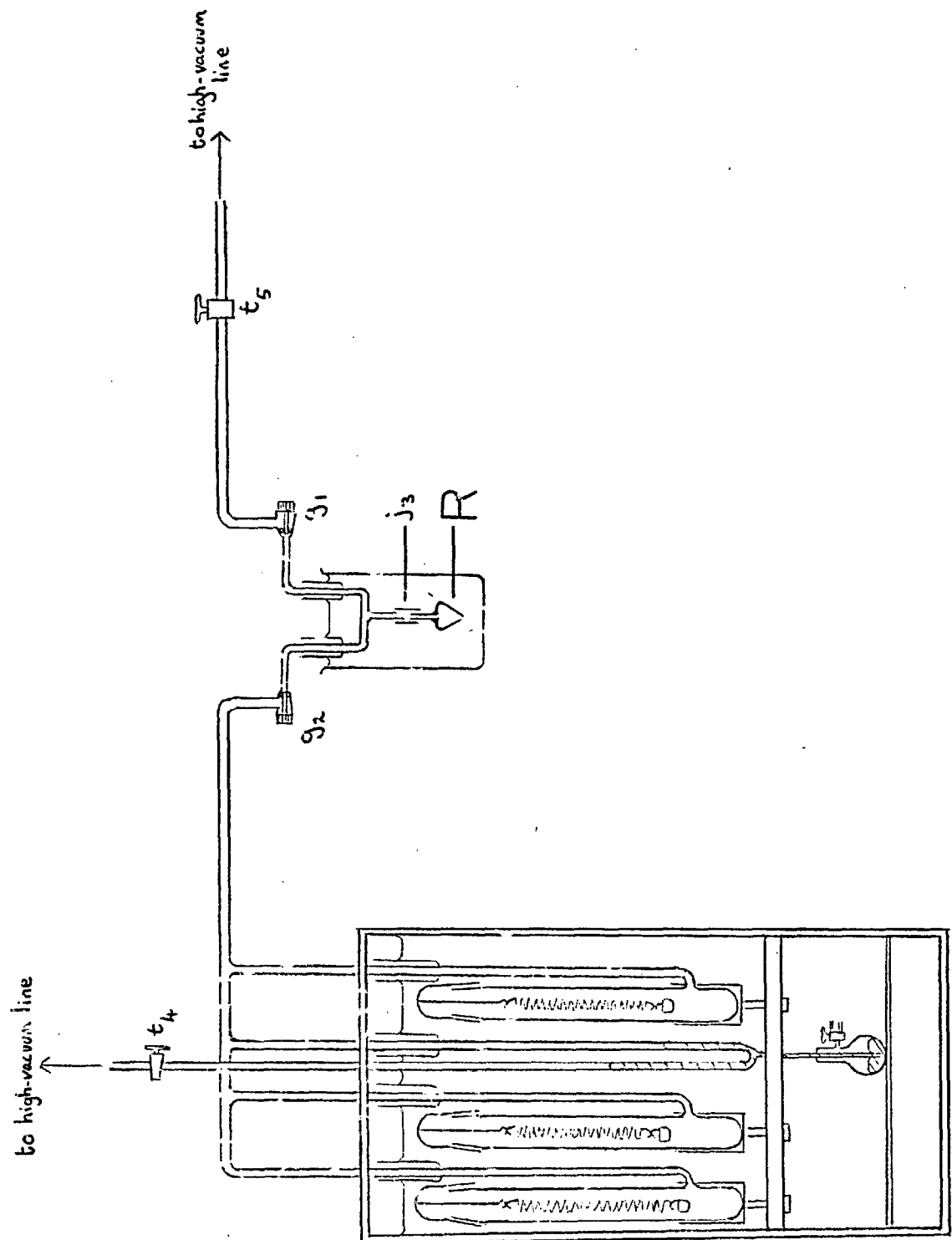
Desorption isotherms were determined in a similar manner from the gas volume which remained adsorbed as the pressure was lowered.

3.4.5 Gravimetric sorption apparatus

Three independent sets of gravimetric sorption systems were used, each set consisting of three 5 cm bore pyrex glass balance cases connected in parallel to a sorbate reservoir by heated pyrex glass tubing. One such set is illustrated in figure 4. The B45 cone and socket assembly at the top of each balance case was greased with Edwards high vacuum silicone grease. Apiezon hydrocarbon greases were less satisfactory because it was very difficult to separate the assembly after prolonged periods using these greases. Silicone grease has a larger operating temperature range and is not so readily squeezed out of the joint, but it has the disadvantage that glass-breakages in the vicinity of a silicone greased joint are more difficult to repair (this grease creeps along the glass surface and hinders subsequent glass-blowing). The two greaseless stopcocks, g_1 and g_2 (supplied by Young and Co.) were of 4 mm internal bore and were fitted with P.T.F.E. 'o'-rings. They were satisfactory provided that their 'o'-rings were kept very clean, the greaseless sliding joint j_2 was also satisfactory if the 'o'-rings were kept in good condition. Replacement of the rings was in any case a fairly simple operation.

Sorbent, contained in glass buckets suspended on silica springs (Thermal Syndiotac Ltd., $\frac{1}{2}$ maximum load, 25 cm g^{-1} sensitivity), was outgassed by lowering the mercury in the manometer through the tube into a mercury reservoir below the base of the thermostat tank and opening stopcock t_4 to high-vacuum. When, to renew sorbents, the balance-case taps had been removed, air at atmospheric pressure was present over both arms of the manometer as well as over the mercury reservoir. High-and-low-vacuum lines

Gravimetric sorption apparatus.



had then to be linked and pumping through t_4 and t_5 carried out simultaneously.

After outgassing by heating the samples under vacuum (this was achieved by surrounding the balance cases by tubular glass furnaces wound with resistance wire) some time was required before the springs cooled to the temperature required for the experiment. The temperature of the springs and of the sorbents in their buckets was controlled by filling the tanks with water, heating this to a temperature of about 2°C below the one required, using a high power output immersion heater supplied through a variable transformer, and controlling the temperature accurately with a 'Sunvic' unit and 'Red-rod' heater. The water was agitated by electrically driven stirrers and temperatures measured with thermometers calibrated at the National Physical Laboratory.

An improvement in the performance of the 'Sunvic' units was effected if the relay wiring was altered so that a 30 volt a.c. transformer supplied the expanding-metal contact-breaker instead of the normal mains supply. This modification prevented arcing across the points and allowed the temperature to be controlled to within $\pm 0.2^{\circ}\text{C}$.

All springs were calibrated at the various temperatures at which isotherms were to be measured. Pressures were measured by observing the differences in meniscus height of the mercury manometer through a cathetometer. Account was taken of capillary depression in the manner described previously.

Sorbate, which was in every case freshly distilled, could be introduced into the reservoir R by removal of the glass bulb at the sliding joint j_3 . It was then outgassed by freezing in

liquid nitrogen and pumping through g_1 and t_5 . When necessary sorbate could be thermostated by immersing the reservoir in a beaker of water controlled at the required temperature. If this temperature was above room temperature, particular care had to be taken to prevent condensation on cooler parts of the tubing by covering all tubing and stopcocks with heating wire and asbestos rope.

3.4.6 Measurement of isotherms

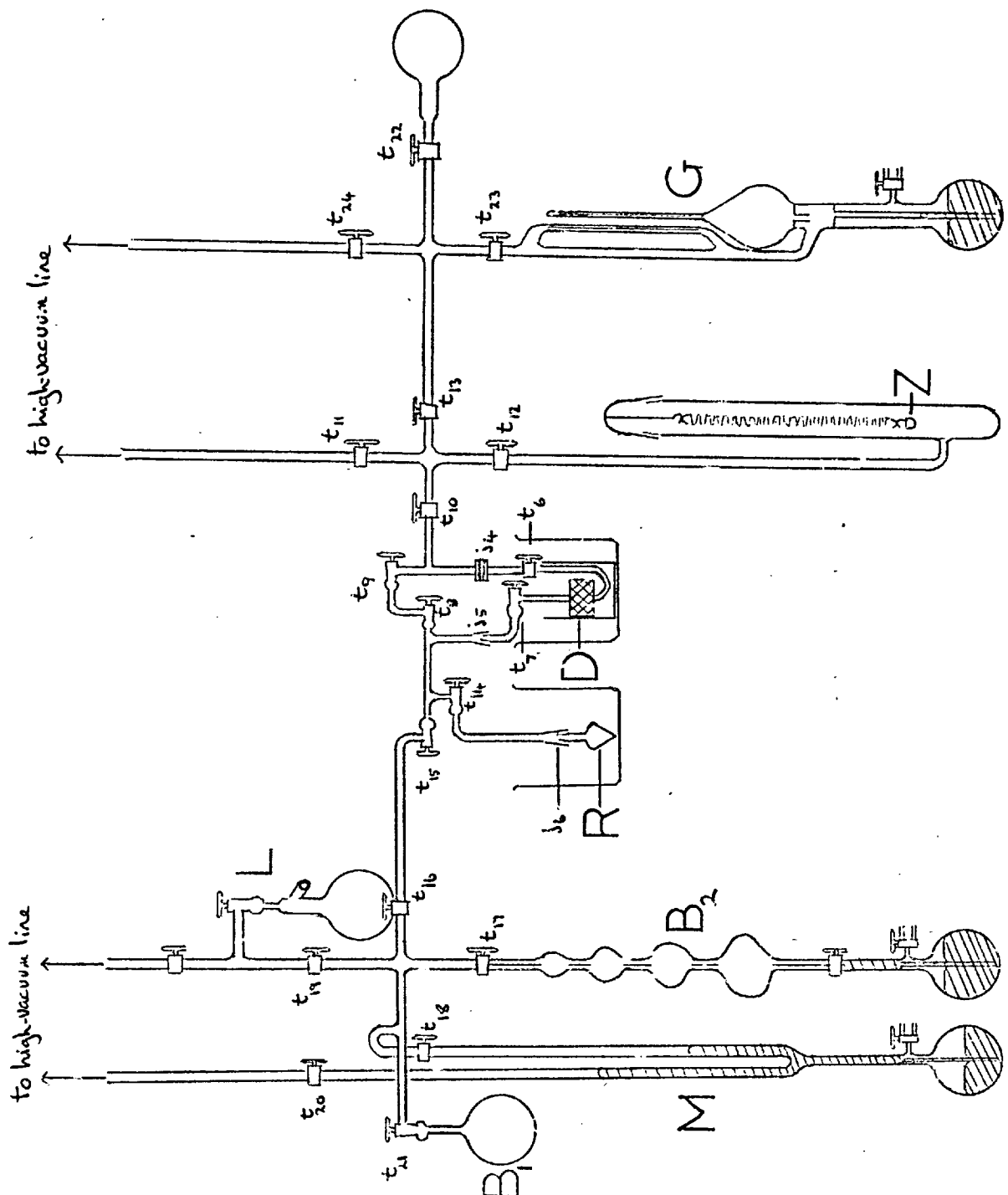
A weighed glass bucket was loaded with sorbent and reweighed. It was then attached to a silica spring and carefully lowered into the balance case on a hook fixed to the balance case top. After outgassing and thermostating to the temperature required for the experiment the sorbent was reweighed by calculation from the spring length (measured through a cathetometer). Doses of sorbate could then be admitted through g_2 and an isotherm determined. Immersion of the reservoir R in liquid nitrogen enabled vapour to be withdrawn from the system and in this way a desorption isotherm could be determined.

3.4.7. Permeation apparatus

Two independent permeation systems were employed, each being designed so that the membrane container section could be isolated and detached from the rest of the apparatus. Both systems could be used for water-vapour as well as for permanent gas transport measurements.

A diagram of one permeation system is shown in figure 5. All stopcocks and greased joints were, unless otherwise stated,

Permeation system.

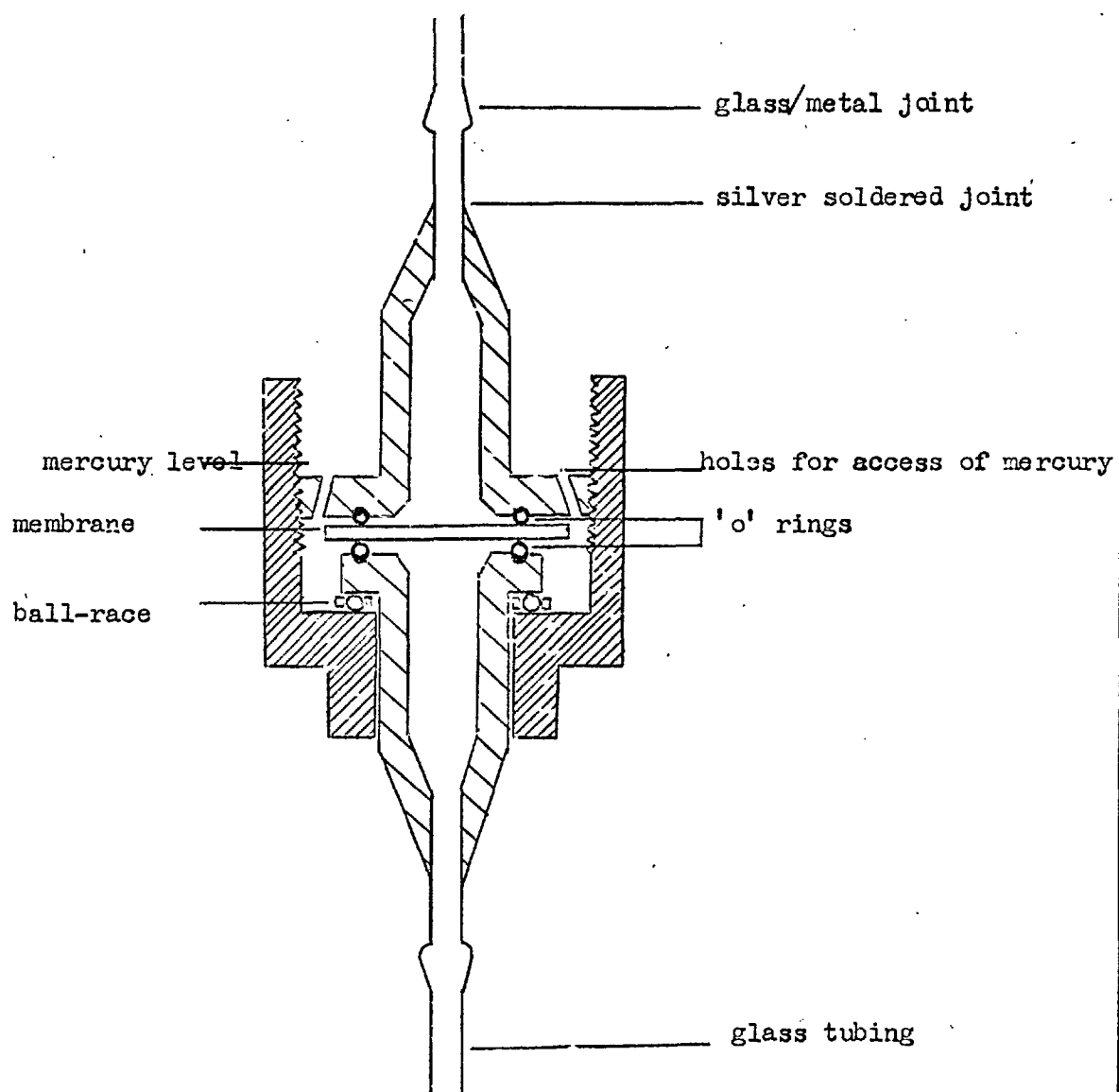


lubricated with 'Apiezon N' grease. A stainless steel diffusion cell, marked as D in figure 5, is shown in detail in figure 6. It is similar to those used previously in this department (e.g. references 169 and 172). The cell, of circular cross-section, consisted of three major parts, the outer casing with an internal screw thread and the upper and lower flanged sections between which the membrane was held. Circular depressions in both flanged faces located two neoprene 'o'-rings to ensure a good fit. The membrane was held firmly when the outer casing was screwed down, pressing the upper, screw-threaded flange against the lower flange. A gas-tight seal was effected by pouring mercury through the holes in the upper flange, and the entire cell was placed in a narrow cylindrical metal vessel which was immersed in a thermostatically controlled water bath.

The thickness of the membrane was determined from the mean of several readings recorded on a micrometer screw gauge, its area was obtained by measuring the inside diameter of marks made on the membrane by the neoprene 'o'-rings after its removal from the cell (this diameter was always close to 26 mm).

The diffusion cell assembly was detachable from the rest of the apparatus at the 'o'-ringed screw-joint j_4 and the cone and socket joint j_5 . After fitting a membrane into the cell inside a dry bag, the stopcocks t_6 and t_7 were closed and the assembly could then be reattached to the apparatus. With t_6 and t_7 remaining closed the glass tubing between the closed stopcocks t_{14} and t_{15} and the high vacuum line was outgassed through t_8 , t_9 , t_{10}

Stainless steel diffusion cell.



and t_{11} , with t_{12} and t_{13} kept closed. This part of the apparatus was then filled with dry air at atmospheric pressure (air allowed into the high-vacuum line through a silica-gel tube) and the two stopcocks t_6 and t_7 reopened. The membrane could then be outgassed through t_{11} , it was essential to ensure that both sides of the membrane were evacuated simultaneously by leaving both t_8 and t_9 open. Outgassing generally took a considerable length of time and was continued until no significant increase in pressure could be measured on the McLeod gauge G when the membrane was isolated from the high-vacuum line. (In most cases membranes were outgassed for about a month at 80°C before permeation experiments could be carried out.)

3.4.6 Measurements of gas and vapour flow through membranes.

So that gas and vapour permeation experiments could be carried out in series on the same membrane, the apparatus was designed to include a permanent gas supply L, ingoing pressure measuring manometer M and outgoing pressure McLeod gauge G. Water vapour from a water reservoir R, contained in a thermostatically controlled water bath, was included in the ingoing side and a zeolite sorbent Z contained in a bucket suspended from a calibrated silica spring was in the outgoing side. This spring-balance was used to measure the mass of water passing through the membrane. Change over from gas to vapour permeation studies involved, after outgassing the membrane, only alteration of stopcock settings.

Water vapour permeation

Freshly distilled water in the reservoir R was frozen and evacuated to remove absorbed air, the stopcock t_{14} closed and the reservoir brought to temperature in its thermostated bath. The water vapour pressure was then determined from tables⁽¹⁸⁰⁾. If the temperature of the reservoir was above room temperature it was necessary to warm all the tubing carrying vapour to the membrane and this was effected by covering all tubing from above the water level of the bath up to and including stopcocks t_8 and t_{15} and to the upper glass to metal joint of the diffusion cell with heating wire. The temperature of this wire was controlled using a variable transformer.

The initial length of the spring-balance was measured using a cathetometer.

When both water reservoir and membrane had been brought to temperature, stopcocks t_{15} , t_8 , t_9 and t_{11} were closed with t_6 , t_7 , t_{10} and t_{12} open. Then as t_{14} was opened a stopwatch was started. The rate at which the water vapour passed through the membrane was determined by measuring the mass of water taken up by the zeolite and plotting these values against time. Measurements were continued until the steady-state flow rate had become established.

Gas permeation

The stopwatch was started when t_{15} was opened, t_{14} remaining closed throughout. The ingoing pressure was measured on the

manometer M and, if the flow rate was high, the volume of gas on the ingoing side could be enlarged by opening t_{21} to the buffer B_1 or by opening t_{17} to the burette B_2 . The outgoing pressure was measured on the McLeod gauge G , with t_{12} closed. Again if the flow rate was large, the volume available for the outgoing gas could be increased by opening t_{22} to the calibrated buffer B_3 .

Since pressure measurements were made as functions of time it was necessary to know the outgoing volume of the apparatus. The volume of gas at S.T.P. passing through the membrane with time could then be determined. This volume was established by replacing the membrane in its cell with a piece of sheet steel and admitting a small amount of gas into the volume bounded by t_9 , the steel sheet, t_{11} , t_{24} and t_{22} . Its pressure was then measured on the gauge both before and after expanding into the outgassed buffer B_3 . The outgoing volume could then be calculated using the perfect gas law, the procedure was repeated to provide a reproducible value for the outgoing volume.

3.5 Other apparatus and techniques used in this work

Chemical analyses of some zeolites were carried out using classical methods by Analytical Services Ltd., in the Department of Metallurgy. Organic analysis of certain membranes was carried out, using the microanalytical methods for carbon determined as carbon dioxide and for hydrogen determined as water, by the microanalytic laboratory in this department.

X-ray powder diffraction photographs of ion-exchanged zeolites were made by Dr. I. S. Kerr in order to check that the zeolitic structures had not been altered.

A Stanton TR11 thermogravimetric balance was used to determine weight loss as samples were heated from room temperature to temperatures up to 1000°C . The slow cam was employed which allowed a temperature rise of about 10°C per minute and the charts obtained were used chiefly for two purposes:

- (i) to estimate the loss of water of zeolites at atmospheric pressure up to about 600°C where a plateau was usually observed.
- (ii) to burn away polymer material from composites in order to determine the weights of zeolite and polymer per unit mass of composite.

The results of using the Stanton T.G. balance to determine the weight fraction of zeolite in composite materials could be checked by determining carbon contents of samples of the same composites. The two methods gave good agreement and since T.G.A. is far quicker and easier to carry out than chemical analysis it was used for most of the determinations.

CHAPTER 4Results and Discussion

A variety of organic reactants and catalysts have been investigated and the results of these investigations will be discussed in the following order of monomers:

<u>Section</u>	<u>Name of monomer under investigation</u>	<u>Page</u>
4.1	Methyl methacrylate	107
4.2	n-Butyl methacrylate	164
4.3	Acrylonitrile	167
4.4	Styrene	169
4.5	α -Methyl styrene	172
4.6	Ethyl vinyl ether	176
4.7	n-Butyl vinyl ether	182
4.8	iso-Butene	185
4.9	Ethylene	188
4.10	Acetaldehyde	191
4.11	Denzoruran	191
4.12	Acenaphthylene	194
4.13	diazo Methane	198
4.14	diazo Ethane	200

Polymerization reactions of these monomers, the effectiveness of various catalysts to promote reactions, and sorption and permeation

results will be discussed under the appropriate section. General observations and conclusions will be dealt with in the final chapter.

4.1 Investigation of methyl methacrylate polymerization reactions.

Introduction

Preliminary work involved the preparation of poly(methyl methacrylate) membranes containing zeolite fillers. This followed a previous investigation⁽¹⁸¹⁾ in which the fillers included pure and chemically modified synthetic hydroxyapatite, pure and chemically modified Wyoming bentonite and the zeolites (Na, K) L and NaY. In each case, chemical modification was effected by prior treatment of the solids with ethereal solutions of diphenyl diazomethane. This organic compound renders the otherwise hydrophilic hydroxyapatite far less attractive to water vapour⁽¹⁸²⁾. Reduction in water uptake of synthetic hydroxyapatite when included in a polymer matrix was interpreted as the result of a certain amount of adhesion between these two phases in the composite. This adhesion was improved somewhat by chemical modification of the apatite. Irreproducibility of the water sorption results for pure and modified bentonite filled polymers was attributed to the layer-type structure of this filler⁽¹⁸¹⁾. At high relative pressures of adsorbate, swelling of the bentonite would cause the displacement of surrounding polymer. On removing the adsorbed water, bentonite shrinks and physical contact between the phases would be reduced resulting in an increase in subsequent water uptake.

The uptake of water by NaY zeolite filler was considerably reduced from the maximum capacity of the free powder. This reduction in water uptake after inclusion in a polymer matrix was not as marked when the zeolite was (Na,K)L, probably because this zeolite presents smaller and less accessible cavities for the formation of intracrystalline polymer (181).

In a study of the transport of water vapour through poly(methyl methacrylate) membranes, the graphical relationship between steady-state flux and relative pressure was linear for the homopolymer but underwent an upward inflexion, at a relative pressure above 0.7, for flow through filled membranes (181).

Attempts have been made during the present investigation to prepare filled membranes containing a wide range of concentrations of filler. It was during the course of some of these preparations that an unexpected effect of the presence of NaY zeolite on the polymerization of methyl methacrylate was observed. This zeolite was apparently responsible for a faster rate of reaction, one consequence of which was a difficulty in estimating the correct time for transferring the polymerizing solution from its reaction vessel to the casting mould. A test experiment was conducted in which two tubes of monomer were corked and left for two days. The tube to which some outgassed NaY zeolite had also been added contained a solid polymer but the tube containing only monomer showed no sign of any increase in the viscosity of its contents. A repetition of this experiment at 333 K showed that monomer polymerized within two or three hours in the presence of NaY zeolite at this higher temperature.

Zeolites (Na,K)L and NaA were also investigated to see if they had any catalytic activity on methyl methacrylate. The former zeolite behaved similarly to NaY while the latter had no observable effect on the monomer.

At an early stage in the investigation, when methyl methacrylate was being purified by the removal of its inhibitor by washing with sodium hydroxide solution, an attempt to dry the monomer over metallic sodium was made. In accordance with the results of earlier work⁽⁷¹⁾, the monomer turned pale blue and over a period of about ten hours became a hard polymer. The ease with which this polymerization reaction occurred suggests that if metallic sodium could be incorporated within zeolitic cavities, a particularly useful way of preparing filled membranes may be developed. The ability of such ionic reactions to occur at low temperatures would allow much greater control over the polymerization reaction. It could also reduce the number of vapour bubbles within the polymer.

Two methods of producing sodium rich forms of NaY zeolite were investigated. The first method in which sodium vapour was condensed in the outgassed zeolite was abandoned because of the hazards involved in such a procedure. The second method involved the preparation of a sodium azide solution in which NaY zeolite was shaken. After air drying at the pump, the zeolite was heated gently under vacuum to remove nitrogen from the sodium azide. This outgassing took place within a balance case so that the loss in weight as nitrogen was evolved could be followed. The residual zeolite was used to adsorb methyl methacrylate vapour but the isotherm was very similar to the ones illustrating the adsorption

of the monomer vapour on free NaY zeolite and shown in figure 9.

Whatever precautions are taken during outgassing, it is most unlikely that the structure of NaY zeolite could be maintained and all water molecules removed. A sodium rich zeolite may therefore contain a small amount of sodium hydroxide. In view of this, the effect of sodium hydroxide on methyl methacrylate has also been investigated. Two pellets of sodium hydroxide were added to a test-tube half-full of the monomer. The tube was corked and shaken, but before this could be done, a blue colour could be clearly seen on the edges of the pellets. Within one-and-a-half hours the liquid had become pale green and cloudy, and a viscous substance was forming on the walls of the tube. After three hours the lower half of the tube's contents had become a greasy polymer. Continued shaking at room temperature completed the reaction, and after two days the tube contained a hard, white solid. The colour of the reactants suggests that the reaction is ionic, and in fact the free-radical inhibitor had not been removed from the monomer. A blank test in which monomer, but not sodium hydroxide pellets, was shaken for a similar period did not produce any polymer even when the inhibitor had been removed. This result implies that the hydroxide was actively involved in the polymerization reaction and was not merely responsible for eliminating the free-radical inhibitor, allowing the monomer to polymerize thermally. In the absence of a free-radical initiator, thermal polymerization of methyl methacrylate at room temperature is extremely slow.

Methyl methacrylate will polymerize quite rapidly over sodium Y zeolite, sodium and sodium hydroxide.

Methyl methacrylate sorption experiments.

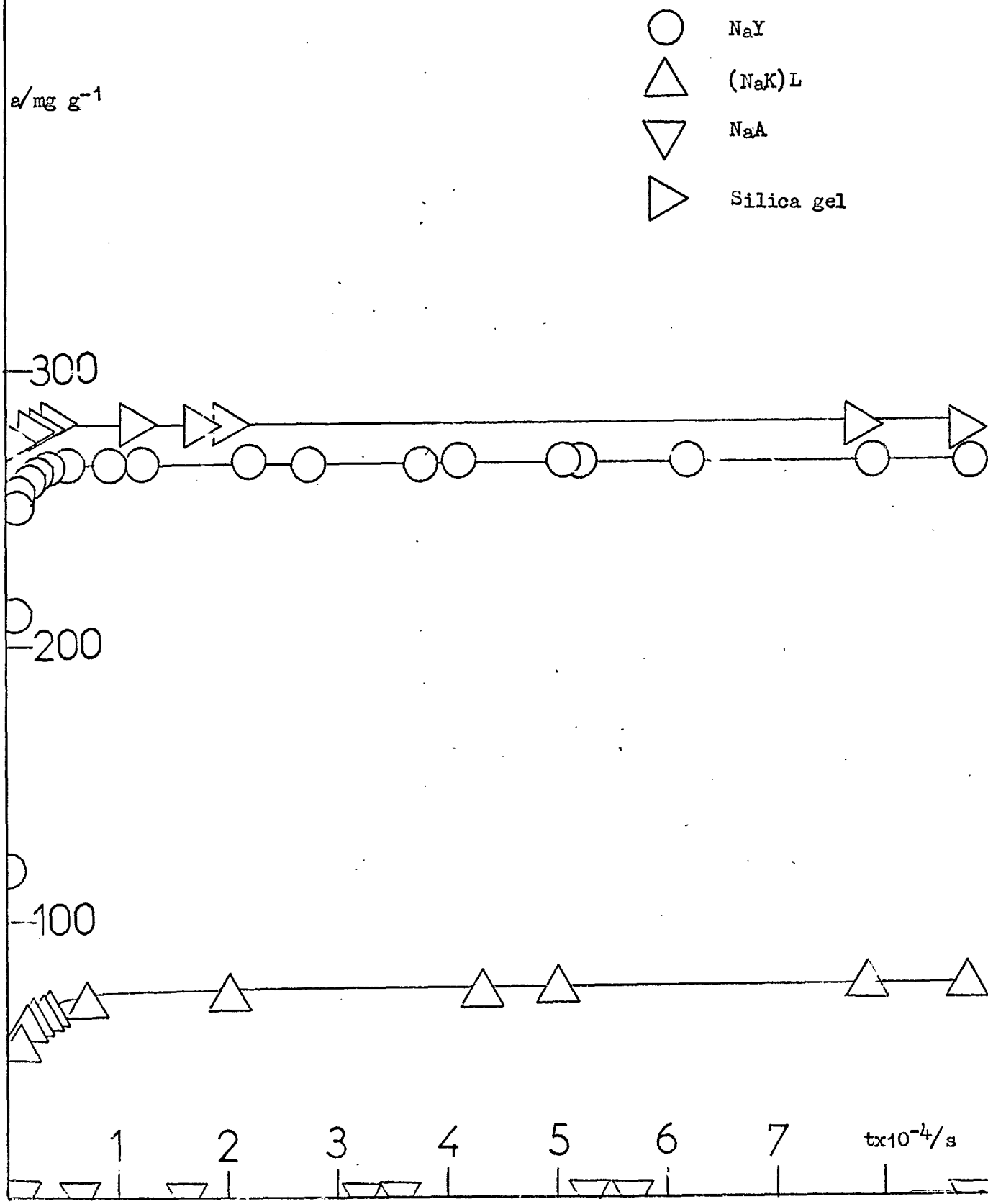
Sorption of freshly distilled methyl methacrylate by zeolites and other sorbents has been studied primarily in order to find out if adsorption is reversible, or, if it is not, to investigate the nature of the undesorbed material.

In order to determine steady-state adsorption isotherms it is necessary to find out the length of time required for an adsorbed dose of methyl methacrylate to reach a state of equilibrium with the vapour phase. Accordingly, kinetic experiments were conducted in which the course of the sorption process was followed by observing the change in length of the silica spring of a gravimetric balance from the time of admission of a dose of vapour. Figures 7 and 8 show that a steady-state is reached within several hours even at quite high relative pressures. This observation was general for all of the sorbents investigated. Exposure of sorbents to methyl methacrylate for extended periods revealed no measurable changes in mass of adsorbed sorbate.

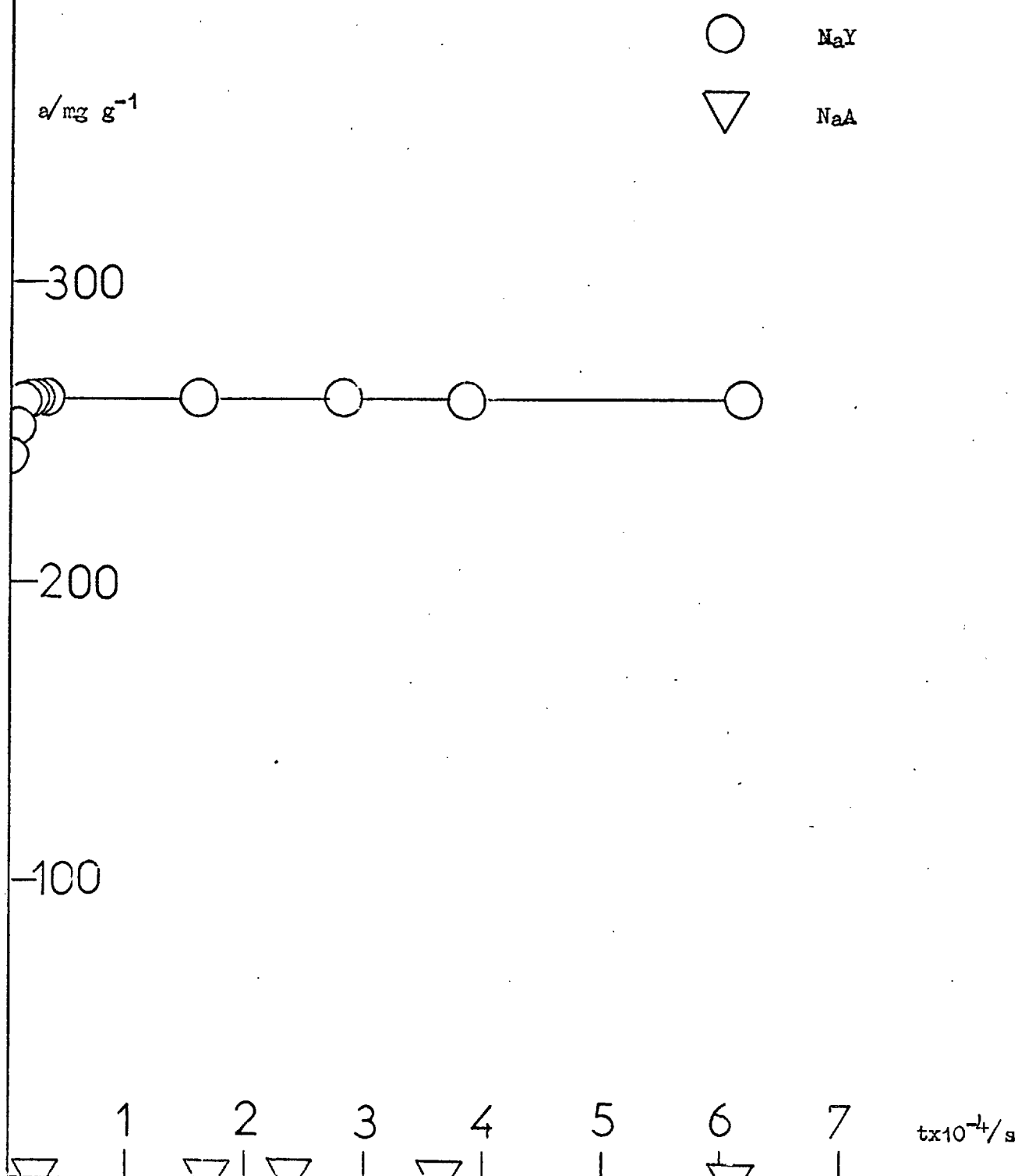
One other point of interest about these figures is the absence of any measurable adsorption on the zeolite sodium A. The entry pores of this zeolite are too narrow to permit entry of a branched-chain molecule, or even a straight-chain hydrocarbon, and it is apparent that no significant amount of monomer is present on the external surface at the relative pressures investigated. If adsorption was irreversible and if this was because polymerization was occurring at the zeolite-monomer interface, then a measurable quantity of monomer would probably have been adsorbed on the external surface.

Adsorption measurements were generally not made at high values of relative pressure because at such pressures a coating

Adsorption of methyl methacrylates in zeolites

 $T = 303 \text{ K}$ $\frac{p}{p_0} = 0.735$ 

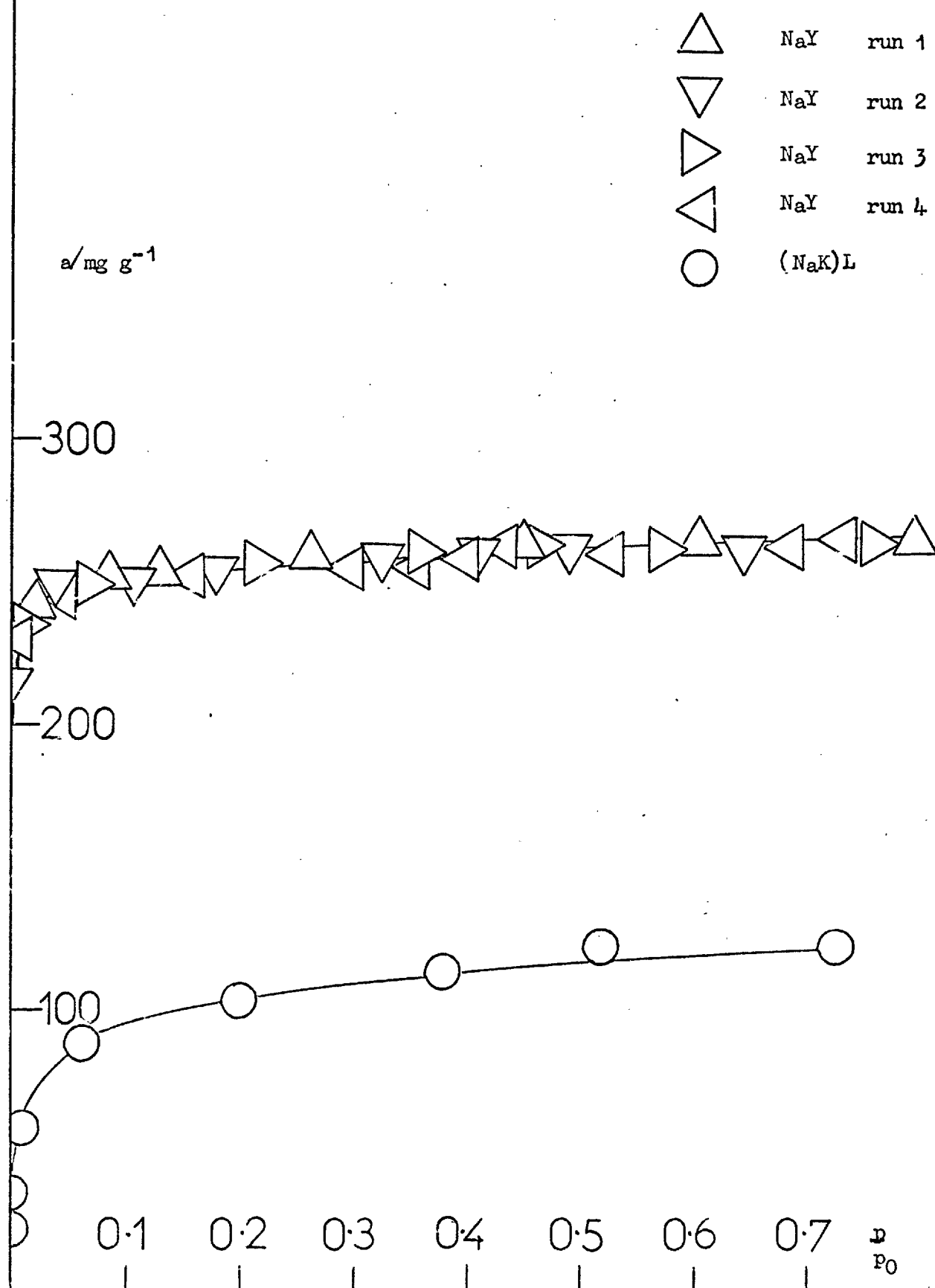
Adsorption of methyl methacrylates in zeolites

 $T = 323 \text{ K}$ $p = 0.435$
 p_0 

of polymer rapidly formed on the glassware. This coating was clearly visible on the walls of tubing and balance cases when relative pressures were greater than about 0.8 and there are several reasons why such coatings should be avoided. The presence of polymer on the silica spring would probably alter its sensitivity and the extra weight on the spring and bucket could not be accounted for. A blank experiment in which vapour was admitted to a balance case and spring supporting a bucket containing glass balls demonstrated that the concentration of monomer (or polymer) depended not only on the pressure of the vapour phase but also on the time of exposure. Clearly the controls necessary for the determination of methyl methacrylate isotherms at high relative pressures would be complicated and the time and effort involved would not be justifiable for this investigation. The coating is in any case difficult to remove from glassware and its vapour interfered with subsequent isotherms. It also caused difficulty in determining the positions of spring ends.

An adsorption isotherm of methyl methacrylate in sodium Y is shown in figure 9, recorded values are on adsorption-only branches of four runs on separate samples. Desorption, from a sorbent which had been at equilibrium with a monomer vapour phase at relative pressure of between 0.65 and 0.8, followed the adsorption branch down to a relative pressure of about 0.1. Below this pressure considerable time was necessary for desorption to reach a steady state and values on the desorption branch in this low relative pressure region are uncertain. Evacuation of the sorbent

Adsorption-branch isotherms of methyl methacrylate in zeolites.

 $T = 303 \text{ K}$ 

from a relative pressure of 0.1 for periods between one and three days reduced the amount of sorbed phase by only about 5%.

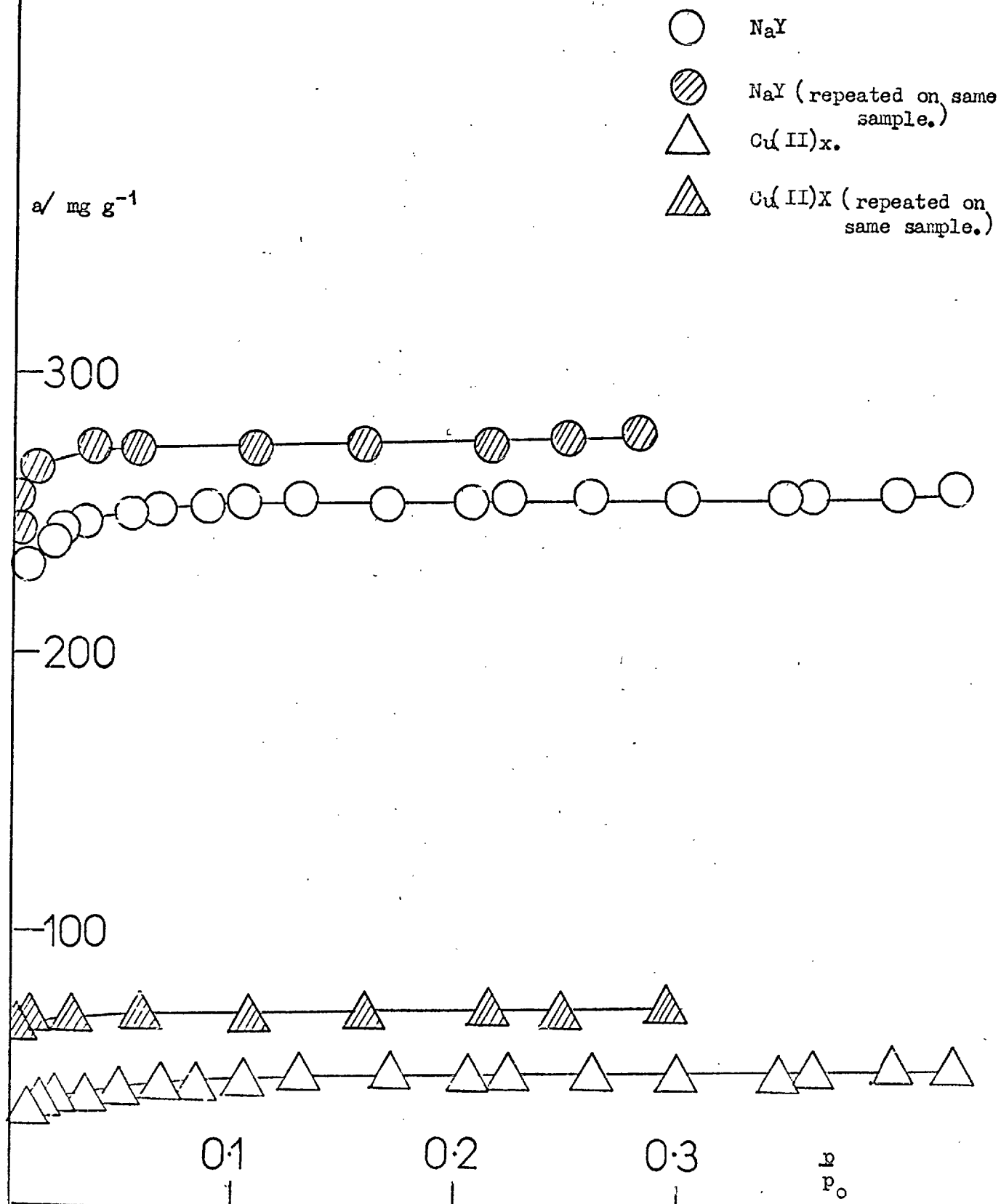
The amount of methyl methacrylate retained by sodium Y after pumping at $<10^{-3}$ Nm⁻² for 24 hours at the temperature of the isotherm (303 K) was, in the four experiments referred to in figure 9, 234 mg g⁻¹, 232 mg g⁻¹, 237 mg g⁻¹ and 235 mg g⁻¹ respectively. The near reproducibility of these results suggests that methyl methacrylate is strongly adsorbed by sodium Y and that a particular amount of the sorbate is held sufficiently strongly within the zeolite to remain undisturbed by these outgassing conditions.

Adsorption-branch isotherms of methyl methacrylate on sodium, potassium L zeolite are also shown in figure 9.

A number of experiments were devised in an attempt to distinguish between strongly adsorbed monomer and polymerized sorbate molecules. If an adsorption-desorption run followed a similar run on the same sorbent with outgassing between the runs, the second run should follow the first if the residue is merely strongly adsorbed monomer. This was not the case and figure 10 shows that, for both sodium Y and copper(II)X zeolites, the second branch values are higher than the first. The choice of a cupric ion-exchanged zeolite was made because of the high carboniogenic activity of such zeolites.

One explanation of the results of figure 10 is that any monomer retained from the first run and converted to polymer would occupy a smaller volume than the same mass of monomer. The volume made available could be occupied by more monomer in the second run. This argument assumes that polymerization must occur much later than

Adsorption-branch isotherms of methyl methacrylate in zeolites

 $T = 313 \text{ K}$ 

within the 24 hour period allowed for sorption to reach a steady-state for otherwise subsequent vapour doses would gradually fill all the available internal volume, including the volume made available by contraction of the sorbed phase. This hypothesis does seem to be rather unlikely and is not supported by the earlier observation that, after the first few hours, no measurable increase took place in the amount of vapour sorbed by a zeolite over a period of several days. The polymerization of monomer on the glass bucket would also, had it been responsible for this apparent increase in sorption capacity, have been detected in this earlier experiment. It is also very unlikely that any change in the structure of the zeolite itself takes place. Apparently, some conformational change must have occurred to the adsorbed material under the conditions employed for outgassing. This change makes more volume available for further sorbate molecules.

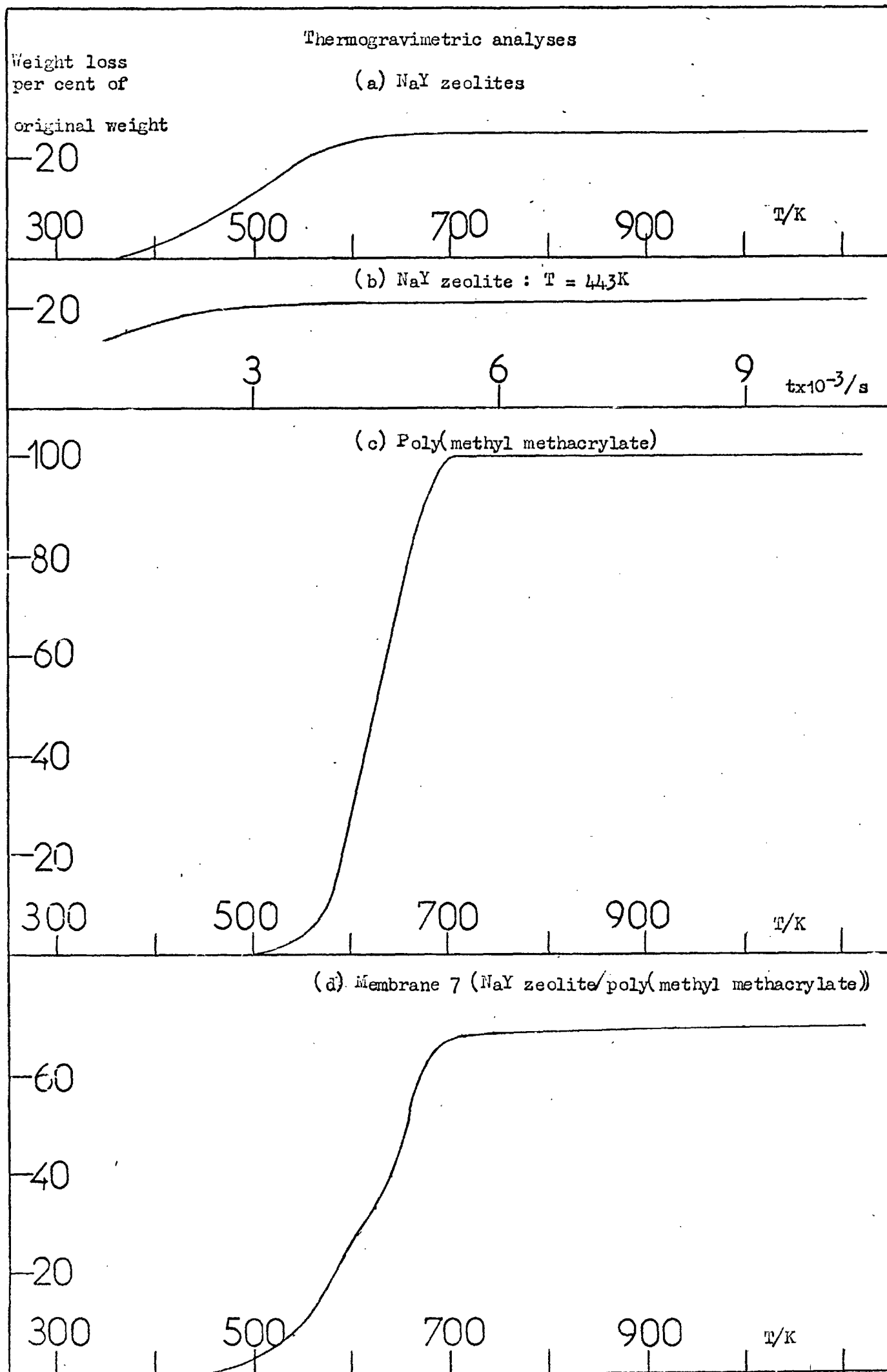
Another feature of figure 10 is an increase in the concentration of adsorbed phase in the copper exchanged zeolite which occurs during the outgassing procedure which separates the runs. In this experiment, however, balance cases containing the two sorbents NaY and Cu(II)X were side by side and shared a common monomer reservoir and manometer. It is therefore possible that a reduction in the volume of the sorbed phase within Cu(II)X, occurring as described above, would make space available to monomer from the other zeolite. Certainly, the shape of the second Cu(II)X isotherm is consistent with the view that much of the volume otherwise available to monomer during the second adsorption run had been filled. A transport of volatile matter from one

sorbent to another in an interconnected gravimetric sorption apparatus has been observed previously⁽¹⁸²⁾.

In spite of the objections raised earlier to the hypothesis that monomer slowly becomes the more dense polymer thus making further space available for sorbate, this argument is supported by many of the observed measurements. The consideration of volume of sorbate per unit volume of sorbent lends further support to the idea. In the intermediate pressure region, 0.39 cm^3 sorbate (if the liquid monomeric form is assumed) per 1 cm^3 of NaY sorbent would become $0.32 \text{ cm}^3 \text{ cm}^{-3}$ when the sorbate becomes a polymer. The second run in figure 10 shows that $0.42 \text{ cm}^3 \text{ cm}^{-3}$ of polymer are present at intermediate relative pressures, and if some of this additional sorbate is still in monomeric, liquid form then the volume of sorbate would be lower and nearer to the $0.39 \text{ cm}^3 \text{ cm}^{-3}$ of liquid present during the first run. Such a description is necessarily based on many assumptions, but it is at least plausible. (The densities of liquid, monomeric methyl methacrylate and solid poly(methyl methacrylate) are assumed to be 0.944 g cm^{-3} and 1.17 g cm^{-3} respectively.)

If, as is suspected, polymeric methyl methacrylate is present within the zeolitic cavities the question arises, are these chains of high, intermediate or low molecular weight. The type of material which would be of most use in the adhesion of a zeolite to external polymer would be an internal, high molecular weight methyl methacrylate polymer chain extending through the windows and into the external matrix. If the internal phase polymer were of low molecular weight, however, one would expect it to have been outgassed during the evacuation procedure which followed the measurement of isotherms. Any attempt to raise the temperature of outgassing may give rise to complications, for although it could allow the desorption of strongly adsorbed monomer or low molecular weight polymer it could also be responsible for inducing further polymerization thermally.

Before any further experiments were conducted on the adsorption of methyl methacrylate in zeolites, it was decided that an investigation of the range of temperature over which the monomer residues in zeolites were stable should be made. A series of thermogravimetric analyses were made under atmospheric conditions and some of these results are shown in figure 11. Diagrams (a), (b) and (c) of figure 11 show TGA curves for NaY zeolite and a sample of poly(methyl methacrylate) respectively while diagram (d) shows the curve for a composite of these materials. In all runs the temperature was increased at a rate of 0.16 K s^{-1} . Under atmospheric pressure, a sample of NaY zeolite lost nearly all of



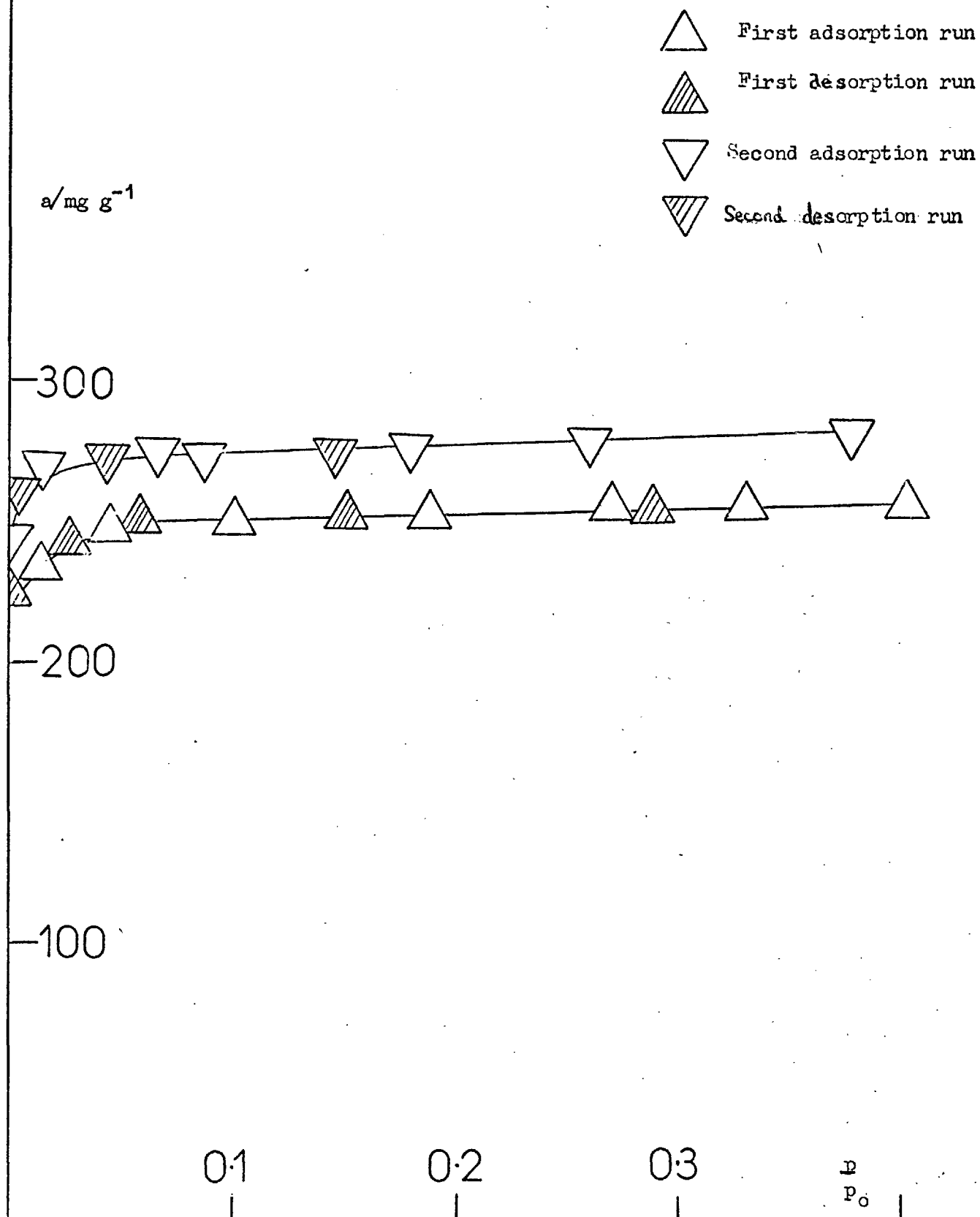
its water at 720 K, a temperature it reached after about three-quarters of an hour.

Poly(methyl methacrylate) decomposes rapidly after a temperature of 470 K has been reached. Clearly a lower temperature has to be employed when outgassing this polymer. Of even greater significance to a study of composite materials was the observation that poly(methyl methacrylate) discoloured and became viscous when heated to about this temperature under vacuum. A temperature of 443 K was about the highest which a membrane could withstand before losing shape. Accordingly, TGA of NaY zeolite at this temperature was conducted and the result is shown in figure 11(b). About 90% of water is lost after about three hours at this temperature under atmospheric pressure. A similar test for loss in weight when the polymer was maintained at this temperature for some time showed that the material was able to withstand this treatment with no measurable weight loss.

The rather low temperature at which the composite material begins to lose weight could be interpreted in two ways. Water from the filler zeolite could be evaporating, or perhaps monomer or low molecular weight polymers could be evaporating. The slight shoulder at about 25 to 30% weight loss is probably due to completion of an evaporation process while the second shoulder is the completion of polymer decomposition.

A further investigation was made of the behaviour of the residue present in NaY zeolite after methyl methacrylate sorption under reduced pressure. After two consecutive adsorption-desorption isotherms had been determined, as represented by figure 12, the

Adsorption isotherms of methyl methacrylate on NaY zeolite

 $T = 313 \text{ K}$ 

NaY sorbent was outgassed for 48 hours under a pressure of $< 10^{-3} \text{ Nm}^{-2}$ at the temperature of the experiment (313 K). The amount of organic residue per gramme of anhydrous zeolite was 244 mg or 17 mg above the amount contained after outgassing for 48 hours under a similar pressure following the first adsorption-desorption run.

After the third adsorption-branch of figure 9 had been measured, the sodium Y zeolite sorbent was outgassed for 48 hours at the temperature of the isotherm (303 K) followed by a further period of 24 hours at 443 K. Over the whole 72 hour outgassing period the pressure was less than 10^{-5} Nm^{-2} . As was mentioned earlier, the amount of residue left after the first outgassing treatment was 237 mg g^{-1} while the higher temperature removed further residue to leave 170.4 mg g^{-1} . It is noteworthy that a repetition of this experiment (the fourth adsorption-branch recorded in figure 9) yielded the respective residue concentrations 235 mg g^{-1} and 170.7 mg g^{-1} at the two outgassing temperatures.

A further isotherm in this methyl methacrylate/sodium Y zeolite system at a temperature of 323 K yielded the following results in the desorption branch:

Temperature of <u>zeolite</u>	Relative pressure <u>of vapour phase</u>	Amount of vapour <u>adsorbed by zeolite</u>
T/K		a/mg g^{-1}
323	0.435	262.0
323	$< 10^{-7}$	237.3
443	$< 10^{-7}$	173.4
573	$< 10^{-7}$	54.3

These values were measured 24 hours after the temperatures had been reached in the case of the low pressure results. In other cases 24 hours was allowed between successive measurements of amount sorbed and relative pressure.

From this evidence, there can be little doubt that polymeric material is present within the zeolite and that it cannot be removed by evacuation even at elevated temperatures. From the TGA curve shown in figure 11(d) it may be seen that temperatures in excess of 700 K are needed to decompose the polymeric material in air.

Whether or not the undesorbed phase was of intracrystalline polymer and if it could remain in the same position in the presence of water was the subject of further investigations. Clearly polymer is associated with the zeolite after monomer sorption, but the location of this polymer has yet to be determined.

One way in which this subject was investigated was by argon adsorption isotherms at 77.6 K, adsorption runs being repeated after (i) outgassing the NaY zeolite at 620 K for 24 hours (ii) contact with methyl methacrylate vapour and (iii) further contact with both vapour phase and liquid phase water. Figure 13 shows the results of this series of isotherms. Curve 1 shows the adsorption of argon on pure sodium Y while the circular symbols of curve 2 show the isotherm after the same sorbent had been in contact with methyl methacrylate vapour at $T = 323$ K and $\frac{p}{p_0} = 0.35$ for 24 hours followed by outgassing at 443 K, $< 10^{-3} \text{ Nm}^{-2}$ for 24 hours. Such a considerable reduction in the volume available to argon, after contact of the sorbent with monomer, may

Adsorption of argon in NaY zeolite after various treatments

 $T = 77.6 \text{ K}$ $a/\text{cm}^3(\text{STP})\text{cm}^{-3}$

○, □ First experiment
⊙, ▨ Second experiment

400

1

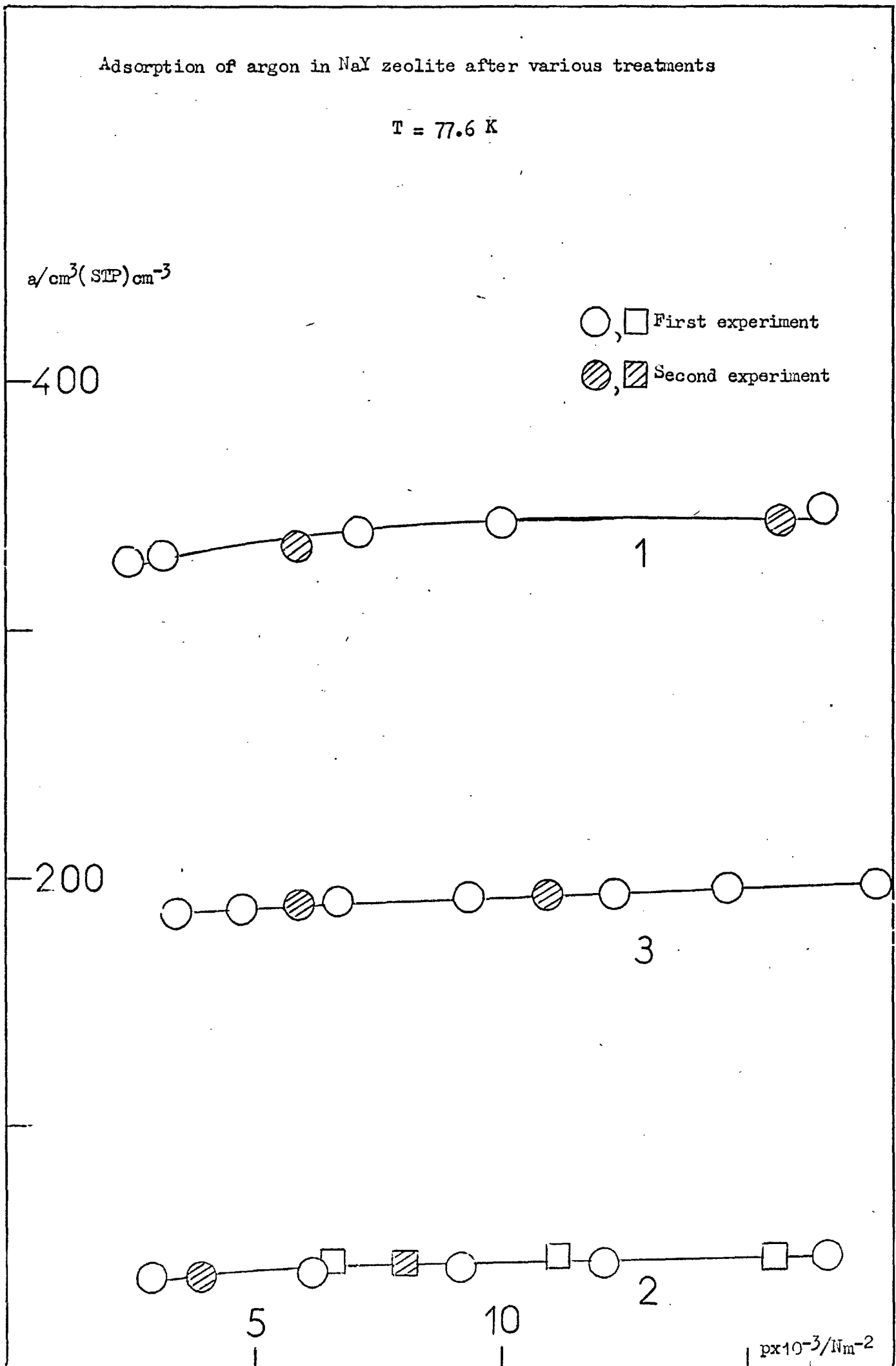
200

3

2

5

10

 $\text{px}10^{-3}/\text{Nm}^{-2}$ 

be accounted for if the polymer produced is contained within the zeolitic cavities. No slow process of argon adsorption was observed, in fact each value of the isotherm marked on curve 2 took about 10 minutes to reach a steady state although an hour was allowed for the determination of each value.

The square symbols of curve 2 represent the adsorption of argon on the sorbent after it had been in contact with water vapour at $T = 323 \text{ K}$ and $p = 0.34$ for 24 hours followed by outgassing at 443 K and $< 10^{-3} \text{ Nm}^{-2}$ for 24 hours. The difference between the two sets of values for curve 2 is slight and could be accounted for by experimental errors. In any case, the adhesion between NaY zeolite and poly(methyl methacrylate) is stable in the presence of water vapour at this temperature and pressure.

Curve 3 shows the result of a much more severe testing of the bond between an organic material and an hydrophilic substance. Liquid water was condensed into the chilled sorbent cell from a reservoir, the cell was isolated, surrounded by insulating material and maintained at 323 K for 48 hours before being outgassed under the conditions described above. Some change in the nature of the adhesion between the phases must have occurred under these conditions. Curve 3 was reproducible and reversible.

A point of particular interest with regard to this experiment is that after the removal of the sorbent from its cell, it was thermogravimetrically analysed and found to contain 171 mg of polymer per gramme of zeolite. This value is very close to those found after other methyl methacrylate sorption experiments followed

by similar outgassing treatments (170.4 mg g⁻¹, 170.7 mg g⁻¹ and 173.4 mg g⁻¹).

The conclusion drawn from this experiment was that the presence of liquid water was sufficient to break down polymer-zeolite adhesion but that this and subsequent outgassing did not remove any organic material from the composite.

A parallel sequence of experiments was conducted on a zeolite of very different structure, sodium-potassium L zeolite. The results of these experiments are shown in figure 14. The effects of water vapour and liquid water on polymer within this zeolite are not apparent from this adsorption isotherm of argon, but reduction in the internal volume available to argon molecules due to the presence of polymer in the L zeolite is less than in the Y zeolite.

At this stage the sodium Y experiment was repeated on a fresh sample in order to confirm the values obtained earlier. The hatched symbols of figure 13 are the results of this second run.

These argon isotherms suggest that the formation of polymer in sodium Y reduces the volume available to argon very considerably and that a mild hydrothermal treatment renders this polymer more mobile. An increase in volume available to argon is thereby effected. Polymer formation in sodium potassium L zeolite is either unaffected by this mild hydrothermal treatment, or the adhesion between polymer and the host structure has no effect on the capacity of the composite for argon molecules.

Complementary experiments involving measurements of water sorption isotherms on poly(methyl methacrylate), the zeolites and

Adsorption of argon on (NaK)L zeolite after various treatments

$T = 77.6 \text{ K}$

Curve 1 Pure zeolite

Curve 2 After treatment with methyl methacrylate

Curve 3 After subsequent treatment with water vapour

Curve 4 After treatment with liquid water at 323 K

$a/\text{cm}^3(\text{STP})\text{cm}^{-3}$

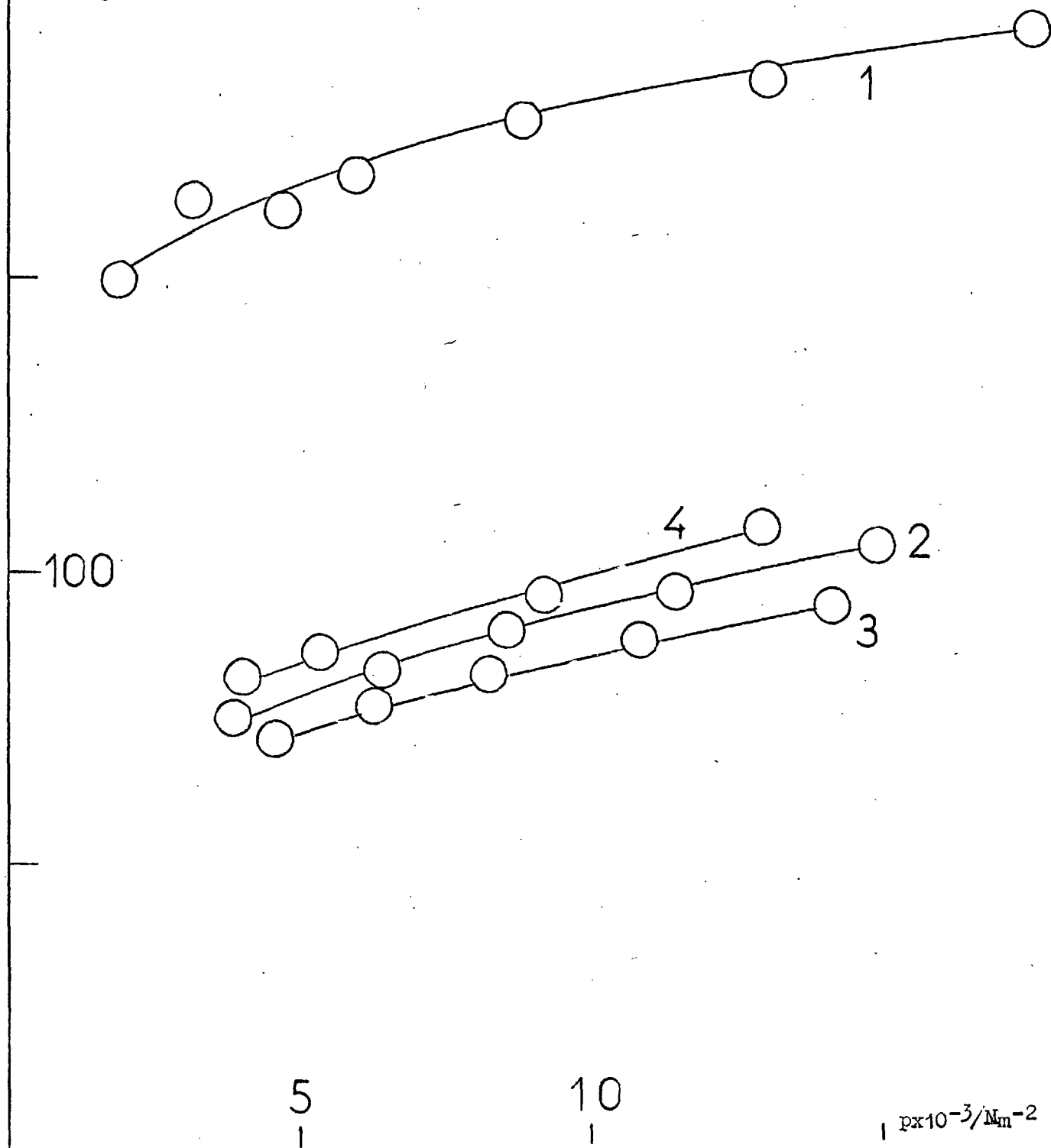
200

100

5

10

$\times 10^{-3}/M_m^{-2}$



zeolite - poly(methyl methacrylate) composite materials were attempted in order to study other effects of water on these substances. Figures 15 and 16 show water sorption isotherms on the various fillers which have been included in poly(methyl methacrylate) based composites. These isotherms have been measured at single temperatures only, but changes in the shape of the curves caused by temperature changes would be apparent in the very low pressure region. Figure 17 shows the sorption isotherm for poly(methyl methacrylate), the values shown are of two runs at different temperatures on the same example. The values are representative, and the four samples which were examined for water sorption all had rather similarly shaped isotherms. In agreement with other determinations⁽¹⁸³⁾, there is no measurable difference between water sorption isotherms at different temperatures. The heat of water adsorption in poly(methyl methacrylate) is presumably very close to the heat of condensation of water.

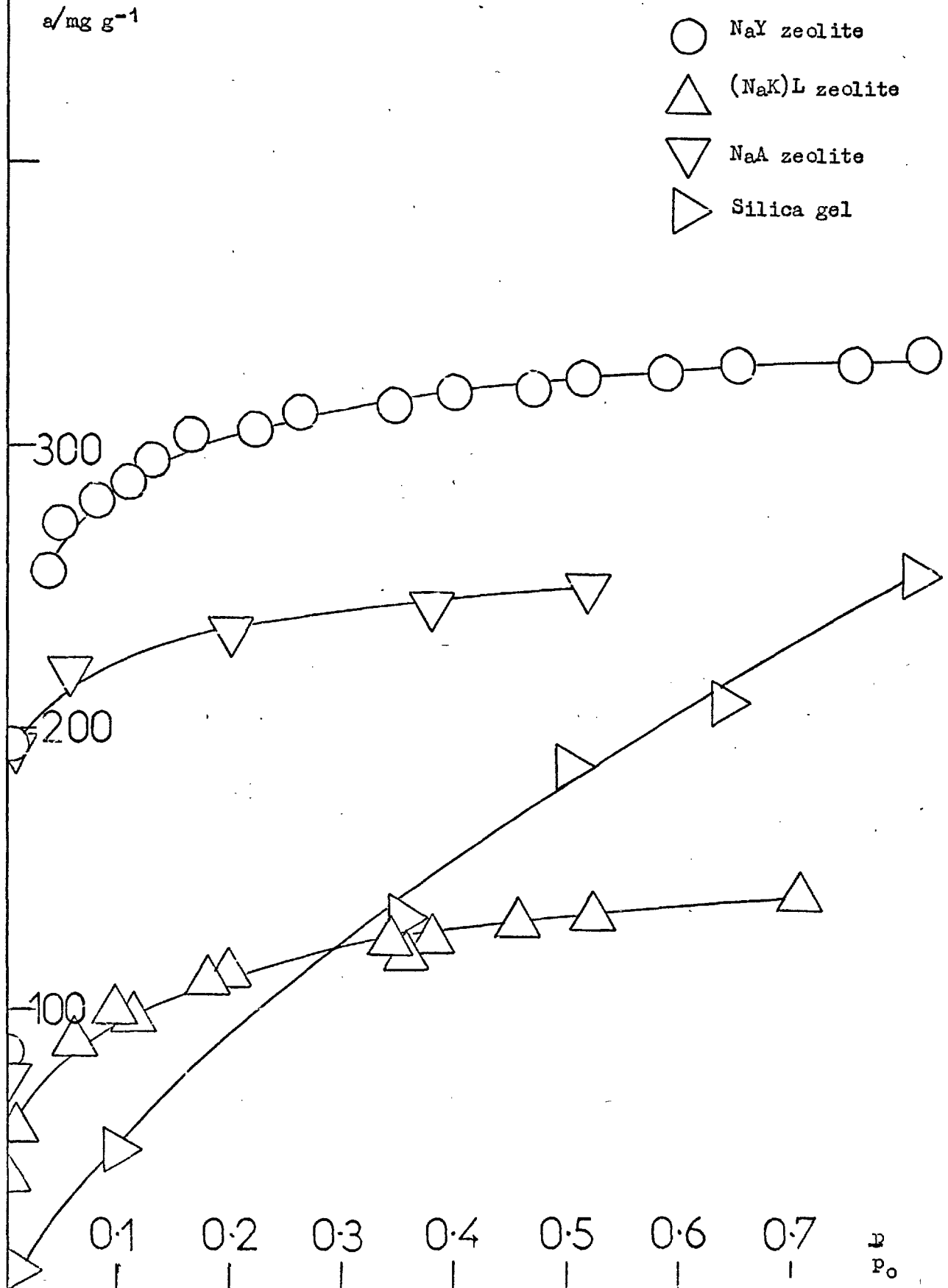
To obtain a more general view of the sorption of water in composite materials which include poly(methyl methacrylate), a wide range of compositions was employed. In the case of NaY filled composites, the weight fraction of zeolite is in the range

$$0.05 < w_z < 0.86$$

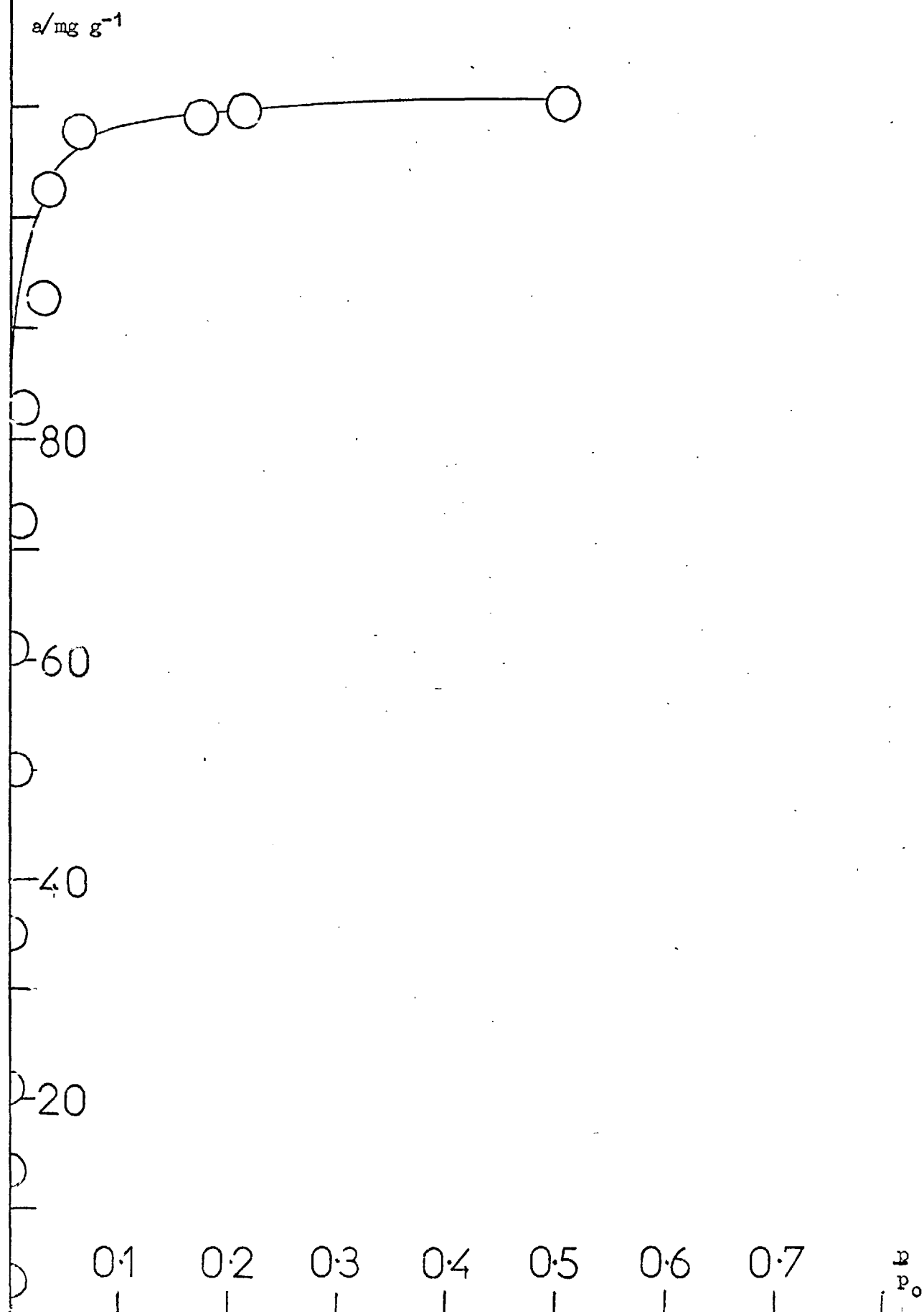
Weight fraction of zeolite, w_z , is defined as the mass of zeolite per unit mass of composite. Values of w_z can be determined directly from TGA runs, although some results were checked by chemical analysis of the composite materials.

Table 4 shows the composition of some of the composite materials whose water sorption isotherms were measured. Some of

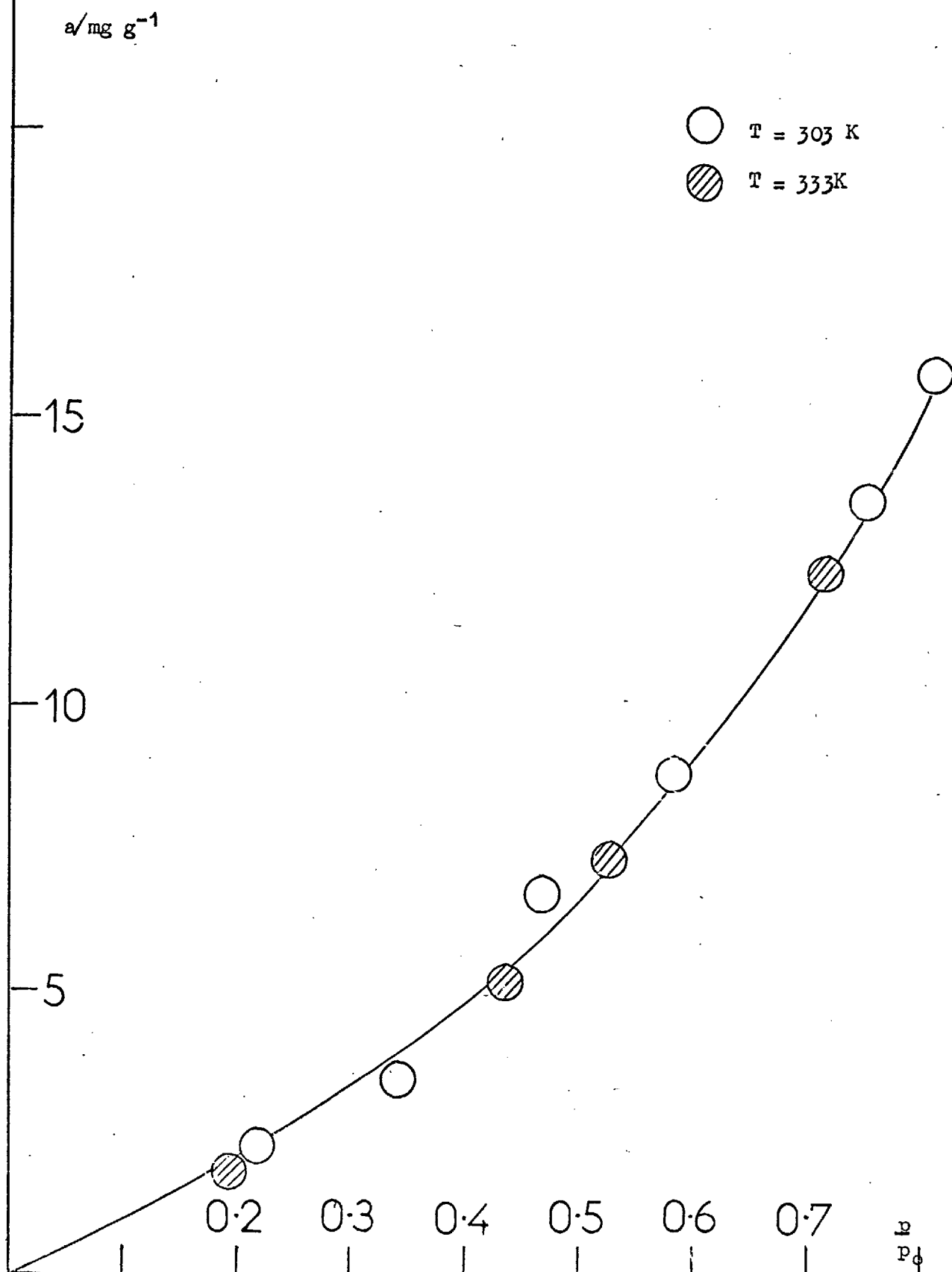
Adsorption-branch isotherms of water in various sorbents.

 $T = 303\text{ K}$ 

Adsorption-branch isotherms of water in Cu(II)X zeolite.

 $T = 313\text{ K}$ 

Adsorption-branch isotherms of water in poly(methyl methacrylate)
(membrane IV)



these materials were in the form of membranes while others were zeolites containing residual polymeric material after monomer sorption experiments. These latter materials are referred to as powders.

Table 4

Composite materials containing poly(methyl methacrylate).

<u>Name of filler</u>	<u>Weight fraction of zeolite, w_z^*</u>	<u>Volume fraction of filler, ϕ_f^*</u>	<u>Description of material</u>
NaY zeolite	0.327	0.306	Membrane 1
NaY zeolite	0.048	0.040	Membrane 2
NaY zeolite	0.269	0.244	Membrane 6
NaY zeolite	0.710	0.825	Membrane 7
NaY zeolite	0.178	0.131	Membrane 8
NaY zeolite	0.346	0.326	Membrane 9
NaY zeolite	0.852		Powder A
NaY zeolite	0.855		Powder B
(Na,K)L zeolite	0.117		Membrane 10
(Na,K)L zeolite	0.973		Powder C
(Na,K)L zeolite	0.984		Powder D
NaA zeolite	0.237		Membrane 11
NaA zeolite	0.983		Powder E
6u(II)X zeolite	0.936		Powder F
Silica gel	0.283		Membrane 12
Silica gel	0.996		Powder G

(* See Appendix A)

Water sorption isotherms for the composite materials containing NaY, (Na,K)L, NaA, Cu(II)X and silica gel are shown in figures 18 to 22 respectively. In each case, an isotherm for the free powder is shown for comparison. According to expectations, the uptake of water in a sequence of composites of different composition is reduced as the weight fraction of zeolite is lowered.

A more interesting comparison of water uptake by the composites may be made if allowances are made for the proportions of polymer matrix and zeolite as well as for the uptake of water in the polymer phase. A simple model, in which gas gaps are ignored, allows the amount of water taken up by a composite material, a_c , to be expressed in terms of the weight fractions of zeolite and of polymer (both external and intracrystalline), w_z and w_p respectively, and the amounts of water taken up by the zeolite and polymer-phases, a_z and a_p respectively.

$$a_c = w_z a_z + w_p a_p$$

This model allows a comparison to be made directly between a derived value of a_z and the amount of water taken up by the zeolite as a free powder, a_o .

$$\frac{a_z}{a_o} = \frac{a_c - w_p a_p}{a_o w_z}$$

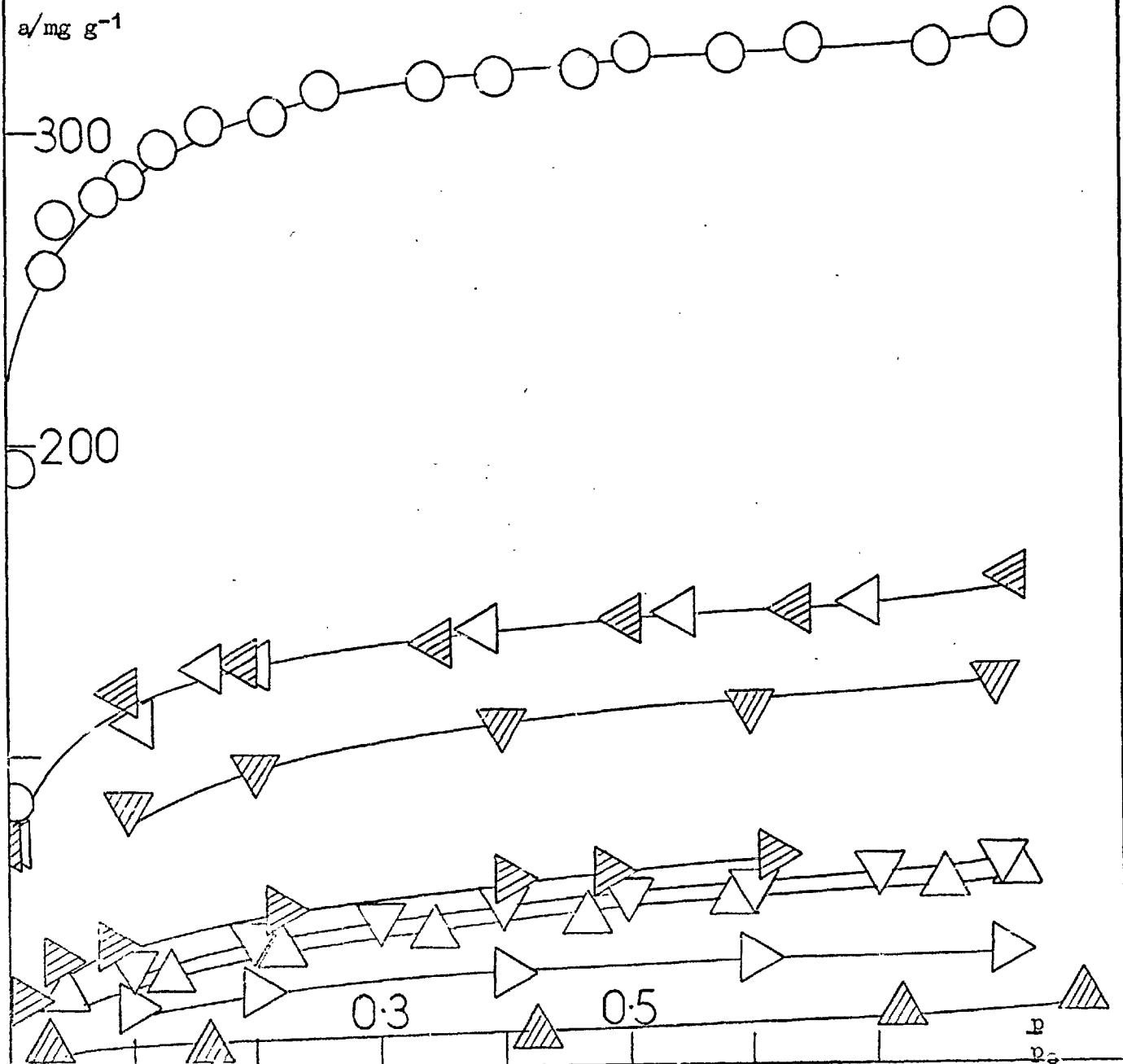
The value of a_p is assumed to be independent of filler concentration and w_p is related to w_z by the expression:

$$w_z + w_p = 1$$

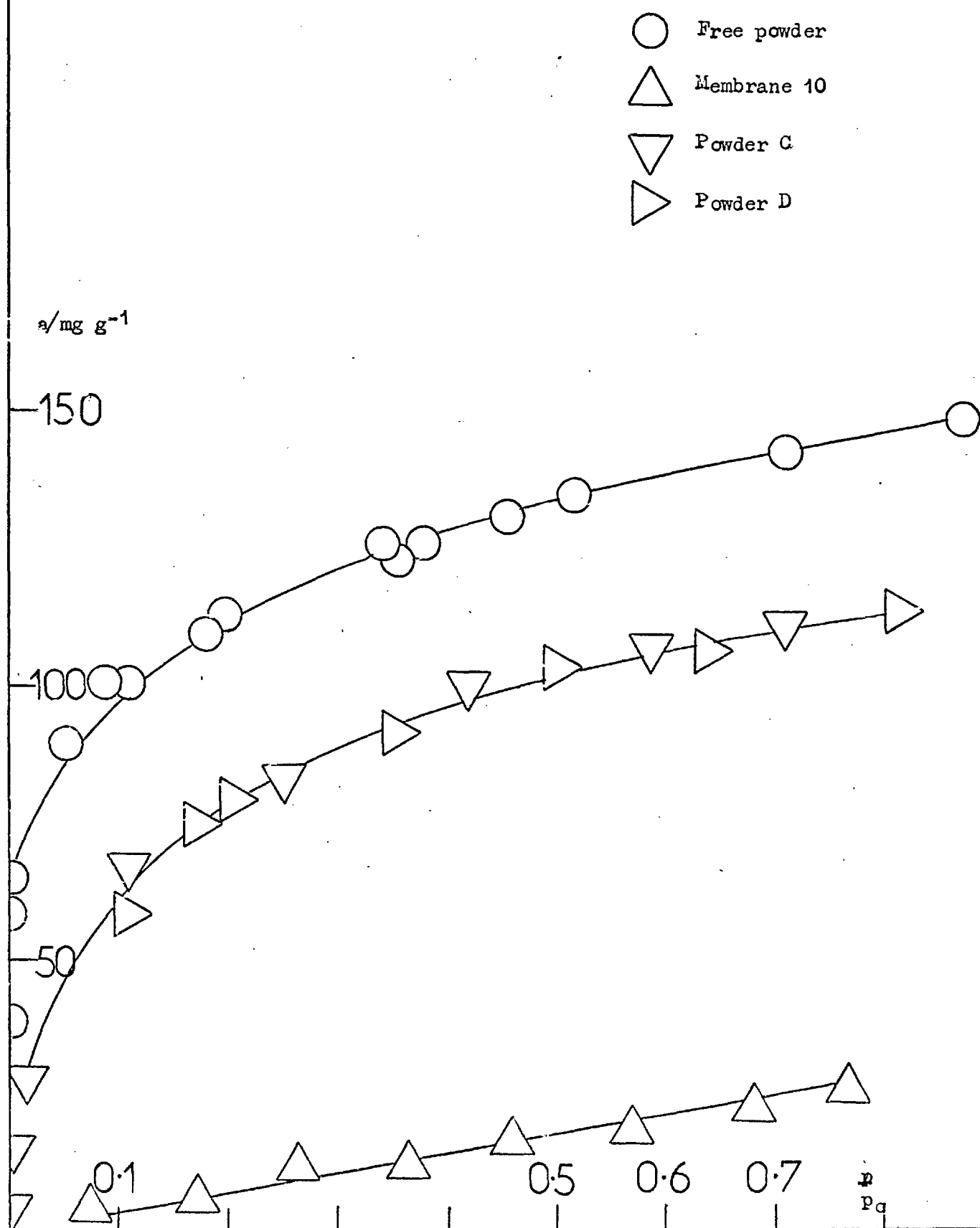
Adsorption-branch isotherms of water in NaY zeolite filled composites.

$T = 303K$

- | | | |
|---------------|--------------|--------------|
| ○ Free powder | ▽ Membrane 6 | ▤ Membrane 9 |
| △ Membrane 1 | ▨ Membrane 7 | ◁ Powder A |
| ▧ Membrane 2 | ▷ Membrane 8 | ▥ Powder B |



Adsorption-branch isotherms of water in (NaK)L zeolite filled composites

 $T = 303 \text{ K}$ 

Adsorption-branch isotherms of water in NaA zeolite filled composite.

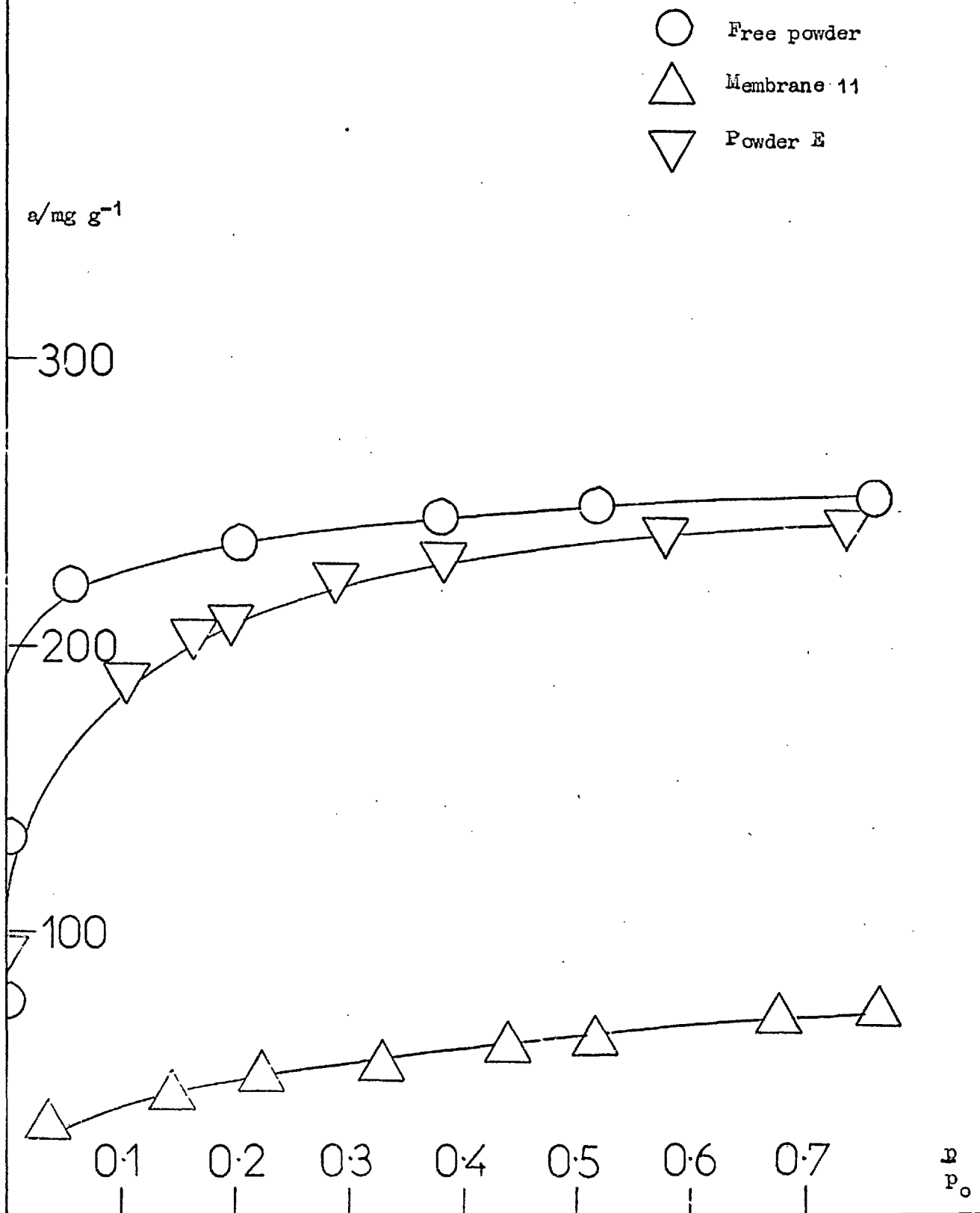
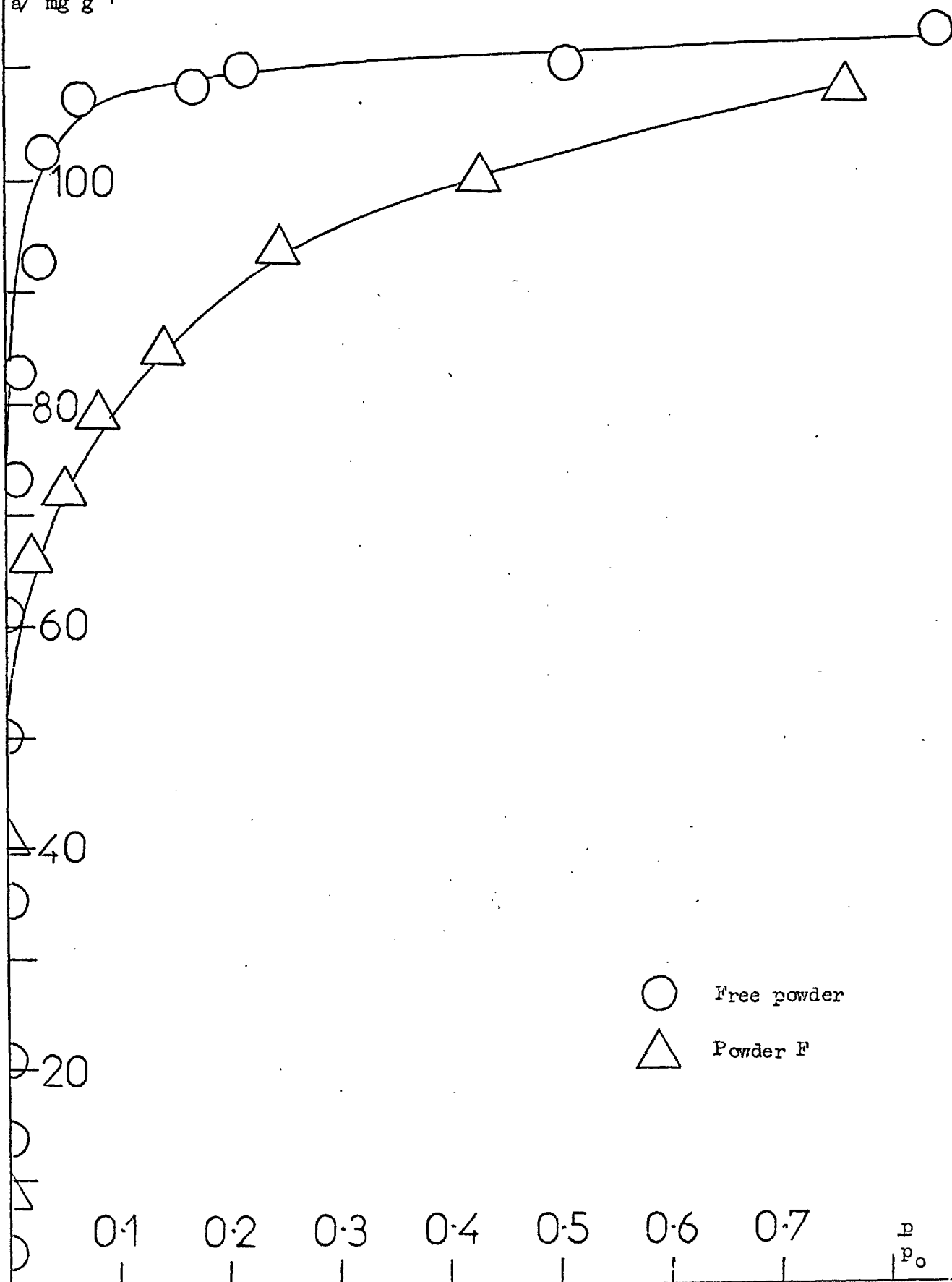
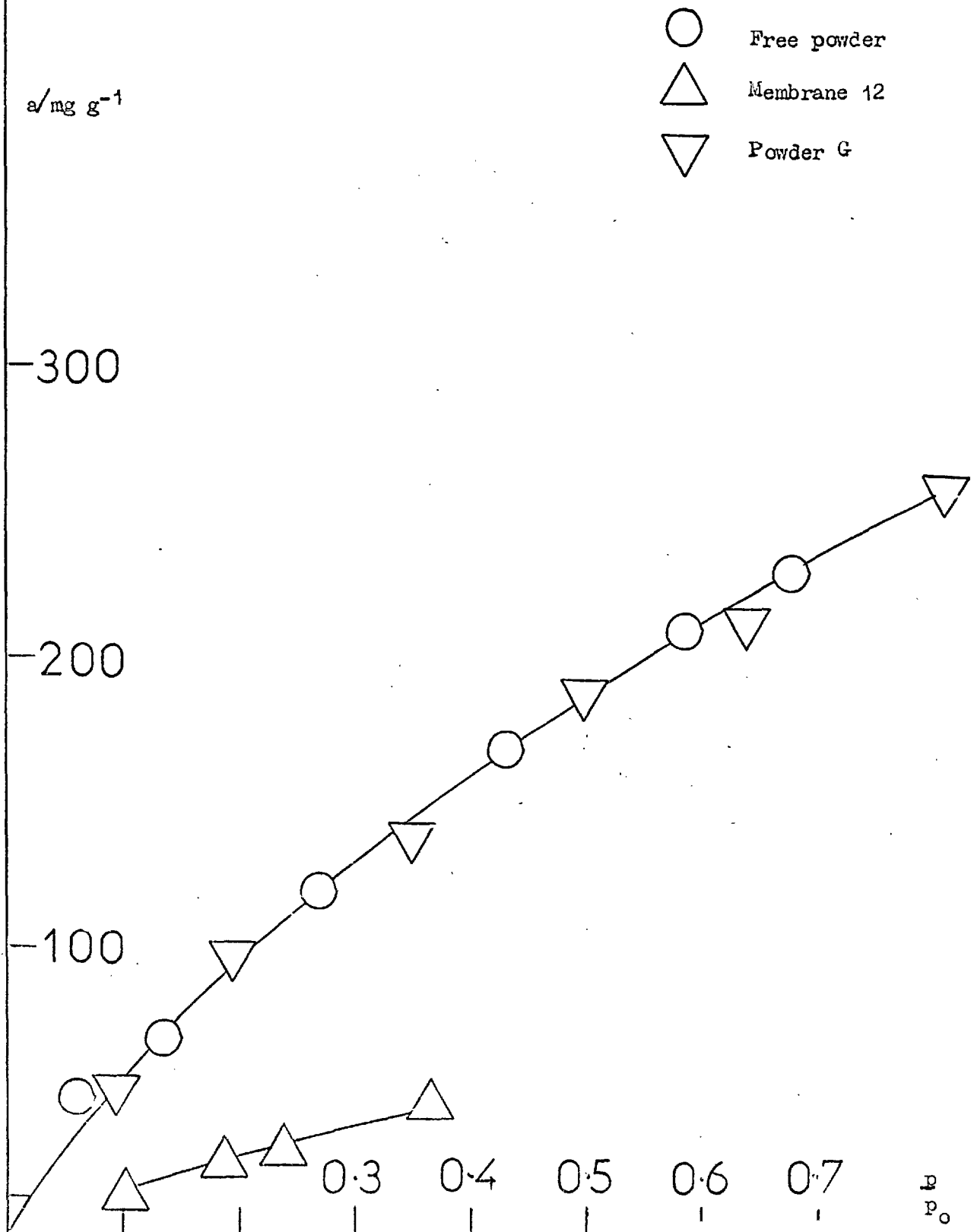
 $T = 303 \text{ K}$ 

Figure 21

Adsorption-branch isothermas of water in Cu(II)X zeolite filled composites. $T = 313 \text{ K}$ $a / \text{mg g}^{-1}$ 

Adsorption-branch isothermas of water in silica gel filled composites.

 $T = 303 \text{ K}$ 

Consequently,

$$\frac{a_z}{a_o} = \frac{a_c - (1-w_z) a_p}{a_o w_z}$$

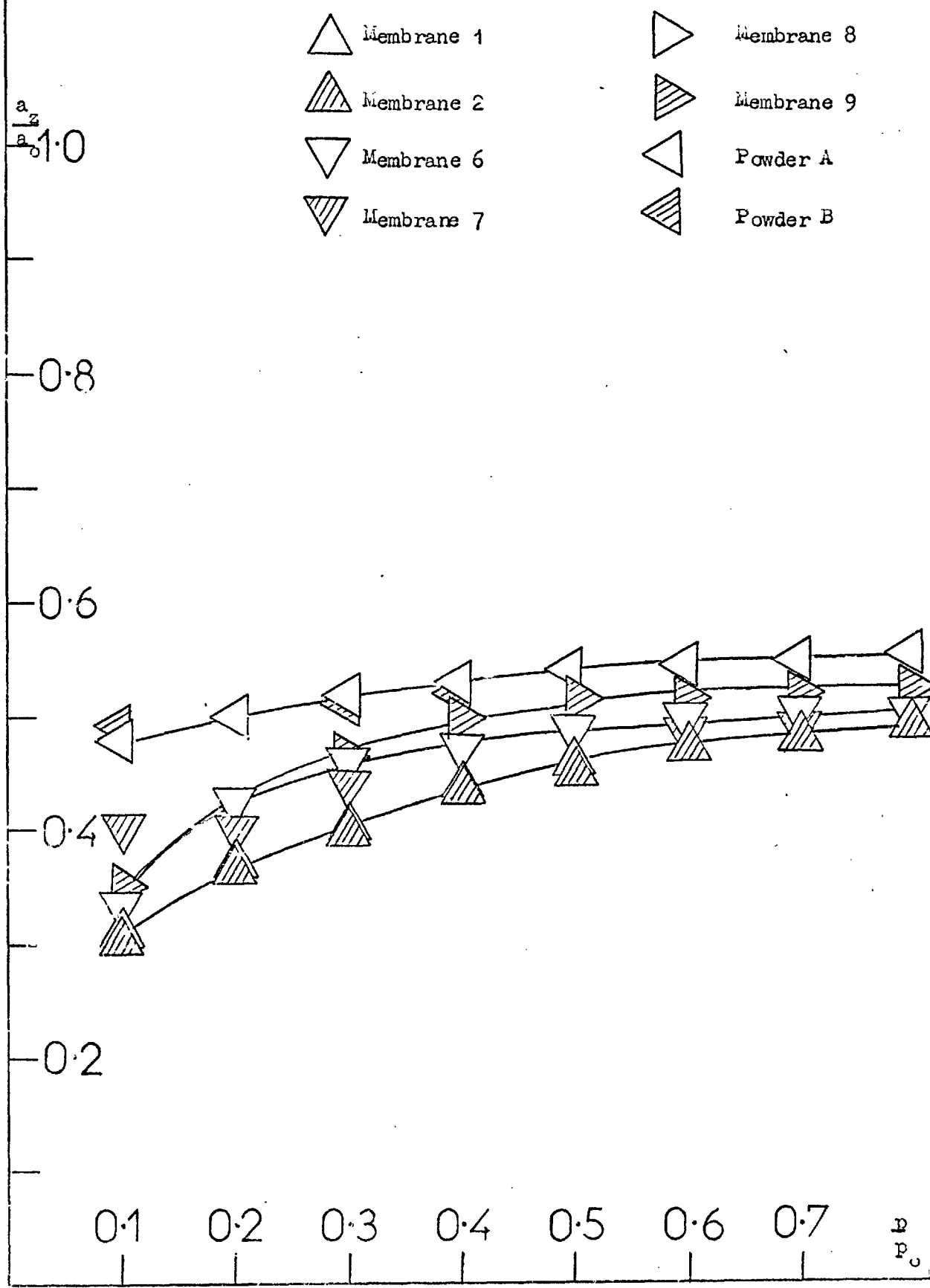
and a_c , a_p and a_o are measured directly from isothermal experiments on the composite, homopolymer and free zeolite respectively. The value of w_z is calculated from a TGA run or chemical analysis.

The value of this model is that it allows a plot of $\frac{a_z}{a_o}$ to be drawn against relative pressure, and this graph yields most important information. If the internal cavities of the zeolite are unoccupied by polymer then water molecules would enter these cavities, increasing the value of $\frac{a_z}{a_o}$ towards unity. The presence of external gas gaps would also increase the value of $\frac{a_z}{a_o}$, and if these two conditions of internal and external cavities available for water adsorption were fulfilled the value of $\frac{a_z}{a_o}$ would be higher than unity.

Reference to figures 23 to 27 shows that in some cases the value of $\frac{a_z}{a_o}$ is well below unity which suggests that in these cases (notably NaY and (Na,K)L filled composites) much of the internal zeolitic volumes are occupied by polymer and gas gaps are not present.

The largest decrease in the ratio occurs when the filler is NaY zeolite. This is probably because this zeolite includes large cavities affording plenty of space for polymer molecules. As the internal cavities of the zeolites become smaller, a lower proportion of the total internal volume would be available to large molecules such as methyl methacrylate, and the reduction of $\frac{a_z}{a_o}$ would be less great. Figures 23 to 25 illustrate this trend.

Adsorption-branch isotherms of water in NaY zeolite filled composites.

 $T = 303 \text{ K}$ 

Adsorption-branch isotherms of water in (Na,K)L zeolite filled composites.

$T = 303 \text{ K}$

$\frac{a_z}{a_0}$

1.0



Membrane 10



Powders C and D

0.8

0.6

0.4

0.2

0.1

0.2

0.3

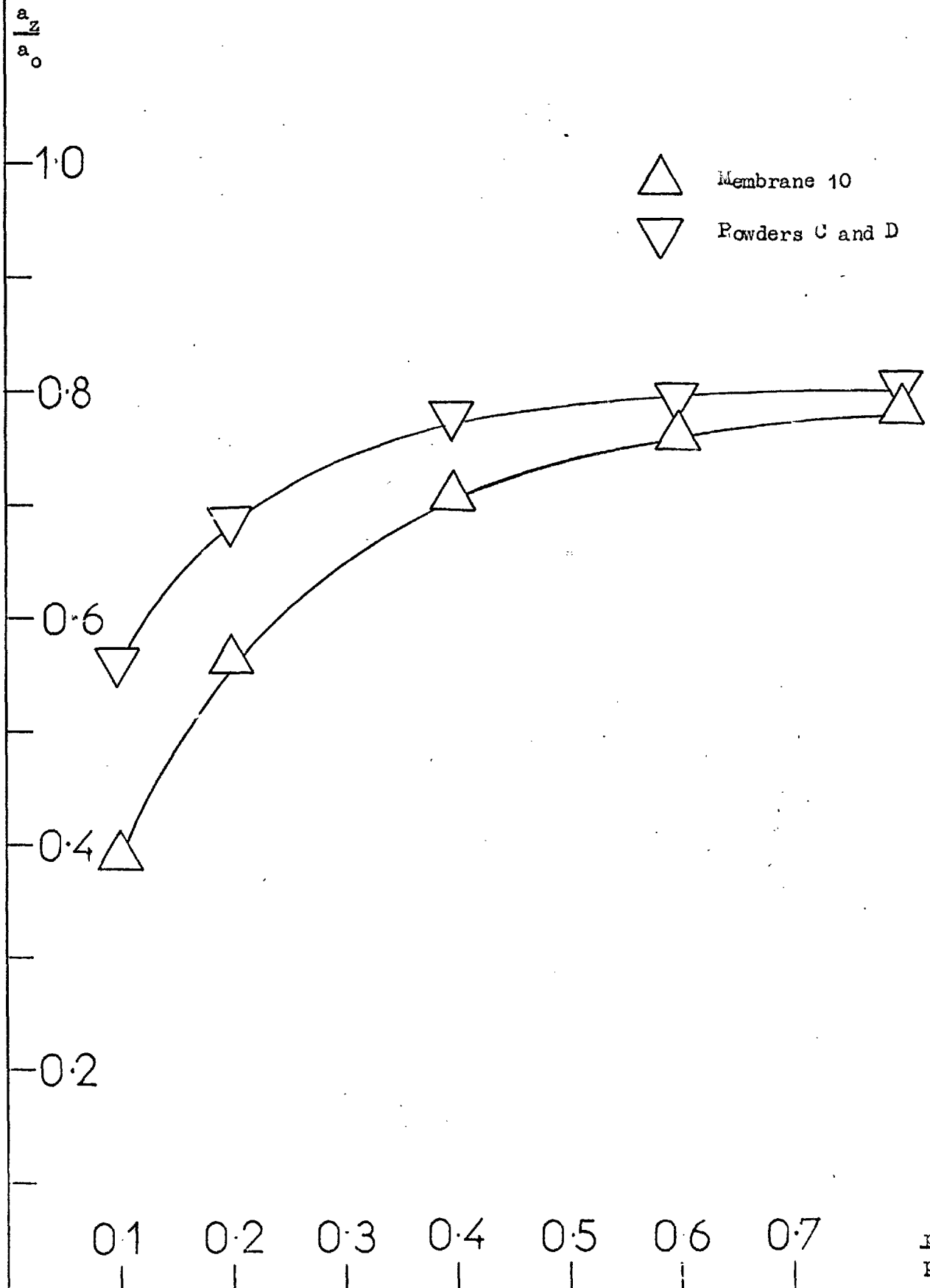
0.4

0.5

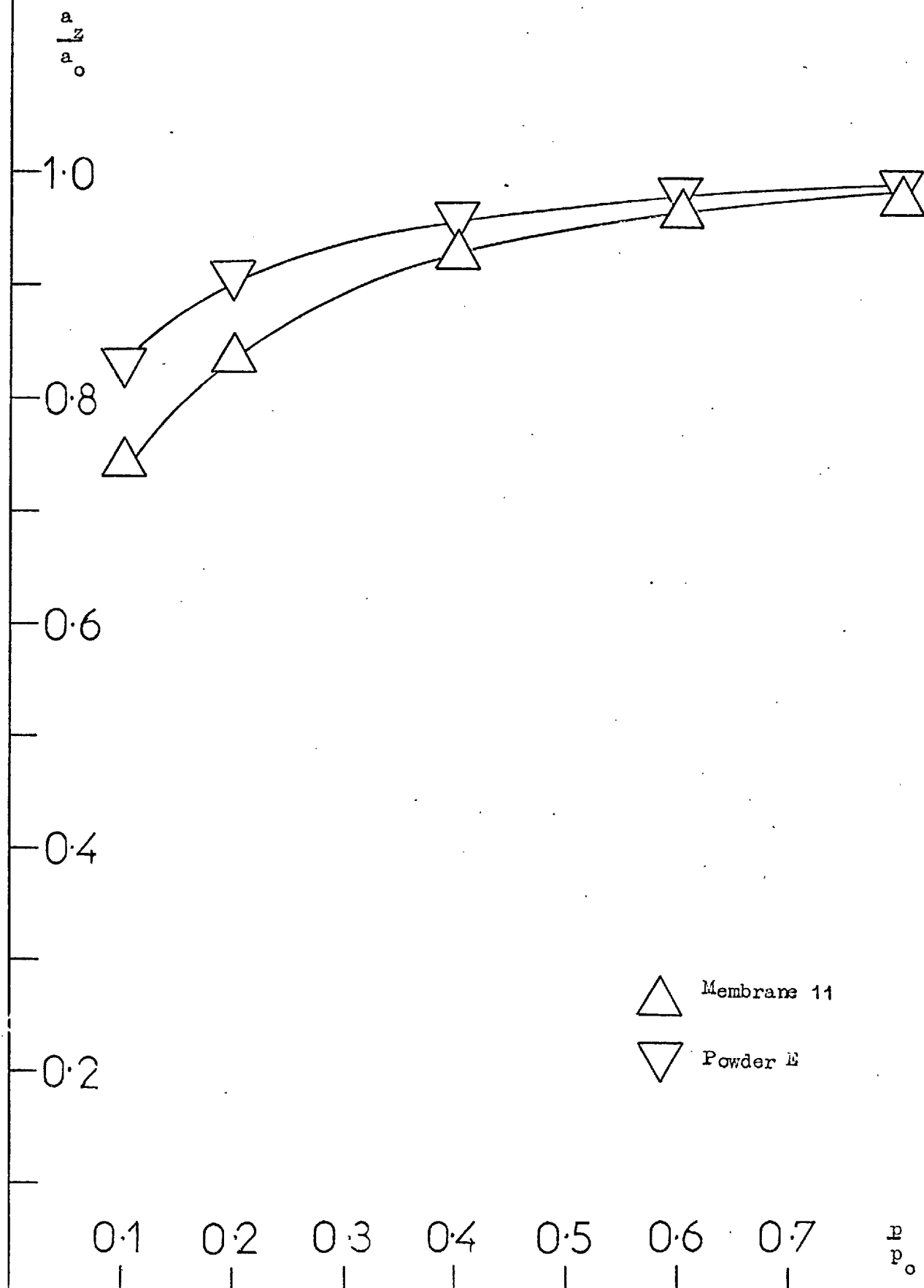
0.6

0.7

$\frac{p}{p_0}$

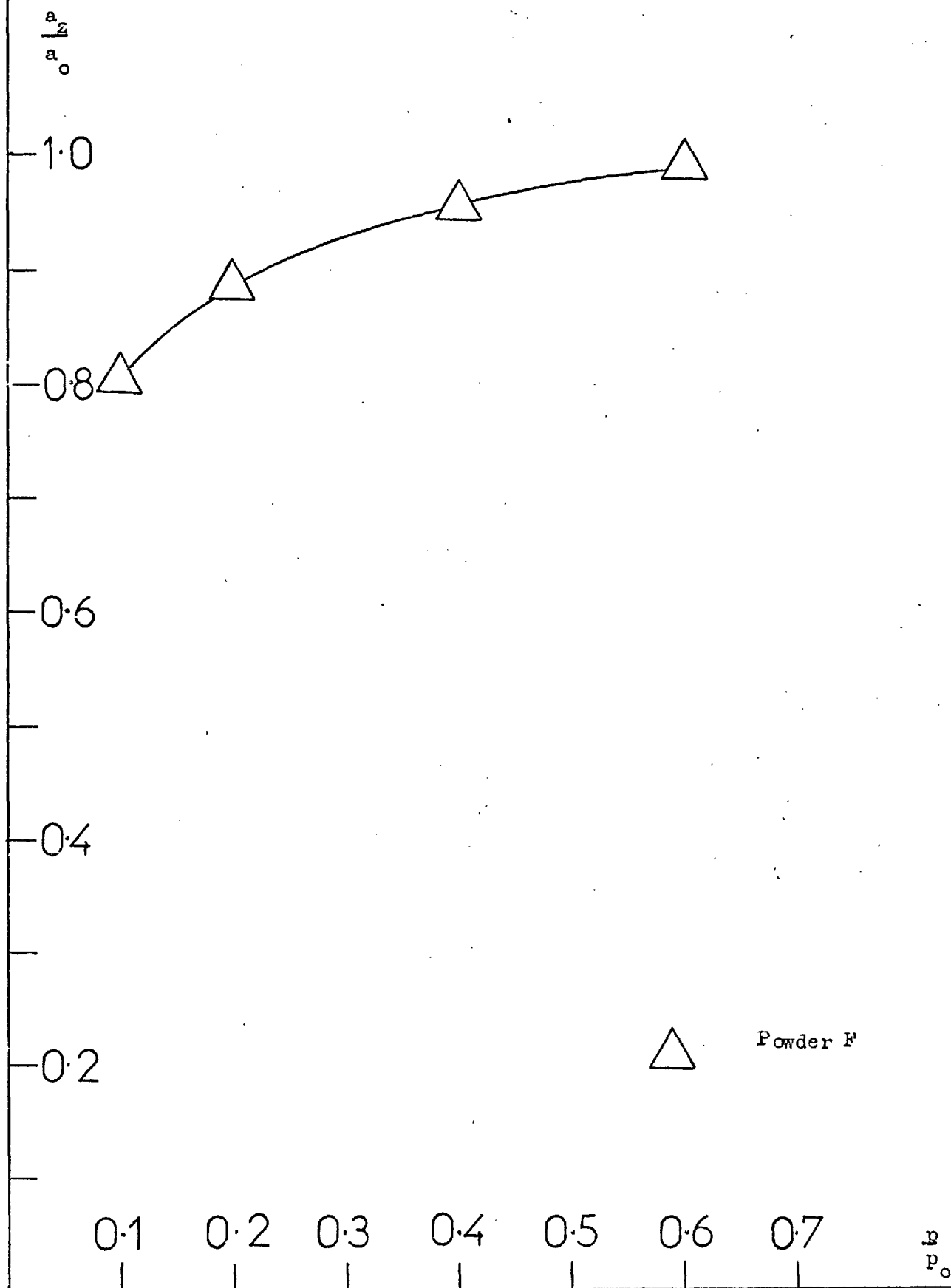


Adsorption-branch isotherms of water in NaA zeolite filled composites.

 $T = 303 \text{ K}$ 

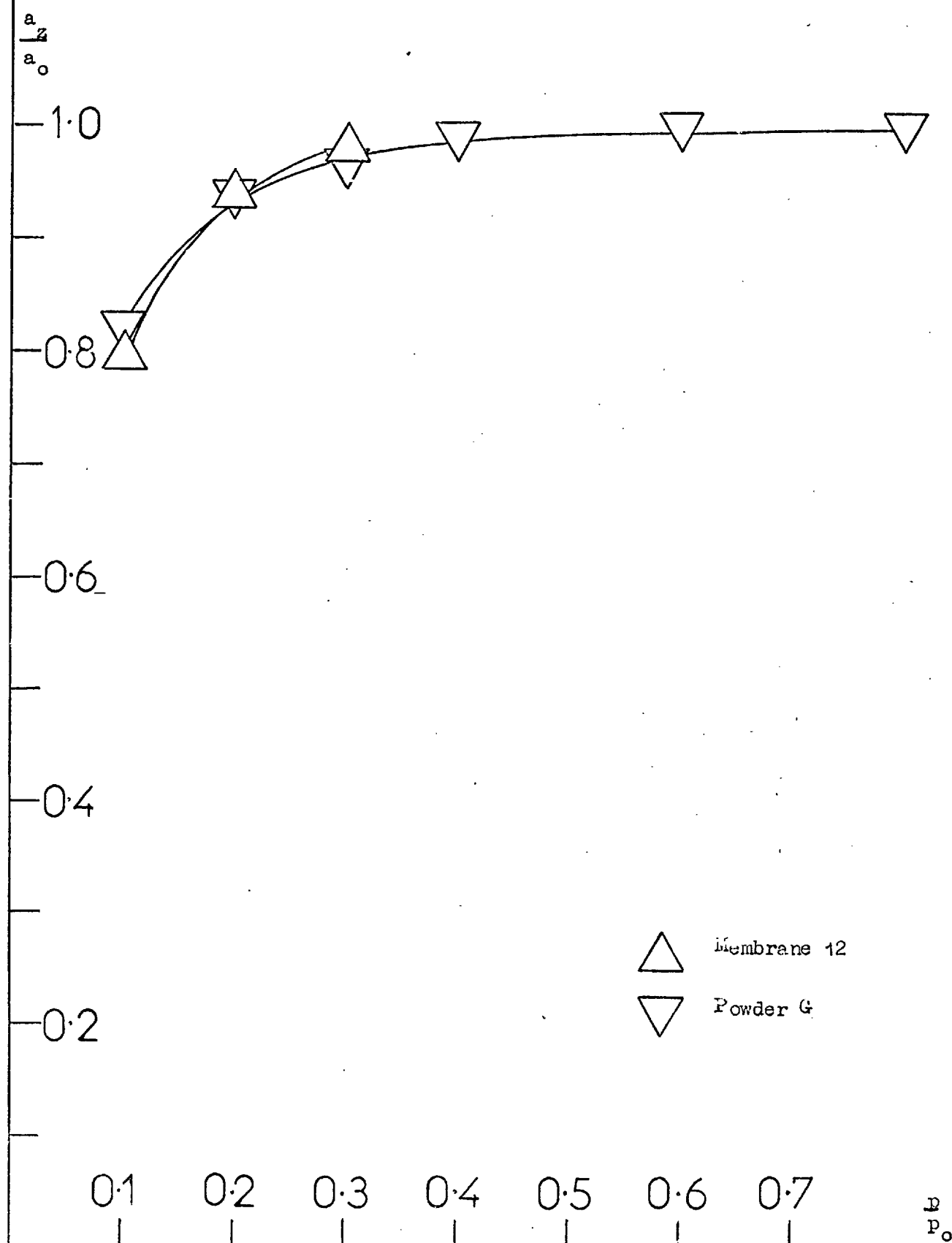
Adsorption-branch isotherms of water in Cu(II)X zeolite filled composites.

$T = 313 \text{ K}$



Adsorption-branch isotherm of water in silica gel filled composites.

$T = 303 \text{ K}$



Silica gel has a hydrophilic surface which may adhere to the polar carbonyl groups of poly(methyl methacrylate). At low values of the relative pressure, water molecules would not compete for the silica surface with the polymer and the value of $\frac{a_z}{a_o}$ would be low. As the relative pressure is raised, however, water molecules would break down this adhesion and $\frac{a_z}{a_o}$ values would approach unity. Figure 27 illustrates this $\frac{a_z}{a_o}$ effect.

Water vapour transport through poly(methyl methacrylate) membranes.

The flow of water through homopolymer membranes has been investigated in much detail previously^(150,183), but some work has been done in this investigation to see what sort of spread of permeability results can be expected using different samples of the same polymer.

Figure 28 shows a determination of one value of the permeability coefficient of water through the homopolymer. The steady-state permeability coefficient from this single run is

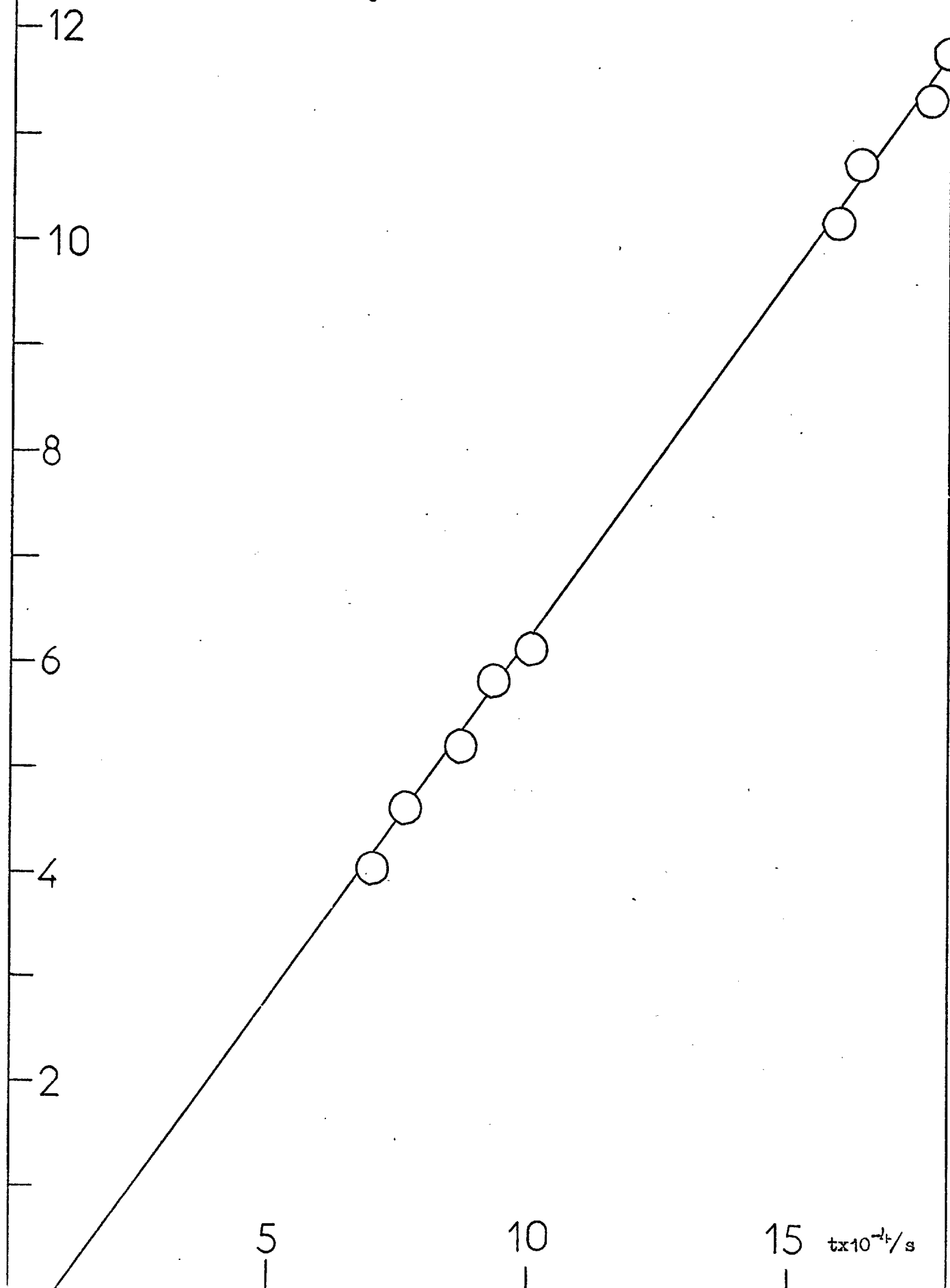
$$P = 0.86 \times 10^{-7} \frac{\text{cm}^3(\text{STP})\text{cm}}{\text{cm}^2\text{s cmHg}}$$

For this particular membrane, membrane IV, there was no measurable variation in the permeability coefficient with temperature, at least over the range of temperatures investigated. Figure 29 shows P values measured at several values of temperature and relative pressure. The very low value of E_p , the energy of activation for permeation and the closeness of the enthalpy of solution to the enthalpy of sorption implies that E_D , the energy of activation for water diffusion in membrane IV, will be close

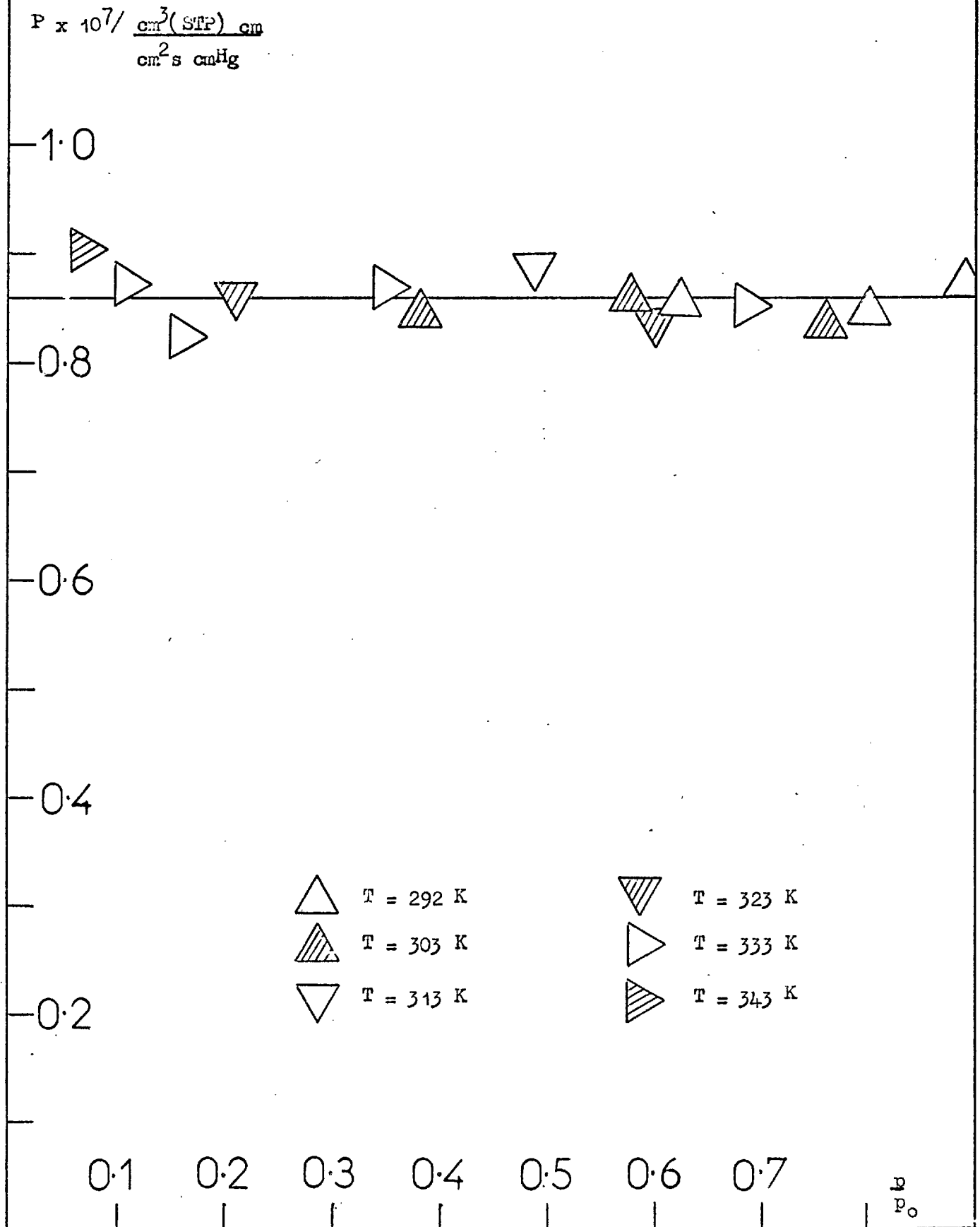
Figure 28

148.

Volume of water flowing through poly(methyl methacrylate) membrane IV

 $V/\text{cm}^3(\text{STP})$ $T = 303\text{K}, \frac{p}{p_0} = 0.575, l = 0.012$ 

Permeability coefficients for water vapour through membrane IV



in magnitude to the enthalpy of sorption of water. E_D will also be independent of water concentration within the membrane.

Figure 30 shows the variation of the steady-state flux per unit area, J , of membrane IV with the concentration of water within the membrane, c . The slope of this curve at any particular concentration is the steady-state diffusion coefficient at that concentration, D . A plot of D against c is shown in figure 31 and D is clearly dependent upon c .

The decrease in the steady-state diffusion coefficient as water concentration increases may be accounted for by the formation of water molecule clusters within the polymer's microcavities. The concentration independence of E_D throughout the range of c implies that clustering occurs predominantly in existing microcavities and neither water molecules nor temperature changes cause any appreciable disturbance of the polymer matrix. This is not unexpected since the polymer is well below its glass transition temperature.

Some values for the other homopolymer membranes are shown in table 5.

Steady-state flux of water vapour through membrane IV.

$T = 303 \text{ K.}$

$J_1 \times 10^7 / \text{cm}^3(\text{STP}) \text{ cm}^{-1} \text{ s}^{-1}$

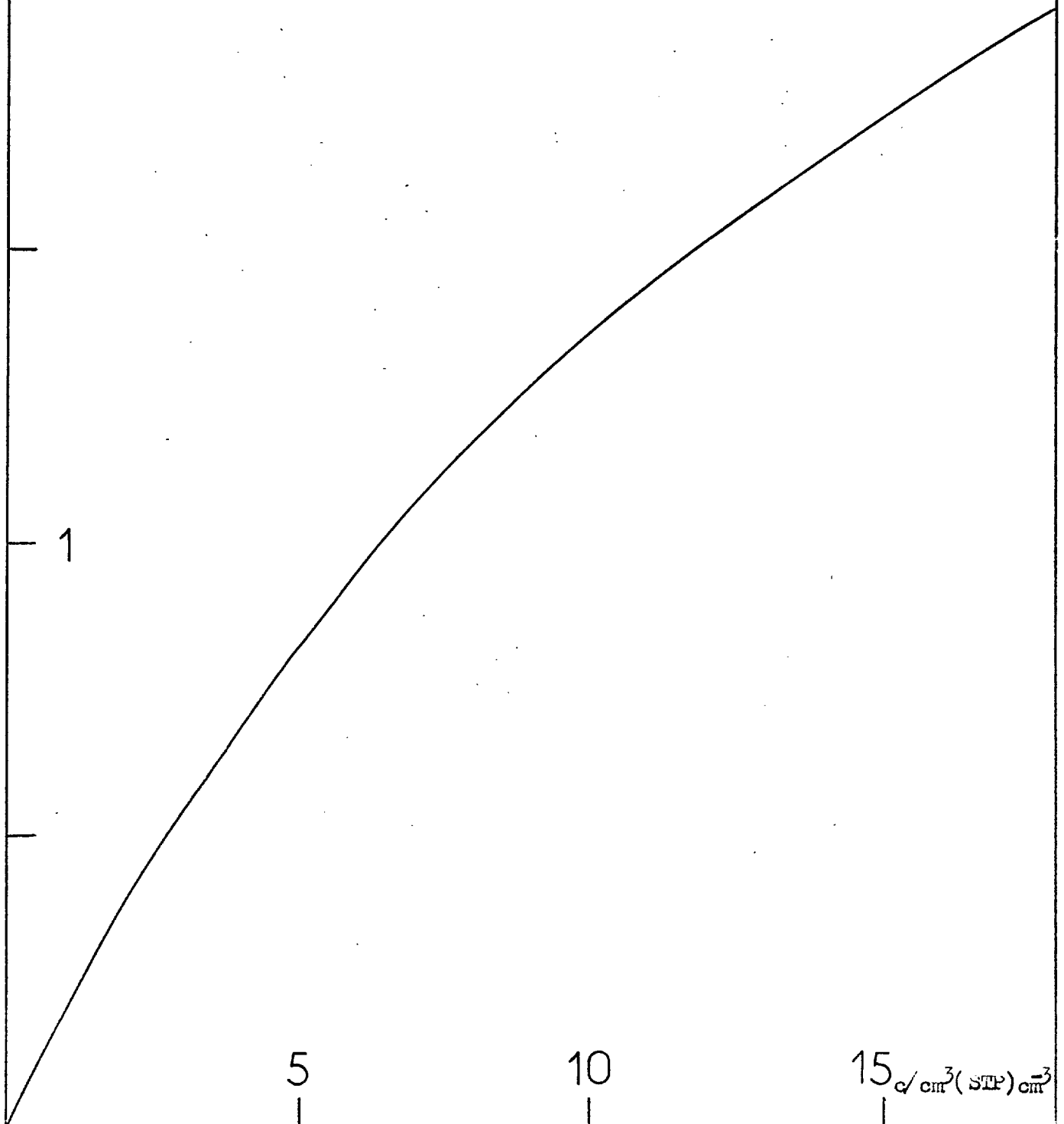
— 2

1

5

10

15 $\text{cm}^3(\text{STP}) \text{ cm}^{-3}$



Steady-state diffusion coefficient of water through membrane IV.

$$T = 303 \text{ K}$$

$$D \times 10^8 / \text{cm}^2 \text{ s}^{-1}$$

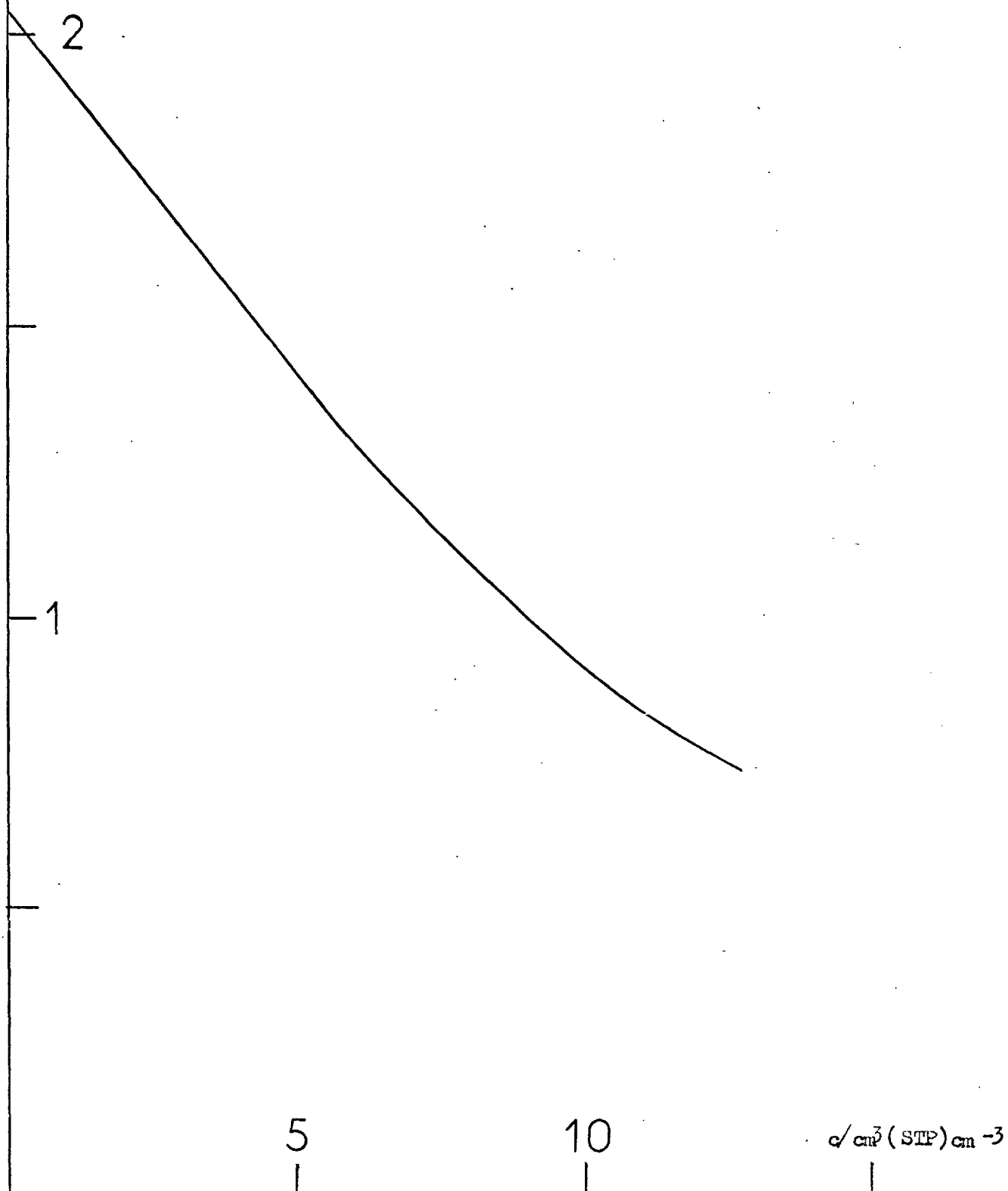


Table 5Permeability and diffusion of water in poly(methyl methacrylate)

Membrane	Thickness	$P \times 10^7$ $\frac{\text{cm}^3(\text{STP})\text{cm}}{\text{cm}^2\text{s cmHg}}$ ($T = 303\text{K}$)	E_p kJmol^{-1} ($293\text{K} < T < 343\text{K}$)	$D_{c \rightarrow o} \times 10^7$ cm^2s^{-1} ($T = 303\text{K}$)
Poly(methyl methacrylate)	$1/\text{cm}$			
I	0.019	1.83	3,7	0.57
II	0.022	1.04	1.3	0.33
III	0.016	1.62	3.8	0.48
IV	0.012	0.87	0.0	0.20

A considerable variation in the values of these permeability and diffusion constants for different samples of the same polymer is apparent. This variation is unfortunate because it will restrict any interpretation of such constants for composite membranes, especially if the results are close to the values for the homopolymer membranes. One way of overcoming this difficulty would be to cast membranes from a solution of a well characterized sample of polymer, but the practical problems involved in the preparation of composite membranes by this method were not investigated in this work.

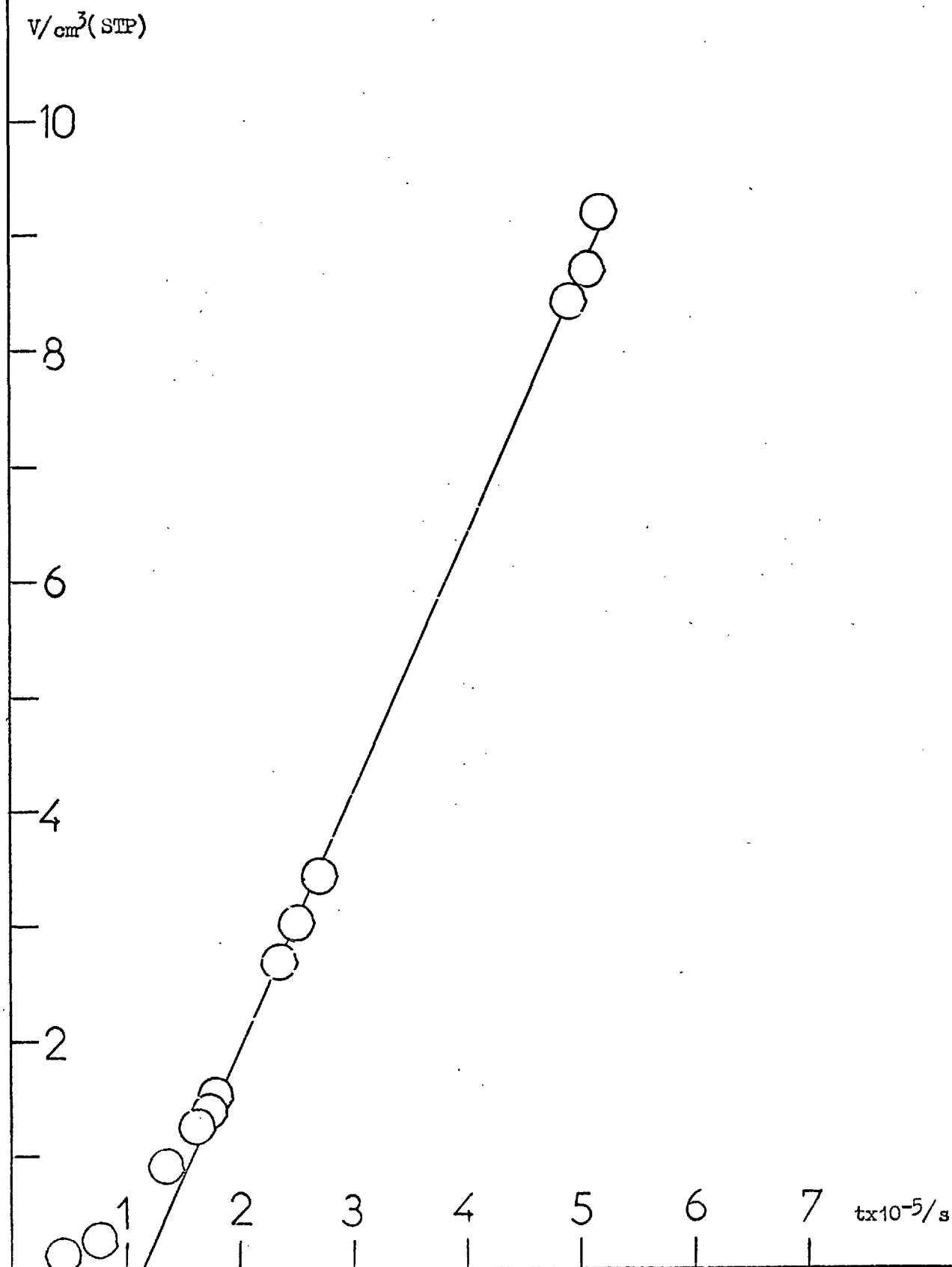
In spite of these limitations, the flow of water through some composite membranes has been studied and figure 32 shows the rate of flow of water through membrane 6 (see table 4). One difference between this curve and that in figure 28 is that the time-lag for the filled membrane is about ten times greater. Even this large time-lag is probably an underestimate, for it is unlikely that all the water could be removed from the zeolite in the composite before a run was commenced. Various values of the steady-state permeability coefficient for water through membrane 6 were determined and are shown in figure 33. Values were measured at two temperatures and again there is no obvious temperature dependence of the permeability coefficient. Above a relative pressure of about 0.5, the permeability coefficient increases with increasing relative pressure.

Figure 34 shows the curve of J_l versus c for water in membrane 6 while figure 35 shows the dependence of D upon the water concentration. For homopolymer membrane IV, D decreased steadily as the water concentration increased, but for membrane 6 D increases with c over most of the concentration range. This dependence of D upon c for the composite membrane is interpreted as follows. Through the range of concentration $0 < c < 4.0 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ which corresponds to the relative pressure range $0 < \frac{p}{P_0} < 0.08$ at 303K, water molecules would be very strongly bound to the zeolite. (The maximum concentration in this range corresponds with 26 mg of water per gramme of composite and at a relative pressure of 0.08 the amount of water held by the filler could be as high as 25.9 mg g⁻¹.) As the pressure increases a greater proportion of

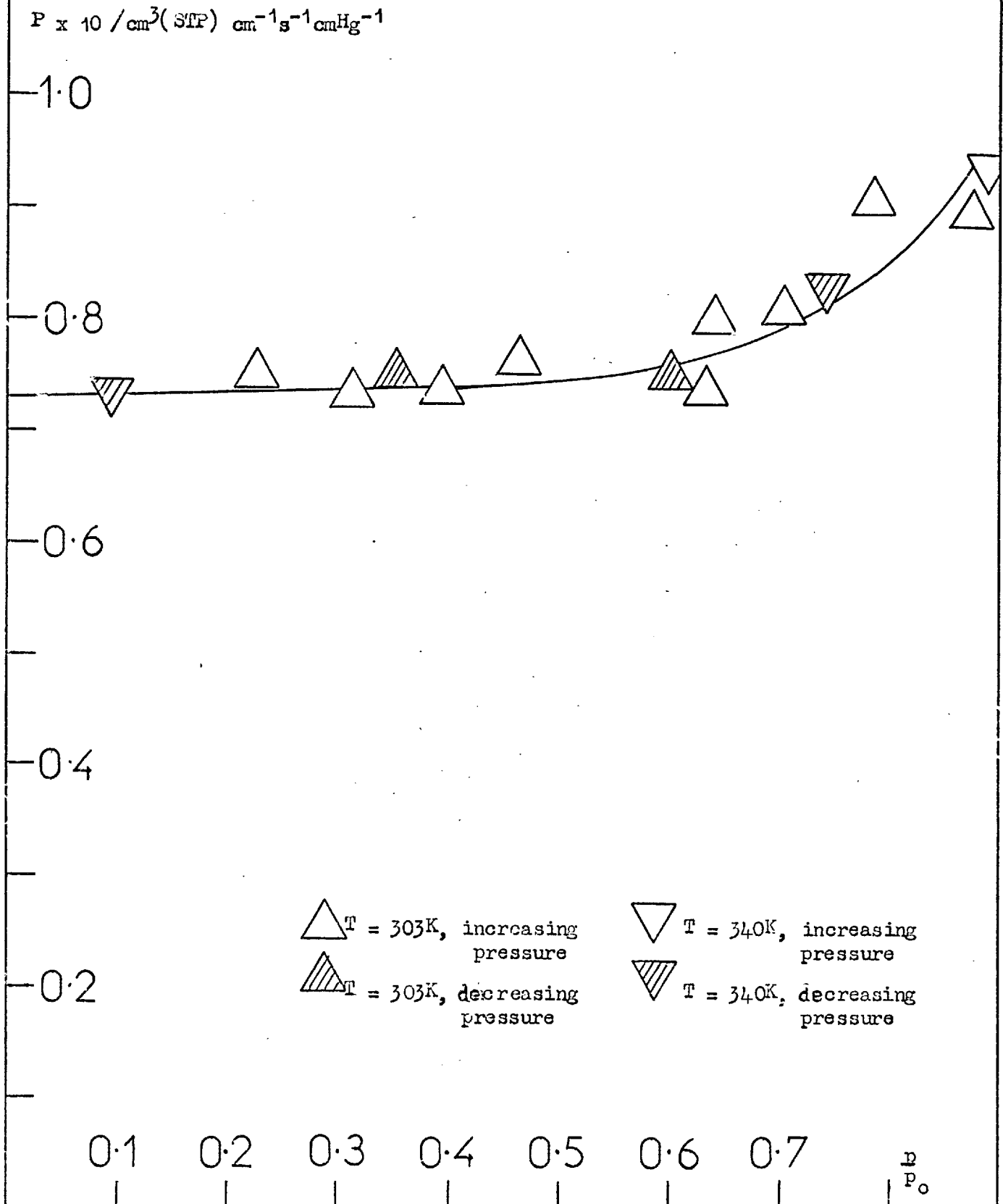
Figure 32

Flow of water through filled membrane 6.

$$T = 303 \text{ K}, p = 0.463, l = 0.032 \text{ cm}, \rho_f = 0.244 \\ p_o$$



Flow of water through filled membrane 6.



Steady-state flux of water vapour through membrane 6.

$$T = 303 \text{ K}$$

$$J_1 \times 10^7 / \text{cm}^3 (\text{STP}) \text{cm}^{-1} \text{s}^{-1}$$

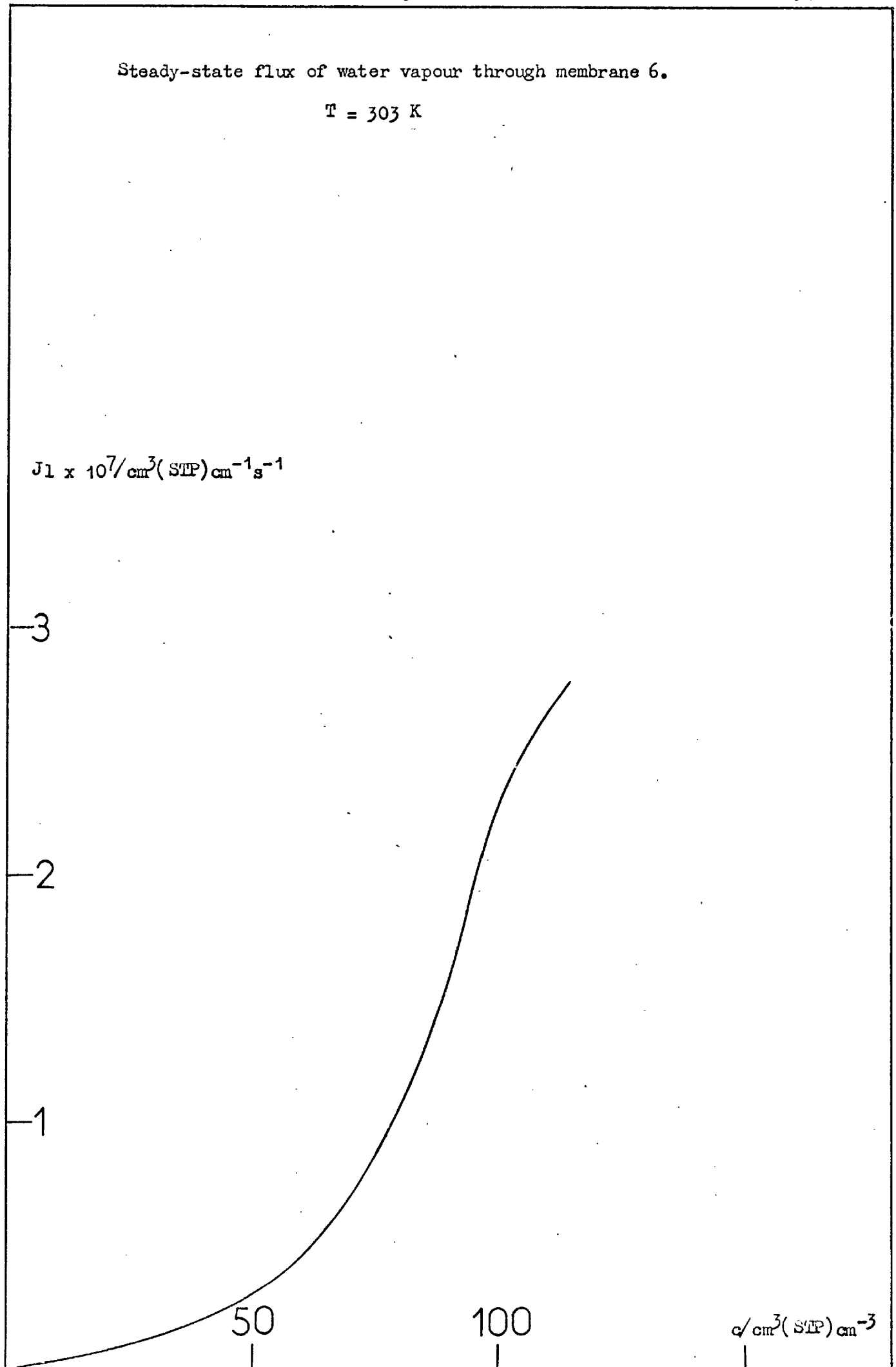
-3

-2

-1

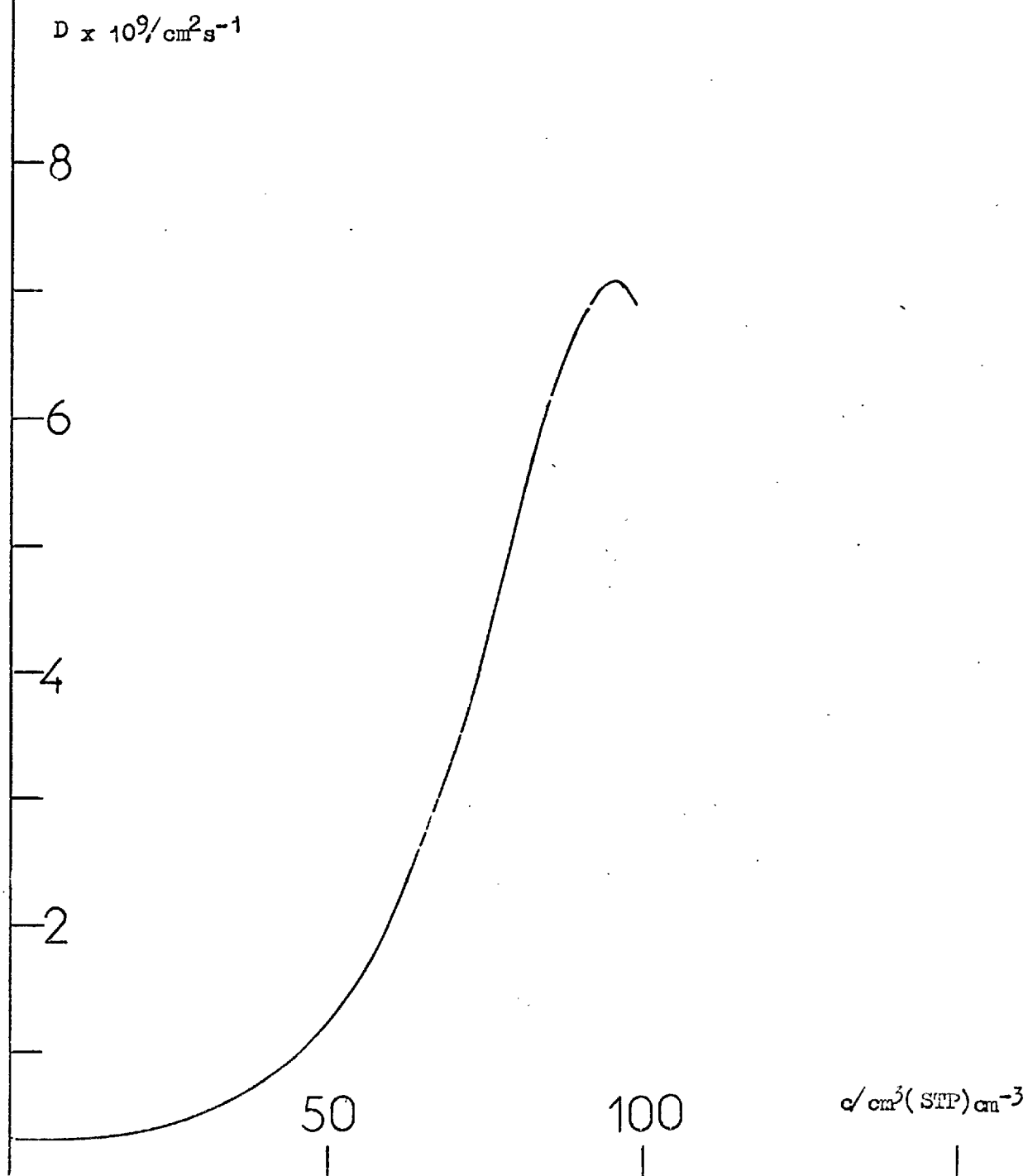
50

100

 $c / \text{cm}^3 (\text{STP}) \text{cm}^{-3}$ 

Steady-state diffusion coefficient of water through membrane 6.

$$T = 303 \text{ K}$$



the water molecules in the membrane would be present in the polymer phase. Such molecules would be expected to be more mobile than those in the zeolite and if so would give rise to an increase in D . Beyond a certain concentration, the clustering of water molecules in polymer micro-cavities would become a dominant feature in the diffusion process and D may fall once more. Although errors in measurement are unavoidable at high pressures of c , the magnitude of D at high concentration is similar to the lowest value of D measured for the homopolymer (see figure 31).

A quantitative examination of D and P for composite polymers is restricted by the lack of knowledge of these constants for the polymer phase of the material. Although membrane 6 has a volume fraction of filler of 0.244 and therefore, in the absence of any gas gaps with polymer, a volume fraction of external polymer of 0.756, nothing can be said about the magnitude of D or P through this external polymer phase. One observation which can be made is that the inclusion of a large volume fraction of filler reduces the permeability coefficient to a value lower than any of the values found for homopolymer membranes at low and intermediate relative pressures, but that the coefficient increases considerably at high relative pressures.

Permeability results for other composite membranes are shown in table 6.

Table 6Permeability results in poly(methyl methacrylate) filled membranes

Membrane	Filler	ϕ_f	Thickness l/cm	$P \times 10^7$ $\frac{(\text{c} \rightarrow \text{o})}{\text{cm}^3 (\text{STP}) \text{cm}}$ $\text{cm}^2 \text{s cmHg}$	T /K	$D \times 10^7$ $\frac{(\text{c} \rightarrow \text{o})}{\text{cm}^2 \text{s}^{-1}}$
1	NaY	0.506	0.021	0.91	332	0.003
2	NaY	0.040	0.039	0.94	303	0.010
6	NaY	0.244	0.032	0.73	303	0.003
8	NaY	0.131	0.066	(a)	303	—
9	NaY	0.326	0.083	0.65	312	0.002
10	(NaK)L		0.062	(b)	303	—
11	NaA		0.069	(b)	303	—
12	Silica gel		0.089	0.24(c)	317	0.001

(a) Membrane gave high, irreproducible values of P and was subsequently found to contain hair-line cracks

(b) Irreproducible values of P but no evidence of cracks in these membranes.

(c) As the concentration in the membrane increased, P values became high and irreproducible. No evidence of cracks in the membrane was found.

An increase in P at high concentration of water vapour, especially when it is associated in some cases with the commencement of irreproducibility of results, does suggest that adhesion between the polymer and its filler is reduced under such conditions, and easy diffusion paths around the filler particles are formed thereby.

In the preliminary stages of this investigation water flow experiments were conducted using a different experimental technique. The method involved fixing the membranes across the flattened end of glass tubing with "Araldite". The results obtained for a membrane containing NaY zeolite in a poly(methyl methacrylate) matrix at a temperature of 323 K and where $w_z = 0.285$ and $l = 0.013$ cm are shown in table 7.

Table 7Permeability coefficients measured on membrane (i)

<u>Date of determination</u>	<u>Relative Pressure</u>	$\frac{P \times 10^7}{\frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \text{ s cmHg}} \text{ cm}}$
9th November 1969	0.34	4.41
12th November 1969	0.35	4.62
15th November 1969	0.47	3.82
19th November 1969	0.54	16.84
22nd November 1969	0.39	20.41
26th November 1969	0.54	22.35
29th November 1969	0.54	19.80

These results demonstrate the unsuitability of this method for water vapour flow experiments, and in any case the manufacturers do not recommend "Araldite" as a suitable agent for bonding poly(methyl methacrylate). As the "Araldite" - polymer adhesion is reduced, easy diffusion paths around the membrane would be formed.

Argon and helium flow through composite membranes.

If adhesion between a filler and the external polymer matrix is reduced permanently by water vapour, then this would be revealed if argon or helium flow experiments were carried out before and after water vapour flow experiments. A break-down of adhesion would cause an increase in permeability of the composite membrane to the permanent gas.

One problem in this aspect of the work was that no satisfactory method was found for outgassing the membranes before flow experiments were conducted. Blank experiments in which a zero pressure differential was maintained across the membranes always produced a pressure of gas which was measurable on the McLeod gauge and which increased proportionally with the duration of a run. Moreover, this pressure must have been greater than the pressure of gas resulting from flow across the membrane for when a differential did exist the apparent flux was of the same magnitude as the flow in the blank run and in no case could any attempt at determining a flux be made. The possibility of leakage into the systems was discounted because of the care taken with the glassware and all other parts of the system were immersed in mercury baths. Also, a high-frequency electric discharge through the gas in the system was pale blue in colour, probably the effect of water vapour, and not mauve which would be associated with the presence of nitrogen from the atmosphere.

No progress was made with this aspect of the work which, in view of the shortage of time, was abandoned.

4.2 Investigation of n-butyl methacrylate polymerization reactions.

Isotherms of n-butyl methacrylate in NaY and (NaK)L are shown in figure 36. These curves show that n-butyl methacrylate sorption is of a similar character to the sorption of the methyl homologue. The monomer is just as tenaciously held by the sorbents upon outgassing, even at elevated temperatures. Table 8 shows the amounts of material retained by the zeolites after evacuation.

Table 8

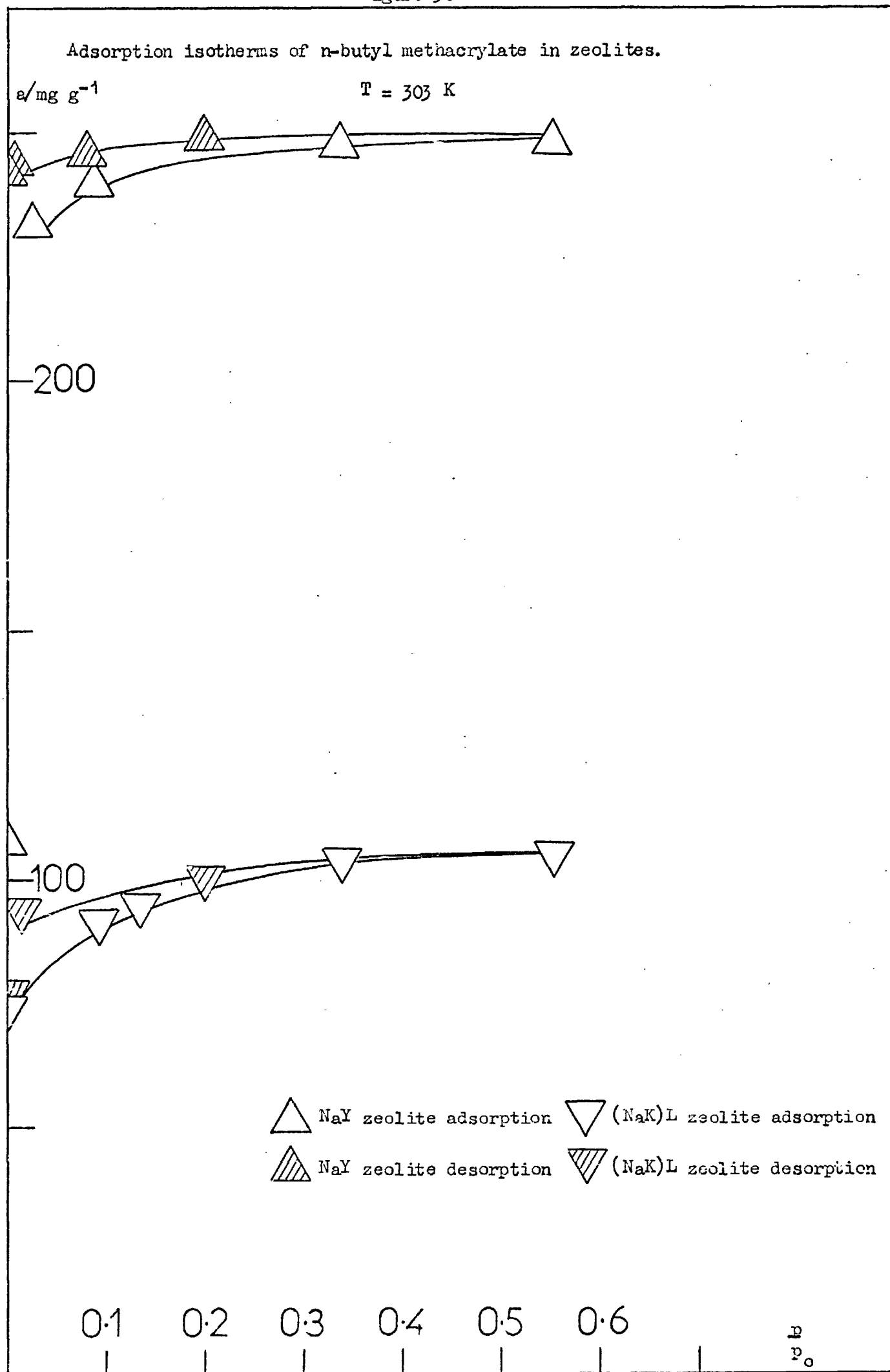
Desorption of n-butyl methacrylate from two zeolites.

Conditions of outgassing	$a(\text{NaY})$ /mg g ⁻¹	$a(\text{NaK})\text{L}$ /mg g ⁻¹
24 hours, 303K, < 10 ⁻³ Nm ⁻²	237	79
Further 24 hrs, 443K, < 10 ⁻³ Nm ⁻²	145	0

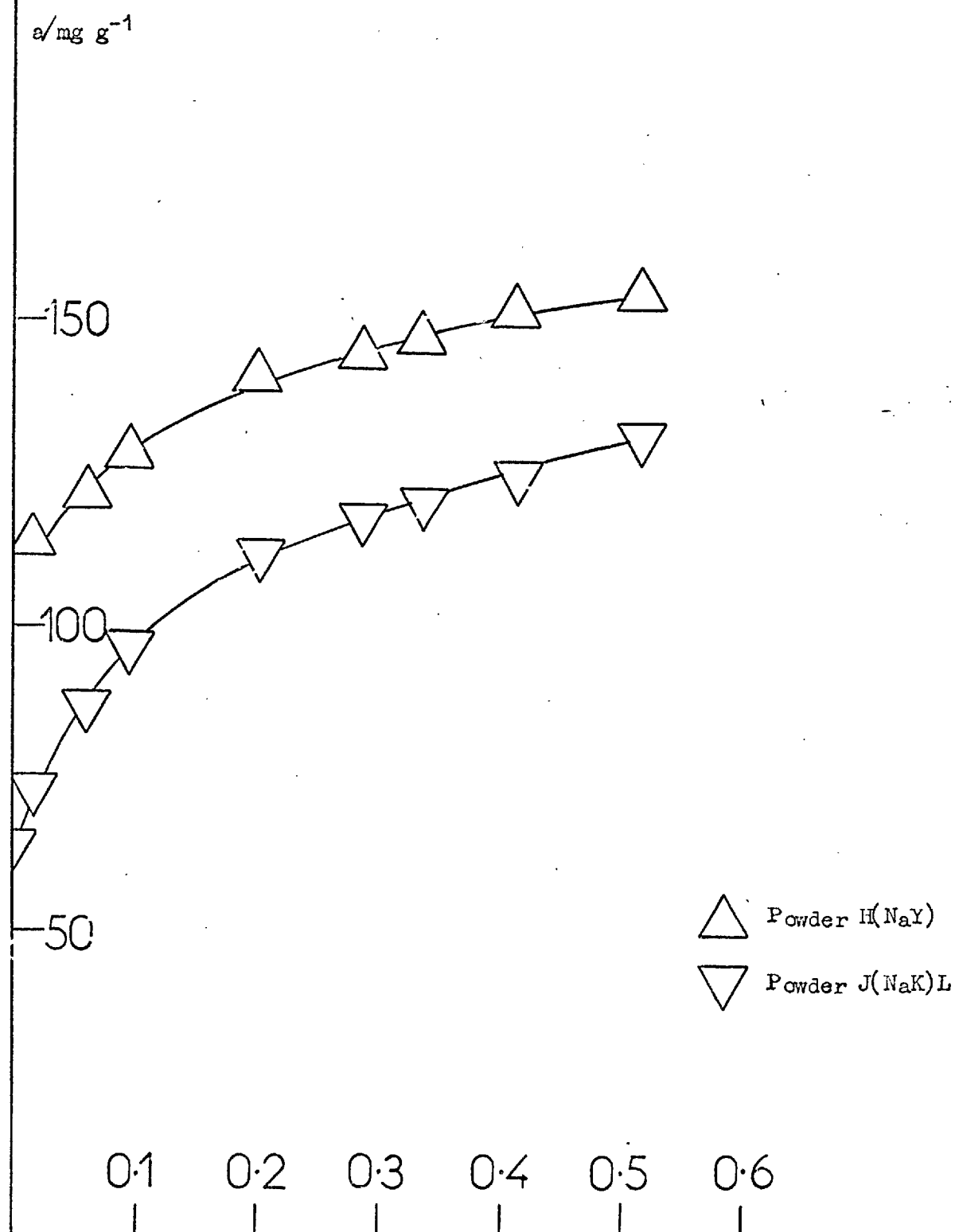
The masses of outgassed residue retained by NaY correspond closely to residual methyl methacrylate values. Furthermore, the increased molecular size of this monomer does not prevent its entry into the cavities of either zeolite.

Water isotherms on the composite materials obtained after outgassing the two zeolites following monomer sorption are shown in figure 37. The uptake of water on powder H (NaY after n-butyl methacrylate adsorption-desorption) is very similar to the uptake on powders A and B (NaY after methyl methacrylate adsorption-desorption).

Figure 36



Adsorption-branch isotherms of water in zeolite filled composites.

 $T = 303 \text{ K}$ 

The water sorption isotherm for powder I ((NaK)L after n-butyl methacrylate adsorption and desorption) is similar to the isotherm for the free powder, the residual mass of monomer, according to table 8, is zero.

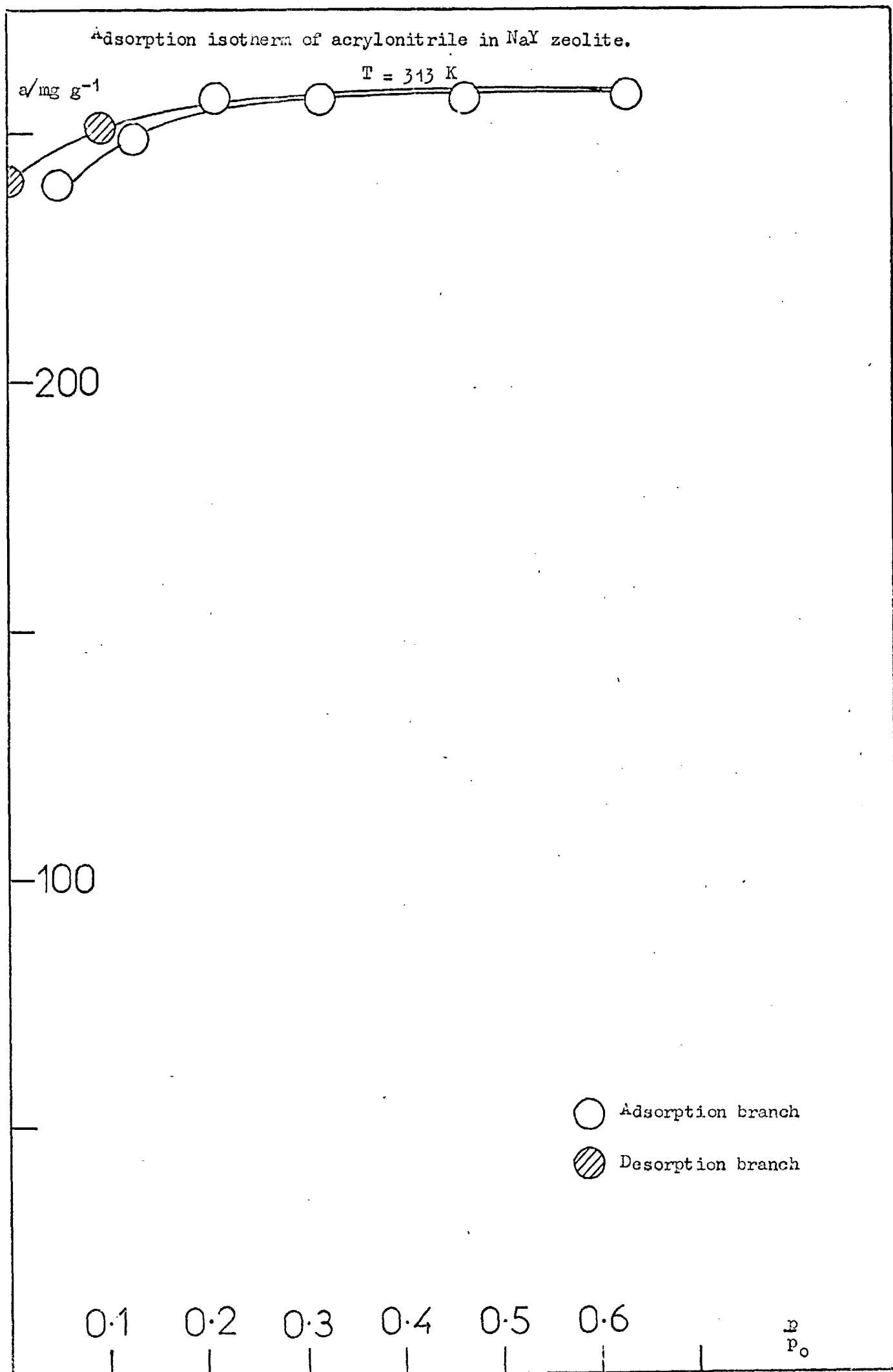
The similarity of n-butyl methacrylate sorption results to the results obtained for the methyl homologue allows no further progress to be made concerning an understanding of the nature of polymerization reactions over zeolites. In view of this, the plan to prepare filled poly(n-butyl methacrylate) membranes for flow studies was abandoned and no further work on this monomer was undertaken.

4.3 Investigation of acrylonitrile polymerization reactions.

A test-tube containing two pellets of sodium hydroxide and half-filled with acrylonitrile was shaken at room temperature. After $1\frac{1}{2}$ hours the colourless liquid had become bright yellow and opaque. Within 24 hours it had become a hard, dark yellow solid.

The smoothness of this reaction and the presence in the monomer of a free-radical inhibitor imply that an ionic process took place. It is at least a simple, non-violent method for preparing polyacrylonitrile.

Figure 38 shows the sorption behaviour of the monomer over NaY and in common with the two monomers investigated earlier, a residue presumably of polymer is retained by the zeolite after evacuation. In view of the toxic nature of acrylonitrile and the similarity of its sorption behaviour to the methacrylates, no further investigations were made.



4.4 Investigation of styrene polymerization reactions

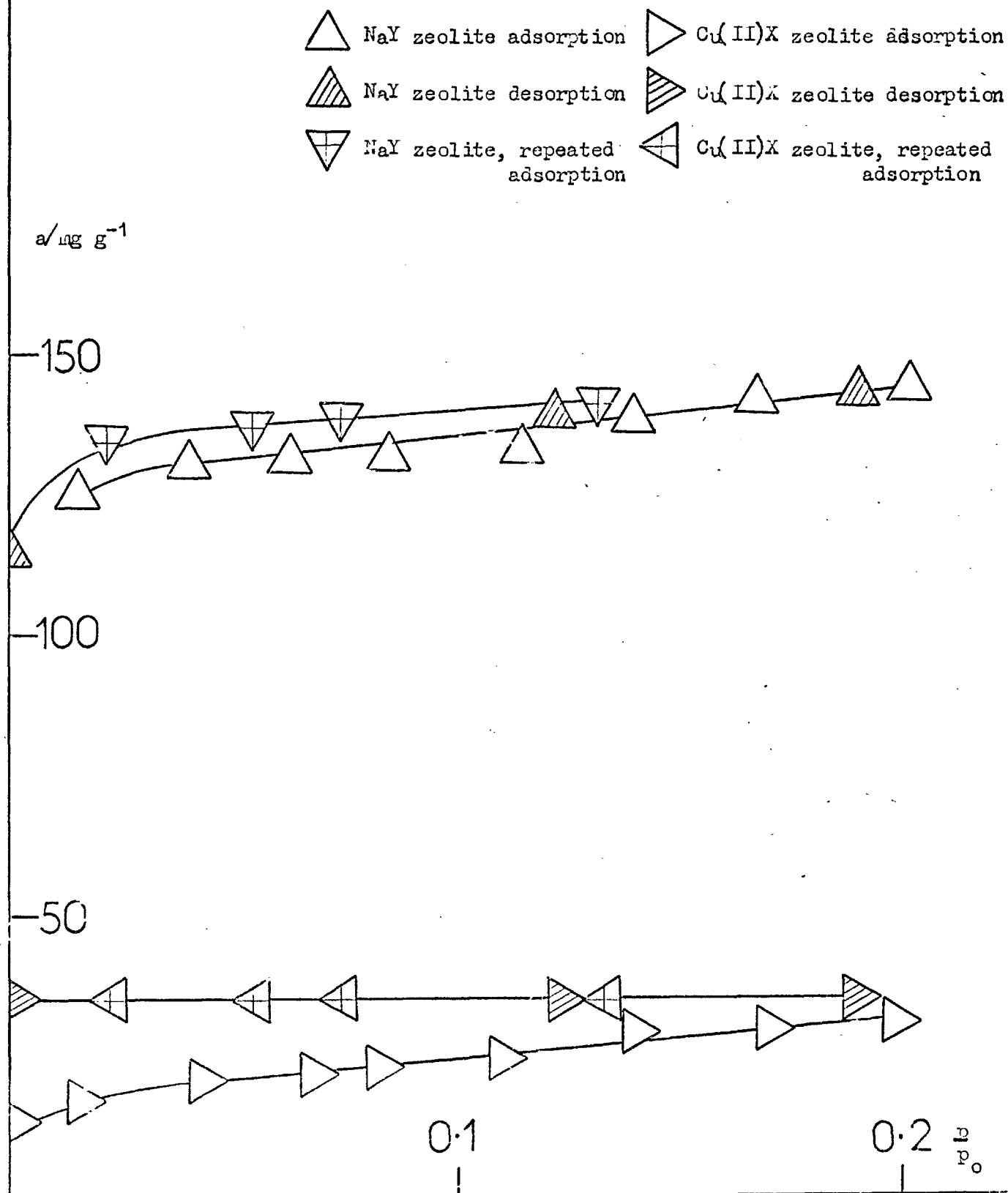
Although styrene polymerizes readily in contact with metallic sodium, shaking the monomer with sodium hydroxide pellets did not induce bulk polymerization. This is in contrast with the effect of this substance on methyl methacrylate and acrylonitrile. A trace of water insoluble solid was found in the mixture after shaking for two days at room temperature, however.

Styrene sorption on two zeolites is shown in figure 39 where open symbols represent points measured on the first run, hatched symbols mark desorption values and crossed symbols represent a second adsorption run which followed outgassing for 96 hours at 333K. Clearly more volume is available for styrene sorption on the second run in NaY, an effect which was observed for methyl methacrylate sorption in this zeolite. The residue of styrene was not removed even after evacuation for a 48 hour period at 373K, suggesting that polymerization had occurred within the cavities.

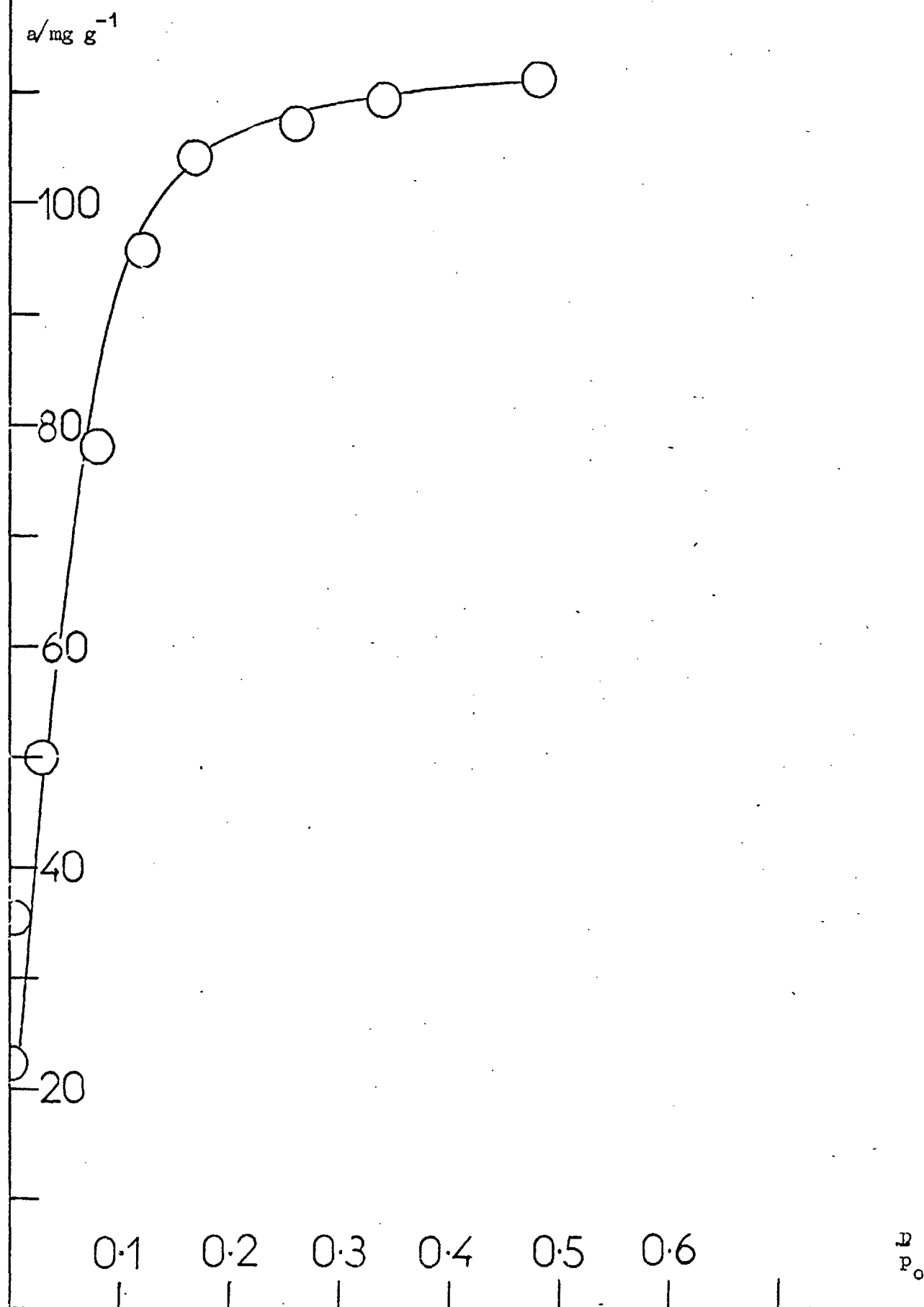
Figure 40 illustrates the adsorption of water in NaY after a double styrene sorption experiment. The material is referred to as powder J. There is a marked reduction in the volume available to water and the isotherm is similar to the one shown in figure 18, for the adsorption of water in powders A and B (NaY after methyl methacrylate sorption).

Figure 39

Adsorption isotherm of styrene in zeolites.

 $T = 333 \text{ K}$ 

Adsorption-branch isotherm of water in NaY zeolite filled composite (Powder J)

 $T = 333 \text{ K}$ 

4.5 Investigation of α -methyl styrene polymerization reactions

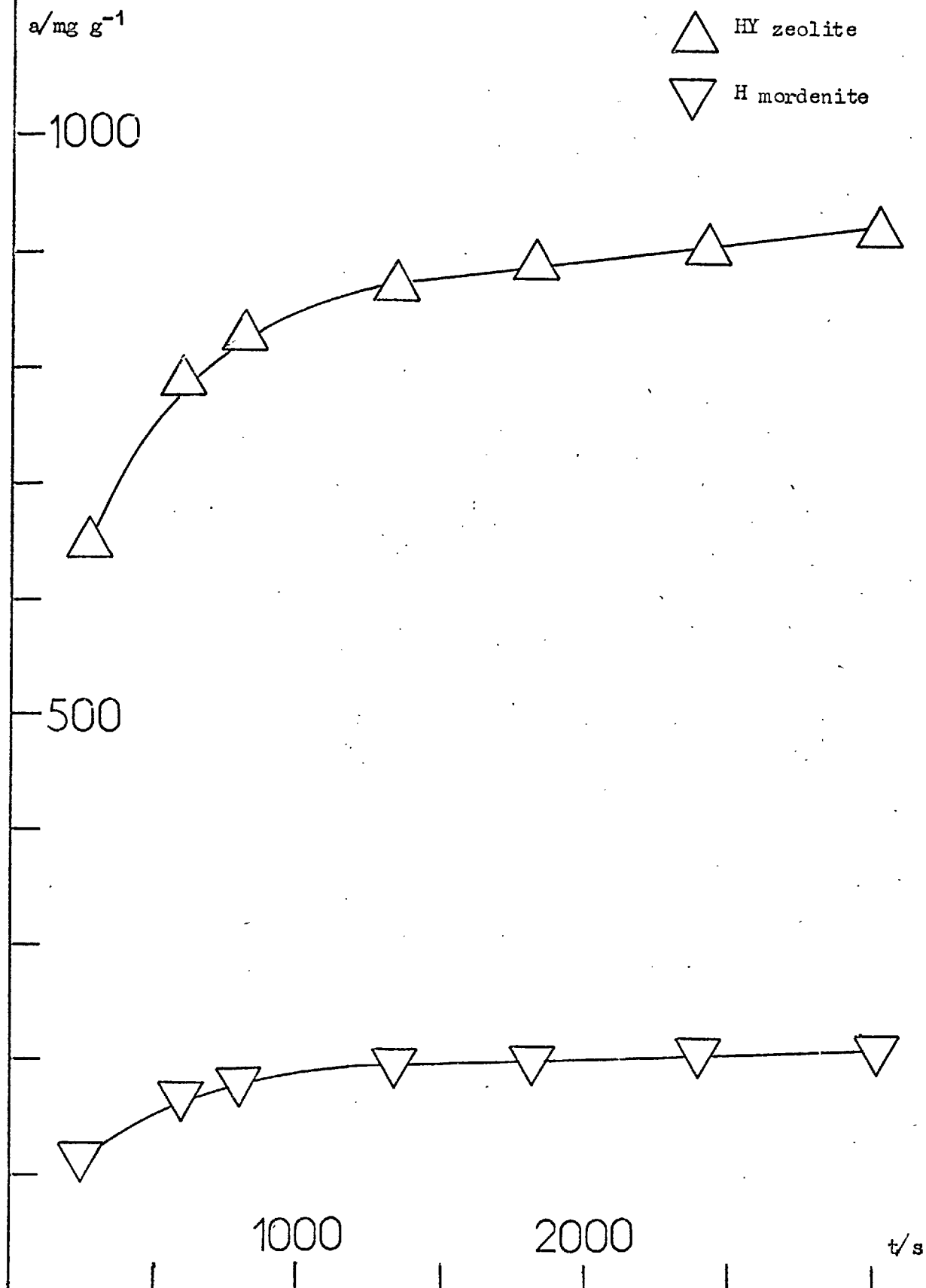
The addition of an α -methyl group to the styrene molecule should impart an increase in electron density at the double bond. Consequently, α -methyl styrene should display a higher activity over cationic catalysts than styrene.

A kinetic experiment, in which α -methyl styrene at relative pressure 0.46 was admitted to two zeolites, is recorded in figure 41. Both HY and H mordenite adsorb more of this sorbate than could be contained within their internal cavities, and since both sorbents became discoloured during the course of the experiment, the occurrence of an external reaction is most likely.

After the admission of further doses of the sorbate, and when the concentrations in HY and H mordenite were 1208 mg g^{-1} and 292 mg g^{-1} respectively, the sorbents were evacuated for 48 hours. At the end of this period 959 mg g^{-1} and 276 mg g^{-1} were still retained, but an increase in temperature to 443 K and a further period of 24 hours under vacuum reduced these concentrations to 13 mg g^{-1} and 9 mg g^{-1} respectively.

Water sorption isotherms on the powders obtained after this sorption-desorption treatment, powders K and L for HY and H mordenite respectively, are shown in figure 42. These isotherms are not greatly different from the isotherms for the free zeolites but this is not surprising in view of the very small residue of polymer present in each powder.

α -methyl styrene was distilled into tubes containing outgassed samples of HY and H mordenite but there was no evidence

Adsorption-branch isotherms of α -methyl styrene in zeolites $T = 303 \text{ K}$ $p = 0.46$ p_0 

Adsorption-branch isotherms of water in zeolites and zeolite filled
composites.

$T = 303 \text{ K}$

$a / \text{mg g}^{-1}$

200

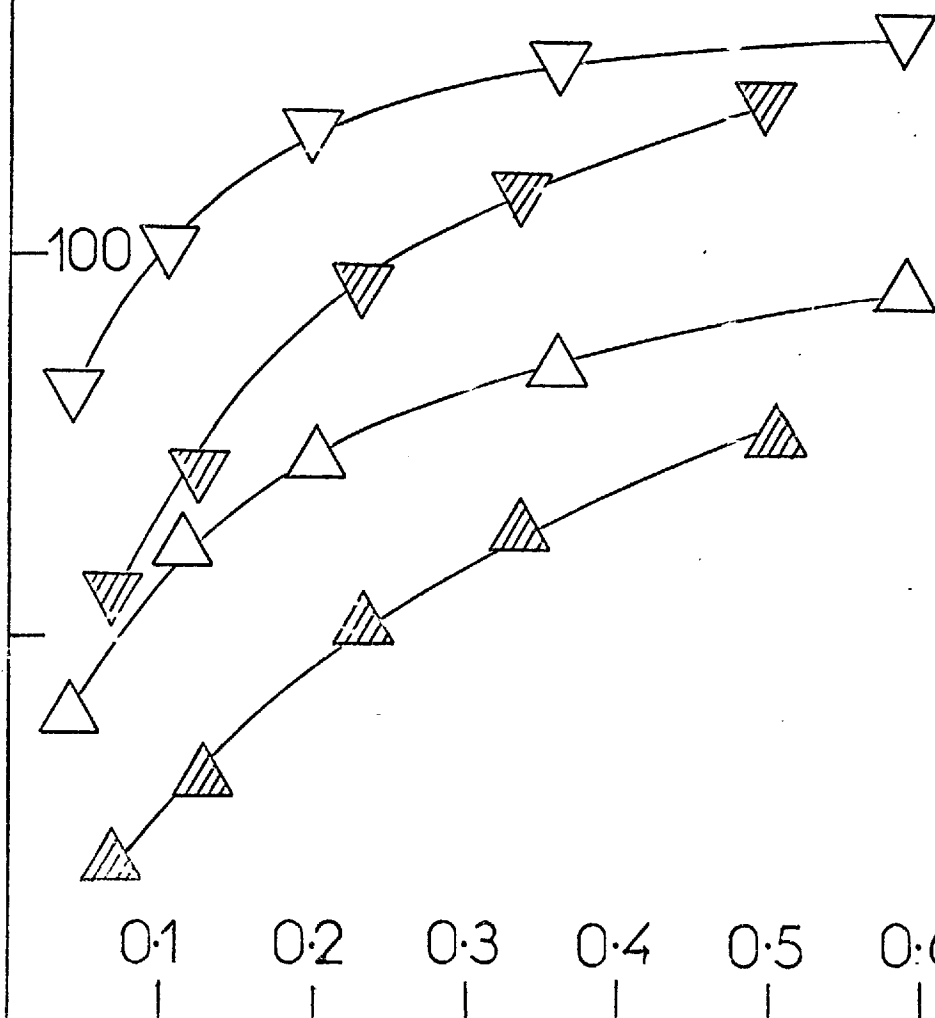
$\triangle$ HY zeolite
 $\triangle$ Powder K (HY)

∇ H mordenite
 ∇ Powder L (H mordenite)

100

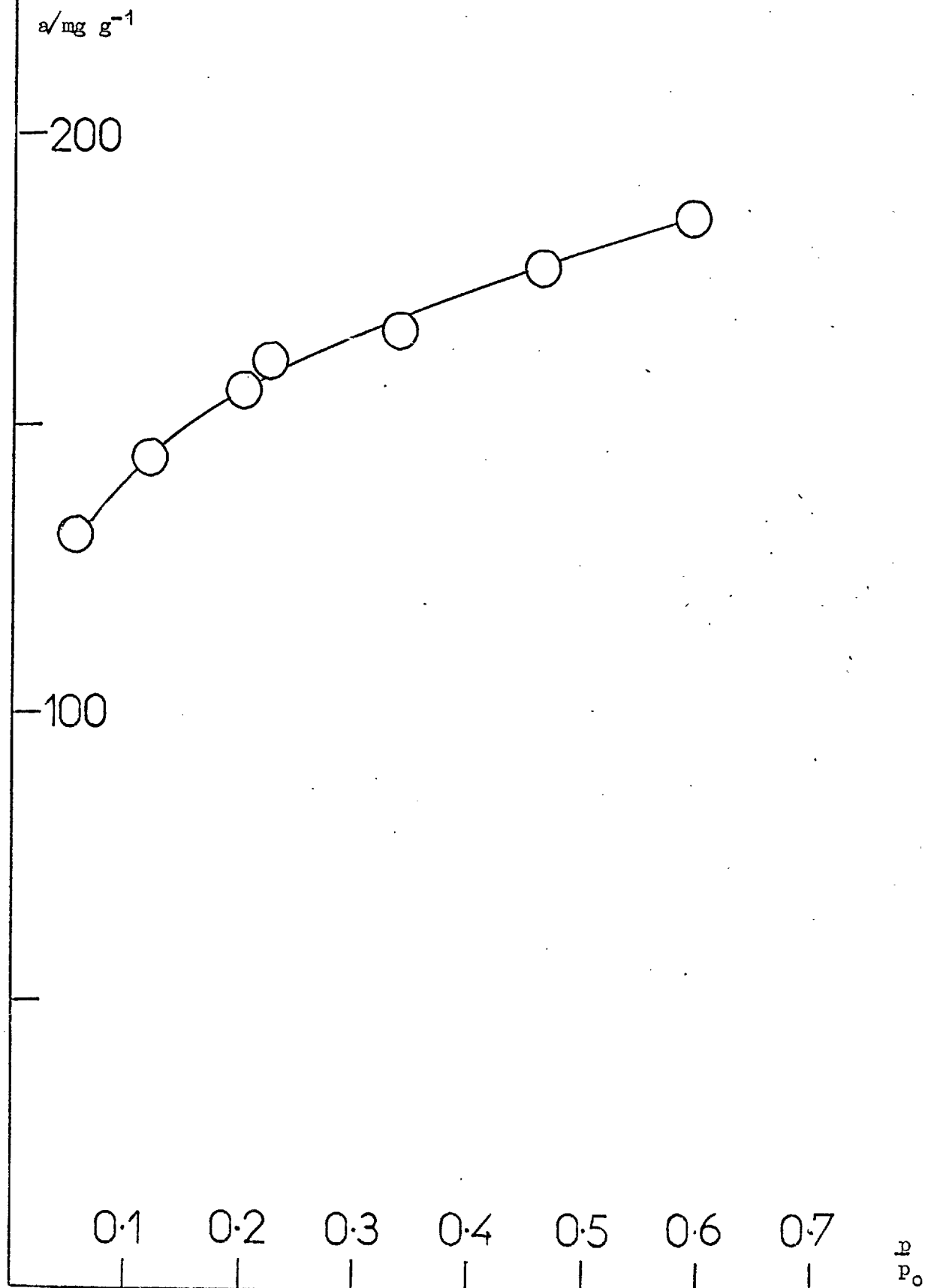
0.1 0.2 0.3 0.4 0.5 0.6

$\frac{n}{n_0}$



Adsorption-branch isotherm of α -methyl styrene in NaY zeolite.

$T = 303 \text{ K}$



of any bulk polymerization reaction. Figure 43 does show that the considerable amount of monomer sorbed by the H exchanged zeolites is not general for other zeolites and NaY shows no such property.

It is most likely that the formation of a low molecular weight poly(α -methyl styrene) does occur over the hydrogen exchanged zeolites.

4.6 Investigation of ethyl vinyl ether polymerization reactions

Introduction

An interesting reaction of ethyl vinyl ether was found by an undergraduate in the organic chemistry department when he attempted to dry the liquid over molecular sieve 4A pellets⁽¹⁸⁴⁾. A rapid polymerization occurred and within a few minutes the ether had become a clear, viscous gum. The experiment was repeatable with fresh samples of reactant and molecular sieve.

Primarily, the active catalyst within the pellets needed to be isolated and it was quickly found that NaA zeolite, which is similar to the dessicant present in 4A pellets, had no effect at all on the ether. The pellets do, however, contain a clay mineral binding agent, probably similar to kaolinite. In view of this, some ethyl vinyl ether was added to a portion of kaolinite and a violent reaction occurred instantly. Much of the ether was ejected from the test-tube and the residual material was blackened and hot. The organic residue was a dark-brown, viscous gum.

Although NaY (and of course NaA) had no obvious effect on the ether, both HY and H mordenite behaved similarly to kaolinite and induced violent reaction. In the case of each of these three aluminosilicates, no special drying was necessary, polymerization occurred just as readily under atmospheric conditions over catalysts brought straight from the bottle as it did over carefully outgassed materials under anhydrous conditions.

The violence of these polymerization reactions could be moderated by diluting ethyl vinyl ether with n-hexane before the addition of catalyst. In this way, and after evacuation and removal of the diluent, a clear sample of the viscous polymer was obtained. The gum was analysed and had the composition $(C_4H_8O)_n$, the empirical formula of poly(vinyl ethyl ether).

Ethyl vinyl ether sorption experiments.

Adsorption of ethyl vinyl ether in NaY zeolite was investigated kinetically and an isotherm is shown in figure 44. Adsorption-desorption is tending towards a steady-state after about 24 hours, although a slow process was apparent. An adsorption isotherm of ethyl vinyl ether in NaY is shown in figure 45 where 24 hours was allowed for a new dose to reach a steady-state before measurements were taken. The figure includes isotherms on other sorbents and while the sorption in NaY and silica gel is unexceptional, the curves for the other two sorbents indicate that a multilayer of sorbate has been formed on the external surface of the sorbents. No kinetic investigation of the sorption character of these other aluminosilicates, HY and kaolinite, was made but the points marked on figure 45 are not equilibrium values and the sorption on these

Adsorption-branch isotherms of ethyl vinyl ether in NaY zeolite.

$T = 308 \text{ K}, p = 0.0025$
 p_0

$a/\text{mg g}^{-1}$

200

100

1

2

3

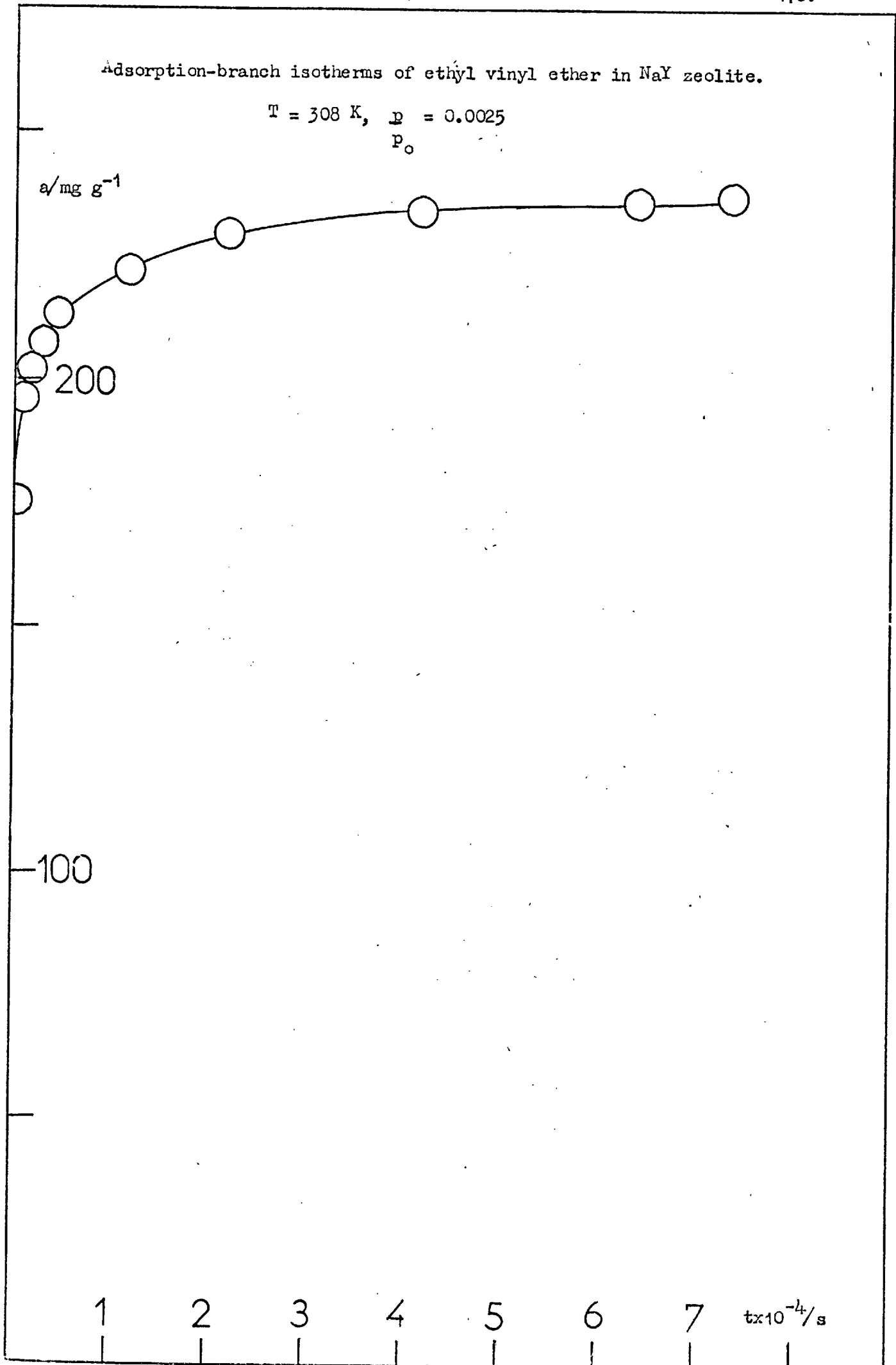
4

5

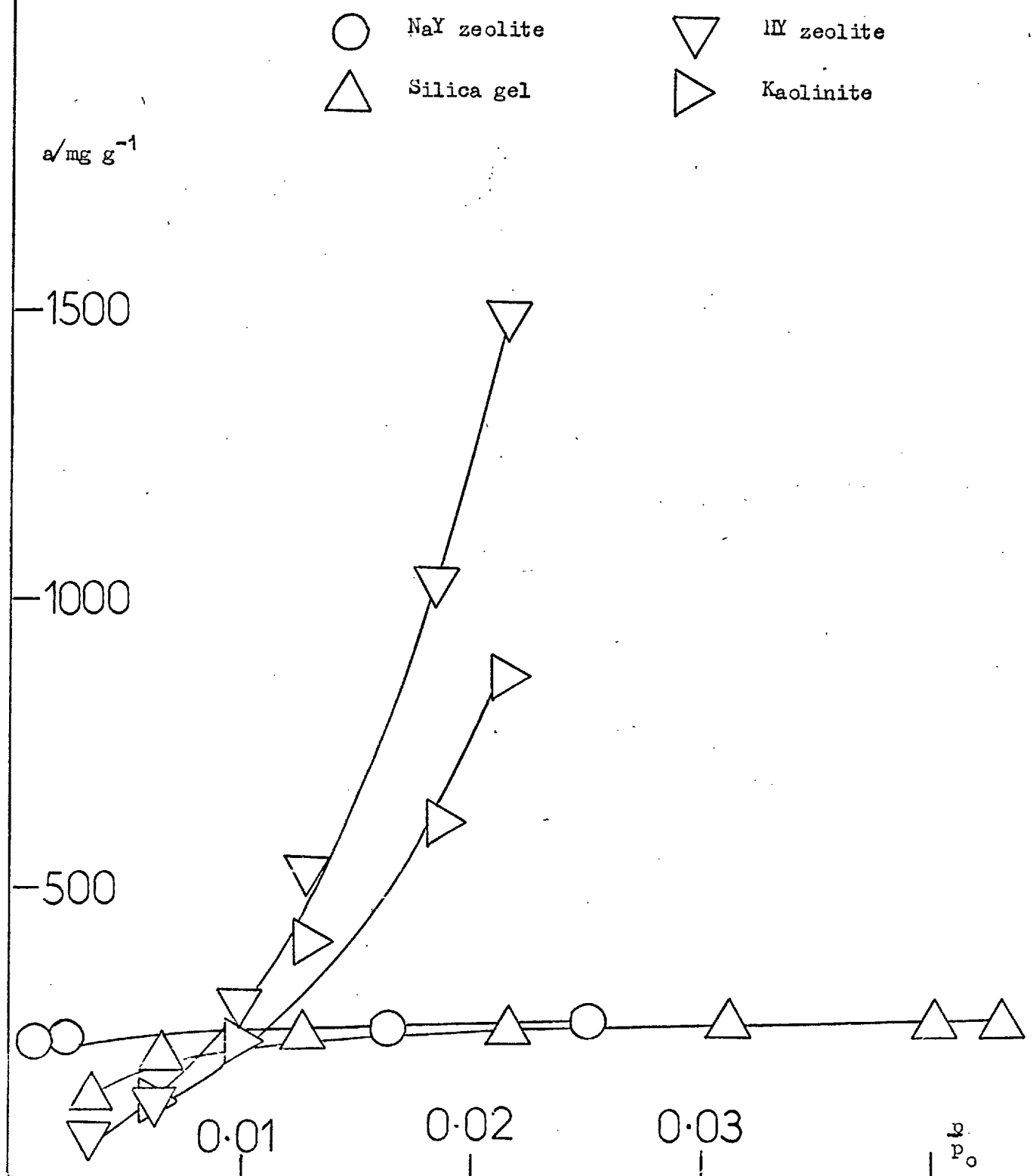
6

7

$t \times 10^{-4} / \text{s}$



Adsorption-branch isotherms of ethyl vinyl ether in various sorbents.

 $T = 308 \text{ K}$ 

materials had not reached a steady-state after 24 hours.

The final measured values on the HY and kaolinite curves of figure 45 are at a relative pressure of 0.215 (the isotherms were measured simultaneously in an interconnected gravimetric sorption apparatus). The dose of monomer vapour which was admitted after these values caused a discolouration of both sorbents and a dark brown layer of liquid or gum was clearly visible in the sorption buckets. When the quantity of ethyl vinyl ether on HY and kaolinite had reached 2245 mg g^{-1} and 1512 mg g^{-1} respectively, the sorbents were evacuated. After 50 hours at a pressure maintained below 10^{-3} Nm^{-2} and at a temperature of 308 K these amounts had fallen to 1981 mg g^{-1} and 1282 mg g^{-1} respectively. After this period of outgassing the temperature was raised to 393 K and evacuation continued for a further 96 hours, even these conditions reduced the amounts of ether to 1004 mg g^{-1} and 796 mg g^{-1} respectively. Clearly polymerization of ethyl vinyl ether has occurred at low pressure and room temperature and moreover polymer was not formed only within the zeolitic cavities.

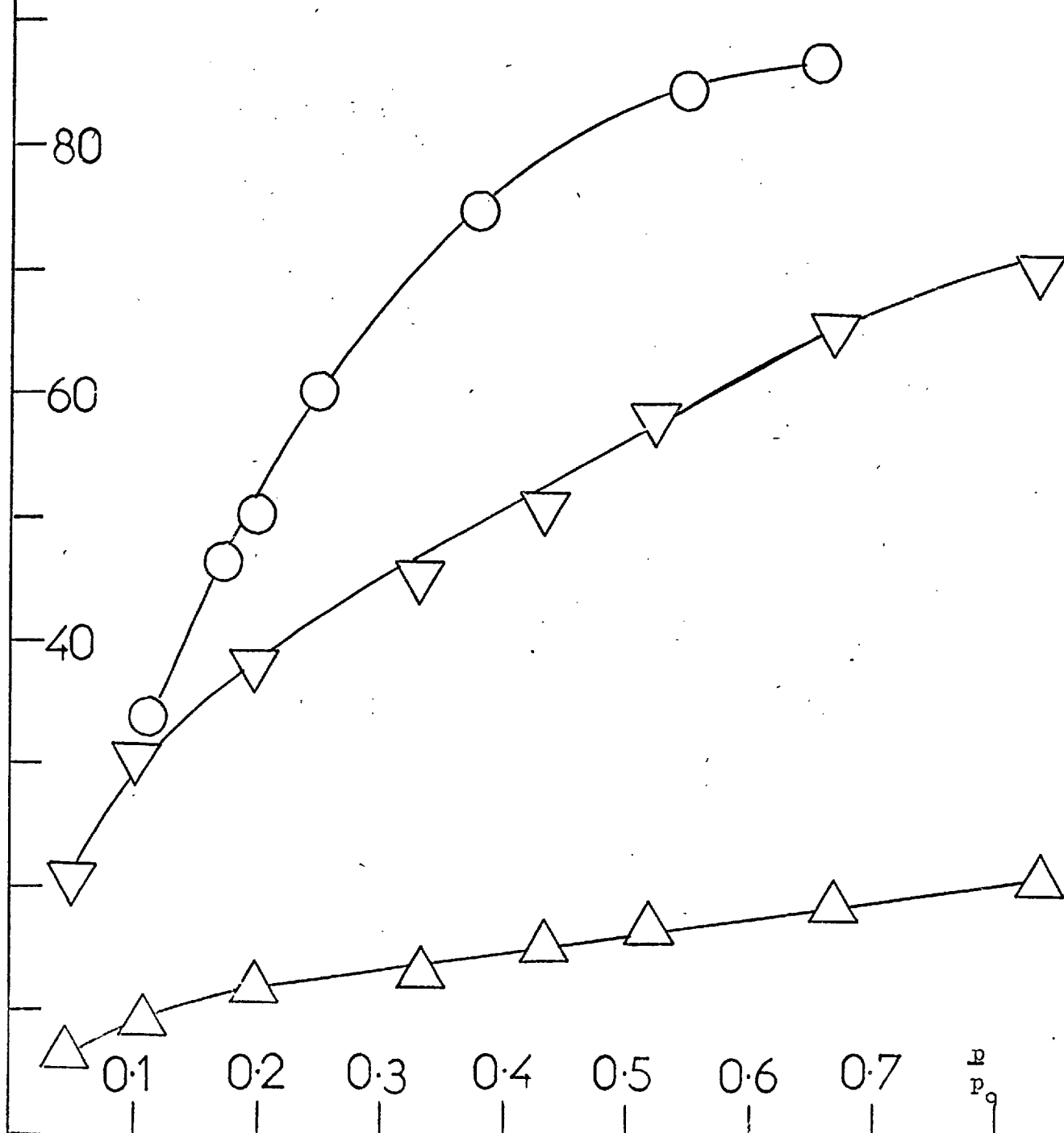
Water sorption isotherms on the sorbent residues after ethyl vinyl ether sorption, powders M, N and O for the residues of NaY, HY and silica gel respectively, are shown in figure 46. The uptake of water in HY is considerably reduced after treatment with ethyl vinyl ether and even the uptake by NaY which did not attract such great amounts of the ether is reduced to less than 30%.

Adsorption-branch isotherms of water on various sorbents after treatment with ethyl vinyl ether.

$T = 303 \text{ K}$

$a/\text{mg g}^{-1}$

- Powder M (NaY)
- △ Powder N (HY)
- ▽ Powder O (Silica gel)



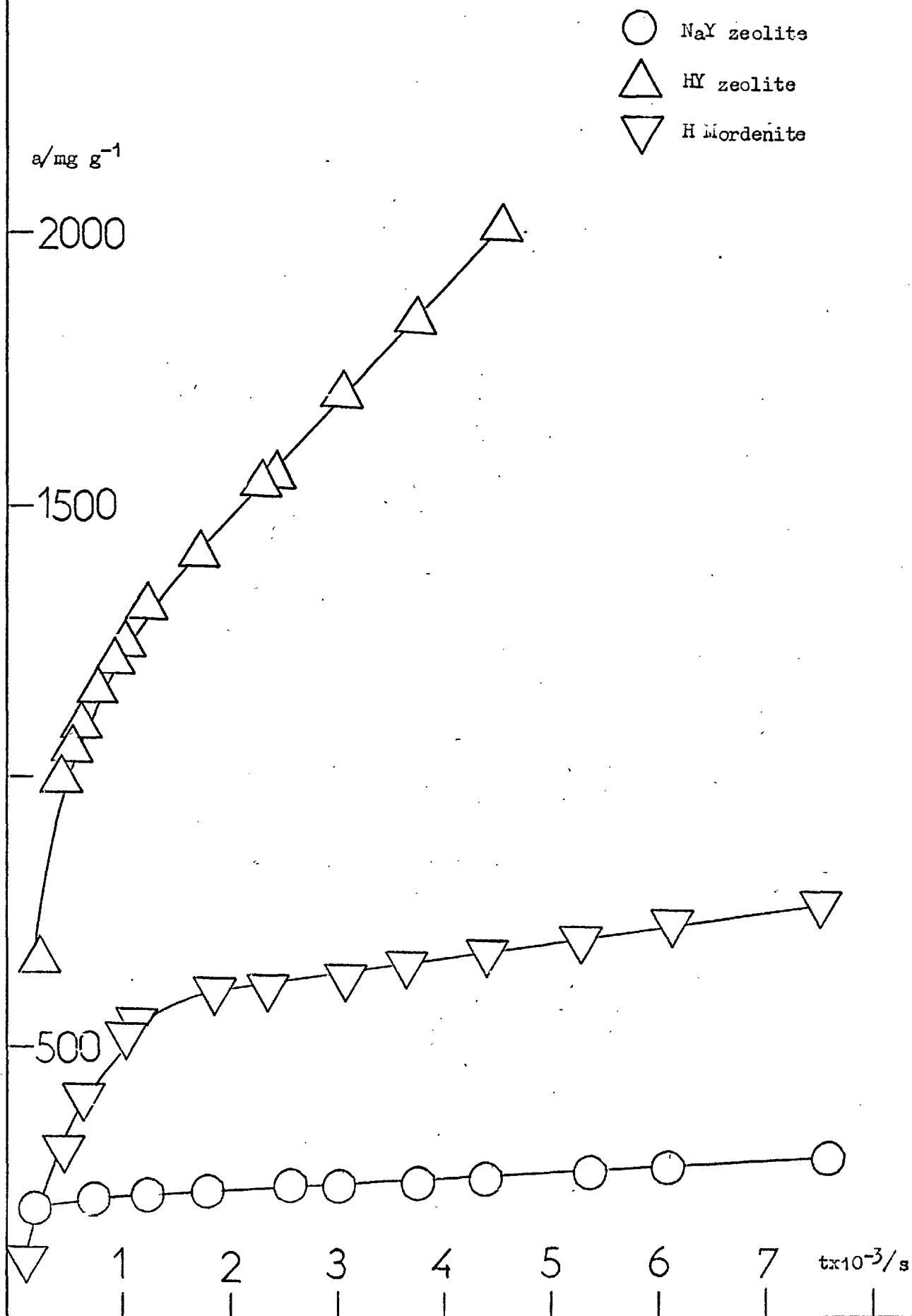
4.7 Investigation of n-butyl vinyl ether polymerization reactions

In view of the ability of hydrogen exchanged zeolite Y to catalyse the polymerization of ethyl vinyl ether, another similar catalyst was investigated in conjunction with this higher vinyl ether. In fact the additional mesomeric effect of the n-butyl group should, according to work reviewed in the first chapter⁽¹⁰⁵⁾, cause a lower rate of polymerization for the higher ether.

Figure 47 shows the adsorption of n-butyl vinyl ether on three zeolites at $T = 304\text{ K}$ and $\frac{p}{P_0} = 0.98$. Sorbents became discoloured as the amount of ether in the zeolites increased, but this discolouration was more pronounced in the hydrogen exchanged zeolites.

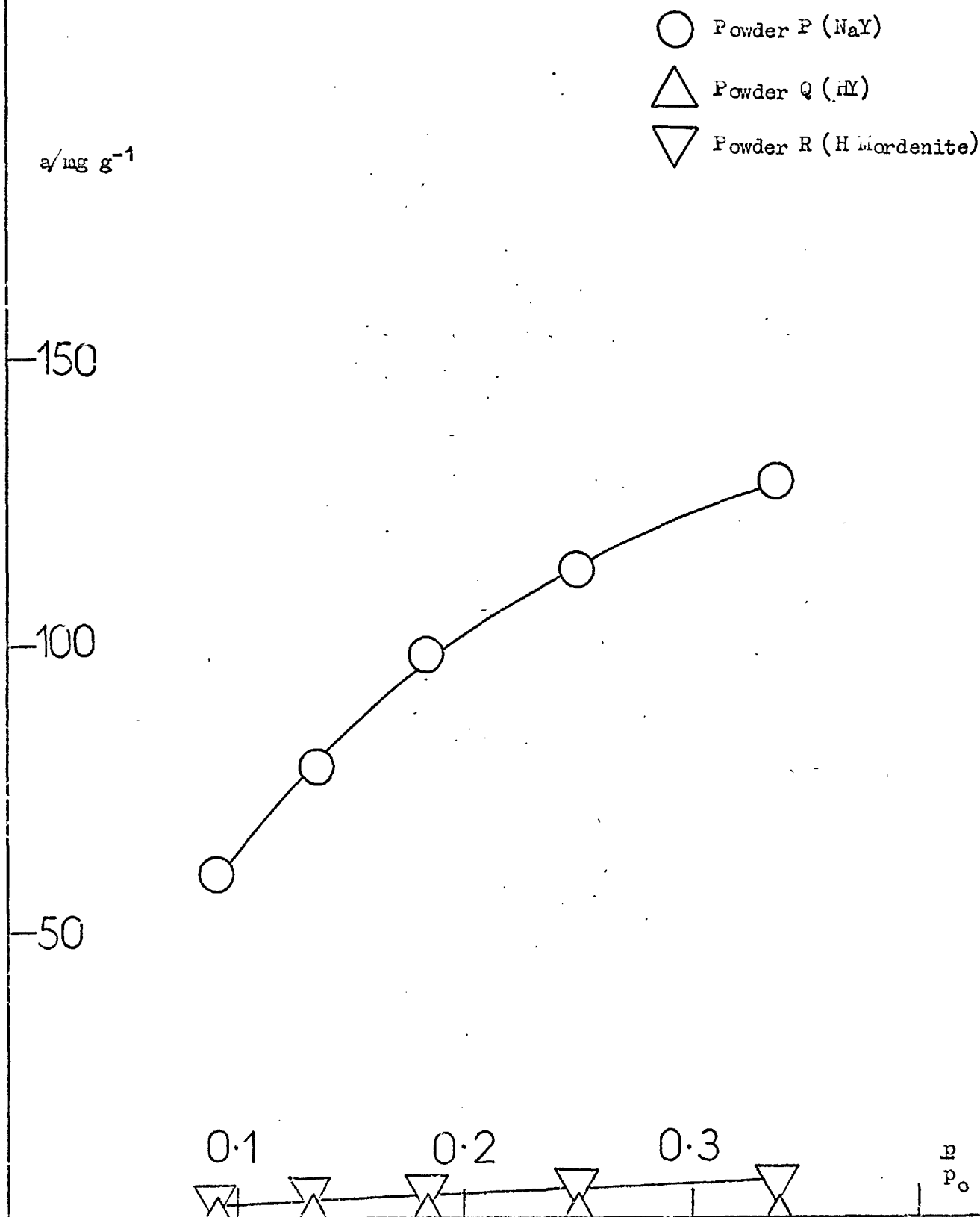
Evacuation of the sorbents for 72 hours at $T = 304\text{ K}$ after the quantities of ether had reached 321 mg g^{-1} , 2990 mg g^{-1} and 860 mg g^{-1} in NaY, HY and H mordenite respectively reduced these values to 281 mg g^{-1} , 2852 mg g^{-1} and 811 mg g^{-1} . Further evacuation at 443 K for 24 hours reduced the amounts sorbed to 180 mg g^{-1} , 1940 mg g^{-1} and 666 mg g^{-1} respectively. Following this treatment, water sorption isotherms were measured and these results are shown in figure 48 (powders P, Q and R denote the residues after ether sorption on the sorbents NaY, HY and H mordenite respectively). It is once more apparent that not only does bulk polymerization of vinyl ethers occur at the external surface of H exchanged zeolites but the internal cavities are largely occupied as well. For both ethyl vinyl ether and n-butyl vinyl ether sorption, little space is available within the zeolites for water molecules, even after

Adsorption of n-butyl vinyl ether in zeolites.

 $T = 304 \text{ K}; \frac{p}{p_0} = 0.98$ 

Adsorption-branch isothermas of water in zeolites after treatment with
n-butyl vinyl ether.

$$T = 303 \text{ K}$$



rigorous outgassing had taken place. It is also apparent that poly(vinyl ethers) are not hydrophilic in character.

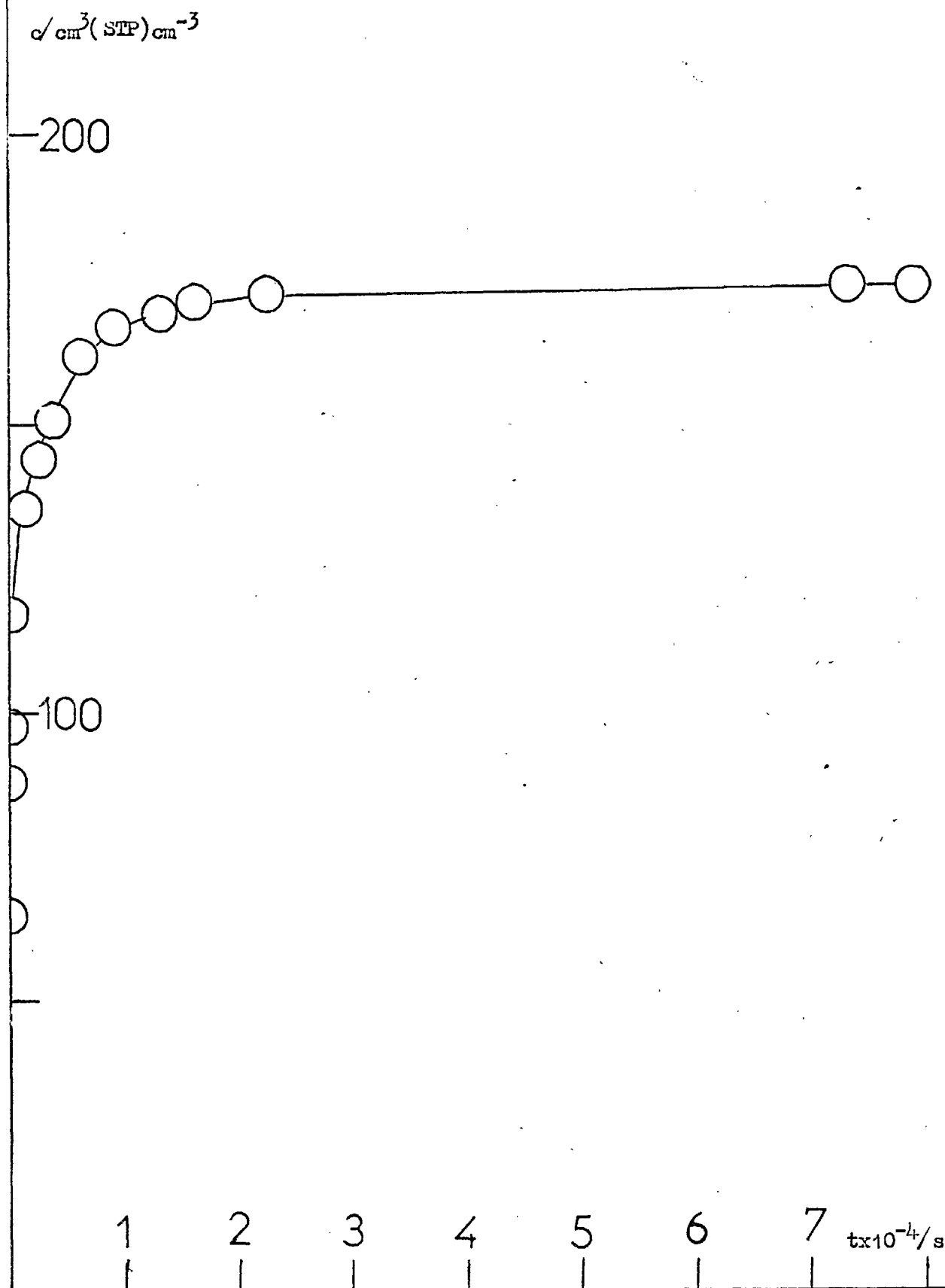
4.8 Investigation of iso-butene polymerization reactions

iso-Butene polymerizes quite readily in the liquid phase at low temperatures over certain cationic catalysts⁽⁶²⁻⁶⁴⁾ and an attempt was made to see if H mordenite could induce gaseous iso-butene to polymerize. A dose of the monomer was admitted to the zeolite at 273K and an initial pressure of 7.15 cmHg. Figure 49 shows that a steady-state is reached after about 8 hours. When the sorbent temperature was raised to 443 K and the system left for 25 hours, the concentration of olefin retained by the zeolite had fallen from 173 cm³(STP)cm⁻³ to 142 cm³(STP)cm⁻³ and the pressure over the sorbent has risen from 0.16 cmHg to 1.29 cmHg. Such behaviour is consistent with the processes of physical sorption.

After iso-butene sorption had been measured, the H mordenite sorbent was outgassed for 24 hours at 443 K. Argon sorption isotherms were then measured on the sorbent and these are compared in figure 50 with an isotherm measured before the iso-butene experiment. Apparently there has been a small retention of hydrocarbon by the zeolite, which would presumably imply that polymer has formed within the zeolitic cavities but only in small quantity. The low pressure at which the monomer was maintained above the zeolite was probably responsible for the small amount of polymer formed and the outgassing conditions were probably rather severe for the low molecular weight polymer formed from the reaction.

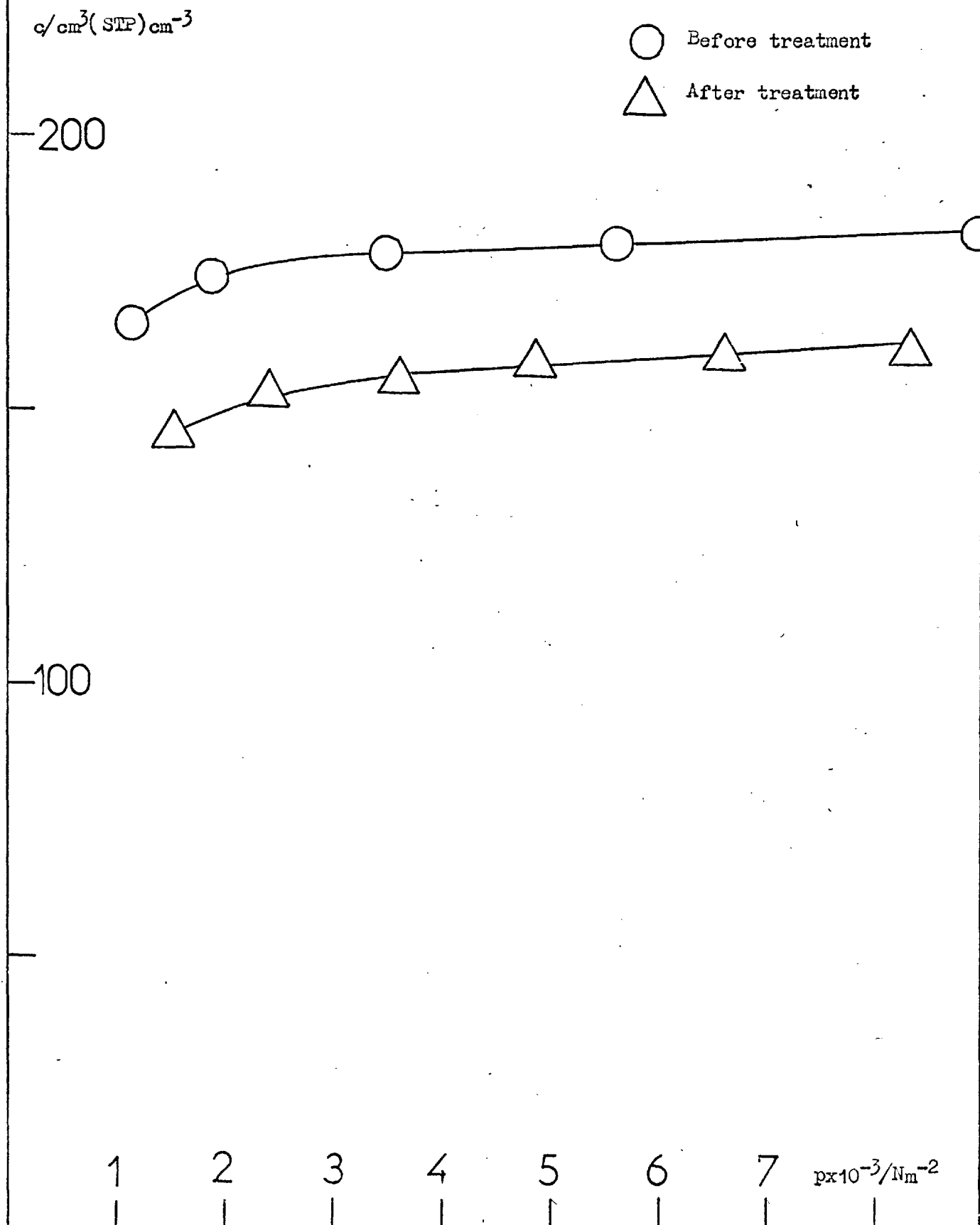
Adsorption of iso-butene in hydrogen mordenite

$$T = 273 \text{ K}; \quad p_{t=0} = 9.53 \times 10^3 \text{ Nm}^{-2}; \quad V_{t=0} = 16.68 \text{ cm}^3(\text{STP})$$



Adsorption isotherms of argon on hydrogen mordenite before and after
treatment with iso-butene

$T = 77.5 \text{ K}$



4.9 Investigation of ethylene polymerization reactions

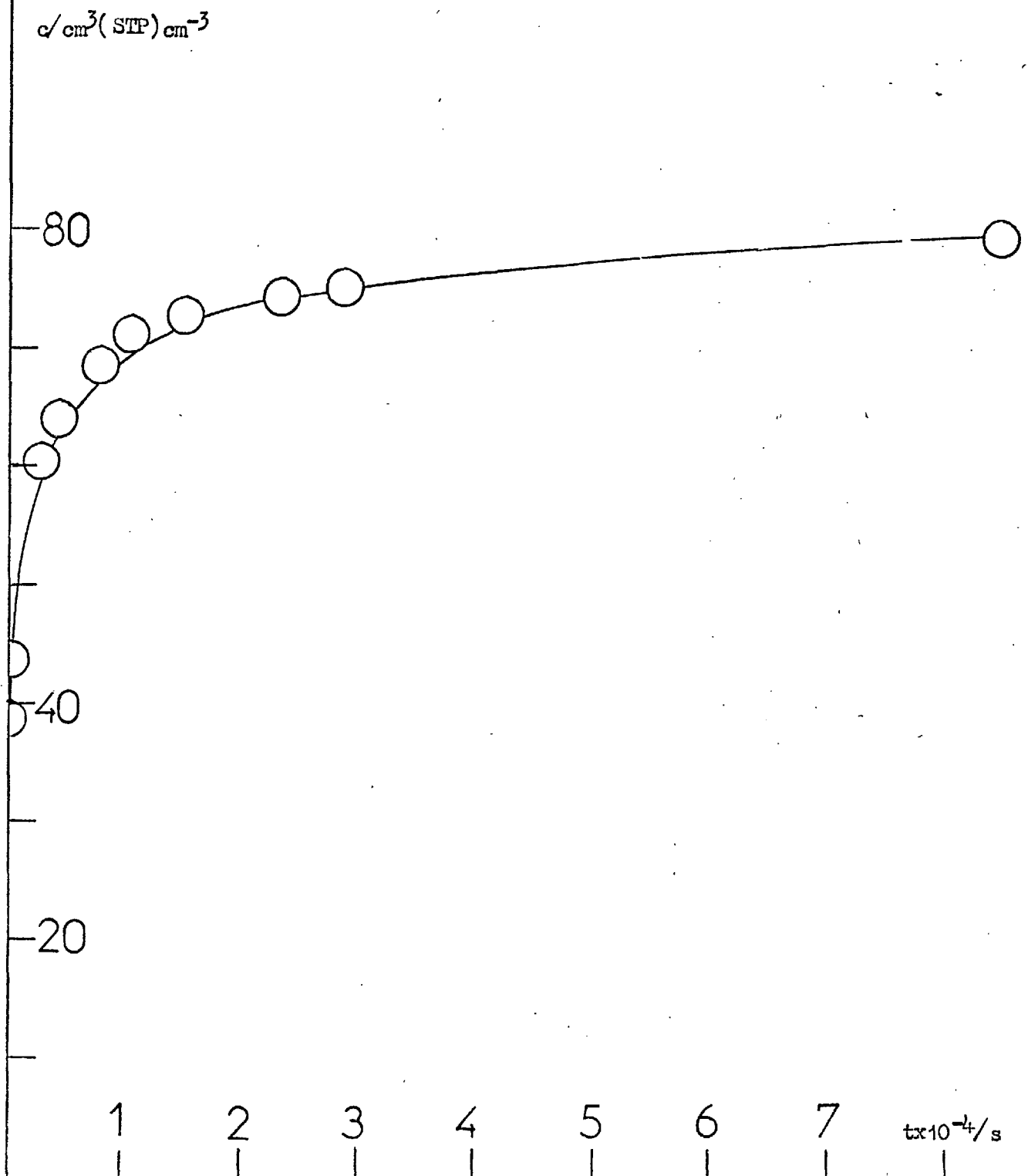
The polymerization of ethylene over HY and dehydroxylated Y at temperatures in the range 373 to 423K has been mentioned earlier⁽⁵⁴⁾. It is of interest to examine the sorption of this olefin in a hydrogen exchanged zeolite at room temperature. A dose of ethylene was admitted to H mordenite at 298K and an initial pressure of 22.4 cmHg and this pressure fell over a period of more than 24 hours. Figure 51 shows the increase in adsorbed ethylene in the zeolite with time. Clearly a slow process is involved.

Argon sorptions on the zeolite residue after ethylene adsorption is shown in figure 52. Curve 2 represents the isotherm obtained after outgassing the zeolite for 24 hours at 298K following ethylene adsorption and it may be compared with the isotherm for argon sorption on pure H mordenite. Clearly there is a considerable amount of ethylene which remains within the zeolite after evacuation at room temperature for 24 hours. This implies that a chemical change of the sorbate has taken place, probably to polyethylene.

A further period of evacuation at 443K for 24 hours was responsible for the removal of most of the organic residue and curve 3 of figure 52 illustrates argon sorption on the product of this treatment.

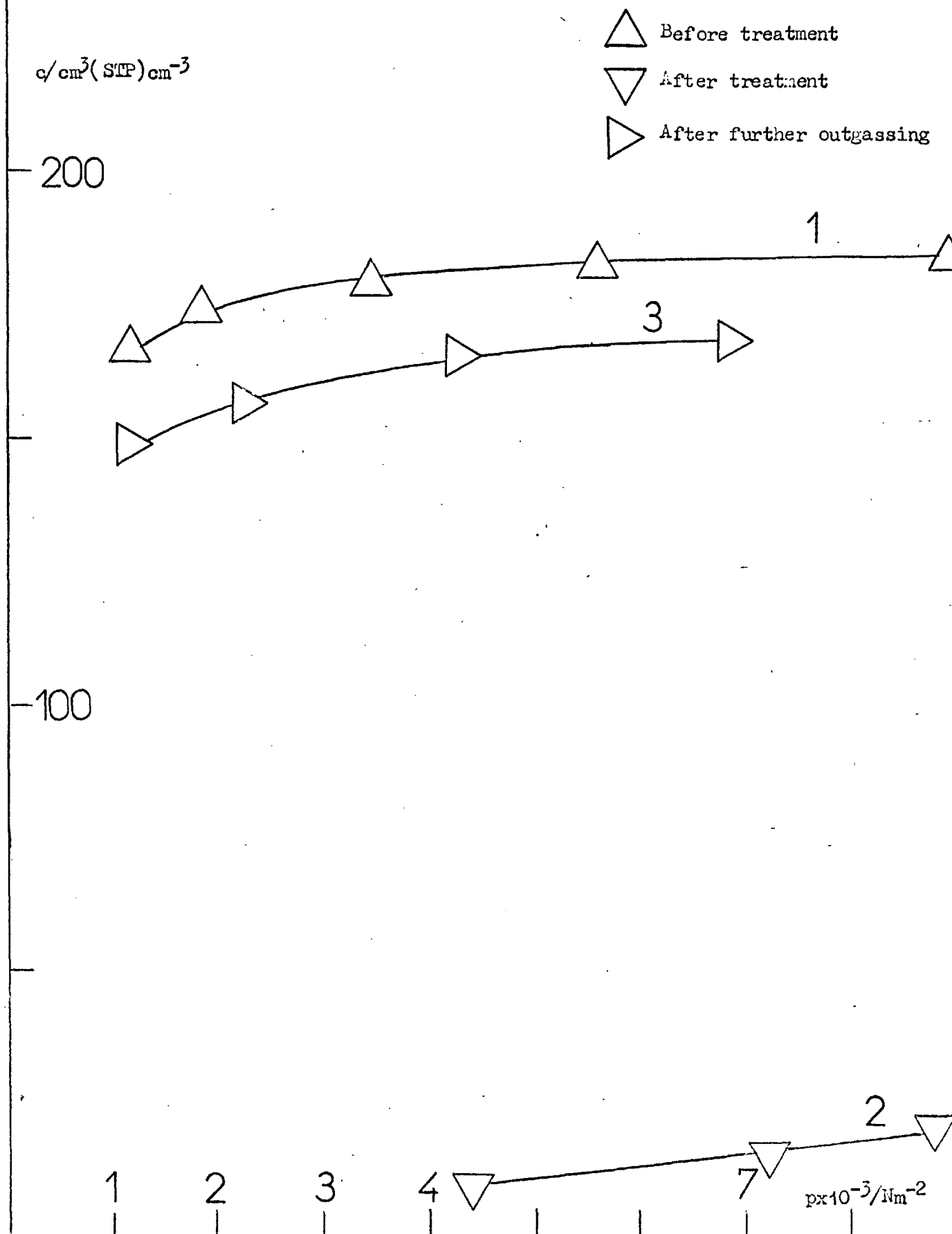
Adsorption of ethylene in hydrogen mordenite.

$$T = 298 \text{ K}; \quad p_{t=0} = 29.91 \times 10^3 \text{ Nm}^{-2}; \quad V_{t=0} = 55.05 \text{ cm}^3(\text{STP})$$



Adsorption isotherms of argon on hydrogen mordenite before and after treatment with ethylene.

$T = 77.5 \text{ K}$



4.10 Investigation of acetaldehyde polymerization reactions.

The cationic polymerization of several aliphatic aldehydes at low temperatures has been mentioned earlier⁽¹¹⁰⁻¹¹²⁾ and an effort was made here to see if acetaldehyde would polymerize over HY at room temperature.

Figure 53 illustrates the adsorption of acetaldehyde by a sample of HY. The isotherm was not reversible and evacuation of the sorbent for 24 hours at the temperature of the isotherms reduced the adsorbed concentration to 164 mg g^{-1} . Even evacuation for 24 hours at 443K reduced this concentration only to 158 mg g^{-1} indicating that acetaldehyde is either abnormally powerfully bound to the sorbent or chemically altered, possibly into a polymer.

The product of this adsorption-desorption treatment, powder S, was then investigated as a water sorbent and curve 2 of figure 54 illustrates this. Comparison with curve 1, the isotherm for water sorption of the same sample of HY before acetaldehyde treatment, shows that the residue from acetaldehyde adsorption prevents the entry of a considerable amount of water into the zeolitic cavities.

4.11 Investigation of benzofuran polymerization reactions.

Benzofuran undergoes polymerization cationically and in a manner similar to the vinyl ethers^(108,109). Sorption of benzofuran in NaY and H mordenite was therefore investigated to see if these zeolites were effective catalysts for benzofuran polymerization at room temperature.

Adsorption isotherm of acetaldehyde in HY zeolite

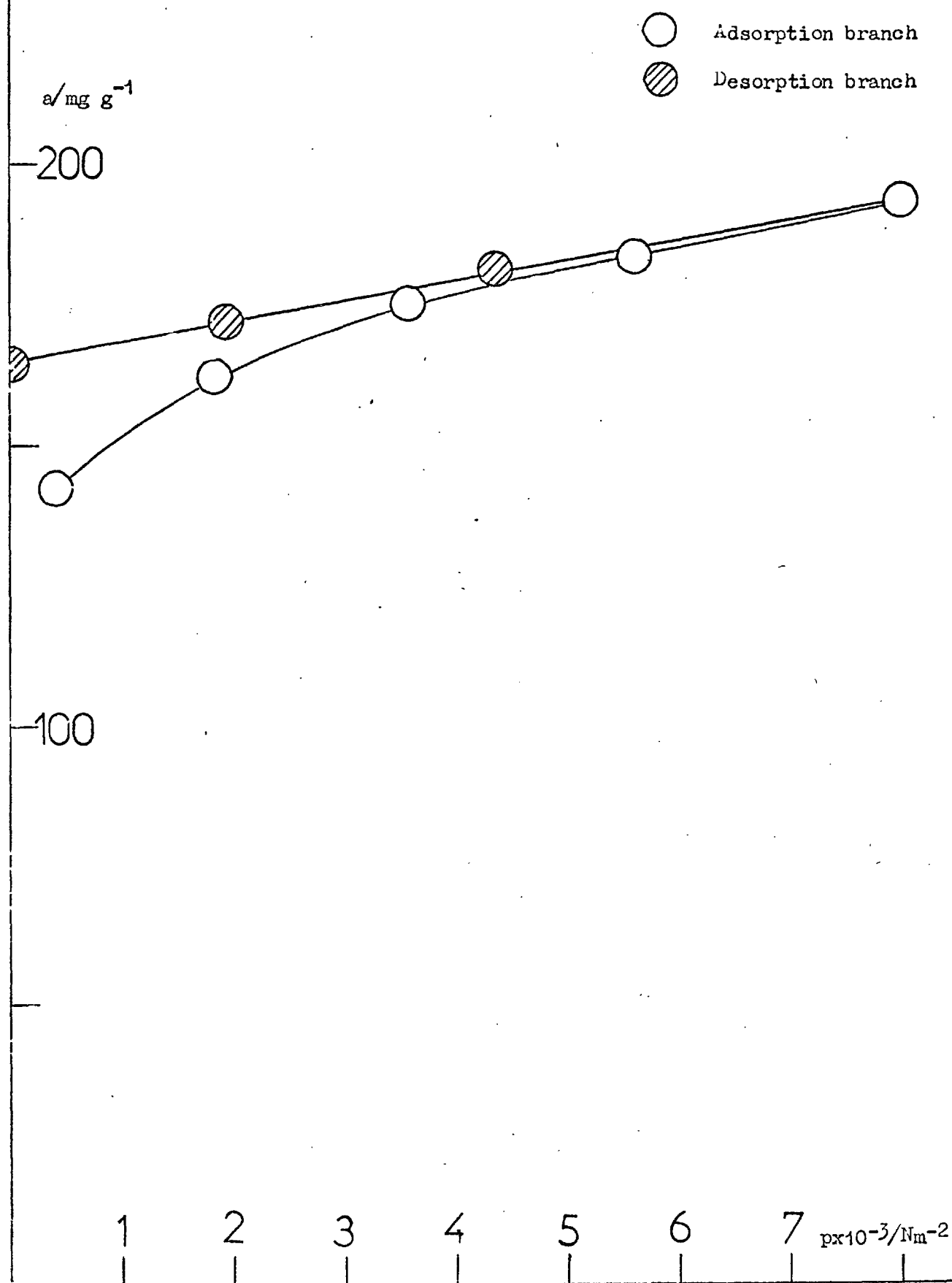
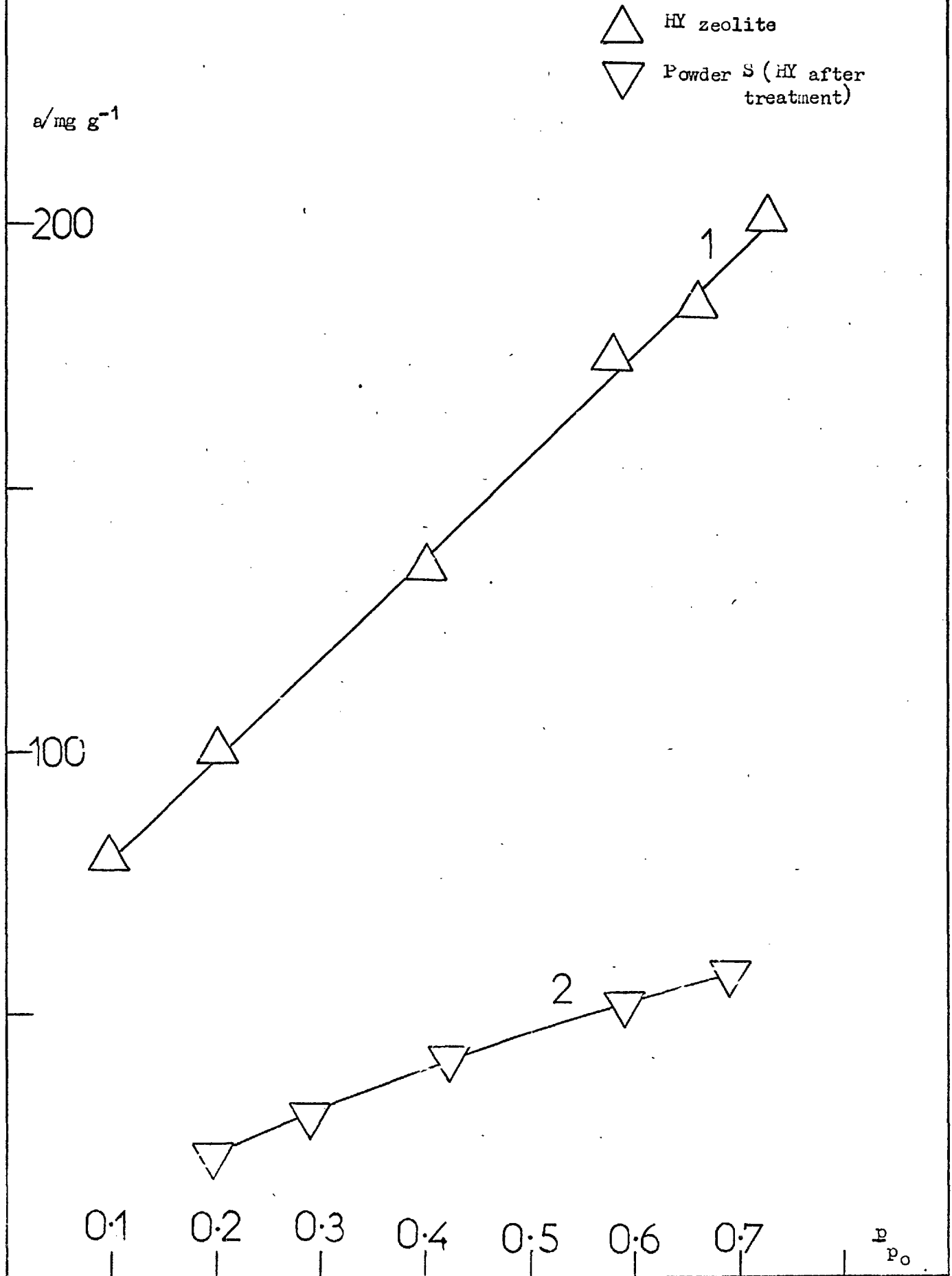
 $T = 303 \text{ K}$ 

Figure 54

Adsorption-branch isotherm of water in HY zeolite before and after treatment with acetaldehyde.

$T = 303 \text{ K}$



Isotherms of benzofuran sorption on NaY and H mordenite are shown in figure 55, clearly adsorption takes place to a very considerable extent at very low pressure in NaY but the channels of H mordenite appear to be too narrow to permit the entry of benzofuran in large amounts.

Evacuation of the sorbents at 443K for 24 hours reduced the amount of organic material in NaY and H mordenite to 195.3 mg g⁻¹ and 15.8 mg g⁻¹ respectively.

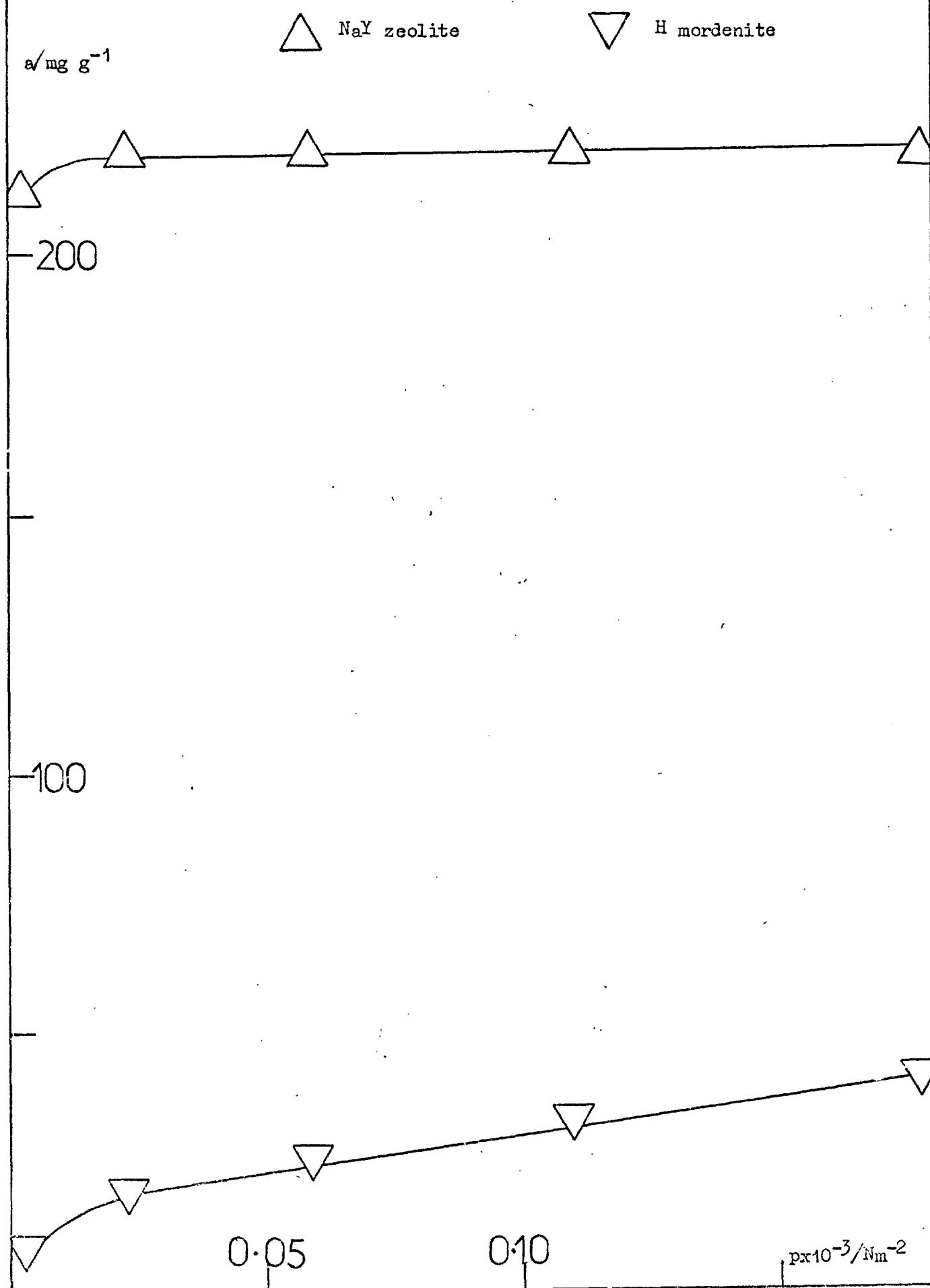
Water sorption isotherms by the products of these two zeolites after benzofuran sorption-evacuation treatment are shown in figure 56. Curves 1 and 2 represent water sorptions on free NaY and H mordenite while curves 3 and 4 show the water sorption isotherms on powders T and U, the products obtained from these two zeolites respectively. A considerable amount of benzofuran or a polymer apparently remains within NaY even after evacuation at 443K. The water sorption of H mordenite is also reduced slightly by treatment with benzofuran.

4.12 Investigation of acenaphthylene polymerization reactions.

Another molecule which polymerizes cationically by head-to-tail linking is acenaphthylene⁽¹⁰⁷⁾. This compound is a yellow crystalline solid which melts at 365K and there was no means of determining a sorption isotherm with the apparatus used in this work. A small quantity of H mordenite was shaken for 72 hours at room temperature with a solution of acenaphthylene in diethyl ether, the product is called powder V.

Figure 57 shows the sorption of water on H mordenite before

Adsorption-branch isotherms of benzofuran in zeolites.

 $T = 303 \text{ K}$ 

Adsorption-branch isotherms of water in zeolites before and after
treatment with benzofuran.

$$T = 303 \text{ K}$$

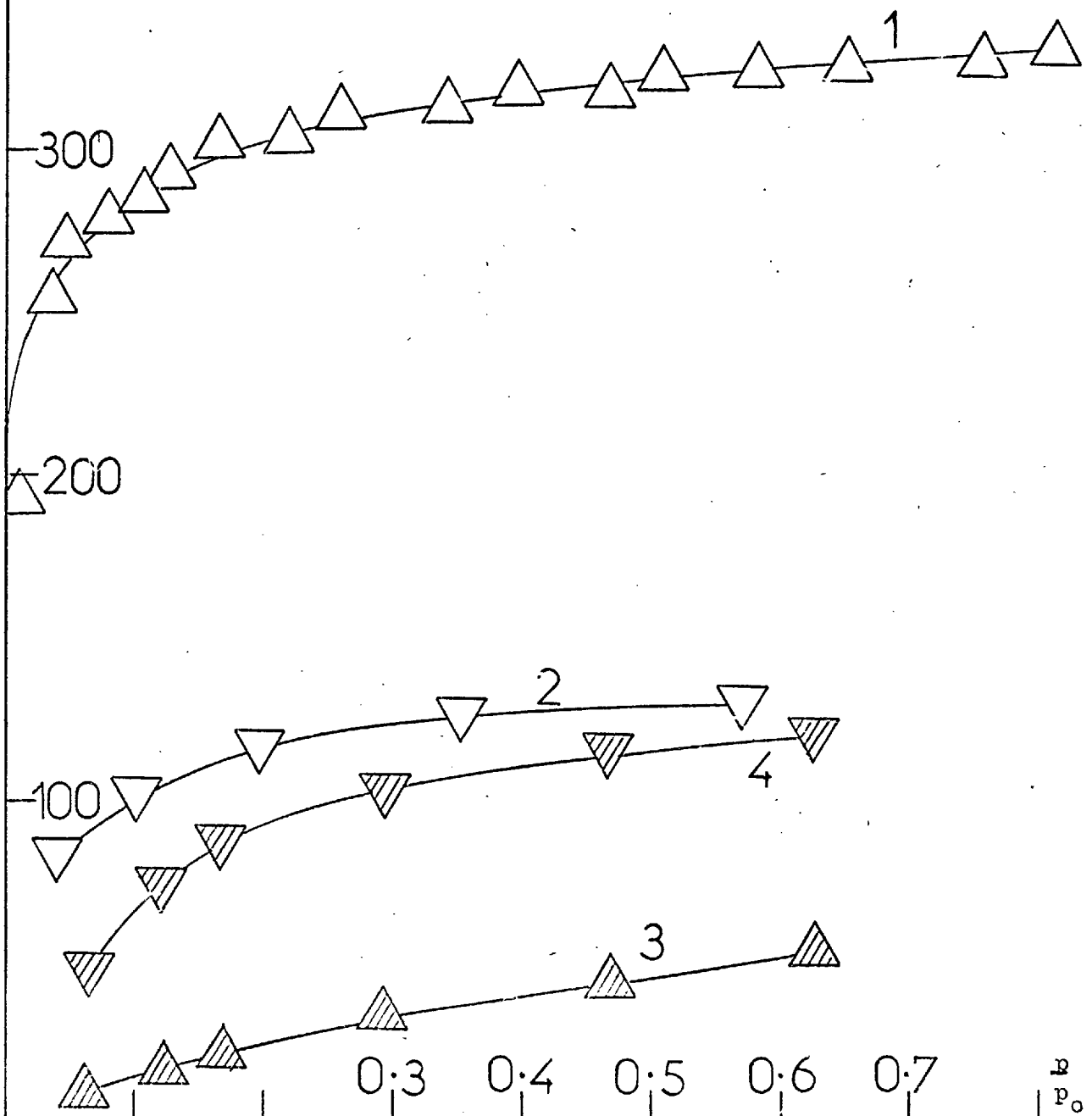
△ NaY zeolite

▽ H mordenite

▨ Powder T (NaY)

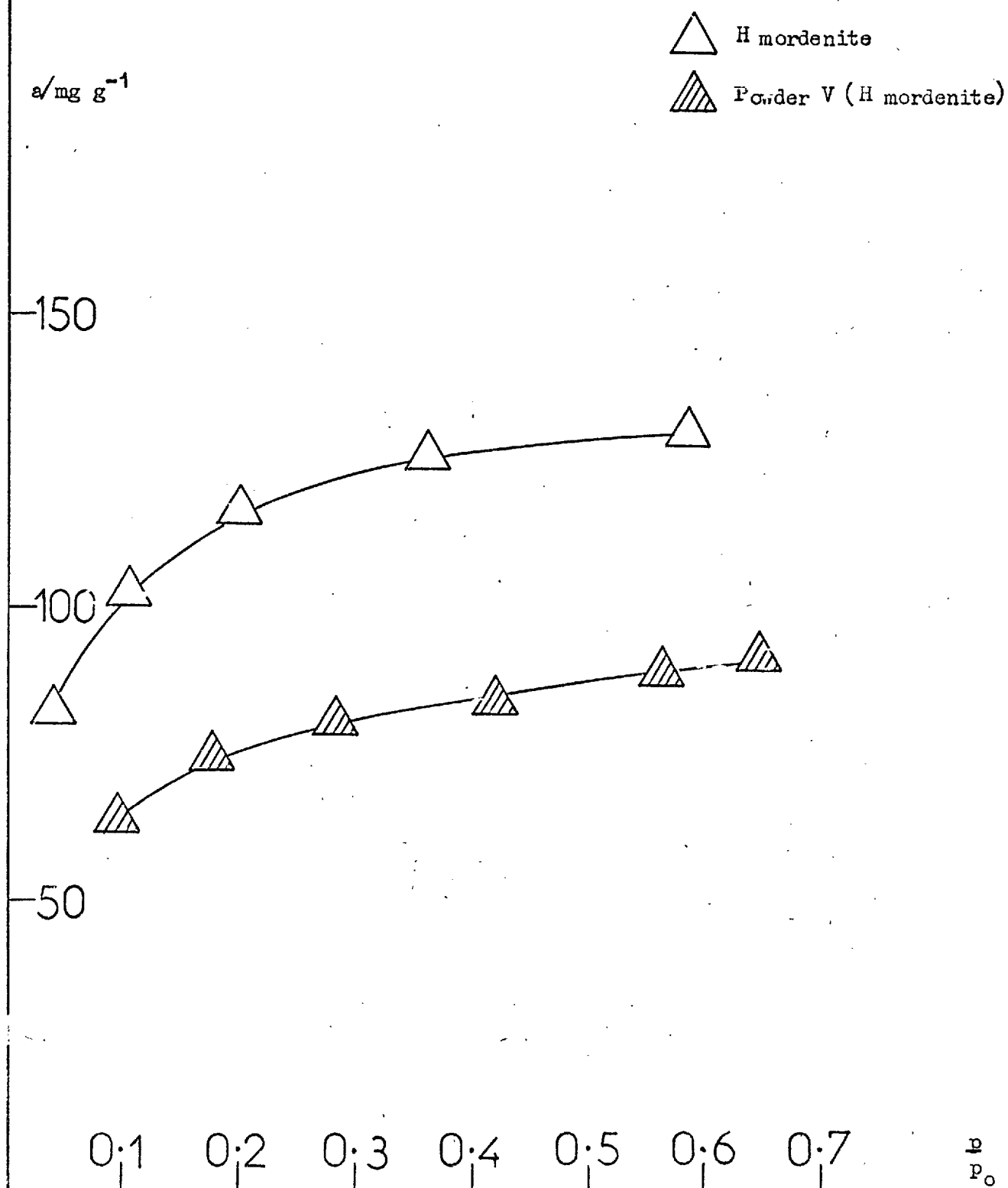
▨ Powder U (H mordenite)

$a/\text{mg g}^{-1}$



Adsorption-branch isotherms of water in hydrogen mordenite before and
after treatment with acenaphthylene.

$$T = 303 \text{ K}$$



and after acenaphthylene treatment. The treated sorbent had been dried and evacuated for 24 hours at 443 K prior to water sorption measurements. In spite of the size of acenaphthylene, which must have restricted its entry to H mordenite, there is a reduction in volume available to water molecules after this treatment. It is likely therefore that polymerization has occurred within the zeolitic cavities to a small extent.

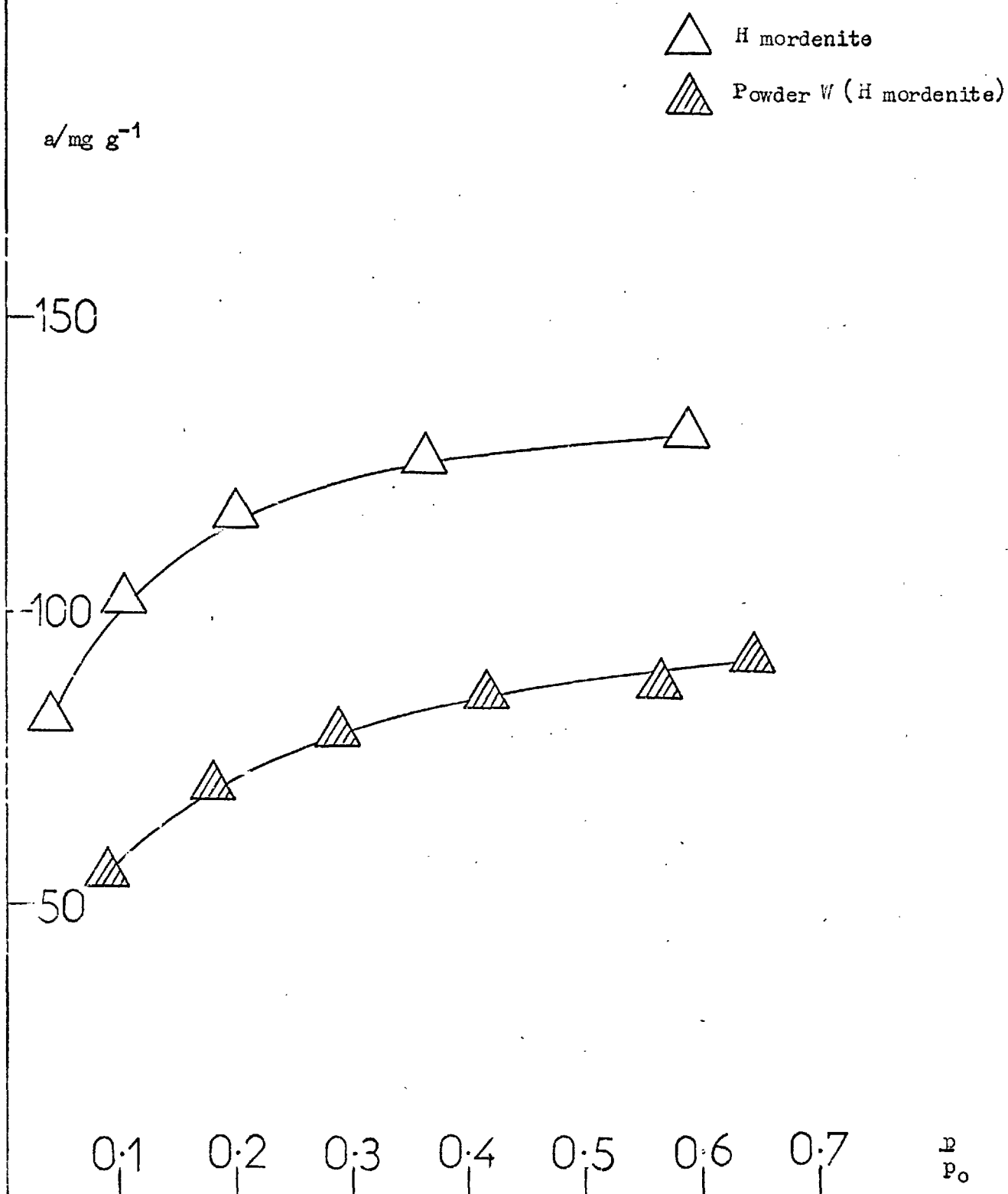
4.13 Investigation of diazo methane polymerization reactions.

Several examples of the polymerization of diazo methane over heterogeneous catalysts were mentioned earlier⁽¹¹⁹⁻¹²³⁾ and the effect of zeolites on this compound has been investigated here. A considerable reduction in the hydrophilic character of hydroxyapatite was observed after the treatment of this material with ethereal solutions of diazomethane⁽¹⁸²⁾. The cause of this change in surface character was associated with the formation of an organic chemisorbed monolayer. This monolayer was more complete and more effective as a water repellent when the apatite had a large concentration of surface acidic sites. In view of this, H mordenite was selected as a suitable zeolite with which to investigate the reaction of diazo methane.

A 0.05 M solution of diazo methane was left in contact with H mordenite for 72 hours at 273K and, after drying and outgassing at 443K for 24 hours, a water sorption isotherm was measured. This isotherm is shown in figure 58, powder W, together with a water sorption isotherm on the free zeolite. A reduction in the water

Adsorption-branch isotherms of water in hydrogen mordenite
before and after treatment with diazo methane.

$T = 303 \text{ K}$



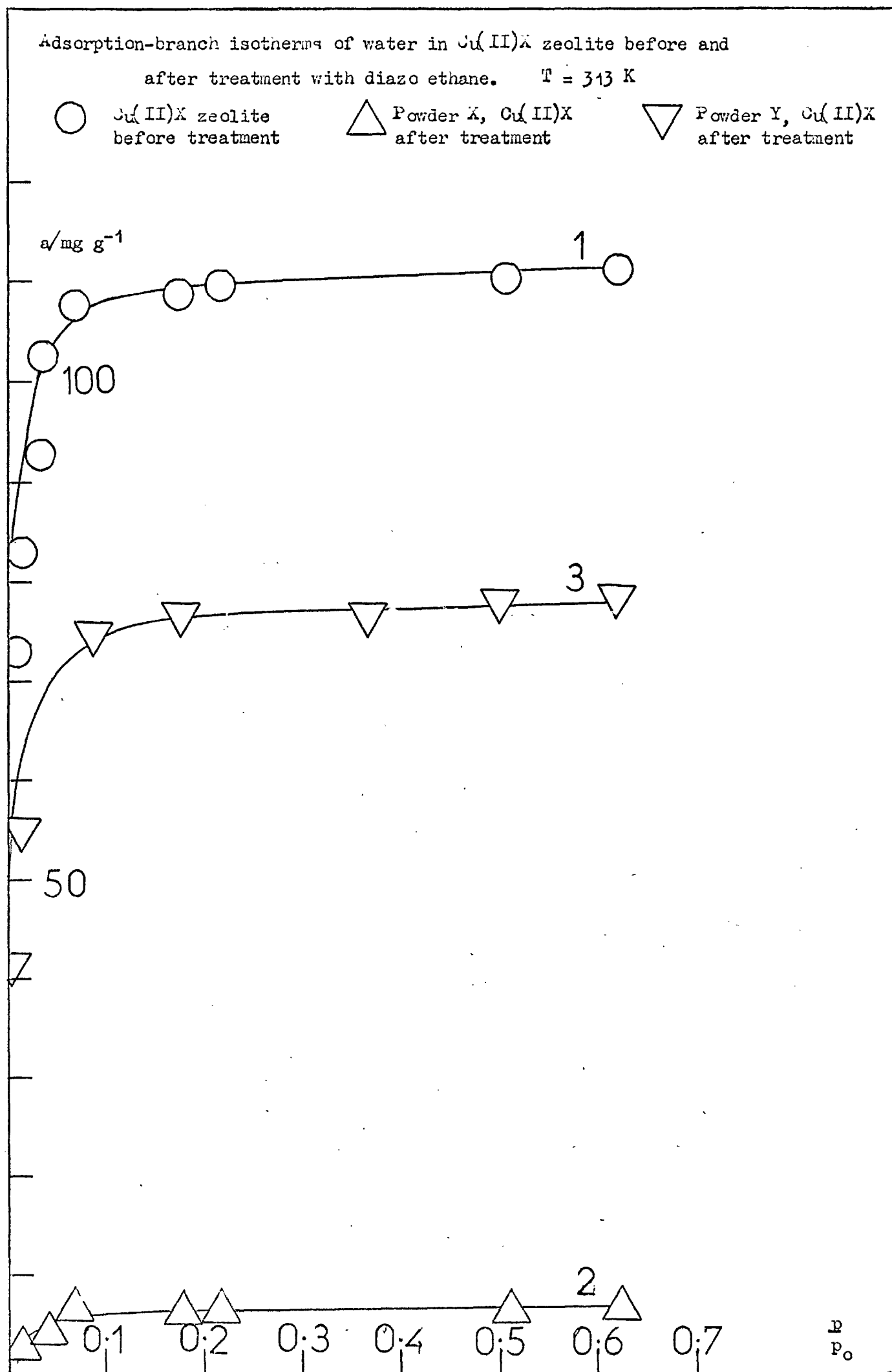
uptake is apparent after such treatment and this could be interpreted in two ways. If polymerization had been induced within the zeolite then much of the zeolitic cavity volume would be unavailable for subsequent water sorption. Alternatively, the reaction with diazo methane may have produced a chemisorbed monolayer of methoxy groups in a manner similar to the reaction with hydroxyapatite⁽¹⁸²⁾. In this second case, the volume of zeolitic cavities available for water molecules may be little changed.

An analysis of powder W revealed that the concentration of organic material present in the zeolite after water sorption was 81 mg g⁻¹.

4.14 Investigation of diazo ethane polymerization reactions.

In a previous investigation of diazo alkane reactions over crystalline aluminosilicates⁽¹⁸⁵⁾ some work was done with diazo ethane and Cu(II)X zeolite. The cupric zeolite was selected because many other copper salts and even copper metal exhibit powerful catalytic activity for diazo alkane polymerization. Although the materials in this study were prepared by this earlier investigator, the water sorption isotherms for the study were measured by the author and are presented here.

Curve 1 of figure 59 illustrates the adsorption of water to free Cu(II)X while the other curves show the effect upon the sorbent of contact with ethereal solutions of diazo ethane. The difficulty of preparing samples to obtain reproducible results is clear from this figure, and some of the difficulties associated



with experiments on diazo alkanes should perhaps be pointed out. These compounds are unstable and can only be stored for short periods in chilled solutions. Considerable care has to be taken when using the solutions which have a toxic, explosive vapour. In addition, the rapid loss of the compounds from solution has to be avoided for it is easy to prepare a solution which upon analysis may be found to contain no diazo alkane at all. In all cases where ethereal solutions of diazo alkanes have been used, work has been done in a fume-cupboard (in more recent work the investigator has also worn a gas-mask manufactured with a diazo alkane filter) and all solutions have been analysed before use and diluted to a concentration of 0.05 M in diethyl ether. Analysis of the solutions was by neutralization of the diazo alkane by the addition of excess benzoic acid followed by an estimation of the excess by titration against a standard methanolic potassium hydroxide solution⁽¹⁷⁵⁾.

The outgassing procedures which preceded the measurement of the isotherms represented by curves 2 and 3 differed. Curve 2 measurements followed evacuation of the sorbents for 48 hours at 423K while the procedure adopted before curve 3 was measured was evacuation for 48 hours at 473K. Probably 473K is rather too high a temperature for the sorbent to withstand for such a period and this may be the cause of the smaller reduction of hydrophilic character of this modified zeolite. A very considerable blocking of the internal volume is apparent from curve 2, however.

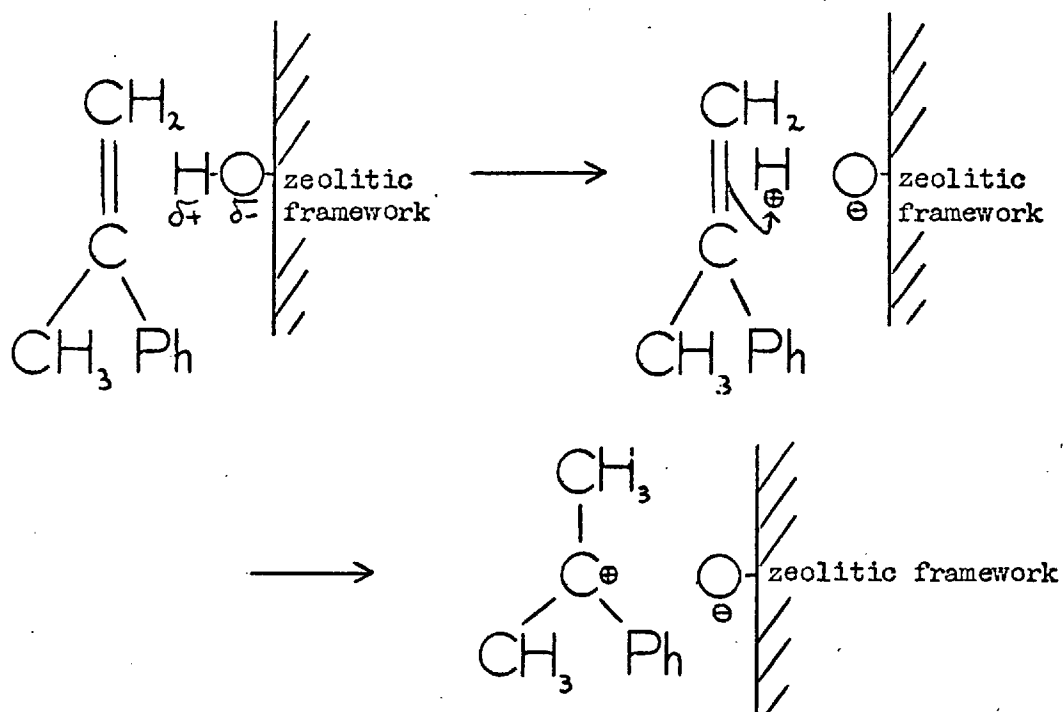
CHAPTER 5

Conclusions

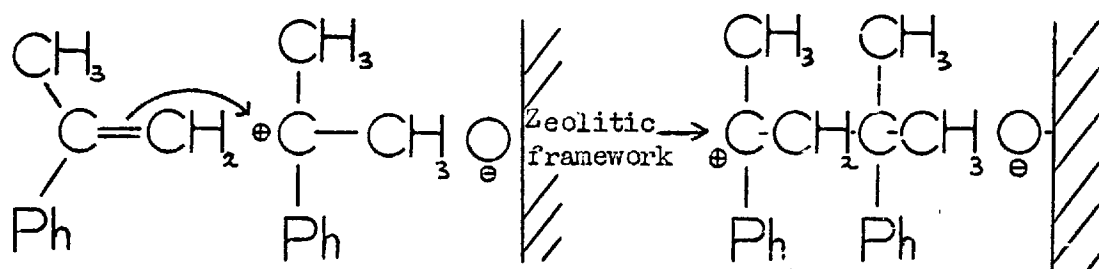
Room temperature reactions over crystalline aluminosilicate catalysts of fourteen organic substances have been studied. The reactions over zeolites were of two main types. Type 1 reactions were those in which monomers were strongly adsorbed into the internal volume of a catalyst. Evidence has been presented for the polymerization of these monomers within the zeolitic cavities. Polymeric materials formed from a type 2 reaction were not restricted to the internal cavities and continued to appear over the catalyst throughout the course of a sorption experiment.

Reactions of the second type are most easily observed and they will be dealt with first. The three monomers which polymerized in this way are α -methyl styrene, ethyl vinyl ether and n-butyl vinyl ether. Reactions took place over either hydrogen exchanged zeolites or the clay-mineral kaolinite.

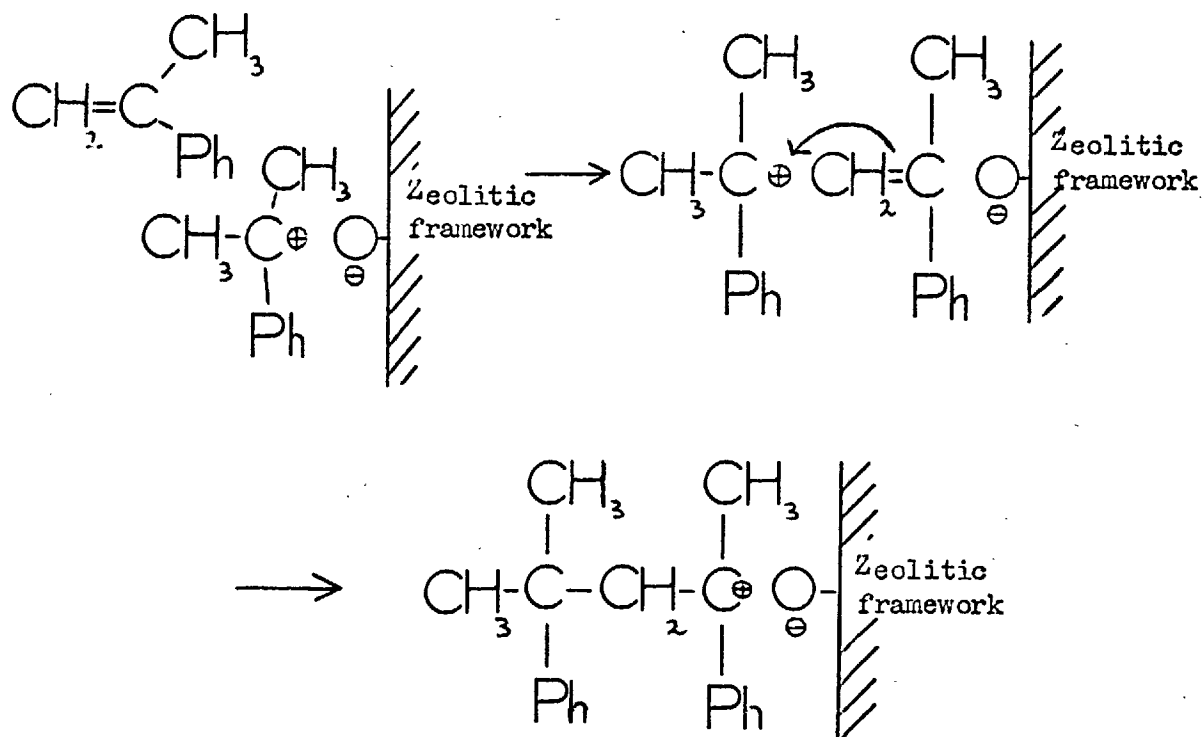
α -Methyl styrene may polymerize after the addition of an electrophilic species such as a proton. The hydrogen exchanged zeolites HY and H mordenite, outgassed under the conditions described previously, would contain residual water molecules. These water molecules would enable the zeolitic surfaces to be sufficiently (Bronsted) acidic for protons to be donated to the organic molecules. Polymerization may be based on the following scheme:



After the addition of a proton to the sorbate, polymerization could take place.

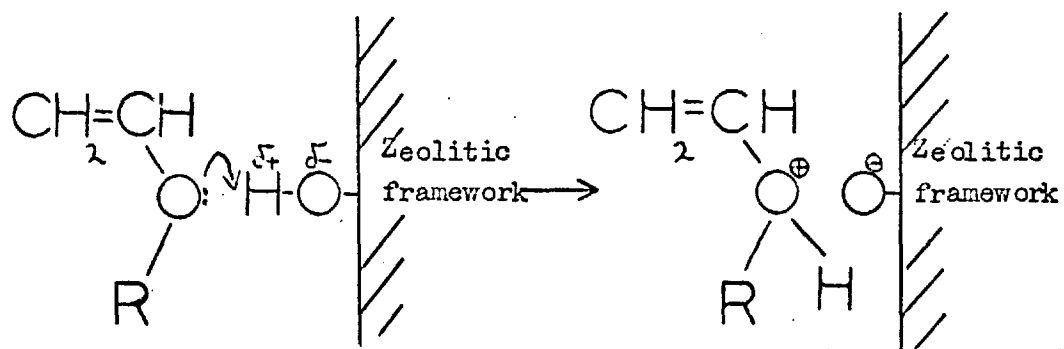


It is more probable, however, that the positive charge of the carbonium ion would be located close to the zeolitic surface. Polymerization could take place after monomeric molecules had diffused through the growing chains of polymeric material.

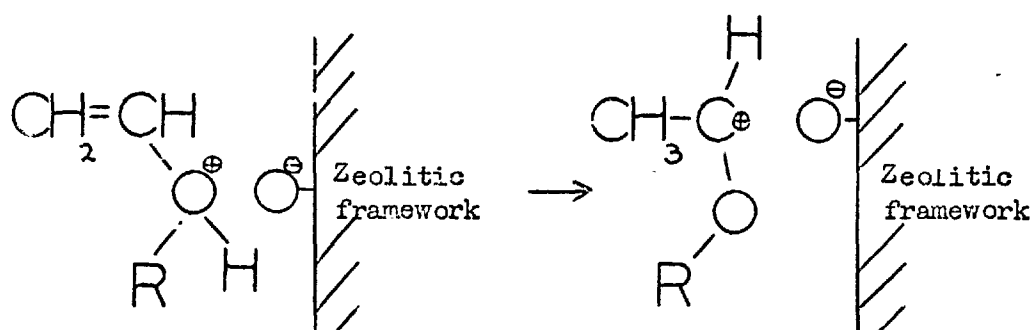


Bulky side chains on both monomer and polymer molecules would hinder the diffusion of monomeric molecules to the reaction centre and the reaction may therefore proceed slowly.

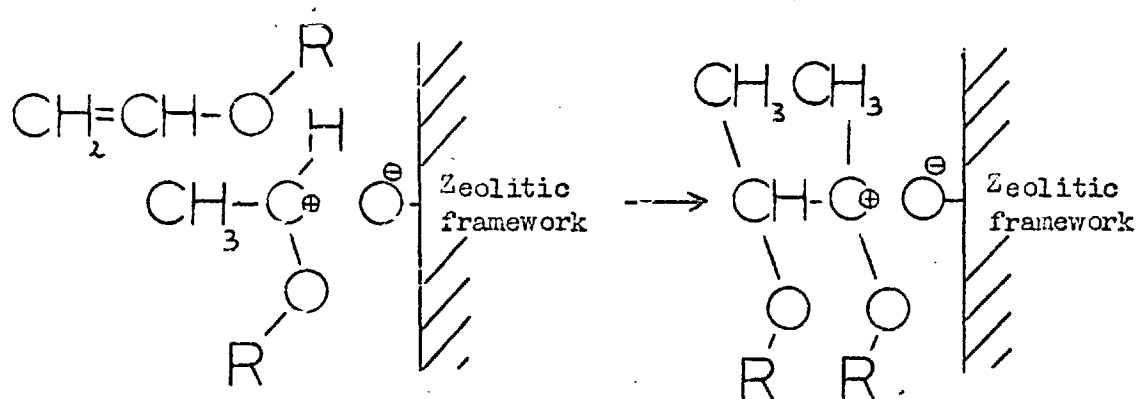
Vinyl esters reacted violently in the presence of even hydrated hydrogen exchanged zeolites. All stages of such reactions as these are therefore fast. The following scheme is proposed. The lone pair of electrons on the oxygen atom of the ether molecule attracts a proton from a surface water molecule. This proton combines with the organic molecule to yield an oxonium ion.



Isomerization of this oxonium ion to a carbonium ion can then take place,



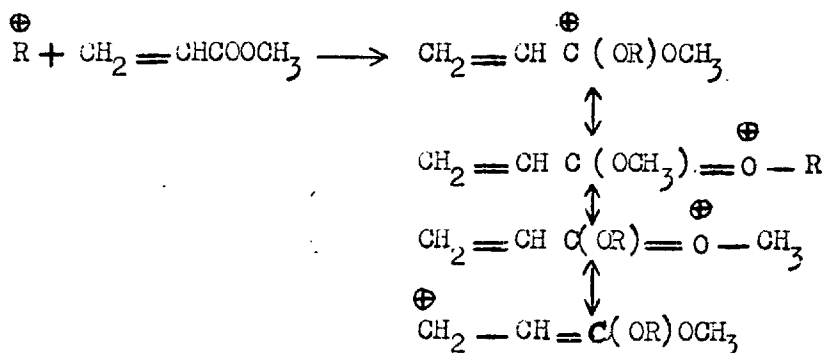
and polymerization may follow.



The chains of poly(alkyl vinyl ether) would be linear and would allow the diffusion of further ether molecules to the zeolitic surface.

Apparently, the necessary conditions for a type 2 reaction to occur are (i) the organic monomer must be able to carry a positive charge (ii) the zeolite should have entry pores of sufficient diameter to allow the entry of the monomer and (iii) the zeolite must have a strongly (Bronsted) acidic surface. Type 2 polymerization reactions are therefore cationically induced and proceed rapidly, probably at the internal surface of the zeolite.

All other monomers investigated in this work underwent a type 1 polymerization reaction with all the zeolites employed. One of the most interesting reactions was between methyl methacrylate and NaY zeolite. This organic monomer does not, according to previous work, undergo cationically induced polymerization reactions. Indeed, a reaction scheme has been suggested which accounts for the inability of this compound to yield an active carbonium ion⁽⁷⁴⁾:



A more probable explanation of the polymerization of methyl methacrylate within NaY and other zeolites is that the reaction

proceeds by a free-radical mechanism. Evidence was presented earlier for the existence of radical species within zeolites^(57,64, 68-70). The possibility of an anionically initiated polymerization reaction should not be overlooked either.

Methyl methacrylate, n-butyl methacrylate and acrylonitrile form one sub-group of monomers which undergo type 1 reactions, for these monomers do not normally polymerize by cationically induced reactions. The other monomers of this group can polymerize cationically and might be expected to undergo type 2 reactions over suitable catalysts. There are, however, several reasons why these monomers should not react in this way.

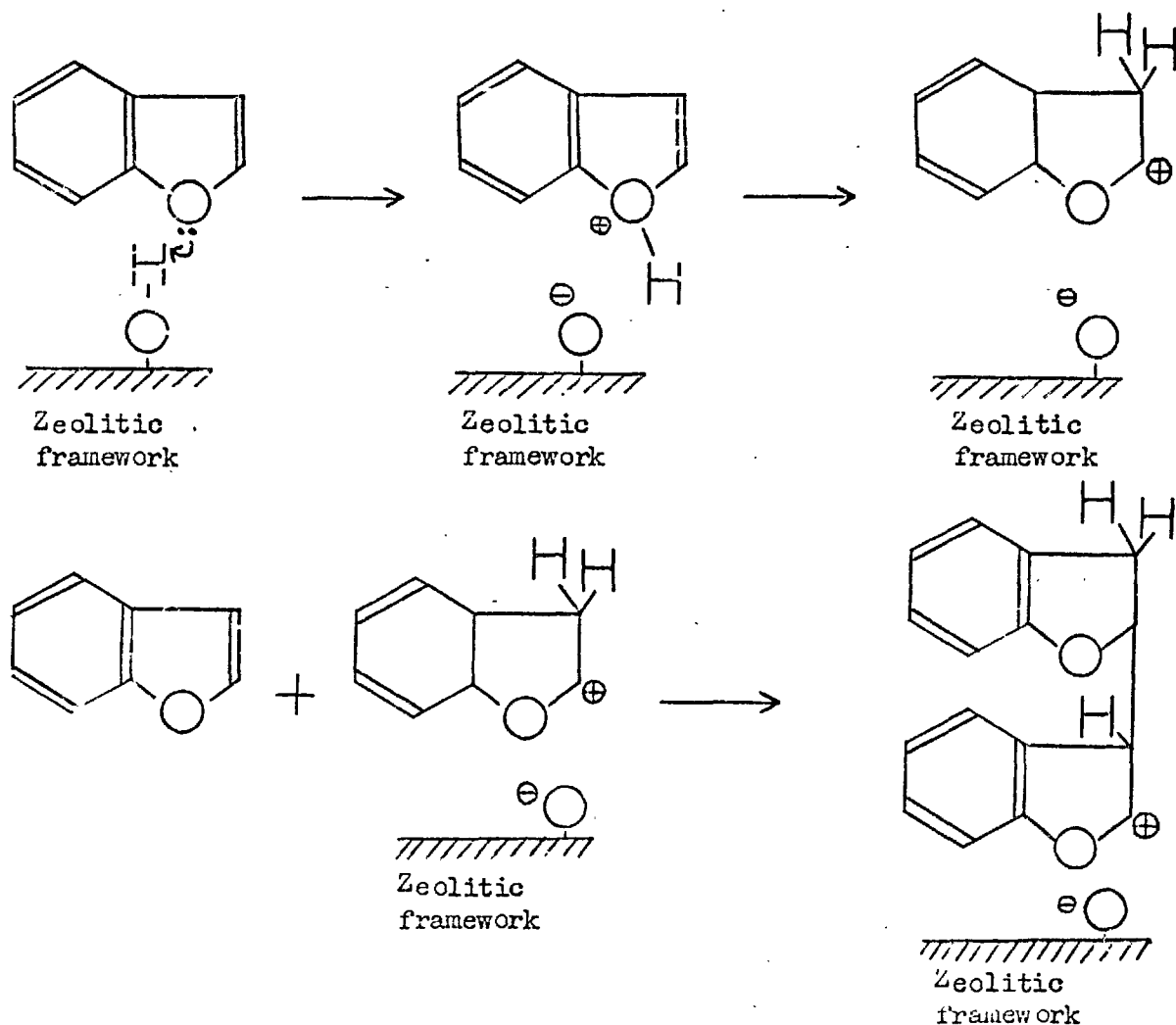
The behaviour of styrene was not investigated by sorption experiments in hydrogen exchanged zeolites and it should be recalled that even the vinyl ethers polymerised by a type 1 reaction over NaY zeolite. It should also be noted that the methyl group of α -methyl styrene renders this molecule more active than styrene for cationically induced polymerization reactions. Even α -methyl styrene was only moderately reactive over hydrogen exchanged zeolites.

The presence of iso-butene in the group of monomers undergoing type 1 reactions over hydrogen exchanged zeolites is less easy to understand. Mineral acid catalysed reactions^(62,64) and clay-mineral and silica-alumina gel catalysed reactions⁽⁶³⁾ of iso-butene are known in which dimers and trimers are produced. These reactions were conducted under high pressure and with the olefin in the liquid phase, however. Although evidence of polymeric material

formed by a type 1 reaction has been presented it is unlikely that the low gas pressures employed in the adsorption of iso-butene would enable a high yield of polymer to be produced.

Ethylene does undergo cationically induced polymerization reactions but the monomer is not very reactive. Similarly, the cationically induced polymerization of acetaldehyde is rather slow.

It was unfortunate that no hydrogen exchanged Y zeolite was available for treatment with benzofuran. This monomer may have reacted in a similar manner to the vinyl ethers over a hydrogen exchanged zeolite into whose cavities it could gain access.



Acenaphthylene molecules are also too large to enter the internal cavities of hydrogen mordenite.

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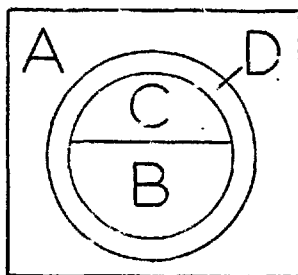
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Appendix A.

Weight fraction of zeolite, weight fraction of filler and volume fraction of filler in a composite material.

Although the weight fraction of zeolite per unit mass of composite is the directly measurable estimation of composite composition, it does not adequately represent the composition in terms of a micro-porous filler such as a zeolite, within an external polymer phase. The reason for this assertion is that a portion of the polymeric phase may occupy the intracrystalline cavities of the filler.

In the diagram below, A represents an external polymer phase, B intracrystalline polymer and C the unoccupied volume within the zeolite, D.



The weight fraction of zeolite, w_z , measured from TGA or chemical analysis is the ratio :

$$w_z = \left(\frac{m_D}{m_D + m_{(A+B)}} \right)$$

where m_D is the mass of D, the zeolite etc.

A more useful ratio would be the weight fraction of filler, w_f :

$$w_f = \frac{m_D + m_B}{m_D + m_{(A+B)}}$$

This ratio w_f could be calculated directly from w_z if m_B was known. If m_B is assumed to be the mass of methyl methacrylate adsorbed within unit mass of NaY zeolite at intermediate values of the relative pressure, the following ratios may be calculated:

$$w_z = \frac{\text{Mass of residue after heating composite to 700K}}{\text{Initial mass of composite}}$$

$$\text{and } w_f = \frac{w_z}{0.81 - 0.19 w_z}$$

The volume fraction of filler, ϕ_f is the ratio:

$$\phi_f = \frac{V_D}{V_A + V_D}$$

where V_D is the volume enclosed by D, the zeolite etc. Clearly

$$V_D = \frac{m_D}{\rho_D}$$

where ρ_D is the density of anhydrous zeolite etc. and consequently

$$\begin{aligned} \phi_f &= \left(\frac{\frac{m_D}{\rho_D}}{\frac{m_D}{\rho_D} + \frac{m_D}{\rho_D} - \frac{x m_B}{\rho_p}} \right) \\ &= \left(\frac{\frac{w_z}{\rho}}{\frac{1-w_z}{\rho_p} + \frac{w_z}{\rho_D} - \frac{x w_z}{\rho_p}} \right) \end{aligned}$$

$$= \frac{w_z}{1.24 - 0.53 w_z}$$

where m_p is the total mass of polymer in the zeolite and x is the mass of sorbate contained by unit mass of zeolite at intermediate values of the relative pressure.

Appendix B

Some non-S.I. units which have been mentioned in this work

<u>Quantity</u>	<u>Non-S.I. unit</u>	<u>Definition in S.I. units</u>
Length	1 Å	$1 \times 10^{-10} \text{ m}$
Pressure	1 cmHg	$13.595 \times 98.0665 \text{ Nm}^{-2}$

MODIFICATION OF THE SURFACE OF SYNTHETIC HYDROXYAPATITES

R. ASH, R. M. BARRER, M. D. BUTLER, AND J. D. W. HUDSON

Communicated by J. D. W. Hudson

SUMMARY

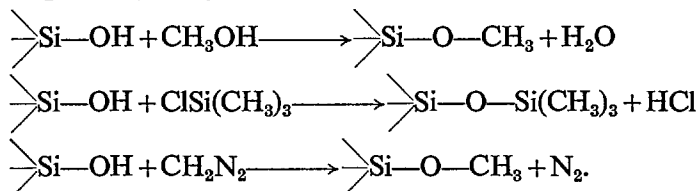
Alkylchlorosilanes, hexamethyldisilazane, and aliphatic diazo compounds have been examined as potential means of attaching chemisorbed hydrophobic groups to the surfaces of apatite crystals.

The silane derivatives appeared to form adsorbed silyl ethers especially in presence of any molecular water, and in no cases were stable chemisorbed films obtained. If appreciable moisture was present chlorosilane derivatives, but not hexamethyldisilazane, could attack and even destroy hydroxyapatite, converting it into CaCl_2 and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

The diazo compounds were found to react with hydroxyapatite to give stable chemisorbed films that reduced the hydrophilic character of the surfaces. Long-chain aliphatic groups produced the largest changes. The surface reaction proceeded best when molecular water was absent, and when the highest concentration of acid phosphate groups was present, as for instance with Ca-deficient apatites.

INTRODUCTION

Various attempts have been made to find adhesives which will permanently adhere to both dentine and enamel in a moist environment (Rose, Lal, Williams, and Falcetti, 1955; Snyder, Wilson, Newman, and Semen, 1967). As a simplification of this problem one may investigate surface reactions of organic molecules with hydroxyapatite powders. To guide the choice of organic reactants one may consider those molecules which modify other surfaces. Thus, methanol (Dzhigit, Kiselev, Mikos-Avgul, and Shcherbakova, 1950), trimethylchlorosilane (Lygin and Kiselev, 1961), and diazomethane (Shcherbakova and Slovetskaya, 1956) form hydrophobic monolayers of chemisorbed groups on hydroxylated silicas:



The trimethylsilyl groups in particular are thermally stable and permanent in presence of water, at least over a period of several months. Also reactions between zinc oxide and some *n*-alkane thiols (Eyring and Wadsworth, 1956), between chromia and methanol or ethanol (Roev and Terenin, 1959), and between alumina and ethanol (Babushkin and Uvarov, 1956) all yield chemisorbed organic groups.

The surface of hydroxyapatite contains calcium, orthophosphate, and hydroxyl ions, water molecules, and probably some associated protons. A reaction at the surface may theoretically involve one or more of these ions or molecules. The principal groups of compounds investigated as surface reagents were silane derivatives and aliphatic diazo compounds. If alkyl or aryl groups can be grafted chemically to apatite surfaces these should confer hydrophobic character on the surface. This behaviour was studied by measuring sorption isotherms of water before and after chemisorption of silanes and diazo compounds.

The grafting of long alkyl chains to apatite surfaces might promote adhesion to polymers since the chains could become entangled with the polymer. Polymer-apatite powder composites might also be prepared, with good adhesion, which could provide possible dental restoratives, since the filler would reduce shrinkage during curing, lessen thermal expansion, and, with good adhesion, improve bulk strength.

Synthetic calcium phosphates may be made which give X-ray diffraction patterns and infra-red spectra like those of stoichiometric hydroxyapatite although the Ca/P ratio may differ from that in the stoichiometric phase. The Ca/P ratios may vary from 10/6 to less than 9/6, depending upon conditions of formation. The stoichiometric hydroxyapatite may be represented by the formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; and the calcium-deficient apatites have the formulae $\text{Ca}_{(10-x)}\text{H}_x(\text{PO}_4)_6(\text{OH})_{(2-x)}(\text{H}_2\text{O})_x$ where $0 \leq x \leq 1$ (Winand, 1961) and $\text{Ca}_{(9-y)}\text{H}_{(1+2y)}(\text{PO}_4)_6\text{OH}\cdot\text{H}_2\text{O}$ where $0 \leq y \leq 1$ (Berry, 1967). Bone and tooth mineral is a Ca-deficient apatite.

An investigation of the dehydration of alcohols over synthetic hydroxyapatite has suggested that acid sites exist on Ca-deficient apatites (Bett, Christner, and Hall, 1967). Acid sites on the surface of biological phosphate crystals may be available to react with aliphatic diazo compounds.

EXPERIMENTAL METHODS

1. Materials. Examples of the apatite powders studied are listed in *Table I*. The hydroxyapatites were prepared by slow addition of aqueous solutions of diammonium hydrogen phosphate to stirred solutions of calcium nitrate at defined pH values. The apatites of *Table I* (and many others, not listed) provided a range of compositions and surface areas. For comparison purposes, aluminas and Aerosil silicas were also used in studies of surface modification, using both silane and diazomethane derivatives. The diazomethane derivatives were synthesized as required, using the methods of de Boer (1954), Smith and Howard (1955), and of Adamson and Kenner (1935). This account will be concerned primarily with the surface-treated apatites.

2. Examination of Treated Powders. The surface areas of the powders were measured using nitrogen adsorption at -195°C . (78°K .) in a volumetric sorption apparatus. The adsorption of specially purified distilled water at 50°C . (and in some cases also at 30, 40, 60, and 70°C .) was determined using silica spring balances. The nitrogen areas and the water uptakes combined served when required to determine absolute adsorptions of water in which the uptake in micromoles of water per unit surface was plotted against the relative pressure (p/p_0). This method of presenting the data showed quantitatively if, and by how much, the water uptake was reduced by the

surface treatments. This in turn provided a measure of the change from the hydrophilic original surfaces to the less hydrophilic treated surfaces.

Table I

HYDROXYAPATITE PREPARATIONS	CONDITIONS OF PRECIPITATION	Ca/P MOLAR RATIO*	S SPECIFIC SURFACE (m. ² g. ⁻¹)
HA4	Precipitated over 3 hr. at pH 11	1.66	79.5
HA5	Precipitated over 3 hr. at pH 11	1.66	58.2
HA6	Precipitated over 3 hr. at pH 11	1.66	71.3
HA9	Precipitated over 1 hr. at pH 5.8	1.52	67.3
HA11	Precipitated over 300 hr. at pH 12	1.67	68.0
HA12	Precipitated over 300 hr. at pH 5.7	1.46	77.3
HA12/600A	HA12 heated in air at 600° C. for 120 hr.	1.46	22.1
HA12/160V	HA12 heated in vacuum at 160° C. for 120 hr.	1.46	66.5
HA12/600V	HA12 heated in vacuum at 600° C. for 120 hr.	1.46	56.9
HA13	Precipitated over 300 hr. at pH 11	1.67	59.3
HA13/600A	HA13 heated in air at 600° C. for 120 hr.	1.67	51.7
OCP 1†	Precipitated over 24 hr. at pH 8	1.47	130.8

* Stoichiometric apatite has value 1.67.

† OCP, octacalcium phosphate.

Other examinations of the powders before and after treatment were made as required. They included chemical analyses (Ca by EDTA; P as phosphomolybdate); microchemical analysis to determine the amounts of surface organic groups after treatment; X-ray powder diffraction; infra-red spectra (using Nujol mulls between KBr windows) and water contents of the powders by outgassing at 300° C. (loosely bound water only).

SUMMARY OF RESULTS WITH SILANE DERIVATIVES (BUTLER, 1966)

Aerosil silicas were variously treated with $(\text{CH}_3)_3\text{SiCl}$ and with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ (hexamethyldisilazane). The adsorption isotherms of water then showed that silica so treated became less hydrophilic while repeated adsorption measurements at 40° C. showed that the silyl groups were stable. Reduction in hydrophilic character was well marked after prior treatment with the disilazane. When alumina was treated with $(\text{CH}_3)_3\text{SiCl}$ there was little loss of hydrophilic character, but with hexamethyldisilazane subsequent water uptake was reduced. The surface modification was not, however, permanent in presence of water vapour at 40° C.

Many experiments were conducted in which dried hydroxyapatites were treated with $(\text{CH}_3)_2\text{SiCl}_2$, $(\text{CH}_3)_3\text{SiCl}$, $\text{C}_{18}\text{H}_{37}\text{SiCl}_3$, and $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ dissolved in solvents or as the pure reagents, in open and sealed vessels and at temperatures ranging from 20 to 200° C. These treatments changed the subsequently measured adsorption isotherms of water, but the changes were not permanent, being progressively reversed over a sequence of sorption runs with outgassing between each pair of isotherms. Moreover, when one evacuated gravimetric sorption unit containing unmodified

apatite was connected to another containing modified apatite, it was concluded that material distilled from the modified to the unmodified apatite because water isotherms measured on the two apatites, while initially different, became more and more alike.

Treatment of apatite with liquid $(\text{CH}_3)_3\text{SiCl}$ in sealed tubes at 60°C ., far from yielding a hydrophobic solid, gave a hygroscopic product which sorbed large amounts of water (Fig. 1 A). This product was found by X-ray examination to contain CaCl_2

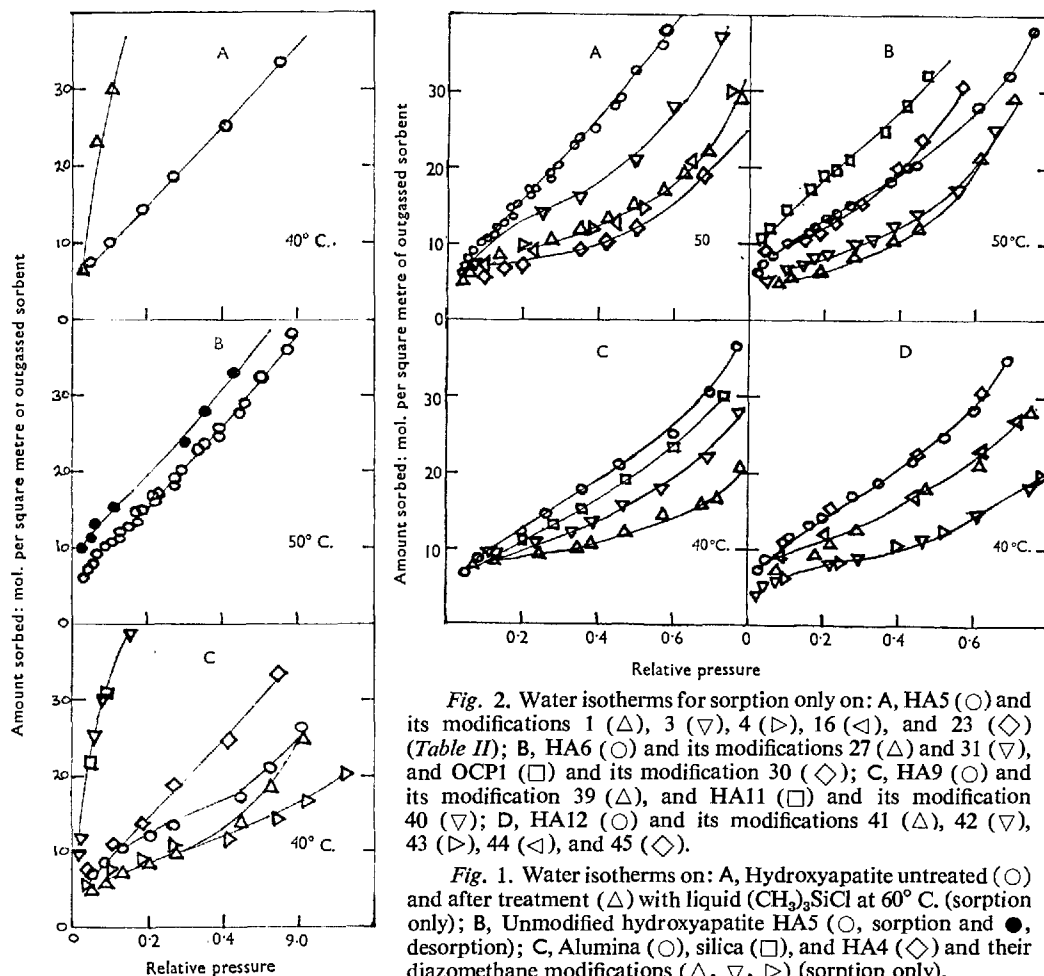
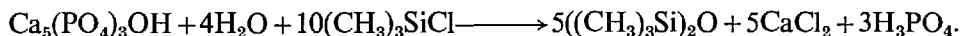


Fig. 2. Water isotherms for sorption only on: A, HA5 (○) and its modifications 1 (Δ), 3 (∇), 4 (▷), 16 (◁), and 23 (◇) (Table II); B, HA6 (○) and its modifications 27 (Δ) and 31 (∇), and OCP1 (□) and its modification 30 (◇); C, HA9 (○) and its modification 39 (Δ), and HA11 (□) and its modification 40 (∇); D, HA12 (○) and its modifications 41 (Δ), 42 (∇), 43 (▷), 44 (◁), and 45 (◇).

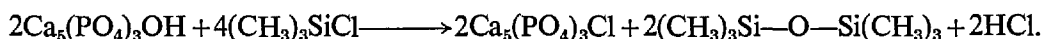
Fig. 1. Water isotherms on: A, Hydroxyapatite untreated (○) and after treatment (Δ) with liquid $(\text{CH}_3)_3\text{SiCl}$ at 60°C . (sorption only); B, Unmodified hydroxyapatite HA5 (○, sorption and ●, desorption); C, Alumina (○), silica (□), and HA4 (◇) and their diazomethane modifications (Δ, ∇, ▷) (sorption only).

and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ but no hydroxyapatite. The residual liquid after the treatment of apatite with $(\text{CH}_3)_3\text{SiCl}$ was examined in the MS9 mass spectrometer. The trace obtained showed the presence of $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$ along with the present compound (both identified by their mass numbers) and fragmentation products of these compounds. The hydrous apatite was believed to decompose according to the overall equation:—



Some of the calcium chloride then reacted with the phosphoric acid and further water to give $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. It may be concluded that apatite and hence tooth enamel will be attacked by chlorosilanes under damp conditions, the attack being effected by hydrochloric acid liberated in reaction between moisture and the chlorosilanes.

This massive decomposition did not occur when molecular water was removed by preliminary evacuation of the apatite. Nevertheless, no stable chemisorbed alkyl silane films were formed, and the materials modifying the surface were considered to be silyl ethers:—



The reaction replaces surface OH^- by surface Cl^- . The formation of silyl ether liberates a little HCl which may further attack the apatite surface. The adsorbed silyl ethers are volatile, which accounts for their transport *in vacuo* from one apatite sample to another as noted earlier, and for the lack of permanence of the surface films.

Hexamethyldisilazane was also very probably converted on moist apatite surfaces to the silyl ether, ammonia being liberated in the process. However, the ammonia does not damage the apatite chemically. Because the effect on the surface is not permanent, due to the volatility of the ether, it is clear that silane derivatives are not satisfactory modifiers, and it is further seen that chlorosilane derivatives damage apatite chemically and in excess may even destroy it. Evidently stable chemisorption involving the bond Si—O—P does not occur. It is noteworthy in this connexion that in hydrothermal reactions involving alkaline magmas with phosphate, aluminium hydroxide and colloidal silica, aluminophosphates, and aluminosilicates crystallized out alongside each other but never silicophosphates containing the above bond (Barrer and Marshall, 1965).

SUMMARY OF RESULTS WITH ALIPHATIC DIAZO COMPOUNDS

Silica, alumina, and the hydroxyapatites of *Table I* were all variously treated with ethereal solutions of diazomethane, and in the case of the apatites with other diazo compounds. The dried solids were in all cases allowed to stand with, or were shaken with, ethereal solutions of the diazo compounds. The solids were then filtered, washed with ether, and dried before outgassing and measuring water and nitrogen isotherms. The variously modified apatites are listed in *Table II*, together with the diazo compounds used and the surface areas, S , derived from the nitrogen isotherms using the BET procedure. The BET equation represented these isotherms well over the important relative pressure range $0.05 < p/p_0 < 0.25$. Water sorption isotherms did not, however, follow the BET equation satisfactorily except in the vicinity of the monolayer capacity. The water isotherms showed hysteresis at all pressures (*Fig. 1 B*).

The first important result was that silica, alumina, and hydroxyapatite were all rendered substantially less hydrophilic by treatment with diazomethane, and that the modified surfaces were this time stable to outgassing and to repeated sorption measurements of water (*Fig. 1 C*). This success led to the use of the other diazo compounds of *Table II*.

It was then established that all the aliphatic diazo compounds of *Table II* gave modified apatite surfaces of reduced hydrophilic character stable to heating and out-

INTERNATIONAL SYMPOSIUM ON TOOTH ENAMEL

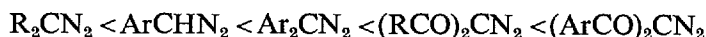
gassing to at least 100° C. Examples of the reductions of water sorption are given in Fig. 2. Moreover, no side-reactions resulting in chemical damage to the apatite could be detected.

Table II

MODIFICATION	PARENT APATITE	MODIFYING MATERIAL (in ethereal solution)	S SPECIFIC SURFACE (m. ² g. ⁻¹)
LXVIII	HA4	Diazomethane	81.1
1	HA5	Diazomethane	68.8
3	HA5	Diphenyldiazomethane	68.0
4	HA5	Diphenyldiazomethane	68.8
16	HA5	Diazo- <i>n</i> -octane	61.5
23	HA5	Diazo- <i>n</i> -octadecane	78.4
27	HA6	Diazo- <i>n</i> -dodecane	56.6
31	HA6	Diphenyldiazomethane	68.8
30	OCP1	Diphenyldiazomethane	126.2
39	HA9	Diphenyldiazomethane	91.9
40	HA11	Diphenyldiazomethane	68.5
41	HA12	Diphenyldiazomethane	80.7
42	HA12/600A	Diphenyldiazomethane	28.9
43	HA12/600A rehydrated	Diphenyldiazomethane	24.7
44	HA12/160V	Diphenyldiazomethane	64.3
45	HA12/600V	Diphenyldiazomethane	56.7

FURTHER INFORMATION ON THE DIAZO REACTION

The aliphatic diazo compounds, which are reactive and relatively unstable, may be arranged in the following order of increasing stability:



where R is an alkyl group (or H) and Ar an aromatic group. Their nature would presumably render them unsuitable for *in vivo* modification of tooth enamel, but not for producing modified synthetic apatite powders for subsequent incorporation in dental resins.

The extent to which alkyl groups modified the apatite surface tended to increase with the size of the alkyl chain. Thus the reduction in hydrophilic character was greater after treatment with diazo *n*-octadecane than with diazo-*n*-octane, and the latter in turn produced a greater decrease than diazomethane (see Fig. 2 A). The reduction of water sorption by diphenyldiazomethane was intermediate between that by diazomethane and diazo-*n*-octane. The extent of surface modification was also more marked when the apatite had been dried overnight at 100° C. than when this preliminary drying had not been given.

Hydroxyapatites HA9 and HA12 had Ca/P ratios of 1.52 and 1.46 respectively, and so were Ca-deficient (*Table I*). HA11 and HA13 were stoichiometric (Ca/P = 1.67). These four preparations were dried under nearly identical conditions and their surfaces characterized by N₂ and H₂O adsorption. The surfaces of HA12 and HA13 were similarly characterized after:—

- i. Heating at 600° C. for 120 hr. in air.
- ii. Heating at 600° C. for 120 hr. at $<10^{-6}$ cm. Hg.
- iii. Heating at 160° C. for 120 hr. at $<10^{-6}$ cm. Hg.

Samples of these pre-treated apatites were then modified with diphenyldiazomethane, and the N₂ and H₂O isotherms determined, with the following results:—

a. The Ca-deficient sample HA9 sorbed appreciably less water per unit area of surface after modification, whereas the difference was quite small for the stoichiometric apatite HA11. This result suggests that, because there are more acidic surface sites on the Ca-deficient than on the stoichiometric apatite, reaction with diazo compounds involves acidic sites (*Fig. 2 C*).

b. The specific surface of Ca-deficient HA12 heated in air at 600° C. for 120 hr. was considerably reduced, presumably by crystal growth. There was, however, little change in the surface of stoichiometric apatite given the same treatment. Acid phosphate groups therefore promote sintering.

c. The apatite HA12 referred to in (*b*) subsequently heated with diphenyldiazomethane showed a proportionately greater change from hydrophilic to hydrophobic character than did HA12 dried overnight in the oven at 100° C. (*Fig. 2 D*). This may indicate that even though heat treatment at 600° C. pyrolyses surface and possibly internal hydrogen phosphate groups to pyrophosphate, the surface pyrophosphate groups on exposure to the atmosphere are hydrolysed to acid phosphate.

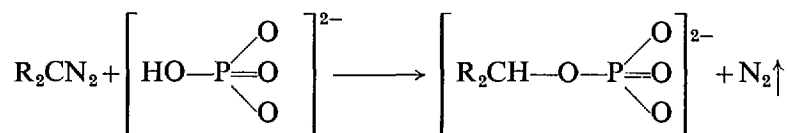
d. HA12 after heating in air to 600° C. was subsequently reheated at 160° C. in an atmosphere of 2 cm. Hg. partial pressure of water vapour for 24 hours. The water adsorption isotherm of this apatite treated with diphenyldiazomethane was nearly identical with that obtained for the HA12, initially heated to 600° C., referred to in (*c*) (*Fig. 2 D*).

e. HA12, heated at 160° C. for 120 hr. at $<10^{-6}$ cm. Hg, was treated at room temperature in an atmosphere of petroleum ether vapour with Na-dried diphenyldiazomethane. The subsequent water adsorption was found to be reduced and these conditions of outgassing were accordingly believed to remove molecular water without breaking down acid phosphate groups. HA12 heated at 600° C. for 120 hr. at $<10^{-6}$ cm. Hg and treated with diphenyldiazomethane as above gave almost an identical water sorption isotherm to that obtained on HA12 similarly heated but not treated with the diazo compound. This supports the view advanced in (*c*), since no opportunity was now provided for subsequent hydrolysis of surface pyrophosphate to acid phosphate.

Moreover, the specific surface of HA12 heated at 600° C. for 120 hr. at $<10^{-6}$ cm. Hg was hardly changed, whereas that of HA12 heated for the same time and temperature in air was very much altered (*see (b)*). This indicates that atmospheric moisture promotes sintering.

CONCLUSION

All these experiments support the view that the modification reaction involves acid phosphate groups at the surface of the apatite:



The richer, therefore, such surfaces can be made in acid phosphate groups the greater should be the concentration of chemisorbed organic groups. The C—O—P surface bond, unlike the Si—O—P bond, can readily be formed. It was moreover found to be stable, from the reproducibility of water sorption isotherms, in the presence of water vapour at temperatures up to 70° C. The hydrophobic nature of the surfaces was found to persist for periods of at least 18 months in air at room temperatures and the films were not decomposed by outgassing at 100° C.

In another part of this programme composite membranes of polymethyl-methacrylate resins and modified and unmodified apatites have been prepared (Ash, Barrer, and Coughlan, 1971), and the reproducibility of their water permeability investigated, in order to see how far the permanence of the resin-apatite bond is improved by modifying the apatite surfaces with chemisorbed organic groups, utilizing the diazo reaction.

Acknowledgements. This work formed part of an investigation of synthetic materials of potential use as dental restoratives supported by the Science Research Council and the Ministry of Technology. M. D. B. and J. D. W. H. acknowledge financial support by the Science Research Council which made possible their participation in this programme.

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MR. J. D. W. HUDSON (London): The purpose of our work has been centred mainly around an investigation of some organic molecules which may react with the surface of

hydroxyapatite. We have looked at a few other surfaces, particularly silica, which has a fairly acidic surface, and studied the types of molecule which react with this material. The silane derivatives which react with silica surfaces to form stable chemisorbed groups which are hydrophobic do not react with synthetic hydroxyapatite surfaces. We think this is due to the fact that there is not sufficient acidity at the surface of hydroxyapatite and also perhaps to the decomposition of the apatite by silane derivatives. We have found, however, that the aliphatic diazo materials containing a nitrogen unsaturated group react vigorously especially with the Ca-deficient apatites; these are apatites that we would expect to contain surface acid groups. We found that the stoichiometric samples of hydroxyapatite—samples that would not be expected to contain surface acid groups—do not react with these diazo compounds. Another study has concerned heating the Ca-deficient apatites at high temperatures in order to pyrolyse any acid phosphate groups to pyrophosphate. Provided no subsequent hydrolysis is allowed to occur this should eliminate acid groups. The subsequent reactions with diazo compounds did not occur. The evidence which is summarized in the paper leads to the conclusion that acid groups are essential before these organic reactions can occur at the surfaces studied.

PROF. R. M. BARRER (London): Mr. Chairman, I would like to make one small addition to these comments. It was our purpose in conducting this work to see whether it was possible to attach groups by strong chemisorption bonds to the surface of apatite which might then serve as additional bonds if apatite crystals were dispersed in organic polymers such as have been employed in dental restoratives. The work has now ceased but you can see that there has been a considerable measure of success in this direction, and this work has been supplemented by measurements or studies of composites with modified and unmodified apatites in organic matrices.

DR. S. L. ROWLES (Birmingham): I was very interested in the observation that with defect apatites heated at 600° C. there was a considerable decrease in the apparent surface area; also in the suggestion that the presence of an acid phosphate group would promote sintering. There is an empirical law (Tamman and Sworykin, 1928) which states that for sintering to occur the temperature must be raised at least half-way to the melting point (degrees K). Now 600° C. is considerably below half the melting point of apatite. I heated a number of defect apatites at 600° C. for periods of up to 4 days and I never observed any obvious reduction in the broadening of apatite lines. I am wondering if Professor Barrer's group has any confirmatory observations of their X-ray diffraction patterns as well as these observations on the surface area? Also, have they any quantitative information from their aliphatic diazo compounds on the proportion of acid phosphate groups on the surface of these defect apatites?

TAMMAN, G., and SWORYKIN, A. (1928), *Z. anorg. Chem.*, **176**, 46.

MR. J. D. W. HUDSON (London): Sintering is largely temperature-dependent and occurs at slower rates at lower temperatures. At 600° C., after, I think, 120 hr. in air, we noticed, by nitrogen adsorption studies, a reduction in the surface area of a Ca-deficient apatite from around 77 to 22 m.² per g. This sintering did not occur with stoichiometric apatite.

DR. S. L. ROWLES (Birmingham): But was this also seen in the X-ray diffraction patterns? Did the lines sharpen?

MR. J. D. W. HUDSON (London): We have not done any X-ray diffraction studies on this.

DR. G. S. INGRAM (Isleworth): I would like to inquire about the Imperial College apatites, Mr. Hudson; how pure were they in terms of possible contaminants such as alkali metals, because these are very good at promoting sintering? I have heated relatively pure Ca-deficient apatites at 600° C. for 120 hr. and one, rated at 8 m.² per g., then gave an area of 9 m.² per g.; another at 18 m.² per g. went up to 20 m.² per g. This was concerned with another surface-controlled reaction and it was not altered to a great extent by the heat treatment. So I would

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contend that you may have some other factor than acid phosphate groups promoting sintering. That the acid phosphate groups had changed during our treatment was quite clear, since we determined pyrophosphate in the solids afterwards. But I would like you to bear a thought about other possible impurities in those apatites.

PROF. A. S. POSNER (New York): When you heat Ca-deficient apatites to about 500–600° C. pyrophosphate is formed. Whether you form a separate pyrophosphate phase or get a condensation of orthophosphates to pyrophosphate within the apatite structure is not clear at present. This reaction may be involved in some way with the change in surface resulting from heating.

DR. S. L. ROWLES (Birmingham): Yes, indeed. In fact, at the last Symposium I mentioned that I had found that a crystalline phosphate phase formed if you heated for a long enough period. On the other hand, for the apatite phase itself, the lines do not seem to change at all and the surprising thing is that apparently here the surface area has decreased. Could there be some other explanation?

PROF. W. G. PERDOK (Groningen): If there is sintering and if these crystals are not orientated then there will not be any increase in crystal size. Therefore, to see sharper lines in your X-ray diffraction pattern would mean that sintering would be occurring between orientated crystals and this is not the case, I think. So surface is only lost because crystals grow together, but not in an orientated way, so that you don't get large crystallites because these are not orientated preparations.

You can have a decrease in surface and have no sharpening on your X-ray diffraction pattern.

MR. J. D. W. HUDSON (London): The surface area of the material we prepared was 55–80 m.² per g., and a typical value was reduced to about 20 m.² per g. after heating. These particles had a considerably larger surface area than those of the samples just mentioned; I don't know whether this might have any effect on the sintering. Some preliminary i.r. studies indicated that pyrophosphate groups were present in the material.

DR. M. V. STACK (Bristol): We might remind ourselves of the surface area work done on anorganic bone by Beebe and co-workers (Holmes, Davies, Meath, and Beebe, 1964). Out-gassing procedure resulted in an increase in surface area of about 15 per cent with increasing temperature up to 300° C., but there was a comparable decrease as the temperature was raised to 500° C. They suggested that some of the small pores were opened up to nitrogen adsorption as the surface area reached the peak value, after which partial collapse of capillaries or grain boundaries was considered to account for a sintering which reduced the surface area back to the value evident at normal temperature.

HOLMES, J. M., DAVIES, D. H., MEATH, W. J., and BEEBE, R. A. (1964), *Biochemistry*, **3**, 2019.

PROF. A. S. POSNER (New York): In a recent surface area study on whole bone by Holmes and Beebe (unpublished results) it was shown that low-temperature nitrogen adsorption on the mineral phase was blocked by collagen. As the collagen was removed by 1,2-ethanediamine refluxing, followed by an ethanol wash, the specific surface of the bone calculated from nitrogen adsorption was found to increase impressively. The value went from about 2 m.² per g. for whole bone to about 132 m.² per g. for partially extracted bone. Small angle X-ray scattering, a technique which does not require the removal of collagen, showed the bone mineral to have a true specific surface of about 200 m.² per g. To remove the collagen fully one must reflux the extracted bone in water. However, this would certainly alter the mineral phase and produce a specimen of questionable value. In summary, it would seem that collagen may screen mineral from interaction with body fluids.

DR. G. H. DIBDIN (Bristol): It's interesting to hear of this difference in surface area; it fits very nicely with the difference we find in the surface area of enamel, using krypton and water.