"AN INVESTIGATION OF SOME PROPERTIES OF SODIUM SILICATES AND THEIR USE IN ZEOLITE SYNTHESIS"

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For Mum and Dad

ABSTRACT

In this work, two main areas of silicate chemistry have been considered and these are "Fundamental studies of the sodium metasilicate hydrates and their solutions" (PART I) and "The use of sodium metasilicate in the synthesis of zeolite X" (PART II).

In part one, the thermal properties of the hydrates of sodium metasilicate containing 9, 8, 6 and 5 moles of water per mole of metasilicate and the thermodynamics governing the solid state equilibria between them were investigated by vapour pressure and differential scanning calorimetry (d.s.c.) techniques respectively. In addition, the solutions of sodium metasilicate in water were investigated by viscosity, density and isopiestic vapour pressure techniques and the results compared with aqueous sodium carbonate. Part one is concluded by a study of some relevant sodium silicate, carbonate and aluminate systems using Fourier Transform nuclear magnetic resonance spectroscopy observing ^{29}Si, ^{13}C and ^{27}Al nuclei.

Part two describes an investigation of the use of sodium metasilicate in large scale synthesis of zeolite X, an aluminosilicate of wide industrial application. This work was prompted by the discovery of "active" silicate, the use of which greatly facilitates preparation of essentially pure zeolite X on an industrial scale. Effort in this area was directed towards identifying the reason(s) for "activity" of particular samples of silicate, and development of methods for preparation of "active" material not previously disclosed in the patent literature.

DECLARATION

I declare that this thesis, which is of my own composition, is an accurate record of work carried out by myself in the Department of Chemistry, University of Edinburgh, and at I.C.I. Ltd., Agriculture Division, Billingham, between October 1972 and August 1975. During this period I was supervised and guided by Drs. R O Gould, B M Lowe and T V Whittam. Prior to submission of this thesis, material contained in Part I, chapters 3, 4 and 7, was published in the scientific literature, reprints of which are included in Appendix F.

In addition I attended the following lectures/courses :-

"Introductory Fortran" (2 weeks) - E.R.C.C. staff.
"High Speed Liquid Chromatography" - Prof J H Knox and Dr J N Done.
"Thermal Analysis" - Drs B M Lowe and F Leach.
"^{13}C Fourier Transform n.m.r." - Varian Associates
"Chemical aspects of the Petroleum Industry" - Shell Research Ltd.
"Industrial Research and Development" - Dr Gravenor (Univ of Swansea).
One week C.R.A.C. course at Keele University, Easter 1974.
Environmental Chemistry 2h - one terms lectures.

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INTRODUCTION

0.1 THE SOLUBLE SILICATES

Silicates are compounds which contain a metal or quaternary ammonium cation with a silicon oxide species as anion. When the cation is an alkali metal or quaternary ammonium ion, the silicates are often soluble in water, unlike insoluble mineral silicates containing heavy metal cations. The most common soluble silicates are those of sodium and potassium which are exploited commercially, although large scale production of the lithium and quaternary ammonium compounds has recently become viable. The composition of alkali metal silicates can be varied widely and is commonly expressed as the molar ratio of silica to metal oxide i.e. SiO_2/M_2O (= r). Compounds with ratios greater than 3.75 are, however, relatively insoluble. The properties of a solution of a particular soluble silicate depend on r and on the concentration. The metasilicates are one of the most important classes of soluble silicate, and are defined by r = 1. Thus, the empirical formula for sodium metasilicate may be expressed as Na_2SiO_3, although, as will be demonstrated later, this in no way implies the existence of the SiO_3^{2-} ion. The sodium silicates have been prepared commercially for over 100 years[1] by the fusion of sand with sodium carbonate or with sodium sulphate and carbon at 1300°C in large, open-hearth furnaces, to produce a water-soluble glass.

0.2 PROPERTIES AND APPLICATIONS OF SOLUBLE SILICATES

The sodium silicates have been widely studied over many years and many uses have been reported.[2,3,4,5] Their main applications are as detergents, adhesives, and as raw materials in industrial processes.

Sodium silicates, such as sodium metasilicate form solutions which are more alkaline than those of sodium carbonate, sodium orthophosphate, tetrasodium pyrophosphate and sodium tripolyphosphate although less alkaline than those of sodium hydroxide.[6] In addition, the solutions of the sodium silicates exhibit a buffer capacity which is more than twice as great as that of most other alkalies, particularly the phosphates. These two properties are the main reasons why sodium silicates are widely used in detergent and cleaning mixtures along with phosphates, soaps or synthetic surfactants, bleaching agents and optical brighteners. In addition to the maintenance of a stable, high pH, they contribute to the overall cleaning action by saponification of animal and vegetable oils and fats, deflocculation and suspension of solid dirt particles, and by the removal from solution of free Ca^{2+} and Mg^{2+} ions through formation of soluble and insoluble complexes i.e. "building". The presence of silicate in a formulation is of extra advantage in powder processing, since it facilitates preparation of crisp, dry, granules.

Aqueous solutions of soluble silicates in which r is greater than 1.5 are generally called waterglasses. The sodium silicate waterglasses are mostly tacky, and this adhesive nature increases as the water content is reduced. These materials are easily dehydrated but, in contrast, the rehydration is very much slower. Consequently, solutions of sodium silicate, particularly those with a high SiO_2/Na_2O ratio, are used extensively as adhesives in the manufacture of materials such as plywood, corrugated paper, wood-chip board and laminated metal foils. Sodium silicates are also used as bonding agents in many ceramic and refractory applications because of heat stability and resistance to chemical degradation.

An important use of soluble silicates is as a raw material in the formation of silica gels and sols and in the synthesis of the crystalline aluminosilicate materials called zeolites. The addition of any acidic material to a silicate solution results in precipitation of silica and, under appropriate conditions, sols or gels may be prepared. The silica gels which are widely used as desiccants are prepared as above, washed thoroughly to remove all ionic species and oven dried. Zeolites are materials with pores of specific size and shape and, consequently, are of great importance as absorbents and catalysts, especially in petrochemical applications. Many zeolites, some of which are structurally related to naturally occurring minerals have been prepared by the hydrothermal reaction of silicate and aluminate solutions.

0.3 SCOPE OF THIS WORK

The work which is described here divides naturally into two parts. Some fundamental studies of the sodium metasilicate hydrates and their solutions are described in part I. The use of sodium metasilicate in the large scale synthesis of zeolite X, a synthetic analogue of the natural mineral, faujasite, is discussed in part II.

Parts I and II are largely self-contained entities although reference from one to the other does occur and is denoted by I or II used as a prefix to the section, table or figure number. For example, table I.2.1 appearing in part II, refers to table 2.1 in part I.

CHAPTER 1

INTRODUCTION

1.1 THE HYDRATES OF SODIUM METASILICATE

There have been many investigations[7,8,9,10,11] of the system $Na_2O.SiO_2.xH_2O$ and these have shown the existence of five crystalline sodium metasilicates which are the hydrates containing 9, 8, 6 and 5 molecules of water in addition to the anhydrous material. The hydrates are relatively labile and few studies have been made of their properties.

Many of the mineral silicates have been investigated by techniques which include X-ray diffraction, Raman spectroscopy[12] and analysis of trimethylsilyl derivatives.[13,14,15] Their structures are based on tetrahedral SiO_4 units which can share two, three or all four corners to form, for example, the fibrous amphiboles or pyroxenes, sheet-like micas or framework silicates respectively.[16] An example of the last case are the zeolites, some of which are discussed in part II.

Anhydrous sodium metasilicate has been shown[17] to have infinite chains of silicate units $(SiO_3^{2-})_n$ as in the amphiboles. The crystal structures of the hydrates which contain 9, 6 and 5 water molecules per metasilicate group have been determined by X-ray[18,19] and neutron diffraction[20] and the main conclusion is that all of these hydrates contain discrete silicate species in distinct contrast to the highly polymerised structure of the anhydrous material. These studies show the absence of Si-O-Si bonding and the detection of Si-O bonds of different lengths is related to the hydrogen bonding between silicate species. The diffraction studies suggest that the $[(HO)_2\ SiO_2]^{2-}$ species exists in the metasilicate hydrate lattice, particularly in the nonahydrate, but subsequent studies using wide-band nuclear magnetic resonance do not confirm this.[21] In conclusion, it seems likely that many of the hydrogen atoms are partially disordered within the lattice. The crystal structure of the octahydrate has only recently been determined[22] and is shown to contain discrete silicate species like the other metasilicate hydrates.

Some thermal and thermodynamic properties of the hydrated metasilicates have been measured or estimated by McCready and these are summarised by J G Vail.[23] Few other investigations of the hydrates have been carried out.[24]

1.2 AQUEOUS SOLUTIONS OF SODIUM SILICATES

The identification of the species which exist in the aqueous solution of a sodium silicate has been, for many years, a main aim of workers in this area. The difficulties which have been encountered in these studies have arisen mainly because of the undoubted existence of an equilibrium distribution of species in such systems and because of the inherent instability of many silicate solutions. This results in the formation of colloidal silicate aggregates, as has been discussed by Nauman and Debye.[25] Silicate solutions are also susceptible to contamination by atmospheric carbon dioxide, which promotes the formation of colloidal particles of silica, and is the reason why most solutions of commercial silicates are cloudy. Filters which are capable of removing these colloidal particles have only recently become available, and, since a large number of those studies which have been published used commercial material, it seems likely that many of the results obtained are not completely applicable to the pure system.

One of the pioneers of what has been termed "silicate science" was R W Harman, who investigated several properties[26-31] of the solutions of sodium silicate, such as conductivity,[26,27] hydrolysis,[28] and depression of freezing point.[29] Harman concluded that hydrolysis[28] was of great importance in dilute solution and that aggregation increased with concentration, especially if materials with $r > 2$ were used. Light scattering and viscosity measurements of carefully filtered solutions were made by Nauman and Debye[25] who found no evidence of particles with molecular weights greater than 400. They concluded that the measured viscosities could be adequately explained by a system which contained small species with an average size of four silicate units. Some later work[32] showed that the turbidity of solutions of sodium silicate stored in sealed containers increased very slowly over several months, and that, in many cases, this was accompanied by a small pH increase. This effect was found to be more prevalent with dilute solutions with $r > 1.0$, and was attributed to a very slow polymerisation of small silicate species. Conductivity[33] and viscosity[34] studies were carried out by Ukihashi who concluded that the silicate species present in aqueous solution were spherical and not highly polymerised, in general agreement with Náuman and Debye.[25,32] Iler[35] made cryoscopic measurements which confirmed the proposals of Nauman and Debye and subsequently, in a review,[6] proposed that silicate solution species could be considered to be based on a silicon atom octahedrally coordinated by six oxygen atoms. The use of Raman spectroscopy,[36,37] however, produced evidence which was inconsistent with his proposal and several studies suggested that the monomeric silicate species was a silicate atom coordinated by four oxygens, possibly $((OH)_2\ SiO_2)^{2-}$. Lagerström[38] and Ingri[39] studied the equilibria of silicate ions in solutions which contained $NaClO_4$ and NaCl respectively. Both workers concluded that their results were consistent with the existence of the mononuclear species $Si(OH)_4$, $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$ and a three- or four- membered polynuclear species. Both of these publications include extensive reviews of contemporary ideas. Later work by O'Connor,[40] who investigated the reaction rates of polysilicic acids with molybdic acid, suggested that the dilution of a silicate solution resulted in a rapid equilibration of species, indicative of depolymerisation, and that the molecular weights of the species involved were compatible with those proposed by Nauman and Debye.[25,32] A new approach was used by Lentz[13] who prepared the trimethylsilyl derivatives of silicate solution species as well as of mineral silicates. The resultant mixtures of derivatives were analysed by gas-liquid chromatography and, in the case of the solutions of sodium silicate, varying amounts of monomer, dimer, trimer, cyclic tetramer and unidentified polysilicate were detected. Results showed that the yield of discrete silicate ions from 1M solutions of sodium silicate decreased with an increase in r whereas the proportion of polysilicate derivatives increased. Recently, Grant and Masson[41] measured the viscosities of aqueous solutions of sodium silicate (r = 3.4) and concluded that the results were compatible with the presence of silicate polyions of low average molecular weight as suggested by Nauman and Debye.[25,32] They also reported that the results obtained by Lentz[13] had been confirmed by Sharma (unpublished) and suggested that the low yields of monomeric silicate species detected in solutions of large r could be the result of side reactions in the trimethylsilylation reaction.

The broad conclusions described in this introduction are strongly supported by a recent Raman study of the aqueous silicate system carried out by Freund.[42] He observed that the spectrum obtained is independent of the history of the solution and interprets the resonances in terms of the species $SiO_2(OH)_2^{2-}$ and $SiO_3(OH)^{3-}$.

1.3 THE AIM OF THIS WORK

As has been described, solutions of sodium silicates and solid sodium metasilicate hydrates are of world wide industrial importance and have been the object of many investigations. However, several aspects of their chemistry have been inadequately covered.

One aim of this work is to elucidate the relative stabilities of the various solid sodium metasilicate phases. Features studied include the heats of fusion, investigated by differential scanning calorimetry (d.s.c.), and the thermodynamic properties, derived from measurement of the equilibrium vapour pressures of hydrate mixtures. This work is described in chapters 3 and 4 respectively.

A second aim of this work is to clarify the true nature of carefully filtered solutions of purified sodium silicate, comparing them with solutions of sodium carbonate, which contain simple monomeric anions. Measurements were made of the viscosity, density and vapour pressure at 25°C, and the results are discussed in chapters 5 and 6. In addition, investigations of the solutions of sodium silicate, sodium carbonate and sodium aluminate were made by nuclear magnetic resonance spectroscopy using a probe capable of observing the ^{29}Si, ^{13}C and ^{27}Al nuclei, and this work is described in chapter 7.

CHAPTER 2

PREPARATION AND ANALYSIS OF SODIUM METASILICATE AND ITS HYDRATES.

2.1 INTRODUCTION

The preparation of pure, crystalline, samples of sodium metasilicate and the hydrates which contain 9, 8, 6 and 5 molecules of water per metasilicate group has been considered in several publications.[7-11,18] The most convenient method to prepare a pure sample of sodium metasilicate is by crystallisation of the nonahydrate from a dilute aqueous solution at room temperature. In this study, a purified nonahydrate was used as a raw material in the preparation of most of the other metasilicate phases which were required.

2.2 MATERIALS AND APPARATUS

2.2.1 MATERIALS

The only samples of sodium metasilicate which were readily available were commercial grade pentahydrate $Na_2SiO_3.5H_2O$ which is supplied by B.D.H. Ltd. and by Joseph Crosfield and Sons Ltd. who also manufacture commercial grade anhydrous material called "Metso". Alternatively, metasilicates were prepared from pure silica powder type KS300 supplied by AKZO Ltd., Analar sodium hydroxide and distilled water.

2.2.2 APPARATUS

Pyrex glassware was used in all crystallisations since it was considered that any impurities incurred by etching of the vessel surface would be less serious than possible contaminants from stainless steel apparatus.

Etching was, in reality, only observed with boiling concentrated sodium metasilicate solution, an observation in agreement with previous reports.[32] Silicate solutions were filtered, under reduced pressure, through a 350 cm^3 Gelman filter funnel No 4371, which was fitted with "Metricel" filter discs with pore sizes 0.2 and 0.8 µm. Hot, concentrated solutions of sodium metasilicate make the filter discs wrinkle, with a resultant loss of efficiency, but they are otherwise resistant to attack by the solutions used. The filtration of sodium metasilicate hydrate crystals from the crystallising solution was carried out in the absence of carbon dioxide, using a specially constructed filtration system. The basis of the apparatus was a 10 cm sintered funnel which was fitted to a one litre suction flask. The sides of the filter which were extended by 15 cm to give increased capacity, terminated in a 10 cm flange joint. The filter was sealed by a flange lid fitted with a 12 cm soda lime tower.

2.3 CRYSTALLISATION OF $Na_2SiO_3xH_2O$ (x = 0, 5, 6, 8, 9)

2.3.1 INTRODUCTION

In principle, the sodium metasilicate hydrates may be prepared by two different methods : by crystallisation from a dilute aqueous solution of sodium metasilicate, or by the crystallisation of a melt of an appropriate composition, $Na_2SiO_3.xH_2O$. The former technique can be used to prepare purified material, since impurities are concentrated in the mother liquor. The latter method produces material of the same purity as the parent melt, since all impurities are included in the solid which is obtained. As discussed earlier, pure nonahydrate may be obtained by crystallisation of a dilute aqueous solution and, in this work, very pure samples of the other hydrates and the anhydrous metasilicate were prepared from it. In specified cases where absolute accuracy in the ratio of SiO_2 to Na_2O was not necessary, essentially pure samples of the nonahydrate and pentahydrate were easily prepared by the crystallisation of a melt containing stoichiometric quantities of pure silica, sodium hydroxide and water.

2.3.2. CRYSTALLISATION - EXPERIMENTAL DETAILS

Sodium metasilicate nonahydrate was prepared by recrystallisation from a supersaturated aqueous metasilicate solution, containing stoichiometric amounts of pure silica and sodium hydroxide or commercial grade pentahydrate, cooled to room temperature and seeded with a few nonahydrate crystals. The crystals were filtered in the absence of carbon dioxide and dried over the pentahydrate until they contained exactly nine molecules of water per metasilicate group. The normal technique was to prepare a hot saturated solution of sodium metasilicate which was clarified by repeated ultrafiltration through a 200 nm filter before it was cooled and seeded. When crystallisation was nearly complete, sufficient distilled water was mixed into the system to prevent the formation of a solid mass of damp nonahydrate so that an easily filtered slurry of pure material was obtained. This method combines rapid crystallisation with high efficiency of purification. An alternative method for clarification of the parent solution is the addition of approximately 5% by weight of sodium hydroxide[26] but this was only used in early work since it increases the possibility of the occlusion of sodium hydroxide in the crystals formed. The damp nonahydrate crystals were dried over the metasilicate pentahydrate, an arrangement which was found to be effective although rather slow. Conventional drying methods such as the use of silica gel or pumping on the sample were investigated but were found to cause excessive dehydration of the very labile nonahydrate. Details of nonahydrates used in subsequent studies are given in table 2.1.

Sodium metasilicate octahydrate is difficult to prepare and, in this

TABLE 2.1 DETAILS OF SOME SODIUM METASILICATE NONAHYDRATES USED IN THIS WORK

Batch Name	Details of Preparation
H5	Recrystallised three times from an aqueous solution of technical $Na_2SiO_35H_2O$ (B.D.H. Ltd.) to which 5% by weight NaOH was added. Crystals filtered under nitrogen and stored, damp, in a sealed polythene bottle.
H6	Similar to H5 but crystals dried to approximately nonahydrate composition over pentahydrate in vacuo.
H7	Recrystallised three times from an aqueous solution of Na_2SiO_3, prepared from pure silica powder, pure sodium hydroxide and distilled water. Each time, before crystallisation the solution was filtered at least twice through a 0.8 µm filter. No additional sodium hydroxide was used for clarification. Crystals filtered under nitrogen and dried to nonahydrate composition over the pentahydrate in vacuo.
H8	As for H7, except recrystallised four times before crystals were filtered off in the modified sinter funnel to reduce the possibility of contamination by atmospheric carbon dioxide - see text. Crystals carefully dried to nonahydrate composition over the pentahydrate in vacuo.

work, was never prepared free from other metasilicate hydrates.

Sodium metasilicate hexahydrate was prepared by isothermal crystallisation at 52°C of an aqueous solution which contained 47% by weight of purified sodium metasilicate, seeded with a small amount of hexahydrate.

Sodium metasilicate pentahydrate was prepared from its melt which was made by careful evaporation of a pure nonahydrate melt. The crystallisation was induced at room temperature by the addition of approximately 20% by weight of pentahydrate seed to the melt.

Anhydrous sodium metasilicate was obtained by careful evaporation of a pure solution of sodium metasilicate at around 100°C.

In all cases, the purified materials were stored at room temperature in carefully sealed glass or polyethylene bottles.

2.4 ANALYSIS OF THE SOLID SODIUM METASILICATE HYDRATES AND THEIR SOLUTIONS

In this work, two types of analysis were used to determine the water content of solids or solutions and to identify the relative amounts of the different crystalline phases present in a sample of silicate. Analyses for Na_2O or SiO_2 were not carried out since it was assumed that the use of carefully purified sodium metasilicate nonahydrate or materials derived from it, was sufficient to guarantee an adequate accuracy in r.

2.4.1. DETERMINATION OF WATER CONTENT BY WEIGHT LOSS ON IGNITION AT 1000°C

Thoroughly clean 6 cm^3 platinum crucibles with lids were oven dried and equilibrated at room temperature and humidity before use. The sample to be analysed was carefully placed in a weighed, covered crucible, which was then reweighed. It was discovered that the inaccuracy due to loss of material through intumescence of silicate solutions when heated[43] could be completely avoided if the filled crucible was preheated at approximately 95°C for a few hours. This technique was used for the analysis of the solid hydrates and silicate solutions. The final stage of the dehydration was achieved by placing the covered crucible in a furnace at approximately 1000°C for about 5 hours, after which it was removed and allowed to cool over fresh P_2O_5 in a sealed desiccator. When cool, (∿ 45 minutes) the crucible, cover and residue, were weighed and, by combination of the three weighings, the proportion of water (% wt.) was calculated. The high temperature ignition was repeated until satisfactory agreement was obtained between successive final weighings. (± 0.02%). All analyses were carried out in duplicate and agreement between pairs was generally better than 0.02%. In order to minimise weighing errors, large samples compatible with reasonable economy of materials and the possibility of spillage were used and it was found that analyses were reproducible to better than ± 0.05%.

2.4.2. IDENTIFICATION OF CRYSTALLINE PHASES PRESENT

The ability to identify the solid components of a mixture which contained sodium metasilicate or its reaction products was crucial to much of the work. The best known technique is that of analysis by powder X-ray diffraction (X.r.d.) which was used throughout. It was later discovered that differential scanning calorimetry (d.s.c.) is a very useful complement to X.r.d., particularly in the analysis of sodium metasilicate hydrates, as is described in chapter 3.

All powder X.r.d. traces were obtained with a Phillips vertical diffractometer type PW1051 using $Cu_{K\alpha}$ radiation and operating at 1° per minute with a receiver slit of 0.2. The aluminium sample holders which are normally used were badly corroded by the sodium metasilicate hydrates, especially if damp samples were used, and suitable replacements were manufactured from thin perspex sheet. The finely ground sample was placed in the sample holder and compacted slightly to reduce the surface area which was exposed to the atmosphere. Several ways of covering the sample with "sellotape" or celluloid film were investigated but the resultant reduction in intensity of the diffracted beam outweighed any obvious advantages. It was concluded that if the sample was prepared as described and examined immediately at a reasonable scan speed, the adverse effects of contact with the atmosphere such as dehydration and formation of carbonates were minimal. Although most samples which were examined by X.r.d. were dry, crystalline solids, satisfactory analyses were also obtained for viscous slurries such as some of the activation mixtures described in part II. The components of the sample were identified by comparison of the trace obtained, with traces obtained under similar conditions from standard samples, and by reference to published data.[18,43] The approximate composition of mixtures (% mol) was obtained by comparison of the intensities of strong peaks in both sample and standard traces.

CHAPTER 3

THERMAL PROPERTIES OF SODIUM METASILICATE HYDRATES

3.1 INTRODUCTION

All of the sodium metasilicate hydrates are known to melt below 75°C,[9] but, apart from some estimations by McCready,[23] there have been few studies of their thermal properties[24] and no direct measurement of their heats of fusion. In this study, values for their heat capacitites at 25°C and their heats of fusion were obtained by differential scanning calorimetry (d.s.c.). It was discovered that this technique is a very valuable complement to the use of powder X-ray diffraction (X.r.d.) in the analysis of mixtures of sodium metasilicate hydrates. Although differential thermal analysis (d.t.a.) has been used to investigate hydrated sodium polysilicates,[44] the application of d.t.a. or d.s.c. to the metasilicate hydrates has not been reported.

3.1.1. SOME BASIC PRINCIPLES OF D.S.C. AND D.T.A.

Both d.s.c. and d.t.a. employ the same basic procedure. Small quantities of a sample and a reference material are placed in an oven where their temperatures are monitored by thermocouples. When the oven temperature is raised steadily, the temperature of the sample differs from that of the reference by an amount which depends on the difference between their heat capacities and on the heating rate. In both techniques, this temperature difference ΔT or its heat equivalent ΔQ is plotted as the ordinate on an X-Y recorder and the oven temperature T or the time t is plotted as the abscissa. Thus the temperature lag which results from the difference in heat capacities of the sample and reference is detected as a deflection from the chart baseline. In a similar manner, any phase transition such as fusion, undergone by the sample is also observed. (The reference must be carefully chosen so as not to undergo any phase transitions in the temperature range concerned). During a phase transition, the sample temperature remains constant despite the fact that the temperature of the oven and of the reference continues to rise. When all of the sample has undergone the phase change, the sample temperature rises rapidly toward that of the oven. Thus phase changes normally show up as unsymmetrical peaks on the recorder chart.

In d.s.c., the deflection from the baseline and the peak area may be quantitatively related to heat capacity and to heat of transition respectively, provided the machine is calibrated with suitable standard materials.

3.2 EXPERIMENTAL DETAILS

3.2.1. MATERIALS

Pure samples of the sodium metasilicate hydrates which contained 9, 6 and 5 moles of water per mole metasilicate were prepared as detailed in chapter 2. The octahydrate was never obtained free from other hydrates. Technical grade pentahydrate (B.D.H. Ltd) was used for comparison, and its thermal behaviour was not observed to differ significantly from that of the pure pentahydrate. All of the materials were carefully analysed by powder X-ray diffraction and by weight loss on ignition at 1000°C as described in chapter 2.

3.2.2. APPARATUS AND PROCEDURE

Measurements were made with a Du Pont Instruments Ltd. 990 Thermal Analyser used with a Cell Base Module II and Differential Scanning Calorimeter (d.s.c.) cell. Small metal pans 6.5 mm in diameter with lids were supplied as containers for the sample and reference materials and it was found that, in this work, an empty pan with lid was adequate as reference. The oven base is a constantan disc with two circular raised areas onto which sample and reference pans are placed. In all cases, the machine was switched on at least 30 minutes before use to permit adequate thermal equilibration.

The temperature scale was calibrated with $Ca(NO_3)_2\ 4H_2O$, stearic acid, naphthalene and benzoic acid, and in all cases the onset of fusion (obtained by extrapolation of the leading edge of the endothermic peaks) agreed with the melting points reported in the literature to within ± 1.5°C as shown in table 3.1. As described in section 3.1.1., the baseline deflection (ΔY) is related to the difference in heat capacity between the sample and reference material. In this work, the true baseline was obtained by running through the temperature range required with empty pans on both sample and reference positions. Heat capacities were then obtained by placing the sample in its pan but leaving the reference pan empty. Thus ΔY is related to the heat capacity of the sample Cp and, with the machine used in this work, the relationship is

$$Cp = \frac{60.E.\Delta Qs.\Delta Y}{H_r.m} \qquad (3.1)$$

where E is a machine calibration coefficient, ΔQs is the Y-range setting, H_r is the oven heating rate and m is the sample mass. Similarly, when ΔQ is plotted against a time base instead of against oven temperature as in heat capacity measurements, one can obtain quantitative measurements of a phase transition, for example the enthalpy of fusion, since ΔH is related to the area under the endothermic peak, A. With the machine in question, this relationship is

$$\Delta H = \frac{60.A.B.\Delta Qs.E}{m} \qquad (3.2)$$

TABLE 3.1 TEMPERATURE CALIBRATION[a]

Material	$T_f/^oC$ indicated	$T_f/^oC$ corrected	$T_f/^oC$ literature	$\Delta T_f/^oC$ (corr-lit)
$Ca(NO_3)_2 4H_2O$[b]	43.2	43.2	43.0	+0.2
Stearic Acid[c]	68.0	67.0	68.0	-1.0
Naphthalene[d]	82.5	81.0	80.2	+0.8
Benzoic Acid[e]	126.2	123.2	122.2	+1.0

[a] T_f indicated measured from the intersection of the extrapolated leading edge of the endotherm with the base line. T_f corrected obtained from T_f indicated by application of the appropriate thermocouple correction (Chromel Alumel) shown in machine manual. Heating rate = 10°C per minute; samples contained in copper pans with crimped on lids.

[b] B.D.H. Ltd. [c] B.D.H. Ltd. "Specially purified", dried over P_2O_5, T_f literature determined from hot-stage M. Pt. apparatus.

[d] Pure sample, source unknown. [e] Specially purified by sublimation.

TABLE 3.2 THERMAL CALIBRATION - MACHINE E VALUES[a,b]

Material	$T_f/^oC$ literature	$E_{sapphire}$[c]	$E_{material}$	ΔE (Sapph-mat)
Ice	0	0.7915	0.796	-0.0045
Stearic Acid	68	0.812	0.8045	+0.0075
Indium	157	0.896	0.892	+0.004

[a] Heating rate 10°C per minute; Crimped pans used, Cu (Ice) Al (Stearic Acid, Indium) - see text. [b] See text for explanation of E. [c] Units of E : Cal min^{-1} in^{-1}

where B is the time base and ΔQs, E and m are as defined for equation (3.1).

The calibration coefficient was found to be temperature dependent and was conveniently determined in the temperature range of interest, by measurement of the baseline deflection obtained with a carefully weighed sample of synthetic sapphire $(Al_2O_3)^{45}$, a material of well defined specific heat. Substitution of values in equation (3.1) gave E as a function of temperature. E may also be determined from equation (3.2), by measurement of the area of the peak produced on fusion of a sample of a material with a well defined heat of fusion. It was found that E values determined from the fusion of ice, stearic acid and indium, agreed with those obtained by use of synthetic sapphire in a heat capacity mode to within 1% as shown in table 3.2.

During all quantitative heat of fusion measurements, the peak was carefully cut out from the chart, after assessment of the baseline position, and weighed. The area of the peak was then calculated using the weight of a 10 in^2 piece taken from the same sheet of chart paper to reduce the possibility of error through inconsistent paper density. The use of a planimeter was investigated but the uncertainty in the area measured was no less than that incurred by the use of the method described (± 2%).

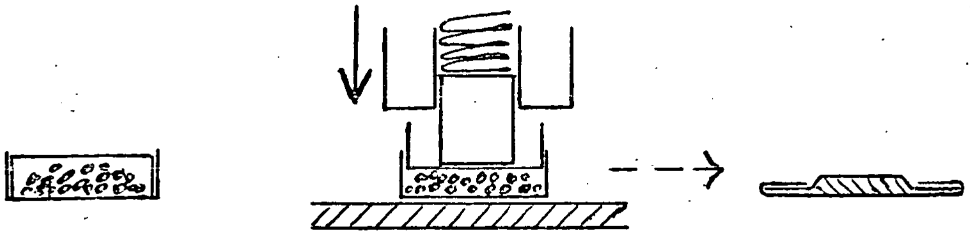
3.2.3. EXPERIMENTAL PROBLEMS

The molten sodium metasilicate hydrates were found to react with the aluminium pans normally used with the d.s.c. cell. The result was that reproducible peak areas could not be obtained. Identical pans and lids made from copper were found to be satisfactorily inert and were used for all measurements which involved silicates. Satisfactory calibration of the temperature scale can be obtained with either type of pan. Reproducible thermal calibration however, could not be obtained for either indium or stearic acid in copper pans. These combinations produced very inconsistent results and, on examination of the used pans, alloy formation and corrosion were observed respectively.

All materials were finely ground before use to ensure good thermal contact between the sample and the pan. It was found that failure to do this resulted in very erratic pen movement and an unsteady baseline. Samples were weighed on a Stanton 5-figure micro-balance, and associated errors were minimised by the use of large samples compatible with good thermal contact and effective pan sealing.

Accurate enthalpy and heat capacity measurements of the silicate hydrates can only be obtained when the sample pans are tightly sealed to prevent the loss of water, but good qualitative analyses can be made with samples in pans with crimped-on lids. Copper pans were only available in the crimped-lid design, which, if used normally, are ineffective in providing adequate water retention for quantitative thermal measurements to be made. However, it was found that these pans and lids could be sealed sufficiently well for this work by judicious use of the encapsulation press, part No 900733-901. Best results were obtained by squeezing the filled pan with lid between the upper die of the hermetic sealing set and a flat steel surface held on top of the lower die mounting. The effect of this was to fold inwards the sides of pan and lid as shown in figure 3.1 so that the encapsulated sample had a completely flat base, a necessary requirement in quantitative work.

FIG. 3.1 METHOD USED FOR SAMPLE ENCAPSULATION



normal use

modified pan use

For quantitative heat measurements, water loss was kept below 0.1% of the sample weight; this is particularly difficult to achieve with the pentahydrate, which has a relatively high melting point.

3.3 RESULTS AND DISCUSSION

3.3.1. THERMODYNAMIC PROPERTIES

The experimental results and their estimated errors are given in table 3.3, along with the values of other workers. The melting points of the three lower hydrates agree within experimental error with the literature values, whilst that of the nonahydrate is slightly higher.

The enthalpies of fusion given in table 3.3 are in each case the mean of at least 4 observations with, in the case of the nonahydrate, hexahydrate and pentahydrate, each of at least 2 independent samples. The value obtained for the nonahydrate lies between the indirect value of Lange and Von Stackelberg[24] and the estimated value of McCready[23], whilst that of the pentahydrate is higher than both earlier values.[23,24] The heat of fusion of the hexahydrate has not been reported previously and lies between those of the penta- and nonahydrates, though closer to the pentahydrate value, as might be expected.

The entropies of fusion, which were calculated from the ΔH_f values ($\Delta S_f = \Delta H_f/T$), increase with the water content of the salt and the entropy of fusion per mole of water (table 3.3) is almost constant. It is thus easy to estimate a value for the entropy of fusion of the octahydrate and hence obtain an approximate value for its heat of fusion. These estimates, which are the only available values for the octahydrate, are shown in table 3.3. The mean value of the entropy of fusion per mole of water based on the results for the 9-, 6- and 5- hydrates (20.9 ± 0.5 J mol^{-1} K^{-1}) is only slightly less than the entropy of fusion of ice (22.0

TABLE 3.3 THERMAL PROPERTIES OF SODIUM METASILICATE HYDRATES $Na_2SiO_3xH_2O$

Hydrate	T_f/°C	ΔH_f/kJ mol^{-1}	ΔS_f/J mol^{-1} K^{-1}	$(\Delta S_f/x)$/J mol^{-1} K^{-1}	10^2C_p/J mol^{-1} K^{-1} (Solid, 25°C)
9	49.8 ± 1.5	59.6 ± 2.5	184.5	20.48	5.3 ± 0.5
	47,8[a]	67.6[d]			4.75[g]
		55.4[e]			
8	49.5 ± 1.5	53.1[f]	164.8[f]	20.6[f]	
	48.4[a]				
6	63.2 ± 1.5	42.0 ± 2.5	124.9	20.82	3.3 ± 0.3
	62.9[a]				3.53[g]
5	73.0 ± 1.5	37.3 ± 3.5	107.6	21.52	3.1 ± 0.3
	72.2[a]	30.7[d]			3.15[g]
		31.5[e]			
0	1088[b,c]	52.0[c]	38.2[c]		1.11 ± 0.05
					1.13[g]
					1.12[c]

[a] Ref. 9. [b] Ref. 46. [c] Ref. 47. [d] Ref. 43.

[e] Ref. 24. obtained indirectly from heats of solution. [f] Estimated, see text. [g] Ref. 43. estimates based on Kopp's law.

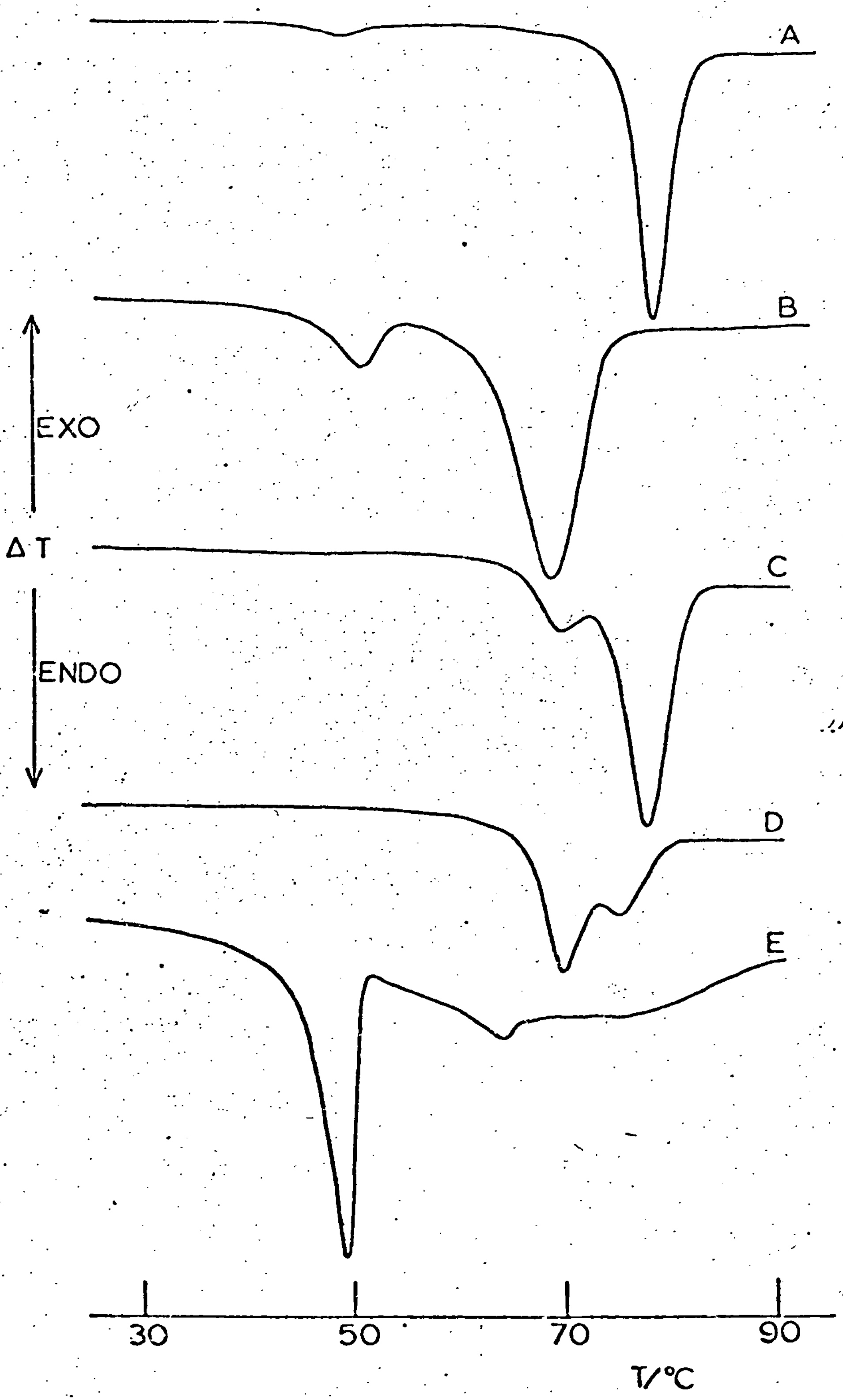
$J\ mol^{-1}\ K^{-1}$)[48] and is consistent with the fact that the metasilicate hydrate lattices are strongly hydrogen-bonded. This behaviour is similar to that observed for many other inorganic hydrates, several of which have entropies of fusion per mole of water within 4 $J\ mol^{-1}\ K^{-1}$ of the pure water value. The fact that the solutions of sodium metasilicate contain significant amounts of polymeric silicates[49] does not appear to have a marked effect on the entropies of fusion of the hydrates.

Within experimental error, the heat capacities obtained at 25°C for the solid hydrates agree with those estimated by McCready.[23] Those of the melts were found to be approximately twice as large as those of the solids, but because of problems, particularly in sample encapsulation, it was impossible to obtain more accurate values.[50]

3.3.2. ANALYTICAL APPLICATIONS

During this work it was found that d.s.c. provides an excellent method for the qualitative analysis of sodium metasilicate hydrates and that, in many cases, it is much quicker, requires a much smaller sample, and is at least as sensitive as the powder X-ray diffraction methods which are normally used. Typical curves obtained with prepared mixtures are shown in figure 3.2 along with the operating conditions. This method is particularly suitable for the detection of small quantities of the higher hydrates present as impurities in lower hydrates, a situation which is often encountered during preparation of these materials. As shown in figure 3.2, trace A, 1% (in moles) of the nonahydrate in pentahydrate is easily detected by d.s.c. whereas experiment showed that this was difficult by powder X.r.d. However, it was found that mixtures which were predominantly high hydrates with small amounts of low hydrates were difficult to analyse by d.s.c., since the predominant high hydrate melted first and the low hydrate impurity (higher M. Pt) then tended to dissolve rather

FIG 3.2 TYPICAL d.s.c. CURVES OBTAINED FOR MIXTURES OF SODIUM METASILICATE HYDRATES.[a,b]



[a] Powdered samples (1-4 m.g.) in Cu pans with crimped on Cu lids. Heating rate : $10^{\circ}C\ min^{-1}$ (A-D), $5^{\circ}C\ min^{-1}$ (E).

[b] Approximate molar compositions : (A) 1% 9, 99% 5; (B) 20% 9, 80% 6; (C) 25% 6, 75% 5; (D) 35% 5, 65% 6; (E) 5% 6, 95% 9

than melt. An example of this is shown in figure 3.2, trace E. It should be noticed that although this method is applicable to a wide range of mixtures, the octahydrate and nonahydrate are indistinguishable, and the anhydrous metasilicate is completely undetectable. Although d.t.a. was not used in this investigation, it seems likely that its performance would be similar.

In conclusion, it is evident that d.s.c./d.t.a. is a very useful complement to powder X.r.d. when used in the analysis of mixtures which contain the hydrated sodium metasilicates.

CHAPTER 4

VAPOUR PRESSURES AND THERMODYNAMIC PROPERTIES OF THE SODIUM METASILICATE HYDRATES.

4.1 INTRODUCTION

Estimated values for the free energies and enthalpies of formation and entropies of sodium metasilicate hydrates at 298.2 K have been given for the four well established hydrates[9,18] by McCready,[23] but the basis on which these estimates were made is uncertain and there are few experimental results available for comparison.[24] Since the properties of anhydrous sodium metasilicate are well established,[47,51] accurate vapour pressures of sodium metasilicate hydrate mixtures would give the thermodynamic properties of the hydrates. In this work a study was made of the equilibria :

$$Na_2SiO_3\ 5H_2O\ (c) \rightleftarrows Na_2SiO_3\ (c) + 5H_2O\ (g) \qquad (4.1)$$

$$Na_2SiO_3\ 6H_2O\ (c) \rightleftarrows Na_2SiO_3\ 5H_2O\ (c) + H_2O\ (g) \qquad (4.2)$$

$$Na_2SiO_3\ 9H_2O\ (c) \rightleftarrows Na_2SiO_3\ 6H_2O\ (c) + 3H_2O\ (g) \qquad (4.3)$$

$$Na_2SiO_3\ 9H_2O\ (c) \rightleftarrows Na_2SiO_3\ 5H_2O\ (c) + 4H_2O\ (g) \qquad (4.4)$$

$$Na_2SiO_3\ 8H_2O\ (c) \rightleftarrows Na_2SiO_3\ 5H_2O\ (c) + 3H_2O\ (g) \qquad (4.5)$$

by direct vapour pressure measurements over the temperature range 290 to 308 K. The technique used was similar to that employed in studies of equilibria between sodium carbonate hydrates.[52]

4.2 EXPERIMENTAL DETAILS

4.2.1. MATERIALS

Samples of sodium metasilicate which contained 9, 6, 5 and 0 molecules of water per metasilicate group were prepared from pure sodium metasilicate as described in chapter 2. The octahydrate was only obtained in combination with the pentahydrate. Care was taken to avoid contamination of the metasilicates by atmospheric carbon dioxide during and after preparation. All of the individual hydrates and hydrate mixtures were assayed by powder X-ray diffraction (X.r.d.) at the beginning of the work. Because of the nature of the experiment, it is not necessary to use samples which contain exactly stoichiometric amounts of water, provided X.r.d. detects the desired crystalline phases and, in most cases, the hydrates used were slightly damp.

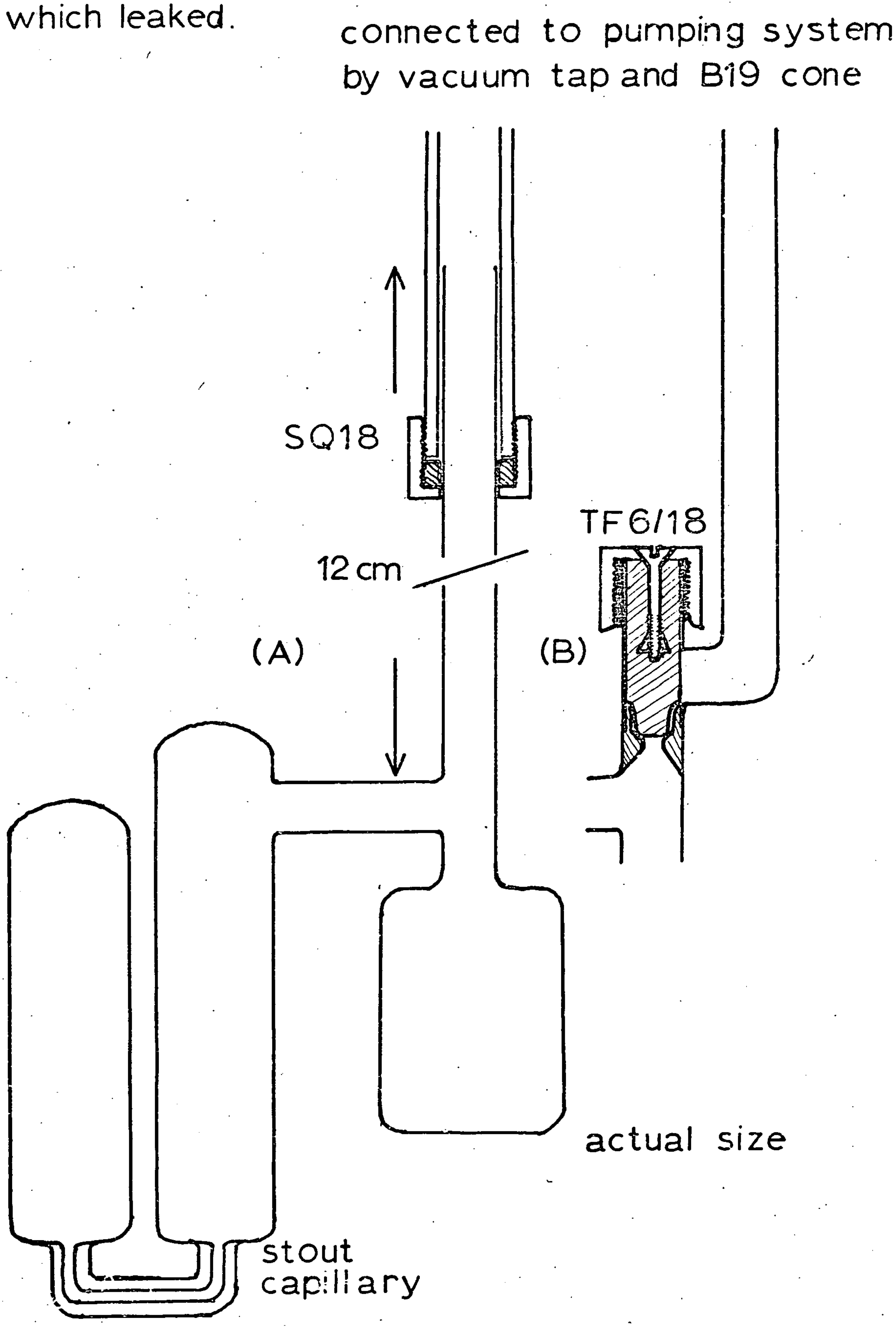
4.2.2. APPARATUS AND PROCEDURE

Vapour pressures were measured with U-tube mercury manometers made from "Veridia" precision bore glass tubing of 20 mm internal diameter. One side of the manometer was sealed and the other was joined to a 25 cm^3 bulb which was half filled with an intimate mixture of two of the salts.

4.2.2.1. Tensimeter - Preparation and Filling

The unfilled apparatus consisted of a manometer and bulb with a long filling-tube which could be attached to a vacuum line by means of an adapter as shown in figure 4.1. Before use, the apparatus was thoroughly cleaned with Analar concentrated nitric acid, washed with distilled water and oven dried. When cold, the bulb was filled with clean mercury, and the apparatus was evacuated to remove air dissolved in the mercury by attachment to a vacuum line. The removal of dissolved air was enhanced if the apparatus was sealed under vacuum, removed from the line and the mercury was swilled around the bulb. The procedure was repeated until no bubbles were apparent in the mercury when the apparatus was evacuated to a pressure of less than 10^{-3} Torr by means of rotary and mercury-diffusion pumps. The apparatus was sealed, removed from the vacuum line,

Fig. 4.1 Diagram showing (A) an empty tensimeter with adapter and (B) the original sealing system which leaked.



and the mercury was carefully poured from the bulb into the manometer. The atmosphere was then slowly admitted to the bulb by careful control of the adapter tap. If more than a very tiny bubble was detectable at the top of the sealed arm of the manometer, the complete evacuation and filling sequence was repeated.

The bulb was half filled with a finely ground mixture of the desired salts after any mercury which remained had been removed by suction. A specially designed funnel with a long, narrow-diameter stem was used to prevent any metasilicate particles from contaminating the mercury surface or from sticking on the sides of the filling-tube. The filled apparatus was attached to the vacuum line and carefully evacuated after the salt mixture had been frozen by a liquid-nitrogen bath. When the system had been completely evacuated, the pumps were isolated from the line and the salt mixture was carefully warmed up to room temperature after removal of the nitrogen bath. The mixture was exposed to the pumps for a few seconds, frozen down again and the system was once more completely evacuated. This sequence of freezing and pumping stages was repeated twice to ensure that no residual air had been trapped in the sample by the use of liquid nitrogen. Finally, the frozen salt mixture was allowed to warm up slowly while exposed to the pumps and, by careful use of a glass-blowing torch, the filling-tube of the apparatus was sealed off. The sealed apparatus, or tensimeter, was drawn away from the line and the sealed end of the filling-tube was annealed in a cool flame. When cold, the tensimeter was placed vertically in a Townson and Mercer Ltd. E270 water thermostat which kept the temperature constant to within ± 0.01°C. Temperatures were measured with a calibrated mercury in glass thermometer and are accurate to ± 0.02°C.

Initial experiments employed a tensimeter which was identical to that described here except that the filling-tube was sealed by a Rotaflo tap, type TF 6/18, as shown in figure 4.1. This version was easier to fill than that which was actually used in this work, and was easily cleaned out and reused. Unfortunately, it was not watertight, and, over a few months at 25°C, most samples picked up water with the result that equilibrium pressures were seldom observed. The apparatus used in this work was found to be completely watertight over periods up to two years.

4.2.2.2. Measurement of Vapour Pressures

The pressure inside the tensimeter was determined by measurement of the vertical distance between the two menisci of the manometer with a Precision Tool and Instrument Co. Ltd. cathetometer which could be read to ± 0.01 mm at each position. The cathetometer was mounted so that the graduated column was exactly vertical by adjustment of the base screws until the column could be rotated through 360° without any appreciable movement of the spirit level in the viewing telescope. In operation, it was found that the necessary vertical movement of the telescope mounting up or down the column often produced a small but significant deviation in the telescope level. As a result, the telescope was carefully levelled before each reading was taken. The errors associated with small changes in the telescope attitude are minimised by having the cathetometer positioned as close as possible to the subject and, in this work, by the use of a close-up lens for the telescope, it was possible to operate 60 cm from the experiment.

It is much easier to focus on the mercury to glass contact line than on the true meniscus, but it became apparent that pressures measured in this way were unreproducible, and this was attributed to two factors. One was that the profile of the meniscus on the sealed side of the manometer was generally shallower than that which was exposed to the water vapour and the other was the slight tendency shown by the mercury to stick to the glass. Consequently, all pressures were determined by observation of the true menisci and, at equilibrium, the value for a particular tensimeter was reproducible to better than ± 0.05 mm. It was found that observation of the meniscus was made easier, with an associated improvement in accuracy, if the tensimeter was illuminated from the rear so that the observed side of the meniscus was dark, in contrast to the bright background. To reduce the tendency of the mercury to stick to the glass, the tensimeter was tilted and repositioned from time to time.

4.2.2.3. Experimental Observations

The metasilicate mixtures $Na_2SiO_39H_2O$ + $Na_2SiO_36H_2O$ (S9 + S6), $Na_2SiO_36H_2O$ + $Na_2SiO_35H_2O$ (S6 + S5), and $Na_2SiO_35H_2O$ + Na_2SiO_3 (S5 + S0) were prepared in duplicate from independent samples of the pure materials. Single preparations of the mixtures $Na_2SiO_38H_2O$ + $Na_2SiO_35H_2O$ (S8 + S5) and $Na_2SiO_39H_2O$ + Na_2SiO_3 (S9 + S0) were also investigated. The eight tensimeters were placed in the thermostat bath and held vertically by a sheet of expanded polystyrene in which slots had been cut to accept the bases of the manometers. Close-up and general views of the experiment are shown in plates 4.1 and 4.2. All of the mixtures were allowed to equilibrate in the sealed tensimeters at 25°C for a minimum of two months, during which the pressures were measured daily. In all cases, relatively steady values were reached within a few days. Subsequently, the equilibrium pressures were measured in turn at 30°, 25°, 20°, 17°, 35° and 25°C allowing approximately two weeks at each temperature. The 25°C pressures were then measured at intervals over a further 16 months after which the apparatus was dismantled and the mixtures were analysed by powder X.r.d. and differential scanning calorimetry (d.s.c.) as discussed in chapters 2 and 3 respectively.

PLATE 4.1 CLOSE-UP VIEW OF TENSIMETERS

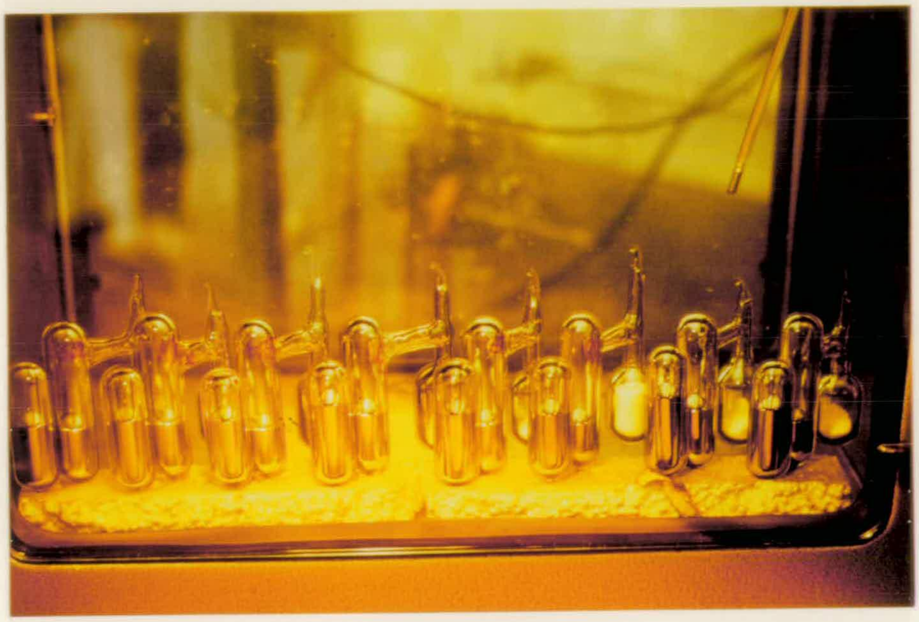
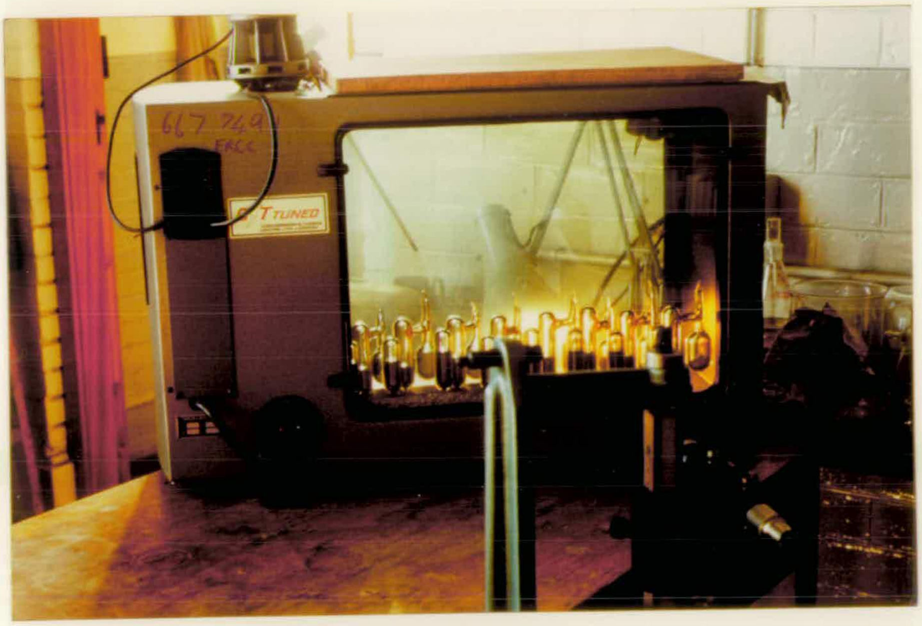


PLATE 4.2 GENERAL VIEW OF APPARATUS SHOWING THE ARRANGEMENT USED FOR MEASUREMENT OF PRESSURES



4.3 RESULTS

By the end of the initial two months equilibration at 25°C, the vapour pressures of the mixtures (S9 + S6), (S6 + S5) and (S8 + S5) were completely steady and those of the (S5 + S0) and (S9 + S0) mixtures were changing by less than 0.2 Torr per month. Twenty months later, at the end of measurements, the 25°C vapour pressures of the (S9 + S6), (S6 + S5) and (S8 + S5) were in exact agreement with the original values whereas those of the (S5 + S0) mixtures had decreased by 0.38 Torr and that of the (S9 + S0) mixture had increased by 0.19 Torr but appeared to be constant. Analysis of the final mixtures confirmed the original compositions in all cases except that of the (S9 + S0) mixture which was found to contain S9 and S5. No crystalline S0 could be detected and it appears that, in this case, the systematic drift in vapour pressure arose from the conversion of S0 to S5. The failure of the (S5 + S0) mixture to reach equilibrium in the first few months is not readily explained. It could, as found with anhydrous sodium carbonate,[52] be due to the physical state of the anhydrous sodium metasilicate. It seems, however, more likely to have arisen from slow equilibration between the two solids, related to the fact that S0,[17] unlike the metasilicate hydrates,[18,19] is extensively polymerised and does not contain discrete silicate ions. The overall downward trend of pressures for the (S5 + S0) mixtures is consistent with the use of slightly damp S5 since the excess water would give rise to higher initial pressures than would be achieved at equilibrium.

The observed vapour pressures are given together with estimated errors in table 4.1. In the case of the (S5 + S0) and (S9 + S5) mixtures, the values given at temperatures other than 298.07 K are believed to be systematically high by about 0.36 Torr and low by about 0.19 Torr respectively.

TABLE 4.1 VAPOUR PRESSURES OF SODIUM METASILICATE HYDRATE MIXTURES, P/TORR[a]

T/K Mixture	289.84[b]	293.07[b]	298.07	303.04[b]	308.09[b]
S5+S0	3.59	4.50	6.53 ± 0.08[c] 6.17 ± 0.08[c,d]	9.17	12.85
S6+S5	5.96	7.44	10.68 ± 0.04[c]	15.11	21.14
S9+S6	7.13	8.86	12.71 ± 0.10[c]	18.06	25.77
S9+S5[e]	6.53	8.17	11.73 ± 0.20[f] 11.92 ± 0.20[d,f]	16.77	24.06
S8+S5	6.73	8.45	12.22 ± 0.20[f]	17.45	24.71

[a] Torr = (101.325/760) kPa. [b] Errors in vapour pressures are unlikely to exceed twice those given for 298.07 K. [c] Estimate of error based on differences between duplicates. [d] Final equilibrium value, see text. [e] Originally (S9+S0), see text. [f] Error estimated by analogy with those for other mixtures.

4.4 DISCUSSION

The only vapour pressures with which those given in table 4.1 may be compared are the estimates of McCready[23] whose values for (S0 + S5), (S5 + S6) and (S6 + S9) (10, 11, 16 Torr) are only in fair agreement (6.2, 10.7, 12.7 Torr). The vapour pressure of the octahydrate $P_{8/6}$ was not measured directly in this work but, by means of the relationship,

$$P^2_{8/6} = P^3_{8/5} / P_{6/5} \qquad (4.6)$$

a value of 13.07 Torr in poor agreement with McCready's estimate (9 Torr) is obtained. The internal consistency of the pressures shown in table 4.1 may be partially confirmed by calculation of the vapour pressure of the S9 + S5 mixture from those of the S9 + S6 and S6 + S5 mixtures with the equation,

$$P^4_{9/5} = P^3_{9/6} \cdot P_{6/5} \qquad (4.7)$$

The calculated value (12.17 ± 0.06 Torr) at 298.07 K is within experimental error of the final equilibrium value (11.92 ± 0.20 Torr) given in table 4.1 but not with that (11.73 ± 0.20 Torr) observed after equilibration for only two months.

Standard molar Gibbs free energy charges for reactions ((4.1) - (4.5)) were calculated from the measured equilibrium vapour pressures shown in table 4.1 by use of the relationship

$$\Delta G^o = -RT\ln Kp \qquad (4.8)$$

$$= -nRT\ln Peq \qquad (4.9)$$

where Kp is the equilibrium constant, R is the gas constant (= 8.31434), T is the temperature in degrees Kelvin, Peq is the equilibrium vapour pressure in atmospheres i.e. (P/Torr)/760 and n is the number of water molecules involved in the equilibrium expression. Values of ΔH^o and ΔS^o

for the reactions ((4.1) - (4.5)) were obtained by a least-squares routine which involved fitting values of ln Kp and T to the equation,

$$R \ln Kp = (-\Delta H^{o}/T) + \Delta S^{o} \qquad (4.10)$$

The values of ΔG^{o}, ΔH^{o} and ΔS^{o} which were obtained are shown, along with their standard errors in table 4.2. In all cases, the deviations of the experimental results from equation (4.10) are not sufficient to justify consideration of the variation of ΔH^{o} and ΔS^{o} with temperature. For reactions ((4.2) - (4.5)) the errors in ΔH^{o} and ΔS^{o} from all sources are unlikely to exceed twice those obtained from the curve-fitting procedure and given in table 4.2. This is also likely to be true for reaction (4.1) since the known uncertainty in the "two month value" of ΔG^{o} (0.71 kJ mol^{-1}) corresponds to an error in ΔH^{o} and ΔS^{o} much less than those given in table 4.2. Best fit values for the constants α and β in the equation,

$$\ln (Peq/760) = \beta - (\alpha/T) \qquad (4.11)$$

are also given in table 4.2 together with the average deviation, δp, between the observed and calculated vapour pressures.

Values of ΔH^{o} and ΔS^{o} for reactions ((4.1)-(4.5)) have not been previously reported. The values per mole of water are almost constant and approximately the same as those observed for the sublimation of ice. A further check on the experimental results is given by the agreement between the values of ΔH^{o} and ΔS^{o} observed for reaction (4.4) and those calculated from the values obtained for reactions (4.2) and (4.3) shown in table 4.2.

Also given in table 4.2 are calculated values for the (S9 + S8) and (S8 + S6) equilibria which were not studied in this work. These values were obtained from reactions (4.4) and (4.5), and (4.2) and (4.5) respectively. Combinations of the equations also give the following values

TABLE 4.2 THERMODYNAMIC PARAMETERS AT 298.15 K FOR SODIUM METASILICATE HYDRATE EQUILIBRIA

Reaction	ΔG^{o}/kJ mol^{-1}	ΔH^{o}/kJ mol^{-1}	ΔS^{o}/J mol^{-1} K^{-1}	$10^{-2}\alpha$/K[b]	β	δp/Torr
(4.1) $S5 \rightleftarrows S0 + 5H_2O$	59.6 ± 0.2	260.6 ± 1.6	677 ± 5	62.68 ± 0.38	16.27 ± 0.13	0.02
(4.2) $S6 \rightleftarrows S5 + H_2O$	10.6 ± 0.1	51.8 ± 0.3	138 ± 1	62.28 ± 0.39	16.63 ± 0.13	0.03
(4.3) $S9 \rightleftarrows S6 + 3H_2O$	30.4 ± 0.1	157.4 ± 1.9	426 ± 6	63.10 ± 0.75	17.09 ± 0.25	0.13
(4.4) $S9 \rightleftarrows S5 + 4H_2O$	41.1 ± 0.2	212.7 ± 2.4	575 ± 8	63.96 ± 0.74	17.30 ± 0.25	0.12
	41.0 ± 0.2[a]	209.2 ± 2.2	564 ± 7			
(4.5) $S8 \rightleftarrows S5 + 3H_2O$	30.7 ± 0.2	159.5 ± 1.1	432 ± 4	63.94 ± 0.42	17.33 ± 0.14	0.05
$S9 \rightleftarrows S8 + H_2O$	10.4 ± 0.3[a]	53.2 ± 2.6	143 ± 9			
$S8 \rightleftarrows S6 + 2H_2O$	20.1 ± 0.2[a]	107.7 ± 1.1	294 ± 4			

[a] Calculated values, see text.

[b] α & β from equation (4.11) : $\ln(Peq/760) = \beta - (\alpha/T)$

for disproportionation of hydrates :

$3S8 \rightarrow S6 + 2S9 \qquad \Delta G^o = -0.7\ kJ\ mol^{-1}$

$4S6 \rightarrow 3S5 + S9 \qquad \Delta G^o = +1.4\ kJ\ mol^{-1}$

$6S5 \rightarrow 5S6 + S0 \qquad \Delta G^o = +6.6\ kJ\ mol^{-1}$

from which it may be seen that only S8 is thermodynamically unstable under experimental conditions.

For comparison with the values in table 4.2, ΔH^o for reactions (4.1) and (4.4) may be calculated from the enthalpies of solution of Lange and Von Stackelberg,[24] and the enthalpy of vapourization of water at 298.15 K (44.02 kJ mol^{-1}).[48] These values are 284.5 and 212.7 kJ mol^{-1} respectively. The value for reaction (4.4) is in excellent agreement with this work, while that for reaction (4.1) is not. A possible explanation is that their [24] anhydrous silicate contained some amorphous material.

Values of the standard Gibbs free energies and enthalpies of formation and the standard entropies at 298.15 K of the sodium metasilicate hydrates calculated from the results in table 4.2 are given in table 4.3. The standard enthalpies of formation are in good agreement with the estimates of McCready,[23] but the standard Gibbs free energies of formation and the standard entropies are not. McCready estimated the increase in entropy per water molecule to be 42 J K^{-1} mol^{-1} whereas the experimental value is approximately 50 J K^{-1} mol^{-1}.

TABLE 4.3 FREE ENERGY AND ENTHALPY OF FORMATION AND ENTROPY OF SODIUM METASILICATES AT 298.2 K[a]

Hydrate	$\Delta G_f^\ominus$/kJ mol^{-1}	ΔH_f^o/kJ mol^{-1}	S^o/J mol^{-1} K^{-1}
S0	-1467 ± 5[b] -1432[c]	-1561 ± 4[b] -1526[c]	113.8 ± 1.3[b] 113.8[c]
S5	-2670 ± 5 -2642[d]	-3031 ± 7 -3021[d] -3006[e]	381 ± 12 322.2[d]
S6	-2909 ± 5 -2879[d]	-3325 ± 8 -3316[d]	431 ± 14 364.0[d]
S8	-3387 ± 5 -3361[d]	-3916 ± 10 -3911[d]	515 ± 20 447.7[d]
S9	-3626 ± 5 -3598[d]	-4207 ± 12 -4205[d] -4158[e]	571 ± 27 489.5[d]

[a] Calculated from the results in Table 4.2 using $\Delta H_f^o(H_2O,g,298.15\ K)$ = -241.8 kJ mol^{-1}, $\Delta G_f^o(H_2O,g,298.15\ K)$ = -228.6 kJ mol^{-1}, $S^o(H_2O,g,298.15\ K)$ = 188.7 J mol^{-1} K^{-1} and the values for anhydrous sodium metasilicate given in the table; all taken from reference 47.

[b] Reference 47. [c] Reference 51. [d] Estimated by McCready, reference 23. [e] Calculated from heats of solution (reference 24) using $\Delta H_f^o(Na_2SiO_3,s,298.15\ K)$ = -1561 kJ mol^{-1} and $\Delta H_f^o(H_2O,1,298.15\ K)$ = -285.8 kJ mol^{-1}.

CHAPTER 5

VISCOSITIES AND DENSITIES OF AQUEOUS SOLUTIONS OF SODIUM METASILICATE AND SODIUM CARBONATE AT 25°C

5.1 INTRODUCTION

The viscosities and densities of aqueous solutions can be analysed theoretically to give a valuable insight into the structure of the hydrated solute and the nature of the solute-solvent interactions. To do this with densities, it is necessary to calculate apparent molal volumes, ϕ_V, and, by extrapolation, obtain the value at infinite dilution, ϕ_V^o.[53] Relative viscosities, η_{rel}, are usually fitted to the Jones-Dole equation (section 5.3.4) in its simple or extended form to obtain values of the viscosity B - coefficient $B\eta$. This parameter is specific to the solute-solvent system in question and its value may be interpreted in terms of the volume and the structure making or breaking properties of the ions concerned.[54,55] The ϕ_V^o and $B\eta$ values obtained for a given electrolyte solution depend on contributions from all the component ions.

In this study, densities and viscosities were measured at 25°C for aqueous solutions of sodium metasilicate and of sodium carbonate over the concentration range 0.01 - 1.7 mol dm^{-3}. The densities of sodium carbonate solutions have been measured by several workers[56,57] but viscosities have not been reported. There have been several studies of the viscosities of aqueous sodium silicate solutions[25,34,41] but few have dealt with the metasilicate[25,34] and, of these, none has been of sufficient accuracy to warrant theoretical interpretation. The densities of aqueous sodium metasilicate have not been reported.

5.2 EXPERIMENTAL DETAILS

5.2.1 MATERIALS

Sodium metasilicate was purified by repeated recrystallisation of the nonahydrate from aqueous solution in the absence of carbon dioxide as described in chapter 2. Because it is difficult to prepare material which contains exactly nine moles of water to one mole of metasilicate, damp material called H5 was used. For comparison one measurement was also made on a solution prepared from pure, dry, nonahydrate, batch H8. Details of these materials are given in table 2.1.

Two sources of anhydrous sodium carbonate were used; Analar (B.D.H. Ltd.) and Suprapur (Merck Ltd.). In both cases the material was carefully dried at 120°C overnight and then stored in vacuo over phosphorus pentoxide.

All solutions were prepared with water freshly distilled from all glass apparatus.

5.2.2 EQUIPMENT

Density measurements were made with a pyknometer of the single capillary type which had a volume of 33.433 cm^3. The capillary was graduated in 0.01 cm^3 intervals and could be read to ± 0.002 cm^3.

Viscosities were measured with an Ubbelohde suspended-level viscometer in which the capillary ends had been flared in order to reduce the kinetic energy correction.[58] Flow times were measured with a Venner stop-watch type A40 which could be read to ± 0.02s. The flow time for water, t_o, at 25°C was 918.20 ± 0.10s.

All measurements were made at 25.00 ± 0.02°C in a Townson and Mercer Ltd. water thermostat bath, type E270 Series III. Most solutions were prepared in Xlon 100 cm^3 polypropylene volumetric flasks to minimise etching effects, but results were indistinguishable from those obtained from solutions prepared in conventional glass flasks, over the times and temperatures involved.

A filling and emptying system which provided a convenient method for handling the solutions during density and viscosity determinations was developed and is shown in figure 5.1.

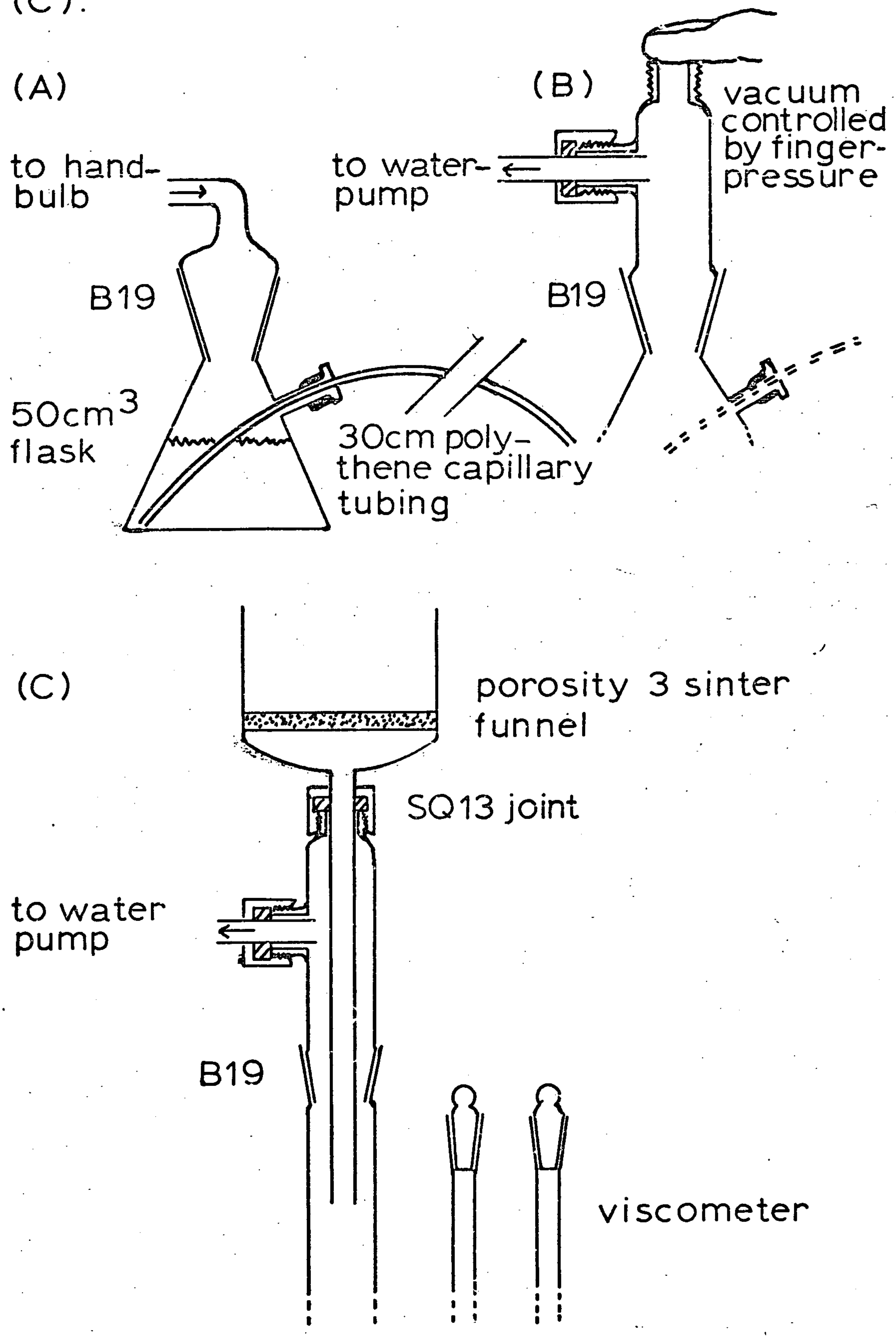
5.2.3 PROCEDURE

5.2.3.1 Solution Preparation

All solutions apart from those of sodium carbonate with m > 1.0 mol dm^{-3} were prepared by dilution of concentrated stock solutions which were stored in the absence of carbon dioxide in tightly sealed polythene bottles. The composition of the metasilicate stock solution was determined by ignition at 1000°C as described in chapter 2 and frequent checks were made over the period the solution was in use. This technique cannot be applied in the case of sodium carbonate stock solution since loss of carbon dioxide occurs at temperatures in excess of 200°C and these solutions were prepared by weight from carefully dried anhydrous material. All stock solutions were carefully filtered through a 0.8μm Gelman filter; in the case of the metasilicates, this was carried out prior to determination of the composition.

All experimental solutions were prepared by weight in dry 100 cm^3 volumetric flasks using 2 cm^3 disposable plastic syringes to transfer the desired amount of standardised stock solution. It was crucial that the flasks used were clean and had been allowed to cool to constant weight; a major disadvantage of the polypropylene flasks was that they took longer to reach constant weight on removal from the drying oven at 120°C (up to five hours at 20°C). The quantity of carbonate stock

Fig. 5.1 Apparatus used for filling (A) and emptying the pyknometer (B), and filling the viscometer (C).



solution which could be prepared by weight was restricted by the maximum capacity (200 g) of the Stanton Unimatic balance. Since the minimum volume with which a concurrent determination of density and viscosity could be made was 100 cm^3, experimental carbonate concentrations in excess of 1.0 mol dm^{-3} were prepared directly from solid electrolyte.

In all cases, the experimental solutions were held at 25°C (bath temperature) for at least 15 hours before measurements were made. All weights used for calculation of solution composition were corrected to the in vacuo values by use of the equation,

$$Wt_{vac.\ corr.} = Wt_{obs} \left(1.0/(1.0 - d\ air/d_x)\right) \qquad (5.1)$$

where the density of air at 25°C, d air, = 0.0012g cm^{-3} and the density of the material being weighed, d_x, was taken as 0.997046 g cm^{-3} for pure water, 1.5 for solid electrolyte or stock solution, and 1.1 for experimental solutions.

5.2.3.2 Density Measurements

Calibration of the pyknometer.

The pyknometer was cleaned in cold, concentrated nitric acid (AR) and then thoroughly washed with distilled water. It was then carefully filled with distilled water to a level approximately 1 cm up the capillary using the apparatus shown in figure 5.1. Care was taken to ensure that no air bubbles were trapped and that the outside was dry before the pyknometer and contents were weighed. The filled pyknometer was fixed vertically in the thermostat bath for approximately 30 minutes to allow thermal equilibration, and the liquid level in the capillary was then measured. After removal from the bath, the apparatus was emptied, dried in the oven, and allowed to come to constant weight at room temperature before it was weighed. From the weights of the pyknometer when empty and when full, the weight of water contained was calculated and corrected for buoyancy as in equation (5.1). The volume of the pyknometer bulb was calculated using the density of water at 25°C (0.997046 g cm^{-3})and the reading from the capillary.

Measurement of Solution Densities.

In order to reduce the occurrence of trapped air bubbles, the pyknometer was kept full of water when not in use. Then, the normal procedure was to rinse the pyknometer with approximately 10 cm^3 of the experimental solution prior to filling. The technique was exactly as for the calibration except that density instead of volume was the unknown. The pyknometer was weighed full and then allowed to reach thermal equilibrium before the level in the capillary was recorded. The calibrations of volume and dry weight were checked at suitable intervals.

5.2.3.3. Viscosity Measurements

Calibration of the Viscometer.

The viscometer was thoroughly cleaned with cold, concentrated, nitric acid (AR), rinsed with distilled water, and placed in the bath with the mounting adjusted so that the capillary was held vertical. It was filled with approximately 50 cm^3 of distilled water which was filtered through a porosity 3 glass sinter by means of the apparatus shown in figure 5.1. The liquid was pumped through the capillary to the upper reservoir by means of a hand-bulb and the time taken for the liquid meniscus to flow from the upper to the lower mark was measured with a stop-watch. This "flow time" was redetermined several times with the same sample of water until two values which agreed to within 0.1 s (∿ ± 0.01%) were obtained. Throughout the subsequent series of experiments, the flow time for water, t_0, afforded a quick check on the state of cleanliness of the capillary.

Measurement of Solution Viscosities.

Solution flow times, t, were measured in a manner similar to t_0 and normal procedure was to rinse the viscometer thoroughly with solution before it was filled with the actual test solution. In order to reduce the volumes of solution required for determination of the density and viscosity of a given solution, densities were measured before viscosities and the solution from the pyknometer was used to rinse the viscometer. With solutions of low concentration, flow times were reproducible to within 0.1 s, as for pure water. At the higher concentrations (> 1.0 mol dm^{-3}), flow times were significantly longer (up to 2700 s for Na_2SiO_3 1.7 m) and an acceptable agreement (± 0.01%) was in some cases ± 0.2 s.

5.2.4 THE EFFECTS OF ETCHING ON GLASS APPARATUS.

At the commencement of this work, it was anticipated that etching of glass surfaces by carbonate or silicate solutions would be an important source of error. Apart from the obvious consequences of etching, on the calibration of pyknometer and viscometer, there was also the possibility of contamination of solutions with products of the etching process. In reality, it was found that, at 25°C, the errors incurred were small provided precautions were taken to reduce the glass-solution contact time to a minimum; in all cases, both pyknometer and viscometer were rinsed carefully with distilled water after each day's experiments. The flow time for water, t_0, was approximately 1.5 s shorter (in 900 s) at the finish of all measurements than at the start, but the actual uncertainty in t_0 used in calculations, was kept to better than ± 0.01%

by frequent recalibration. The pyknometer was recalibrated for weight and volume several times throughout this work and the results obtained on completion of the work agreed with the initial calibrations to well within experimental error.

5.3 RESULTS

5.3.1. INTRODUCTION

As described in section 5.2, concurrent determinations of density and viscosity were made for each experimental solution, and, where the pyknometer and viscometer were reliably calibrated, this normally involved measurement of three parameters; the weight of the filled pyknometer, the equilibrium reading on the pyknometer capillary and the flow time of the solution in the viscometer. All calculations were carried out with the assistance of a computer.

In this work, one of the main reasons for measurement of solution densities was to permit calculation of the apparent molal volume of the solute, ϕ_V, which is defined by the expression,

$$\phi_V = (V - n_o \bar{V}_o) / n_s \qquad (5.2)$$

where V is the total volume of the solution which contains n_s moles of solute and n_o moles of solvent with $\bar{V}_o$, the molar volume of pure solvent.[a] An alternative expression for ϕ_V is

$$\phi_V = [(m.\ F\,w + 1000) / d - (1000 / d_o)] / m \qquad (5.3)$$

where m is the solution molality (moles solute per kg solvent), Fw is the formula weight of the solute and d and d_o are the densities ($g.cm^{-3}$) of the solution and of pure water respectively.

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[a] Since water was used as solvent throughout this work, the subscript $_o$ will be assumed to refer to pure water unless it is stated otherwise.

The relative viscosity of a solution with respect to pure water at the same temperature, η_{rel}, is defined by the relationship,

$$\eta_{rel} = \frac{t.d}{t_o.d_o} \qquad (5.4)$$

where t and t_o are the flow times of the solution and of pure water, densities d and d_o respectively. The experimentally obtained values of d, ϕ_V and of η_{rel} for solutions of Na_2CO_3 and Na_2SiO_3 of molality m, are given in tables 5.1 and 5.2 respectively.

5.3.2. ERRORS

By consideration of the errors in the calibration and in experimental measurement, it is estimated that all densities quoted are accurate to better than ± 0.015%. As shown in equation (5.4), the relative viscosity is dependent on the flow times and densities of both the solution and of pure water. It was found that all flow times were reproducible to within ± 0.01% and this leads to an estimated error in η_{rel} of ± 0.035%.

As described in section 5.2, solutions of sodium carbonate were in all cases derived from carefully dried, pure material and it is estimated that the maximum error in their molalities is ± 0.005%. In contrast, solutions of sodium metasilicate were, in most cases, prepared from damp nonahydrate and analysed by weight loss on ignition at $1000^{\circ}C$ - see chapter 2. By consideration of the spread in molality calculated by this method for duplicate samples of solutions, it is estimated that the error in m Na_2SiO_3 may be as much as ± 0.2%. Differentiation of equation (5.3) with respect to m and d gives an expression of the total uncertainty in apparent molal volume,

$$\Delta\phi_V = \left| \left[Fw / (d.m) - \left(\frac{m.\ Fw + 1000}{d} - \frac{1000}{d_o} \right) / m^2 \right] \delta m \right| + \left| \left[- (m.\ Fw + 1000).\ \delta d / (m.d^2) \right] \right| \qquad (5.5)$$

TABLE 5.1 MOLALITY, DENSITY, APPARENT MOLAL VOLUME AND RELATIVE VISCOSITY OF Na_2CO_3 IN WATER AT 25°C. [a]

m	d/gcm^{-3}	ϕ_V/cm^3mol^{-1}	η_{rel}	Comment
0.0167	0.999	2.699	1.009	stock soln 1[b]
0.0398	1.001	-0.976	1.022	" " "
0.0821	1.006	-2.234	1.044	" " "
0.1244	1.010	-1.841	1.066	" " "
0.2041	1.019	-1.156	1.110	" " "
0.3825	1.037	0.492	1.217	" " "
0.1575	1.014	-1.117	1.084	stock soln 2[b]
0.4695	1.046	1.484	1.272	" " "
0.7815	1.076	3.855	1.505	" " "
0.4332	1.042	1.297	1.247	individual soln [c]
0.7327	1.072	3.608	1.464	" " "
1.0800	1.104	5.880	1.779	" " "
1.2724	1.122	6.919	1.990	" " "
1.4699	1.139	7.952	2.236	" " "
1.7053	1.159	9.056	2.574	" " "

[a] Results before correction for effects of hydrolysis - see text.

[b] Experimental solutions prepared by dilution of concentrated stock solutions (Merck "Suprapur" grade Na_2CO_3 in distilled water).

[c] Individual solutions prepared from AR Na_2CO_3 (B.D.H. Ltd.) and distilled water.

TABLE 5.2 MOLALITY, DENSITY, APPARENT MOLAL VOLUME AND RELATIVE VISCOSITY OF Na_2SiO_3 IN WATER AT 25°C [a]

m	d/gcm^{-3}	ϕ_V/cm^3mol^{-1}	η_{rel}	Comment
0.007	0.998	19.363	1.005	stock soln 1 [b]
0.015	0.999	-1.064	1.010	" " "
0.022	1.000	-5.912	1.014	" " "
0.029	1.001	-8.519	1.018	" " "
0.036	1.002	-10.527	1.024	" " "
0.044	1.003	-10.859	1.029	" " "
0.051	1.004	-11.852	1.033	" " "
0.067	1.006	-12.426	1.043	" " "
0.059	1.005	-11.274	1.037	" " "
0.075	1.007	-11.792	1.048	" " "
0.075	1.007	-11.817	1.048	" " "
0.081	1.008	-11.060	1.052	" " "
0.087	1.009	-11.249	1.056	" " "
0.148	1.017	-10.788	1.097	" " "
0.225	1.027	-9.907	1.151	" " "
0.300	1.036	-8.890	1.209	" " "
0.379	1.046	-8.448	1.273	" " "
0.420	1.052	-7.693	1.309	" " "
0.606	1.075	-5.810	1.487	" " "
0.125	1.014	-11.124	1.081	stock soln 2 [b]
0.261	1.031	-9.302	1.179	" " "
0.379	1.046	-7.917	1.273	" " "
0.516	1.063	-6.578	1.397	" " "
0.645	1.079	-5.518	1.529	" " "
0.671	1.083	-5.320	1.558	" " "
0.787	1.097	-4.324	1.696	" " "
0.897	1.110	-3.508	1.842	" " "
1.121	1.136	-1.968	2.188	" " "
0.191	1.022	-10.447	1.126	stock soln 3 [b]
0.750	1.092	-4.653	1.649	" " "
1.308	1.157	-0.786	2.550	" " "
1.505	1.180	0.298	3.009	" " "
1.706	1.202	1.434	3.584	
0.256	1.030	-7.404	1.171	using H8 nona [c]

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[a] Results not corrected for effects of hydrolysis - see text.

[b] Experimental solutions prepared by dilution of concentrated stock solutions (damp $Na_2SiO_3 9H_2O$, batch H5 and distilled water).

[c] Individual solution prepared from pure, dry nonahydrate - see text.

where the first term gives the error in ϕ_V arising from an error in molality δm, and the second term, the error arising from an error in density, δd. Examination of equation (5.5) shows that the major contribution to the overall error in ϕ_V is the error in density and thus, when m is small, the equation may be approximated by,

$$\Delta \phi_V \sim - (1000/m)\, \delta d \qquad (5.6)$$

In the case of Na_2CO_3, calculated values of $\Delta \phi_V$ from equation (5.6) range from 3.1 $cm^3\ mol^{-1}$ at 0.05m to 0.15 $cm^3\ mol^{-1}$ at 1.0m. Because of the much larger uncertainty in the molalities of the sodium metasilicate solutions, it is incorrect to use this simplified equation and calculation with equation (5.5) shows that errors in ϕ_V are 3.27 and 0.37 $cm^3\ mol^{-1}$ at 0.05 and 1.0m respectively.

5.3.3 DENSITY MEASUREMENTS

Experimental density measurements were curve fitted by a general least-squares procedure and it was found that best agreement between observed and calculated values was obtained using the equation,

$$d = d_o + Am + Bm^2 + Cm^3 \qquad (5.7)$$

where d_o is the density of water at 25°C, and m is the solution molality. The values of A, B and C obtained were, for Na_2CO_3, 0.1085, -0.9924×10^{-2} and 0.1246×10^{-2} ($\sigma = 0.6 \times 10^{-4} gcm^{-3}$) and, for Na_2SiO_3, 0.1338, -0.01028 and 0.13×10^{-2} ($\sigma = 0.83 \times 10^{-4} gcm^{-3}$).

5.3.3.1 Correction for Effects of Hydrolysis

In aqueous solutions of sodium carbonate, hydrolysis occurs, resulting in formation of bicarbonate ion as in the equation,

$$\begin{array}{ccccccc} CO_3^{2-} & + & H_2O & \rightleftharpoons & HCO_3^- & + & OH^- \\ n_s - x & & n_o - x & & x & & x \end{array} \qquad (5.8)$$

and the hydrolysis constant K_H has been estimated[59] to be 2.148 x 10^{-4}. Calculation shows that the extent of hydrolysis, α $(= \frac{x}{n_s})$, increases with reduction in solute concentration and at 0.015m, approximately 11% of the total carbonate content is hydrolysed compared with only 1.4% at 1.0m. Thus it is necessary to apply a correction to the observed apparent molal volumes to allow for the difference between CO_3^{2-}, HCO_3^- and OH^- ions and also for the fact that one molecule of solvent is involved in the hydrolysis reaction.

As shown in equation (5.2), the apparent molal volume of a solute in a solution of volume V which contains n_s moles solute and n_o moles solvent is given by

$$\phi_v = (V - n_o \bar{V}_o) / n_s \qquad (5.2)$$

where $\bar{V}_o$ is the molar volume of the solvent. The volume of the solution, V, may be expressed as the sum of contributions from solvent and all constituent ions and, if hydrolysis occurs according to equation (5.8), this becomes

$$V = vH_2O + vHCO_3^- + vOH^- + vCO_3^{2-} + vNa^+$$

$$= (n_o - x)\bar{V}_o + x\phi_v HCO_3^- + x\phi_v OH^- + (n_s - x)\phi_v CO_3^{2-} + 2n_s\phi_v Na^+$$

Thus, by equation (5.2), the apparent molal volume may be expressed as,

$$\phi_v Na_2CO_{3(obs)} = \frac{-x\bar{V}_o}{n_s} + \frac{x}{n_s}\phi_v HCO_3^- + \frac{x}{n_s}\phi_v OH^- + \frac{(n_s - x)\phi_v CO_3^{2-}}{n_s} + \frac{2n_s\phi_v Na^+}{n_s}$$

$$= -\alpha\bar{V}_o + \alpha\phi_v HCO_3^- + \alpha\phi_v OH^- + (1 - \alpha)\phi_v CO_3^{2-} + 2\phi_v Na^+$$

and, since 2 $\phi_v Na^+$ may be expressed as $2(1 - \alpha)\phi_v Na^+ + 2\alpha\phi_v Na^+$,

$$\phi_v Na_2CO_{3(obs)} = (1 - \alpha)Na_2CO_3 + \alpha[\phi_v NaHCO_3 + \phi_v NaOH - \bar{V}_o]$$

$$= \phi_v Na_2CO_3 + \alpha[\phi_v NaHCO_3 + \phi_v NaOH - \phi_v Na_2CO_3 - \bar{V}_o]$$

Thus,

$$\phi_{vNa_2CO_3} = \phi_v Na_2CO_{3(obs)} - \alpha[\phi_v NaHCO_3 + \phi_v NaOH - \phi_v Na_2CO_3 - \bar{V}_o] \qquad (5.9)$$

Using the notation adopted for the concentrations in equation (5.8), the hydrolysis constant may be expressed, neglecting activity coefficients as,

$$K_H = \frac{x^2}{n_s - x} \qquad (5.10)$$

$$\therefore \quad x^2 = K_H n_s - K_H x$$

$$\therefore \quad 0 = x^2 + K_H x - K_H n_s$$

$$\therefore \quad x = (- K_H \pm \sqrt{K_H^2 + 4K_H n_s}) / 2 \qquad (5.11)$$

Since x cannot be negative, the value of x and thus the extent of hydrolysis, α, may be obtained by taking the positive root of equation (5.11) after substituting for the concentration of solute, n_s and for K_H (= 2.148×10^{-4} for Na_2CO_3 [59]).

By the use of equation (5.10) with some recently reported values for the apparent molal volumes at infinite dilution of some relevant species;[60] $\phi_v^o NaHCO_3 = 23.45$, $\phi_v^o NaOH = -5.20$ and $\phi_v^o Na_2CO_3 = -6.13$ (all in $cm^3 \ mol^{-1}$), experimental ϕ_v values for Na_2CO_3 were corrected for the effects of hydrolysis;

$$\phi_v Na_2CO_3 = \phi_v Na_2CO_{3(obs)} - \alpha (23.45 + (-5.20) - (-6.13) - 18.1)$$

$$= \phi_v Na_2CO_{3(obs)} - \alpha (6.28) \qquad (5.12)$$

The effect of this correction on the ϕ_v results measured for Na_2CO_3 is small and amounts to - 0.445 at 0.04m and -0.07 at 1.7m ($\Delta\phi_V$ in $cm^3\ mol^{-1}$).

In the case of sodium metasilicate, the effects of hydrolysis are much more significant as discussed in chapter 6. The equation thought to describe the major process is very similar to that for carbonate systems and is

$$(HO)_2\ SiO_2^{2-} + H_2O \qquad (HO)_3\ SiO^- + HO^- \qquad (5.13)$$

for which K_H is reported to be 0.02512,[61] 0.063,[62] 0.10233,[39] 0.199.[62] In principle, an analysis similar to that described for the solutions of sodium carbonate can be carried out but, in practice, difficulties arise since values for ϕ_V^o $Na(HO)_3\ SiO$ have not been reported. Therefore, all that can be done is to estimate the correction in ϕ_V by use of the appropriate value of K_H and the ϕ_V^o- values used for the sodium carbonate system. In this analysis, K_H was taken as 0.10233.[39] The effect on ϕ_V is large and amounts to reductions in ϕ_V of -4.9 at 0.4m and -1.4 at 1.7m (all $\Delta\phi_V$ in $cm^3\ mol^{-1}$).

5.3.3.2 Calculation of Apparent Molal Volumes at Infinite Dilution, ϕ_V^o.

Apparent molal volumes as obtained from equation (5.3), are related to solute molarity, c, by the expression;

$$\phi_V = \phi_V^o + Sc^{\frac{1}{2}} + jc \qquad (5.14)$$

where ϕ_V^o is the apparent molal volume at infinite dilution, j is an empirical constant and S is a theoretical constant which depends on the temperature and on the physical properties of the solvent. In this work, S for water was taken to be 9.706 $mol^{-\frac{3}{2}}\ cm^3\ dm^{-\frac{3}{2}}$. Thus ϕ_V^o may be obtained by plotting $(\phi_V - Sc^{\frac{1}{2}})$ against c followed by extrapolation to zero concentration as shown in figures 5.2 and 5.3 for Na_2CO_3 and Na_2SiO_3 respectively. To avoid confusion, only the values obtained

Fig. 5.2 $(\phi_V - Sc^{1/2})$ versus molarity of Na_2CO_3 at 25°C.

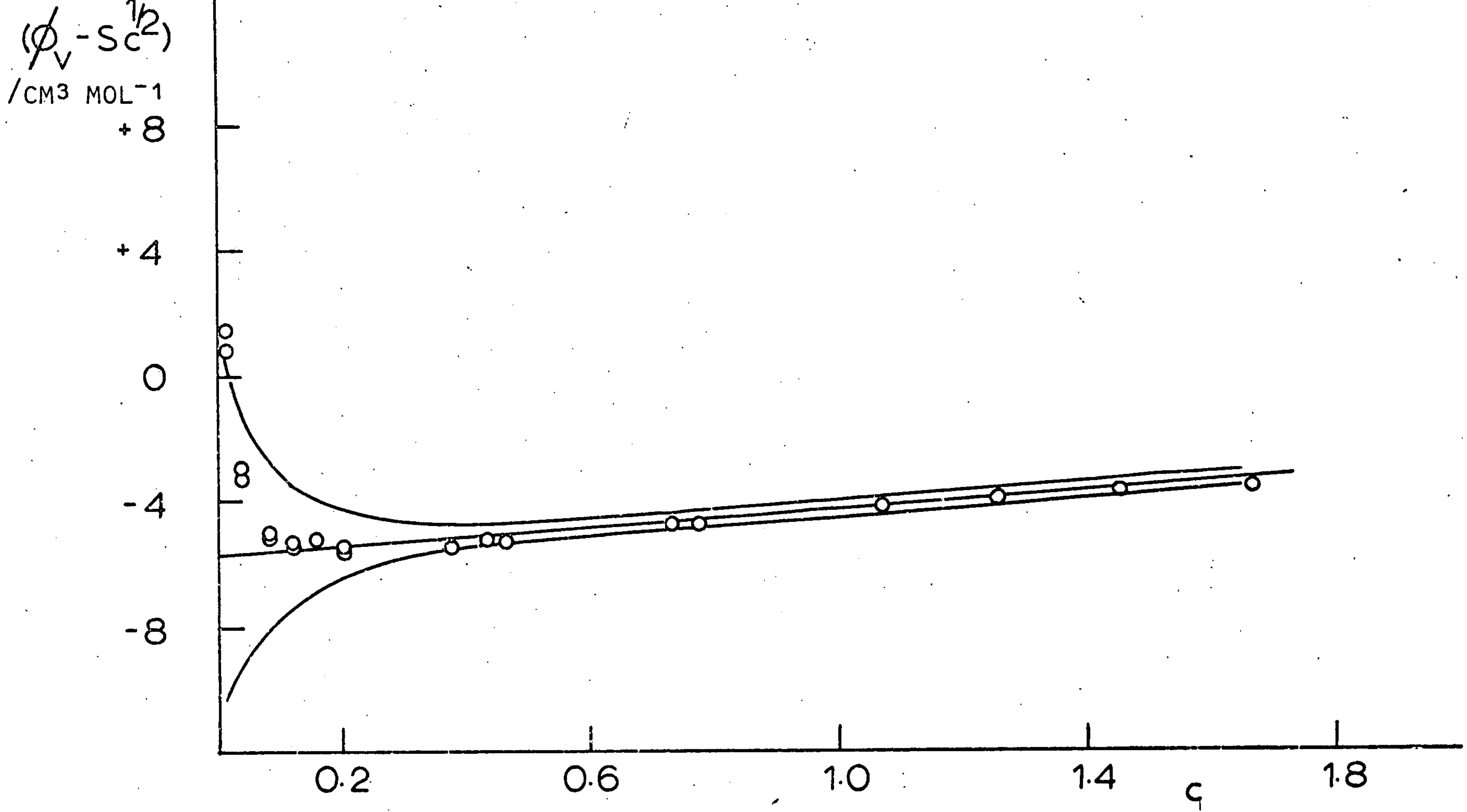
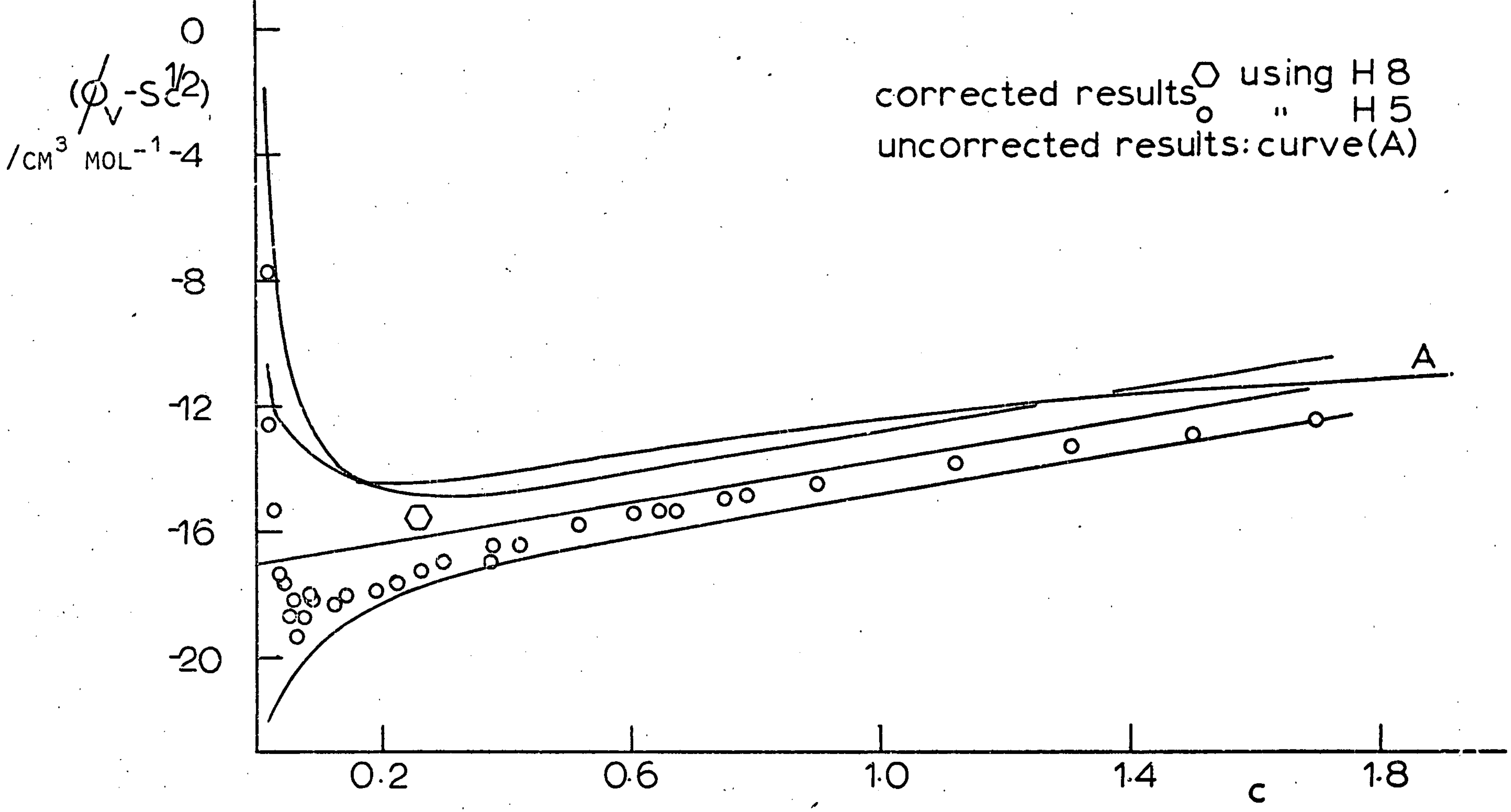


Fig.5.3 $(\phi_V - Sc^{1/2})$ versus molarity of Na_2SiO_3 at 25°C.



after correction for hydrolysis are shown in figure 5.2 (Na_2CO_3). By use of a least-squares computer program which weighted experimental points in proportion to c^2, values of ϕ_v^o and j, together with their standard errors were obtained. These values are:

ϕ_v^o Na_2CO_3 = -5.77 ± 0.09, $j = 1.336 \pm 0.06$

However, in view of the estimated experimental errors which are shown in figure 5.2, a more realistic statement of the results is considered to be:

ϕ_v^o Na_2CO_3 = -5.8 ± 0.3 cm^3 mol^{-1}, $j = 1.34 \pm 0.15$

The results for sodium metasilicate before and after correction for hydrolysis are shown in figure 5.3. The correction applied is large particularly at low concentrations and the slight negative distortion seen in the curve through the corrected points suggests that the correction applied is excessive. One of the less satisfactory aspects of this work became apparent when one of the stock solutions of sodium metasilicate, prepared from damp nonahydrate, batch H5, was used in isopiestic measurements as described in chapter 6. The results obtained suggested that material H5 contained a small amount of sodium hydroxide contaminant as a consequence of the techniques used during crystallisation. Consequently, some of the carefully purified, dry nonahydrate, batch H8, which was used throughout the isopiestic measurements, was used to prepare one solution for use in viscosity and density experiments. As shown in figure 5.3, the result obtained lies significantly above the curve through the other results although just on the limit of estimated experimental error. Unfortunately, the relatively large quantity of the pure, dry material required to repeat this experiment was not available. Thus it seems likely that the apparent molal volumes obtained with batch H5 could be low by approximately 1.5 $cm^3\ mol^{-1}$ and this is reflected in the large error given below for ϕ_V^o Na_2SiO_3. Because of the uncertainty associated with the hydrolysis correction, values of ϕ_V^o and j were estimated from the graph (Fig 5.3). These values are ;

$$\phi_V^o\ Na_2SiO_3 = -17 \pm 1.5\ cm^3\ mol^{-1}, \qquad j = 2.5 \pm 0.3$$

5.3.4 VISCOSITY MEASUREMENTS

The standard equation relating relative viscosity to solute concentration, c, is the Jones-Dole equation,[55]

$$\eta_{rel} = 1 + A\eta c^{\frac{1}{2}} + B\eta c \qquad (5.15)$$

where Aη and Bη are constants specific for the given solute - solvent system. This equation, however, is only applicable to concentrations below 0.1 mol dm^{-3} and is normally extended to higher concentrations by the addition of a further term, to give,

$$\eta_{rel} = 1 + A\eta c^{\frac{1}{2}} + B\eta c + D\eta c^2 \qquad (5.16)$$

Thus, by plotting $(\eta_{rel} - 1 - A\eta c^{\frac{1}{2}})/c$ against c, one may obtain Bη as the intercept and Dη as the slope.

In the analysis of the results obtained in this work, Aη was calculated for sodium carbonate in water as described by Harned and Owen,[63]

$$A\eta = \frac{\beta^*}{80(|Z_1|+|Z_2|)^2}\left\{\frac{\lambda_1^o\, Z_2^{\,2} + \lambda_2^o\, Z_1^{\,2}}{\lambda_1^o\ \ \lambda_2^o} - \frac{4}{\lambda_1^o\ \ \lambda_2^o} \cdot \left[\frac{|Z_2|\lambda_1^o - |Z_1|\lambda_2^o}{(\Lambda^o)^{\frac{1}{2}} + (\Lambda^o + \lambda_1^o|^{Z_2}/_{Z_1}| + \lambda_2^o|^{Z_1}/_{Z_2}|)^{\frac{1}{2}}}\right]^2\right\} \qquad (5.17)$$

where β* depends on the viscosity and dielectric constant of the solvent and, for water at 25°C, $\beta^* = 60.65$; λ_1^{o} and λ_2^{o} are the limiting molar ionic conductances of the ions. It is impossible to calculate $A\eta$ for solutions of sodium metasilicate since accurate conductivity measurements of these systems have not been reported and, consequently results for both solutes were examined using the $A\eta$- value (0.01733 dm $^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$) calculated for Na_2CO_3. The plots of $(\eta_{rel} - 1 - Ac^{\frac{1}{2}})/c$ against c are shown for solutions of Na_2CO_3 and Na_2SiO_3 in figures 5.4 and 5.5 respectively and it is apparent that the results deviate from the linear relationship expected particularly at concentrations in excess of 0.9m and 0.7m respectively.

In order to obtain an equation which related η_{rel} to molarity over the concentration range investigated, an additional term in c^3 was added to the extended Jones-Dole equation (5.16) to give,

$$\eta_{rel} = 1 + A\,c^{\frac{1}{2}} + B\,c + D\,c^2 + E\,c^3 \qquad (5.18)$$

where all parameters including A were allowed to vary. The values of these parameters which fitted the experimental results best were, for Na_2CO_3, 0.006265, 0.5011, 0.1125, 0.0878 ($\sigma = 6.2 \times 10^{-4}$) and for Na_2SiO_3, -0.02386, 0.7172, 0.0261, 0.2698 ($\sigma = 2.7 \times 10^{-3}$). It should be noted that these are purely fitting parameters and no real significance should be attributed to them. Table 5.3 shows values of d and η_{rel} calculated for Na_2CO_3 and Na_2SiO_3 at rounded concentrations by use of equations (5.7) and (5.18) respectively.

Since no viscosity studies of the solutions of sodium bicarbonate or of $Na(HO)_3SiO$ have been reported, it is impossible to correct the viscosity results for hydrolysis effects and experimental results were analysed on the assumption that hydrolysis had a negligible effect except at very low concentrations. Consequently it was difficult to obtain $B\eta$ from the experimental results shown in figures 5.4 and 5.5 by computation,

TABLE 5.3 DENSITY AND RELATIVE VISCOSITY OF SOLUTIONS OF Na_2CO_3 AND Na_2SiO_3 IN WATER AT 25°C.

Molality	Density[a]/gcm^{-3}		Molarity	Relative Viscosity[b]	
	Na_2CO_3	Na_2SiO_3[c]		Na_2CO_3	Na_2SiO_3[c]
0.1	1.008	1.010	0.1	1.053	1.065
0.2	1.018	1.023	0.2	1.108	1.136
0.3	1.029	1.036	0.3	1.166	1.212
0.4	1.039	1.049	0.4	1.228	1.293
0.5	1.049	1.062	0.5	1.294	1.382
0.6	1.059	1.074	0.6	1.365	1.480
0.7	1.069	1.086	0.7	1.441	1.587
0.8	1.078	1.098	0.8	1.523	1.707
0.9	1.088	1.110	0.9	1.612	1.841
1.0	1.097	1.122	1.0	1.708	1.989
1.1	1.106	1.134	1.1	1.811	2.155
1.2	1.115	1.145	1.2	1.922	2.338
1.3	1.124	1.156	1.3	2.042	2.542
1.4	1.133	1.168	1.4	2.170	2.767
1.5	1.142	1.179	1.5	2.309	3.016
1.6	1.150	1.190	1.6	2.457	3.289
1.7	1.159	1.201	1.7	2.617	3.589
1.8	1.167	1.212	1.8	2.787	3.917
1.9	1.176	1.223	1.9	2.969	4.275
2.0	1.184	1.234	2.0	3.164	4.664

[a] Densities calculated from the equation, $d = d_o + Am + Bm^2 + Cm^3$ where $d_o = 0.997046\ gcm^{-3}$ and A, B, C are, for Na_2CO_3, 0.1085, -0.9924×10^{-2}, 0.1244×10^{-2} and, for Na_2SiO_3, 0.1338, -0.1028×10^{-1} and 0.13×10^{-2} respectively.

[b] Relative viscosities calculated from the equation, $\eta_{rel} = 1 + Ac^{\frac{1}{2}} + Bc + Dc^2 + Ec^3$ where A, B, D and E are, for Na_2CO_3, 0.6265×10^{-2}, 0.5011, 0.1125, 0.0878 and, for Na_2SiO_3, -0.2386×10^{-1}, 0.7172, 0.0261 and 0.2698 respectively.

[c] Na_2SiO_3 values based on results from batch H5 nonahydrate only - see text.

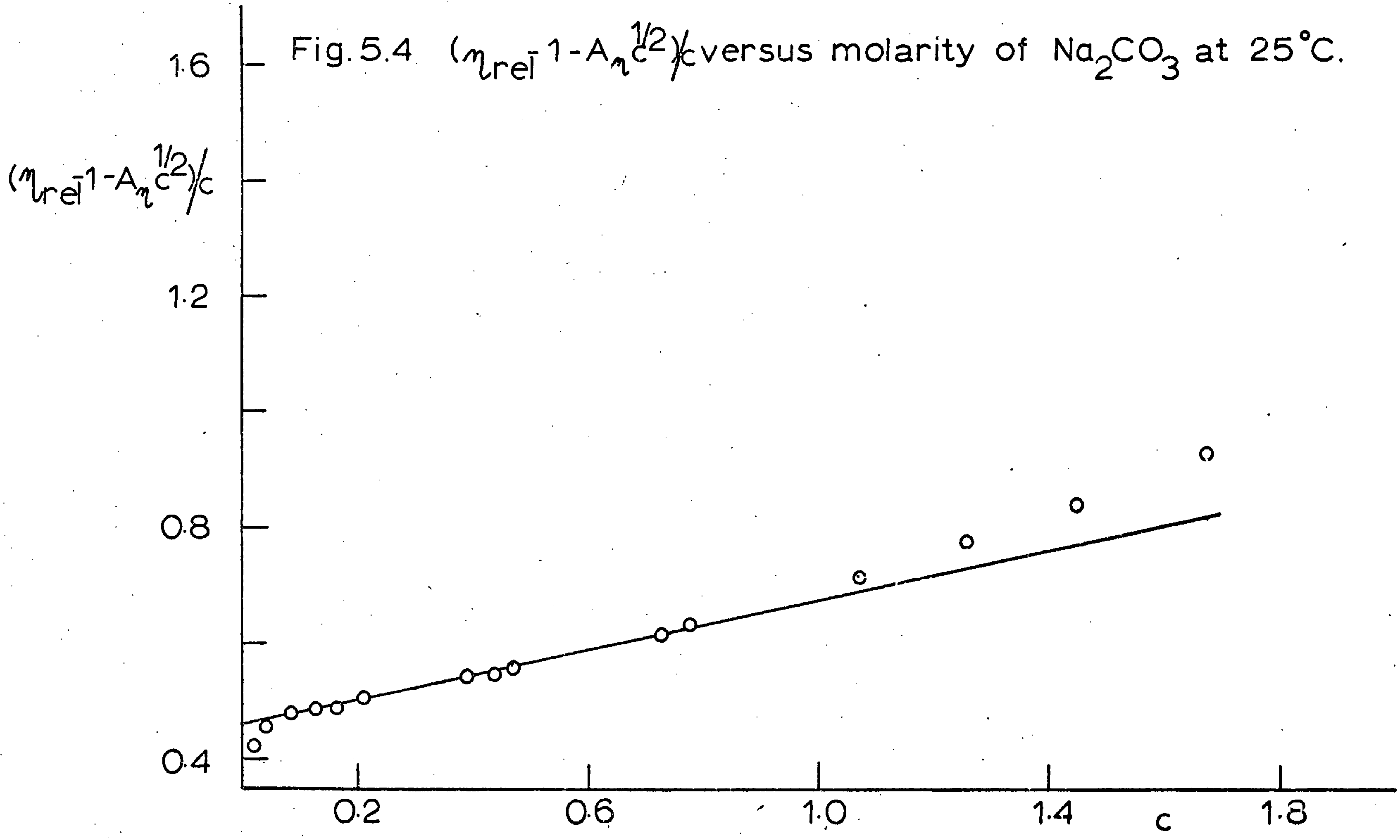


Fig. 5.4 $(\eta_{rel} - 1 - A_\eta c^{1/2})/c$ versus molarity of Na_2CO_3 at 25°C.

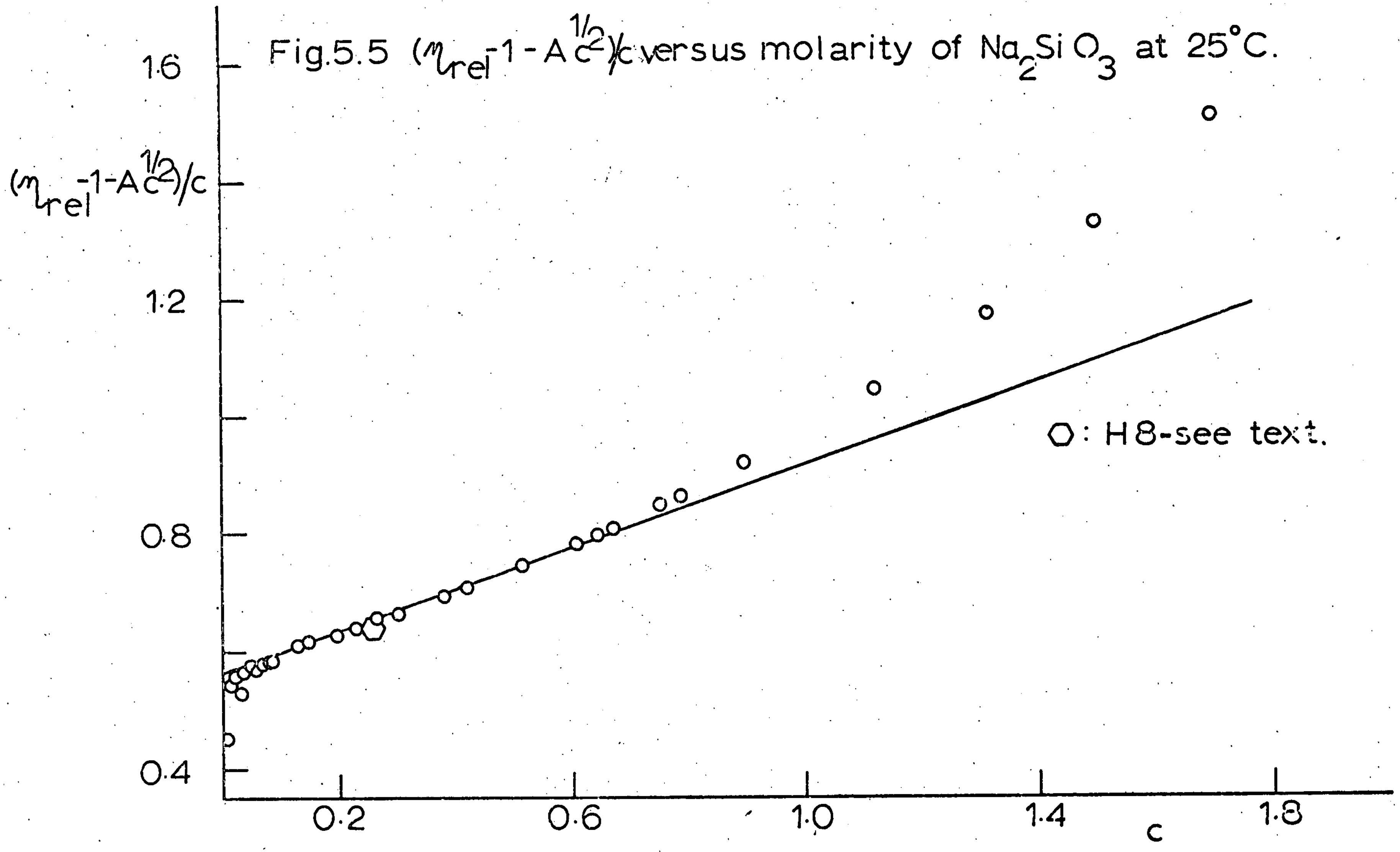


Fig.5.5 $(\eta_{rel}-1-Ac^{1/2})/c$ versus molarity of Na_2SiO_3 at 25°C.

and instead the intercept was obtained graphically, as shown, by drawing the inflection to the two curves. The main error in the function $(\eta_{rel} - 1 - Ac^{\frac{1}{2}})/c$ comes from the error in η_{rel} and may be estimated approximately, from the relationship,

$$\Delta f = \frac{\delta\eta_{rel}}{c} \qquad (5.19)$$

from which it is apparent that for a % error in η_{rel} of ± 0.035%, the actual uncertainty in the function is approximately 0.001 at 1M and 0.18 at 0.02M. Thus the values of B_η with their estimated errors are, for Na_2CO_3, 0.46 ± 0.03 dm^3 mol^{-1} and, for Na_2SiO_3, 0.56 ± 0.03 dm^3 mol^{-1}. An alternative method for estimating the difference between the $B\eta$ values is shown in figure 5.6 where values of η_{rel}/c and d for Na_2CO_3 and Na_2SiO_3 are compared. This figure demonstrates clearly that, for equimolar solutions, the density and relative viscosity are always significantly greater for solutions of Na_2SiO_3 than for Na_2CO_3. As expected, the difference in density is linear with concentration, whereas the values of $(\Delta\eta_{rel})/c$ fall on a curve and intersect the y-axis at 0.125 ± 0.015. Consideration of equation (5.16) shows that the intercept obtained from this plot is in fact $\Delta B\eta(Na_2SiO_3 - Na_2CO_3)$ which is in good agreement with the values obtained by the normal procedure. $(\Delta B\eta = (0.56 - 0.46) \pm 0.06)$.

As shown in figure 5.5, the viscosity result obtained for the solution of nonahydrate batch H8 lies close to the other results and in view of this, the error estimated in $B\eta$ Na_2SiO_3 is considered adequate.

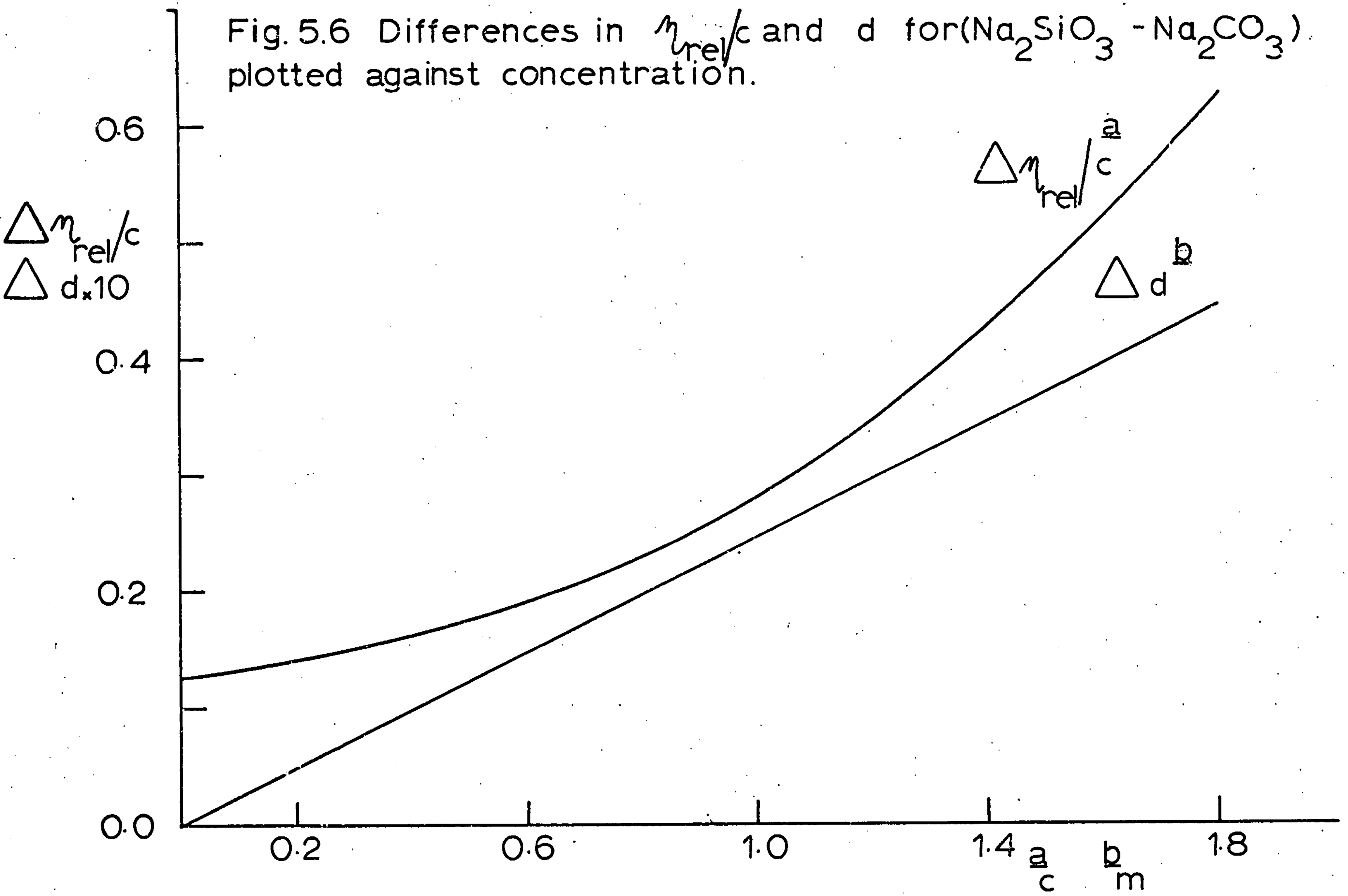


Fig. 5.6 Differences in η_{rel}/c and d for $(Na_2SiO_3 - Na_2CO_3)$ plotted against concentration.

5.4 DISCUSSION

The main results are summarised in table 5.4.

TABLE 5.4

Substance	ϕ_v^o /cm^{3}mol^{-1}	Bη/dm^3 mol^{-1}
Na_2CO_3	-5.8 ± 0.3, -6.13 [a]	0.46 ± 0.03, 0.522 [e]
CO_3^{2-} (aq)[b]	-3.4 ± 0.3, -3.7[a], -4.3[c]	
Na_2SiO_3	-17 ± 1.5, +1.1 ± 1.5[d]	0.56 ± 0.03
SiO_3^{2-} (aq)[b]	-14.6 ± 1.5, +3.4 ± 1.5[d]	

[a] Perron et. al. ref. 60 [b] Calculated taking ϕ_v^o Na^+ = -1.21

[c] Millero ref. 53 [d] Calculated assuming one molecule of water incorporated chemically in the anion - see text. [e] Estimated - see text.

5.41 DENSITY MEASUREMENTS

The value of ϕ_v^o calculated for sodium carbonate (-5.8) lies within experimental error of the value (-6.13) reported recently by Perron and Desnoyers[60] and is close to the mean of four other reports[64] (ϕ_v^o Na_2CO_3 = -6.04 ± 1.3 cm^3 mol^{-1}). No values have been reported for ϕ_v^o Na_2SiO_3. The apparent molal volumes of the silicate and carbonate ions at infinite dilution may be calculated using the conventional ϕ_v^o for Na^+ [53] (-1.21 cm^3 mol^{-1}) and gives ϕ_v^o CO_3^{2-} = -3.4 ± 0.3 and ϕ_v^o SiO_3^{2-} = -14.6 ± 1.5 cm^3 mol^{-1}. Consideration of published results for other dinegative ions[53] showed that the value for SiO_3^{2-} was significantly more negative than that of any comparable ion and suggested that an error had been made in the calculation. It became apparent that the analysis used had taken no account of the well established evidence[36,37,42] which suggests that the predominant silicate species in alkaline solution is not SiO_3^{2-} but is $(HO)_2SiO_2^{2-}$, formed by incorporation of one molecule of water per silicate group. This can be allowed for by use of equation (5.2) as follows;

$$\phi_V = (V - n_o\bar{V}_o)/n_s \qquad (5.2)$$

where the solution volume, V, is unaffected by the type of silicate ion postulated. If it is assumed that each mole of SiO_3^{2-} species incorporates one mole of water, then the actual number of moles of solvent left is $(n_o - n_s)$. Thus the values of ϕ_V^o calculated assuming the existence of SiO_3^{2-}; ϕ_V^o SiO_3^{2-}, or $(HO)_2SiO_2^{2-}$; ϕ_V^o $(HO)_2SiO_3^{2-}$, differ as follows,

$$\phi_V\ (HO)_2SiO_2^{2-} - \phi_V\ SiO_3^{2-} = [-(n_o - n_s)\ \bar{V}_o - (-n_o\bar{V}_o)]/n_s \qquad (5.20)$$

$$= n_s\bar{V}_o/n_s = \bar{V}_o$$

By the use of the molar volume of pure water ($\bar{V}_o$ = 18.1 $cm^3\ mol^{-1}$), ϕ_V^o may be obtained for $Na_2(HO)_2SiO_2$ (+1.1 ± 1.5 $cm^3\ mol^{-1}$) and for the silicate ion, ϕ_V^o = +3.4 ± 1.5 $cm^3\ mol^{-1}$, which is comparable with ϕ_V^o HPO_4^{2-} (= +7.7 $cm^3\ mol^{-1}$). The similarity of these values is significant and supports strongly the evidence from other work that the species SiO_3^{2-} does not exist in aqueous solution. The fact that ϕ_V^o $(HO)_2SiO_2^{2-}$ is small and near zero is in accord with a picture of aqueous silicate systems in which the ion does not possess a strong hydration shell as such, but is actually structurally integrated within the solvent through extensive hydrogen bonding.

5.42 VISCOSITY MEASUREMENTS

Values of $B\eta$ for solutions of sodium carbonate or of sodium metasilicate have not been reported previously. However, by use of published values[54] for KCl (-0.014), NaCl (0.079) and K_2CO_3 (0.336), $B\eta Na_2CO_3$ may be estimated $(0.336 + 2(0.079 - (-0.014)))$ to be 0.522 which is in fair agreement with the value (0.46 ± 0.03) obtained in this investigation.

In the case of sodium metasilicate it is impossible even to estimate a value for $B\eta$ from other results since no suitable data has hitherto been published. The value of $B\eta$ obtained in this study is greater than all other published results for simple sodium salts including the value for sodium carbonate. The most reliable estimate of the difference between $B\eta Na_2SiO_3$ and $B\eta Na_2CO_3$ is likely to be that obtained from figure 5.6 (0.125 ± 0.015 $dm^3\ mol^{-1}$).

For spherical particles which are large in relation to solvent particles, the Einstein equation gives a relationship between effective hydrodynamic volume V_h and the B - coefficient which may be expressed as,

$$2.5\ V_h = B\eta \qquad (5.21)$$

The difference between ϕ_v^o of Na_2SiO_3 and Na_2CO_3 is 6.8 ± 1.8 $cm^3\ mol^{-1}$ and, if this is considered approximately equal to the difference in effective hydrodynamic volume of the two solutes, then equation (5.21) gives the difference in $B\eta$ as 0.017 in comparision with the observed difference of 0.125 ± 0.015. Thus solutions of sodium metasilicate are more viscous than would be expected from their volumes alone. It seems likely that this may be attributed in part to the presence of small amounts of polysilicate species even in dilute metasilicate solutions. However, the fact that the viscosities of aqueous Na_2SiO_3 and Na_2CO_3 are nevertheless of comparable magnitude tends to support the evidence of other workers (eg Naumann and Debye[25,32]) that the polysilicate species present in metasilicate solutions have a low average molecular weight, corresponding to 3 or 4 (SiO_3) units.

CHAPTER 6

VAPOUR PRESSURES OF SODIUM METASILICATE AND SODIUM CARBONATE SOLUTIONS AT 25°C.

6.1 INTRODUCTION

There are two basic ways in which the chemical potentials of the components of an electrolyte solution may be determined. One may either measure the solvent activity and, by application of the Gibbs-Duhem equation (see 6.3.4), obtain the solute activity or vice versa. In general, solvent activity may be measured by vapour pressure and freezing/boiling point methods, whereas solute activity is commonly determined by solubility and by E.M.F. measurements.

In the work which is described here, the solvent activity has been obtained by measurement of solution vapour pressures by an indirect, comparative technique, known as the "isopiestic method".[65] This differs from direct vapour pressure methods in that it involves no manometric measurement, is less temperature sensitive and consequently is, at least in theory, capable of greater precision. The isopiestic method relies upon the principle that if two or more solutions of non volatile solutes are placed in a closed system, then solvent will distil from one solution to another until the vapour pressures of all the solutions are equal i.e. are isopiestic. By careful determination of the equilibrium solution compositions, sets of concentrations of different solutes in the same solvent which have the same vapour pressure, i.e. the same solvent activity, may be obtained. However, in order that these data may be used to give information about the actual solvent activities and, indirectly, the solute activities, it is necessary that solvent activities be known as a function of concentration for at least one of the solutes used - the reference electrolyte. Consideration of a simple example will show the main requirements of an apparatus designed to make isopiestic measurements.

Imagine two solutions A and B, both at the same temperature T, with different vapour pressures such that $P_A > P_B$. Provided that vapour can pass from one solution to the other, solvent will distil from A to B until the vapour pressures of the two solutions are equal. The transfer of solvent results in an increase in the concentration of solution A, and a dilution of solution B with associated changes in the solution temperatures such that $T_A < T_B$. It is well established that a reduction in temperature produces a reduction in the vapour pressure of a solution and vice versa. Thus, P_A is reduced not only by the loss of solvent and resultant increase in concentration but also by the reduction in temperature. The reverse applies to P_B and, as a result, it is possible to attain a false equilibrium situation unless steps are taken to ensure efficient thermal equilibration between solutions.

Many different approaches have been tried in isopiestic work[65,66] and the attainment of good thermal contact between solutions has been one of the main aims. Materials of high thermal conductivity have been used for the dishes containing the solutions as well as for the interconnecting medium which, in most cases, has been a relatively large mass of metal acting as a heat sink or thermal buffer. Rapid equilibration is enhanced if the system containing the solutions is evacuated to a pressure of the same magnitude as water vapour pressure since this permits solvent molecules to pass more freely between solutions. Agitation minimises thermal and concentration gradients within the solutions, and many complicated mechanisms[67] have been used for this. Several workers[68] have attempted to develop apparatus capable of covering the equilibrated solutions before they are removed from the closed system for measurement. The object of this is to minimise the effect of air currents on the solution compositions and it is in this area that the apparatus described here has its main advantages.

In this work, measurements were made of the vapour pressures of solutions of sodium chloride, sodium metasilicate and sodium carbonate in water at 25°C by the isopiestic method. Aqueous sodium chloride has been widely studied and acted as the reference electrolyte in these measurements. Solutions of sodium metasilicate and sodium carbonate have not previously been investigated by the isopiestic technique.

6.2 EXPERIMENTAL

6.2.1 MATERIALS

The sodium chloride and anhydrous sodium carbonate were Merck Suprapur grade. Both compounds were dried by heating to 120°C overnight and were subsequently stored in vacuo over fresh phosphorus pentachloride. Sodium metasilicate was purified as the nonahydrate by repeated recrystallisation from aqueous solution in the absence of carbon dioxide. It was carefully dried over sodium metasilicate pentahydrate until it contained nine moles of water per mole of metasilicate and was stored in a sealed bottle. Full details of the purification and analysis of sodium metasilicate are given in chapter 2. $Na_2SiO_3.9H_2O$ batch H8 (see table 2.1) was used throughout as a source of pure sodium metasilicate and analysis by ignition at 1000°C gave the % H_2O by weight as 56.97 ± 0.03% (pure nonahydrate = 57.049%). All solutions were prepared with water freshly distilled from glass apparatus.

6.2.2 EQUIPMENT

A general view of the experimental arrangement is shown in plate

6.1. Each isopiestic apparatus consisted of a metal block in which eight circular recesses were machined. The experimental solutions were contained in covered metal dishes made from 0.2 mm sheet, which fitted closely into the recesses in the block as shown in plate 6.2. The block and dishes were placed in a 6", type 4, Jencons "Dry-Seal" desiccator which had been modified to allow a lid carrier to be operated from outside of the apparatus. The lid carrier was a perspex disc with recesses to hold the lids, attached to a stainless steel rod which passed through a Quickfit screw-thread joint type SQ18 in the desiccator top. Approximate dimensions of the apparatus are given in figure 6.1.

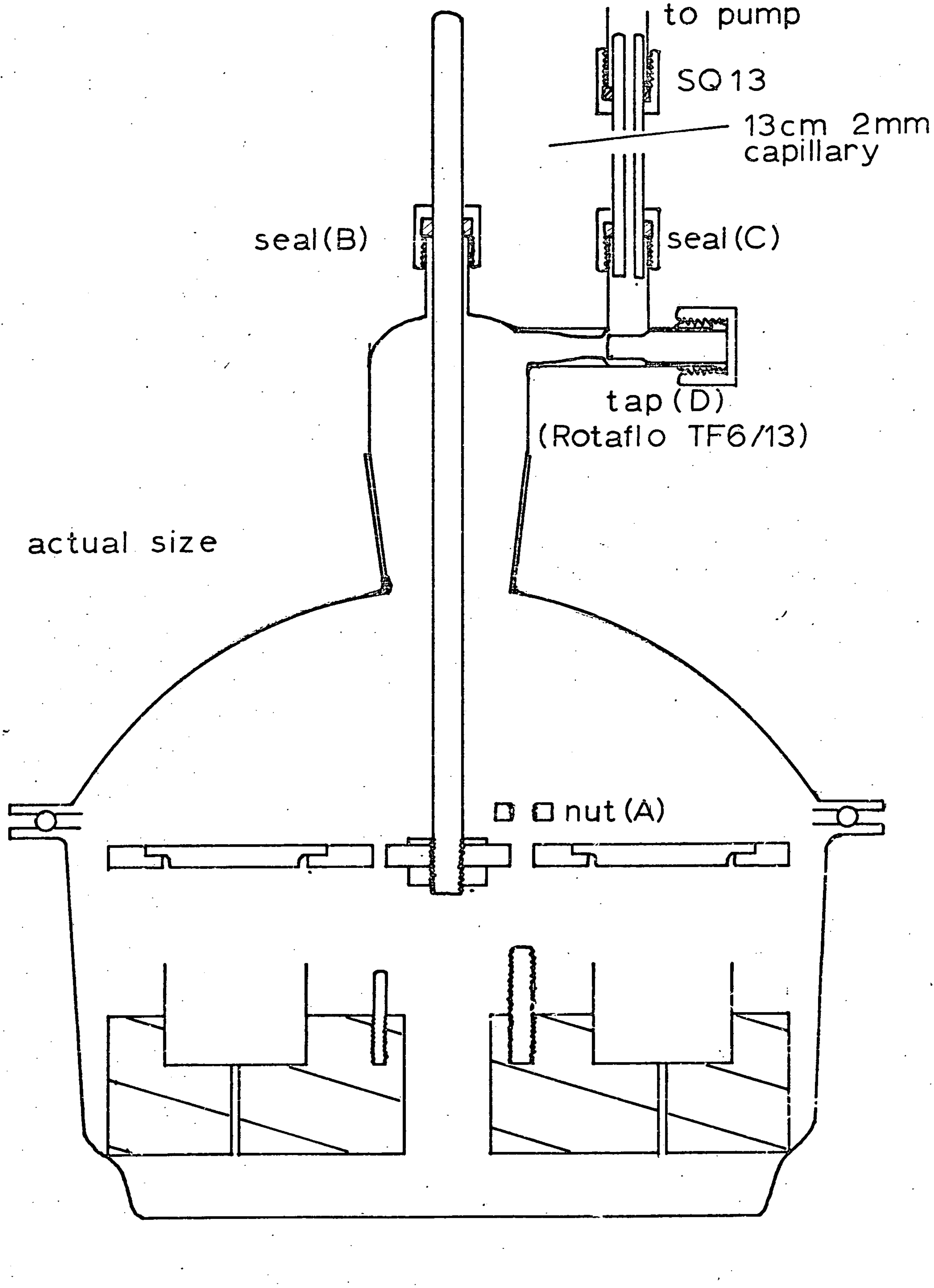
Blocks made from duraluminium, stainless steel and gold-plated copper were all found to give satisfactory equilibration but only stainless steel and copper were used in the work since duraluminium was easily corroded. Dishes pressed from stainless steel sheet were used with the steel blocks and gold-plated silver dishes (Johnson and Matthey Ltd.) were used with the copper ones. Loose-fitting lids of stainless steel and of Teflon were used with the stainless steel and silver dishes respectively. During early measurements, the stainless steel dishes were badly corroded by the solutions of sodium chloride in particular, a tendency thought to be attributable to the annealing stage in their manufacture since the unworked steel sheet was not corroded. However, it was found that oxidation of the dish and lid surfaces by refluxing in concentrated nitric acid for a few days rendered them as inert as the original material. The total capacity of a dish was 9 cm^3 but, in practice, it was found that the use of 4.5 cm^3 solution was the safe maximum if spillage was to be avoided.

The complete apparatus could be evacuated by connection to a pumping system. The pump was an Edwards "Speedivac" type 2520D two-stage model,

PLATE 6.1 THE ISOPIESTIC EXPERIMENT - GENERAL ARRANGEMENT

PLATE 6.2 THE ISOPIESTIC EXPERIMENT - STAINLESS STEEL BLOCK WITH DISHES AND LIDS

Fig. 6.1 The isopiestic apparatus.



and the rate of pumping was reduced to an acceptable level by the use of a 13 cm length of 1 mm internal diameter glass tubing as the connecting link between the apparatus and the pumping system. During the experiment, the apparatus was located on a submerged teak turntable which rotated at an angle of 5° from the horizontal, 15 times per minute, in a thermostatted water bath as shown in plate 6.1. The turntable was driven by a shaft which passed through the base of the water bath from an electric motor fitted with a reduction gear. In practice, it was found to be very difficult to devise a reliable system of seals and bearings for the point where the turntable shaft entered the water bath. Although this problem was overcome by minor modification of the design described by Mallinson,[66] a subsequent mechanism involving a submerged rocking table is felt to be much superior. Two water baths were used and their temperatures were kept at $25 \pm 0.03^{\circ}C$ in one case by a conventional contact thermometer - relay system and in the other by a Fimonitor Temperature control (Fisons Ltd.). Both devices operated satisfactorily. Each bath was equipped with a mechanical stirrer but it was found that the movement of the turntables and desiccators provided sufficient agitation of the bath water.

Disposable plastic 2 cm^3 syringes were used for handling small volumes of solution and distilled water.

6.2.3 PROCEDURE

All dishes and lids were thoroughly washed in distilled water and were then dried in an oven at $120^{\circ}C$ except for the Teflon lids which were dried with Kleenex Medical Wipes. The lids and dishes were allowed to equilibrate at room temperature and humidity for at least one day before use. In most experiments, two dishes contained sodium chloride solution which acted as the reference electrolyte, three contained sodium metasilicate solution and three sodium carbonate solution. After the desired concentration range had been decided, calculation gave the concentrations of the three electrolytes which would be approximately isopiestic.

The solutions were prepared by one or other of two methods which differed in that either solid material or stock solution along with distilled water could be used. In either case, the dish and lid were initially weighed empty. The amount of material required to give approximately 2 cm^3 of a solution of desired concentration was then added to the dish, by syringe in the case of stock solution, and the dish, lid and contents were weighed. This procedure was repeated for all eight dishes which were then placed, carefully, in the recesses in the block. Freshly boiled, distilled water was then added by syringe to each dish to obtain the desired electrolyte concentrations. The use of warm, freshly-boiled water promoted rapid dissolution of solid electrolyte and, because it was relatively free of dissolved air, it avoided spattering which sometimes occurs on evacuation of the apparatus. Stock solutions were used initially to prepare solutions with concentrations less than 1.0 mol dm^{-3} since, in these cases, the weights of solid material required to prepare the desired volume (2 cm^3) were so small that the weighing error was excessive (> ± 0.15%). However, it was shown that this technique is, overall, superior to the use of solid material and could well have been applied to all the solutions prepared in this work. Because of the uncertainty in the water content of the sodium metasilicate nonahydrate used, the composition of sodium metasilicate stock solutions was determined from the weights of solvent and of solid material and checked by analysis of the solution by ignition at 1000°C as described in Chapter 2.

The block, complete with dishes, solutions, lids and lid carrier, was then located in the desiccator base and, when the retaining nut (A) had been removed, the desiccator top was placed in position. (Apparatus components are labelled in figure 6.1). The apparatus was connected to the pumping system through joint (C) and, with tap (D) closed, the pump was switched on. The lids were raised by means of the lid - carrier rod and joint (B) was then secured. When the pumping system had been evacuated, as shown on a manometer, tap (D) was opened and a downward force was applied to the desiccator top until the apparatus had sealed. Evacuation was continued until the pressure measured when the system was isolated from the pump was around 2 cm Hg. Tap (D) was then closed and the apparatus was detached from the pumping system. Connection (C) which was then exposed, was sealed with a small rubber bung to prevent water entering the tap body and the apparatus was firmly located on one of the turntables in the thermostat bath.

When the equilibration was thought to be complete, the apparatus was removed from the bath and the lids were lowered onto their dishes by slackening joint (B) slightly and lowering the lid-carrier rod. Excess water was sucked from the "o"-ring joint and air was let slowly into the apparatus by opening tap (D) with a tightly twisted paper tissue in place of the bung in C. The desiccator top was removed, nut (A) was replaced and the complete block assembly was lifted out of the desiccator base. All eight pots with lids and solutions were successively removed from the block with specially designed, plastic covered tongs, weighed and replaced in the block. This was carried out as quickly as possible and often, all weighings were completed within 3 minutes. The isopiestic concentrations of the different solutes were calculated by combination of the equilibrium weighing with the two previous measurements. The complete block was then replaced in the desiccator base and nut (A) was removed. By use of a plastic syringe, a small amount of freshly boiled water was placed in the bottom of the desiccator base and, after the desiccator top had been replaced, the evacuation and equilibration steps were carried out as before. This successive dilution technique worked very well and, with it, up to eight isopiestic equations were obtained for each experiment. It was found that a suitable amount of water to add each time was 10% of the total water in the apparatus. The time taken to reach equilibrium depends on the inverse of the solute concentration and on the extent to which concentrations differ from the equilibrium values. In this work, a satisfactory interval between measurements was found to be one week for concentrations greater than 1.0 molal and increasing to one month for concentrations around 0.1 molal.

6.3 RESULTS

6.3.1 INTRODUCTION

The water activity of any aqueous solution is related to the fugacities of the solution and of pure water but since, in most cases, the vapour pressures are low, fugacity may be considered equal to pressure and the relationship becomes

$$a_w = P/P_o \qquad (6.1)$$

where P and P_o are the vapour pressures of the solution and of pure water respectively. The water activity is related to a special function, the molal osmotic coefficient of the solution, ϕ, by the relationship;

$$\phi = -(1/\nu m\, M_w)\ln a_w \qquad (6.2)$$

where ν is the number of moles of ions formed when one mole of solute is dissolved, m is the solution molality i.e. moles of solute per kg pure solvent, and M_w is the kg formula weight of the solvent which, for water = 0.018015.

When a number of solutions attain isopiestic equilibrium, the water activity in each solution is the same and thus, considering solutions of two different solutes, A and B, the equilibrium may be expressed as follows, by use of equation (6.2),

$$a_w = e^{-(\phi_A \nu_A m_A M_w)} = e^{-(\phi_B \nu_B m_B M_w)}$$

from which it is apparent that,

$$\phi_A \nu_A m_A = \phi_B \nu_B m_B \qquad (6.3)$$

The isopiestic ratio R is defined by

$$R = (\nu_B m_B) / (\nu_A m_A) \qquad (6.4)$$

where solute B is the reference electrolyte and equation (6.3) thus becomes

$$\phi_A = R.\phi_{ref} \qquad (6.5)$$

This equation is the basis of the isopiestic technique since, provided the reference substance has well defined properties within the concentration range and at the temperature required, ϕ may be calculated for any other electrolyte by measurement of the concentrations of experimental and reference materials which are in isopiestic equilibrium. It is obvious that solutions of more than one experimental solute may be in equilibrium with the same reference solution concurrently.

6.3.2 CALCULATION OF RESULTS

In this work, all weights of solute and solvent (water) were corrected for buoyancy to the in vacuo values by use of the equation,

$$wt_{CORR} = wt(1.0/(1.0 - d_{air}/d_x)) \qquad (6.6)$$

where d_{air} was taken as 0.0012 gcm^{-3} and d_x was taken as 2.0 for solid electrolyte and d_x was taken as 0.997046 for pure water.

Solutions of pure sodium chloride were used as the reference electrolyte and, in all cases, the molality used for calculation of ϕ_{ref} was the mean of the molalities of two duplicate solutions. The equation used for calculation of ϕ_{ref} was as described by Hamer and Wu,[69]

$$\phi_{ref} = 1-2.302585 \left[\frac{|Z_+ \; Z_-| A}{(B^*)^3 m} \left((1-B^*m^{\frac{1}{2}}) - 4.60517 \log. (1+B^*m^{\frac{1}{2}}) - 1/(1+B^*m^{\frac{1}{2}}) \right) - \beta m/2 - \frac{2}{3} Cm^2 - \frac{3}{4} Dm^3 \right] \qquad (6.7)$$

where, for NaCl, $Z_+ \, Z_- = 1.0$, $A = 0.5108$, $B^* = 1.4495$, $\beta = 0.020442$, $C = 0.57927 \times 10^{-2}$, $D = -0.2886 \times 10^{-3}$. Measurements were made of the isopiestic concentrations of sodium chloride, sodium metasilicate and sodium carbonate in water at 25°C from saturation point to 0.1 molal sodium metasilicate. The isopiestic ratios of Na_2SiO_3 and of Na_2CO_3 with respect to the reference substance, NaCl, are shown in figure 6.2. The osmotic coefficient was computed for each experimental solution by use of equations (6.5) and (6.7) and the water activity in each set of solutions was calculated from equation (6.2) using ϕ_{ref} from equation (6.7). These results are given in table 6.1. Solutions of sodium metasilicate and sodium carbonate were prepared in duplicate in experiments S2 to I.P.8 and in triplicate in experiments I.P.9 to I.P.14 inclusive. The values quoted for molality and osmotic coefficient are in all cases the mean of the results obtained from repeat solutions.

6.3.3. SOLUBILITY OF SODIUM METASILICATE IN WATER AT 25°C

The solubility of pure sodium metasilicate in water at 25 ± 0.03°C was determined using pure nonahydrate batch H8 as shown in table 5.1.

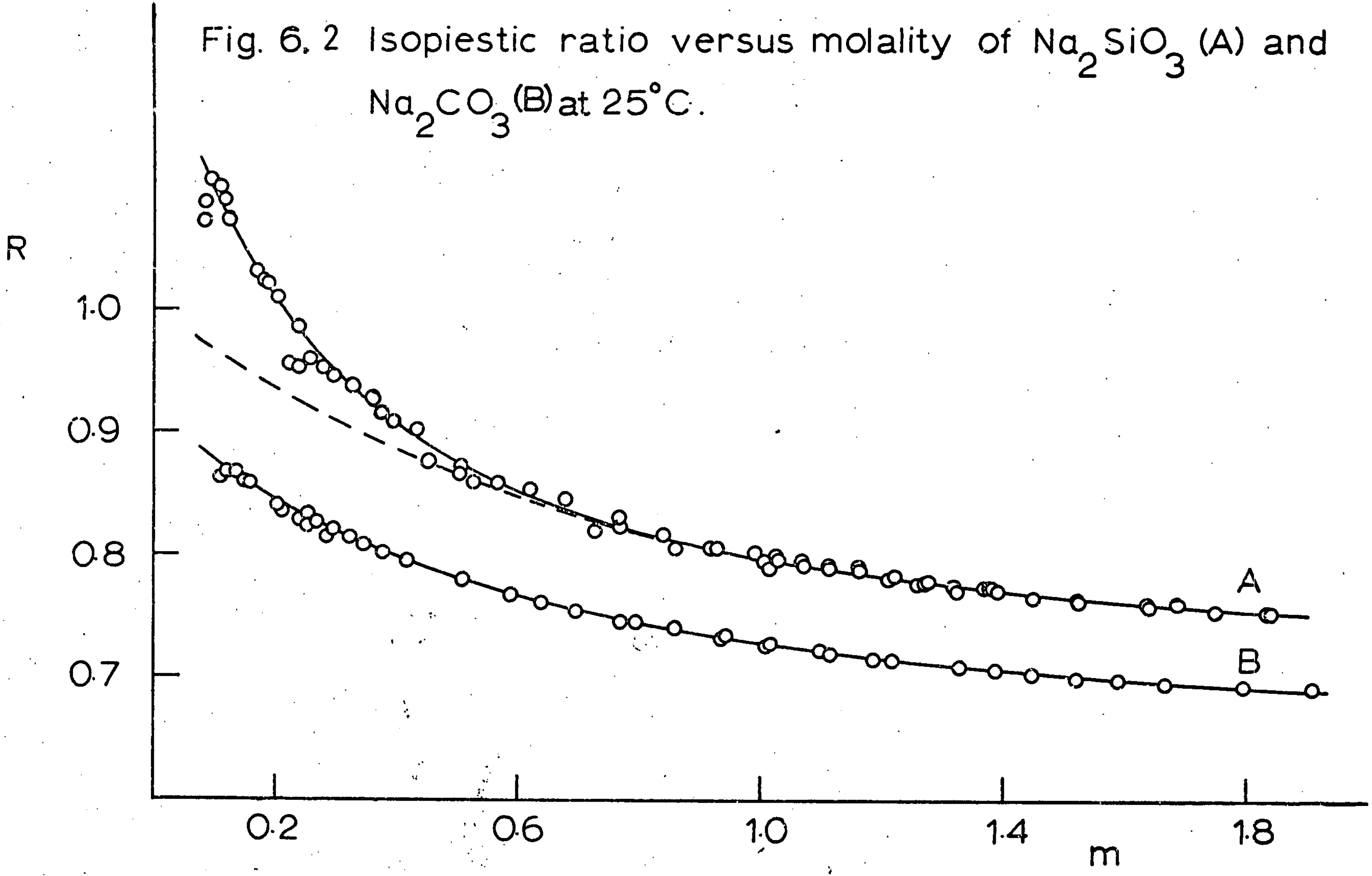


Fig. 6.2 Isopiestic ratio versus molality of Na_2SiO_3 (A) and Na_2CO_3 (B) at 25°C.

TABLE 6.1 WATER ACTIVITY, OSMOTIC COEFFICIENT AND MOLALITY OF SOME ISOPIESTIC SOLUTIONS.[a,b]

Experiment Number	m_{NaCl}	$m_{Na_2CO_3}$	$m_{Na_2SiO_3}$	$\phi_{Na_2CO_3}$	$\phi_{Na_2SiO_3}$	a_w
S2	2.0785		1.8415		0.7456	0.92867
	2.0784		1.8428		0.7450	0.92868
	2.0609		1.8264		0.7447	0.92932
	1.9210		1.6828		0.7453	0.93446
I.P.5	1.5822		1.3590		0.7463	0.94666
			1.3627		0.7443	
	1.5880		1.3656		0.7456	0.94645
			1.3688		0.7439	
	1.5338		1.3149		0.7459	0.94837
			1.3177		0.7442	
	1.4872		1.2710		0.7464	0.95002
			1.2738		0.7447	
	1.4247		1.2111		0.7481	0.95221
			1.2135		0.7466	
	1.3688		1.1522		0.7534	0.95417
			1.1586		0.7492	
	1.3150		1.1067		0.7500	0.95604
			1.1089		0.7515	
	1.2688		1.0630		0.7533	0.95764
			1.0642		0.7525	
	1.2265		1.0221		0.7558	0.95911
			1.0237		0.7546	
I.P.6	1.9787	1.9054	1.7427	0.6802	0.7437	0.93235
			1.7446		0.7429	
	1.8658	1.7909	1.6347	0.6781	0.7429	0.93647
			1.6364		0.7421	
	1.7397	1.6651	1.5174	0.6754	0.7411	0.94103
			1.5183		0.7407	
	1.6650	1.5899	1.4464	0.6746	0.7411	0.94372
			1.4468		0.7408	
	1.5985	1.5207	1.3834	0.6744	0.7413	0.94608
			1.3835		0.7411	
	1.5274	1.4479	1.3164	0.6743	0.7419	0.94860
			1.3159		0.7419	
	1.4677	1.3849	1.2613	0.6754	0.7416	0.95070
			1.2583		0.7433	
	1.4085	1.3240	1.2038	0.6757	0.7434	0.95278
			1.2025		0.7442	
I.P.7	1.2689	1.1803	1.0594	0.6785	0.7559	0.95764
			1.0615		0.7545	

TABLE 6.1 CONTINUED

Experiment Number	m_{NaCl}	$m_{Na_2CO_3}$	$m_{Na_2SiO_3}$	$\phi_{Na_2CO_3}$	$\phi_{Na_2SiO_3}$	a_w
I.P.7 (continued)	1.1846	1.0935	0.9834	0.6711	0.7573	0.96055
			0.9846		0.7564	
	1.1018	1.0107	0.9079	0.6829	0.7602	0.96339
			0.9084		0.7597	
	1.0319	0.9371	0.8405	0.6877	0.7665	0.96577
			0.8414		0.7659	
	0.9471	0.8525	0.7640	0.6920	0.7722	0.96862
			0.7648		0.7713	
I.P.8	0.7208	0.6217	0.5522	0.7142	0.8034	0.97629
			0.5592		0.7940	
	0.6569	0.5626	0.5050	0.7184	0.8045	0.97839
			0.5065		0.7981	
I.P.9^c	0.8585	0.7673	0.6778	0.6940	0.7857	0.97163
	0.7868	0.6955	0.6161	0.6999	0.7903	0.97403
	0.7254	0.6355	0.5631	0.7052	0.7955	0.97608
	0.6772	0.5875	0.5257	0.7109	0.7945	0.97768
	0.5905	0.5048	0.4500	0.7200	0.8078	0.98055
I.P.10	1.3061	1.2178	1.1016	0.6781	0.7496	0.95635
	1.2038	1.1127	1.0083	0.6807	0.7511	0.95989
	1.1121	1.0191	0.9247	0.6838	0.7536	0.96303
	1.0282	0.9330	0.8543	0.6881	0.7516	0.96590
	0.8873	0.7917	0.7233	0.6960	0.7618	0.97066
I.P.12	0.3487	0.2848	0.2362	0.7513	0.9055	0.98851
	0.3095	0.2503	0.2043	0.7591	0.9301	0.98979
	0.2891	0.2325	0.1889	0.7635	0.9395	0.99045
	0.2712	0.2163	0.1772	0.7693	0.9404	0.99104
	0.2538	0.2018	0.1647	0.7729	0.9481	0.99161
I.P.12B	0.4980	0.4165	0.3576	0.7344	0.8552	0.98361
	0.4574	0.3796	0.3252	0.7396	0.8634	0.98494
	0.4227	0.3481	0.2980	0.7450	0.8703	0.98608
	0.3932	0.3216	0.2757	0.7501	0.8750	0.98705
	0.3651	0.2967	0.2540	0.7550	0.8818	0.98797
	0.3324	0.2678	0.2333	0.7617	0.8742	0.98904
	0.3133	0.2514	0.2190	0.7650	0.8779	0.98966
I.P.14	0.1950	0.1520	0.1206	0.7906	0.9963	0.99353
	0.1877	0.1459	0.1148	0.7926	1.0075	0.99377

TABLE 6.1 CONTINUED

Experiment Number	m_{NaCl}	$m_{Na_2CO_3}$	$m_{Na_2SiO_3}$	$\phi_{Na_2CO_3}$	$\phi_{Na_2SiO_3}$	a_w
I.P.14 (continued)	0.1742	0.1348	0.1057	0.7967	1.0166	0.99421
	0.1623	0.1250	0.0981	0.8018	1.0208	0.99460
	0.1571	0.1207	0.0952	0.8037	1.0192	0.99477
	0.1498	0.1152	0.0923	0.8036	1.0030	0.99501

[a] In experiments S2 to I.P.8 inclusive, solutions were prepared from individually weighed amounts of solid electrolyte. Stock solutions were used during preparation of experiments I.P.9 to I.P.14 inclusive - see text.

[b] Purified $Na_2SiO_39H_2O$ batch H8 was used for all measurements on sodium metasilicate. Nonahydrate prepared independently, batch H7 was also used in experiments I.P.5, 6, 7 and 8, and results obtained by use of this material are shown as the second of the two values shown.

[c] Two stock solutions were prepared from $Na_2SiO_3.9H_2O$, batch H8. Solution 1 was used to prepare experiments I.P.9, 10 and 12 : solution 2 was used for experiments I.P.12B and I.P.14.

The method employed was to place two oversaturated and two undersaturated solutions of Na_2SiO_3 in the isopiestic apparatus. The initial water activity in the former is less than in the latter with the result that solvent distils from the undersaturated solution until saturation composition is reached. At saturation, the water activity is the same in the previously undersaturated solution as in the oversaturated solution with the result that distillation ceases. Initially, three weeks were allowed for equilibration before the solutions were measured. The apparatus was replaced in the bath and measured again one month later. It was found that the concentration of the undersaturated solution changed by only 0.06% over this period as shown in the first two measurements in table 6.1. Thus, the solubility of sodium metasilicate at $25^{\circ}C$ in water is estimated to be 1.843 ± 0.004 molal.

6.3.4 CALCULATION OF SOLUTE ACTIVITY COEFFICIENTS

Solute activity is related to solvent activity by the Gibbs-Duhem equation,

$$d \ln a_2 = \frac{x_1}{x_2} d \ln a_1 \qquad (6.8)$$

where a_2 and a_1 are the activities of solute and solvent respectively and x_2 and x_1 are the respective mole fractions. As described by Lietzke and Stoughton,[70] substitution of a semi-empirical equation for the variation of activity coefficient with concentration into the Gibbs-Duhem relationship followed by integration, gives rise to an equation for the osmotic coefficient containing the same parameters as in the original activity coefficient equation. Thus activity coefficient data may be used to calculate osmotic coefficients and vice versa. In this work, the experimentally obtained osmotic coefficients for solutions of sodium metasilicate and for sodium carbonate were fitted to the equation;

$$\phi = 1 - \frac{A|z_+z_-|}{B^3I}\left[(1+BI^{\frac{1}{2}}) - 2\ln(1+BI^{\frac{1}{2}}) - (1+BI^{\frac{1}{2}})^{-1}\right] \qquad (6.9)$$

$$+ Z_1I + Z_2I^2 + Z_3I^3$$

by a least squares procedure and values of mean solute activity coefficient $\gamma \pm$ were obtained from the corresponding expression,

$$\ln\gamma \pm = -A|z_+z_-|I^{\frac{1}{2}}/(1 + BI^{\frac{1}{2}}) + 2\,Z_1I + \frac{3}{2}Z_2I^2 + \frac{4}{3}Z_3I^3 \qquad (6.10)$$

In both equations (6.9) and (6.10), I is the ionic strength of the solution ($I = \frac{1}{2}\Sigma_i c_i z_i^2$) and A is the Debye-Hückel constant which was taken to be 1.17616. When fitting experimental ϕ data, A was kept fixed and parameters B, Z_1, Z_2 and Z_3 were variable. It was found that the relatively low maximum concentrations involved in this work ($\leq$ 1.9m) made the use of the cubic term in equations (6.9) and (6.10) unnecessary and, as a result, all fitting and subsequent calculation of $\gamma \pm$ was carried out using parameters A, B, Z_1 and Z_2 only.

The accuracy of activity coefficients calculated in this manner is largely dependent on the spread of experimental ϕ values since the uncertainty in the parameters of the ϕ - m relationship (equation (6.9)) will be reflected in the uncertainty in $\gamma \pm$ calculated from equation (6.10).

6.3.5 REPRODUCIBILITY AND ESTIMATED ERRORS

No significant difference was observed between results obtained from stainless steel or gold-plated silver dishes whether using Teflon or stainless steel lids. As discussed in section 6.2.3, the weighing errors incurred during preparation of experimental solutions by direct weighing of solid electrolyte into the sample dishes became unacceptable for solutions < 1 molal and consequently, the more dilute solutions investigated were prepared by use of concentrated stock solutions - see footnotes [a] and [c], table 6.1. The agreement between equilibrium molalities of duplicate solutions was better at high solute molalities than at low molalities as summarised in table 6.2 and ranged from ± 0.02% at 1.5m to ± 0.3% at 0.1 molal. The accuracy of the isopiestic molalities calculated depends, however, not only on the agreement between duplicates but on the reliability of the composition of the source material used whether solid electrolyte or stock solution. In the case of sodium chloride and sodium carbonate, material of high purity was readily available and, by the use of stock solutions for preparation of the lower concentrations, the overall reliability of the isopiestic molalities measured is estimated to be better than twice the difference between duplicates ie ± 0.1% at 1.0m. However, in the case of sodium metasilicate, pure material of accurate composition is difficult to prepare and to analyse as is discussed in chapter 2. It is estimated that the water content of the nonahydrate used in all experiments, batch H8, was accurate to better than ± 0.1% overall. This introduces an additional error in the molalities of Na_2SiO_3 and amounts to ± 0.2% at saturation but decreases to ± 0.07% at one molal. However, as with the other solutions investigated, general experimental error is a function of the inverse of concentration. An estimation of the maximum effect of these errors on molality, isopiestic ratio and osmotic coefficient is given in table 6.2.

The water activities shown in table 6.1 are dependent only on the reliability of the reference data and are estimated to be accurate to better than 0.08% overall.

As shown in table 6.1, the results obtained from two independently prepared samples of pure Na_2SiO_3 $9H_2O$, batches H7 and H8 agree within

TABLE 6.2 ESTIMATES OF THE RELIABILITY OF OBSERVED ISOPIESTIC MOLALITIES AND DERIVED PARAMETERS /%±

m	1.5	1.0	0.1
Agreement between duplicate solutions.	0.02	0.05	0.3
Error in true concentration	0.02,[a] 0.2[b]	0.05,[a] 0.07[b]	0.3,[a] 0.68[b]
Total error in isopiestic molality.	0.04, 0.22	0.1, 0.12	0.6, 0.98
Uncertainty in R(dR)	0.08, 0.26	0.2, 0.22	1.2, 1.58
Uncertainty in ϕ[c] (= ϕ.dR)	0.00064, 0.00192	0.0016, 0.0016	0.0096, 0.015

[a] NaCl and Na_2CO_3; [b] Na_2SiO_3; [c] Note that the estimated uncertainty in ϕ is not a % error.

the estimated error inherent in these measurements. However, it should be noted that the systematically higher molalities obtained for solutions of H7 cannot be explained by a small difference in water content of the materials since H7 was observed to be, if anything, slightly drier than H8. As detailed in table 2.1, the preparation of H8 involved extremely careful purification under CO_2 - free conditions and it is possible that a very low level of contaminant was present in the H7 which was used.

6.4 DISCUSSION

6.4.1 SODIUM CARBONATE

As shown in table 6.3 and in figure 6.3, the experimentally observed osmotic coefficients for solutions of sodium carbonate lie on a smooth curve when ϕ is plotted against molality, m. Using the values of B, Z_1 and Z_2 from a least-squares fitting of the results to equation (6.9), values of $\phi, \gamma \pm$ and of a_w were calculated at rounded concentrations and are shown in table 6.4. The variation of solute activity coefficient with molality is shown in figure 6.4. Since this work was carried out, osmotic coefficients and activity coefficients for aqueous solutions of sodium carbonate at 25°C obtained by isopiestic methods have been reported by Khvorostin et. al.[71] and these are shown for comparison in figures 6.3 and 6.4 along with the activity coefficients of C. E. Taylor[72] obtained by E.M.F. measurements.

Comparison of the osmotic coefficients obtained in this work with those of Khvorostin[71] shows that agreement within the concentration range 0.1 to 2 molal is good apart from in the region of 0.5 m where a maximum difference of about 2% occurs. Assuming an uncertainty in the results of Khvorostin[71] similar to that estimated in those described here, both sets of values agree within experimental error. The activity coefficients of Khvorostin[71] agree with those obtained in the present work to within 4% over the concentration range investigated and although those of Taylor[72] agree well at concentrations up to 0.6m, they diverge at higher concentrations. It is possible that the E.M.F. technique employed by Taylor[72] may be responsible for this effect.

6.4.2 SODIUM METASILICATE

The osmotic coefficients obtained for sodium metasilicate are

TABLE 6.3 OSMOTIC COEFFICIENTS (EXPERIMENTAL AND OBTAINED BY LEAST-SQUARES CURVE FIT) AND ACTIVITY COEFFICIENTS FOR Na_2CO_3 IN WATER AT 25°C

m	ϕ	$\phi_{C.F.}$ [a]	$\gamma_\pm$ [b]
1.9054	0.6802	0.6864	0.1891
1.9053	0.6802	0.6864	0.1891
1.7910	0.6781	0.6805	0.1917
1.7908	0.6781	0.6805	0.1917
1.6650	0.6754	0.6759	0.1954
1.6652	0.6753	0.6759	0.1954
1.5891	0.6745	0.6740	0.1980
1.5889	0.6746	0.6740	0.1980
1.5205	0.6745	0.6729	0.2006
1.5212	0.6742	0.6729	0.2006
1.4478	0.6743	0.6724	0.2038
1.4481	0.6742	0.6724	0.2038
1.3829	0.6764	0.6724	0.2060
1.3870	0.6744	0.6724	0.2067
1.3238	0.6760	0.6729	0.2100
1.3248	0.6755	0.6729	0.2099
1.2175	0.6782	0.6748	0.2162
1.2180	0.6780	0.6748	0.2161
1.2178	0.6781	0.6748	0.2162
1.1807	0.6783	0.6758	0.2186
1.1800	0.6787	0.6758	0.2186
1.1123	0.6810	0.6781	0.2233
1.1129	0.6806	0.6780	0.2233
1.1129	0.6806	0.6780	0.2233
1.0939	0.6808	0.6788	0.2247
1.0930	0.6813	0.6788	0.2247
1.0234	0.6805	0.6819	0.2302
1.0168	0.6849	0.6822	0.2308
1.0197	0.6841	0.6821	0.2306
1.0197	0.6835	0.6820	0.2305
1.0191	0.6839	0.6821	0.2306
1.0111	0.6826	0.6825	0.2313
1.0103	0.6831	0.6825	0.2313
0.9375	0.6875	0.6864	0.2378
0.9368	0.6880	0.6865	0.2378
0.9329	0.6882	0.6867	0.2382
0.9333	0.6879	0.6867	0.2382
0.9328	0.6883	0.6867	0.2382
0.8528	0.6918	0.6919	0.2402
0.8522	0.6923	0.6919	0.2463
0.7916	0.6961	0.6964	0.2530
0.7918	0.6959	0.6963	0.2530
0.7917	0.6960	0.6964	0.2530

TABLE 6.3 CONTINUED

m	ϕ	$\phi_{C.F.}$[a]	$\gamma_{\pm}$[b]
0.7675	0.6939	0.6983	0.2559
0.7676	0.6938	0.6983	0.2559
0.7669	0.6944	0.6983	0.2560
0.6957	0.6998	0.7044	0.2651
0.6957	0.6998	0.7044	0.2651
0.6953	0.7003	0.7004	0.2652
0.6354	0.7050	0.7101	0.2738
0.6354	0.7050	0.7101	0.2738
0.6349	0.7056	0.7102	0.2739
0.6213	0.7146	0.7115	0.2760
0.6221	0.7137	0.7115	0.2759
0.5874	0.7111	0.7151	0.2815
0.5875	0.7109	0.7151	0.2814
0.5876	0.7108	0.7150	0.2814
0.5625	0.7186	0.7178	0.2857
0.5628	0.7182	0.7177	0.2856
0.5050	0.7198	0.7244	0.2964
0.5049	0.7200	0.7244	0.2964
0.5047	0.7202	0.7245	0.2964
0.4164	0.7345	0.7359	0.3158
0.4163	0.7347	0.7359	0.3159
0.4166	0.7341	0.7359	0.3158
0.3797	0.7393	0.7412	0.3253
0.3794	0.7400	0.7412	0.3253
0.3797	0.7393	0.7412	0.3253
0.3478	0.7456	0.7461	0.3343
0.3480	0.7451	0.7461	0.3342
0.3485	0.7441	0.7460	0.3341
0.3216	0.7500	0.7504	0.3424
0.3214	0.7506	0.7504	0.3425
0.3218	0.7496	0.7503	0.3423
0.2967	0.7547	0.7547	0.3508
0.2963	0.7558	0.7547	0.3509
0.2969	0.7544	0.7546	0.3508
0.2850	0.7505	0.7568	0.3550
0.2845	0.7520	0.7569	0.3552
0.2682	0.7604	0.7599	0.3614
0.2674	0.7629	0.7601	0.3617
0.2678	0.7616	0.7600	0.3616
0.2509	0.7664	0.7633	0.3685
0.2515	0.7645	0.7632	0.3682
0.2516	0.7642	0.7632	0.3681
0.2503	0.7588	0.7634	0.3687
0.2501	0.7594	0.7635	0.3688
0.2526	0.7632	0.7671	0.3765
0.2324	0.7638	0.7671	0.3766

TABLE 6.3 CONTINUED

m	ϕ	$\phi_{C.F.}$[a]	$\gamma_{\pm}$[b]
0.2163	0.7700	0.7707	0.3842
0.2167	0.7686	0.7706	0.3840
0.2019	0.7723	0.7740	0.3916
0.2016	0.7735	0.7741	0.3918
0.1531	0.7848	0.7870	0.4216
0.1516	0.7926	0.7875	0.4227
0.1512	0.7944	0.7876	0.4229
0.1462	0.7909	0.7891	0.4266
0.1458	0.7930	0.7893	0.4269
0.1457	0.7939	0.7893	0.4270
0.1349	0.7965	0.7928	0.4355
0.1348	0.7967	0.7928	0.4355
0.1348	0.7969	0.7928	0.4355
0.1250	0.8017	0.7963	0.4439
0.1250	0.8015	0.7963	0.4438
0.1249	0.8021	0.7963	0.4439
0.1207	0.8038	0.7979	0.4477
0.1207	0.8034	0.7978	0.4477
0.1207	0.8039	0.7979	0.4477
0.1153	0.8032	0.7999	0.4528
0.1153	0.8029	0.7999	0.4528
0.1151	0.8047	0.8000	0.4530

[a,b] Calculated using equations (6.8) and (6.9) respectively,

with $B = 1.4412$ $Z_1 = -0.064739$ and $Z_2 = 0.006931$

$\sigma = 0.32586 \times 10^{-2}$

Fig. 6.3 Osmotic coefficient versus molality of Na_2CO_3 at 25°C.

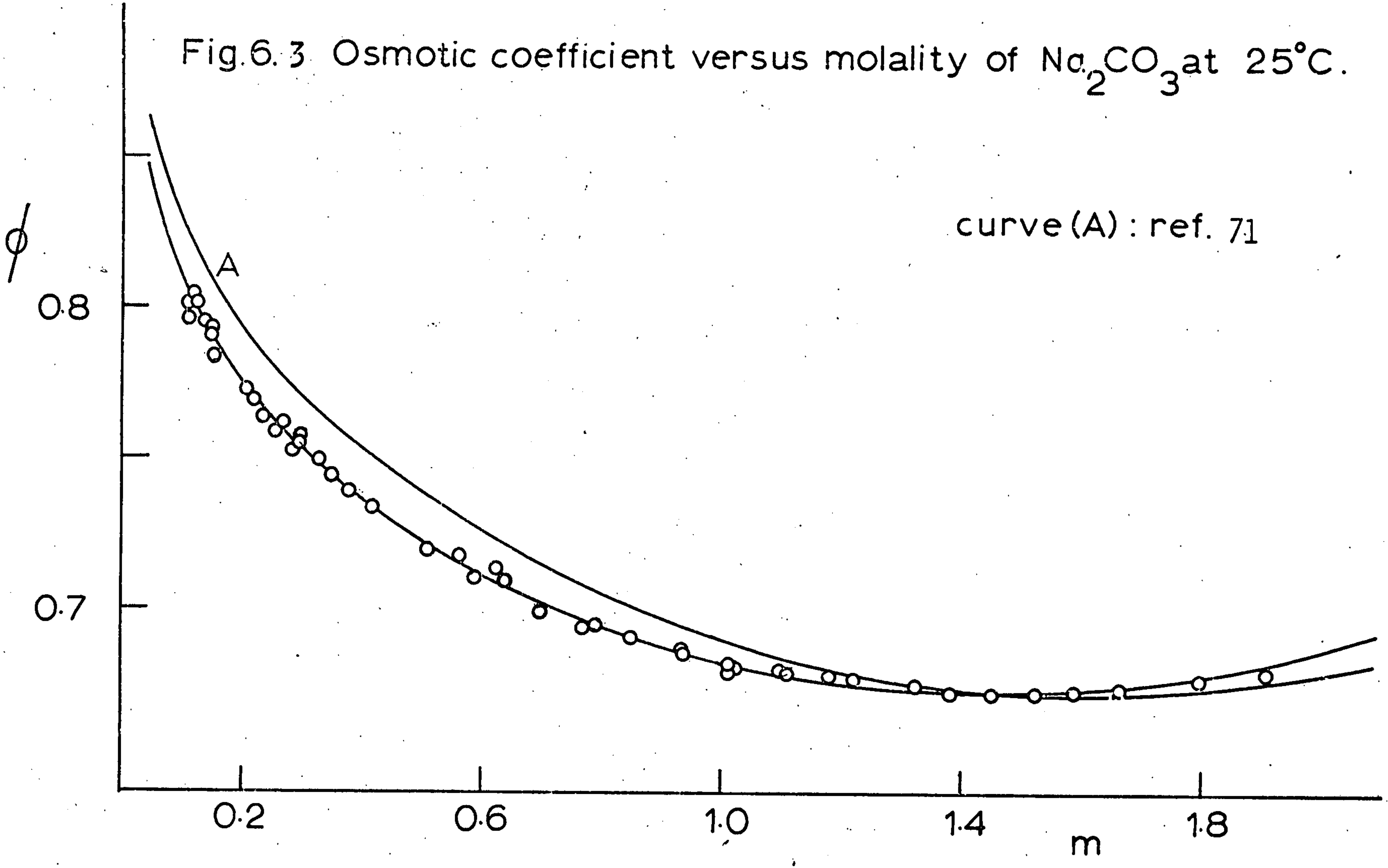


TABLE 6.4 OSMOTIC COEFFICIENT, ACTIVITY COEFFICIENT AND WATER ACTIVITY CALCULATED[a] AT ROUNDED CONCENTRATIONS COMPARED WITH RESULTS OF OTHER WORKERS :- SODIUM CARBONATE IN WATER AT 25°C.

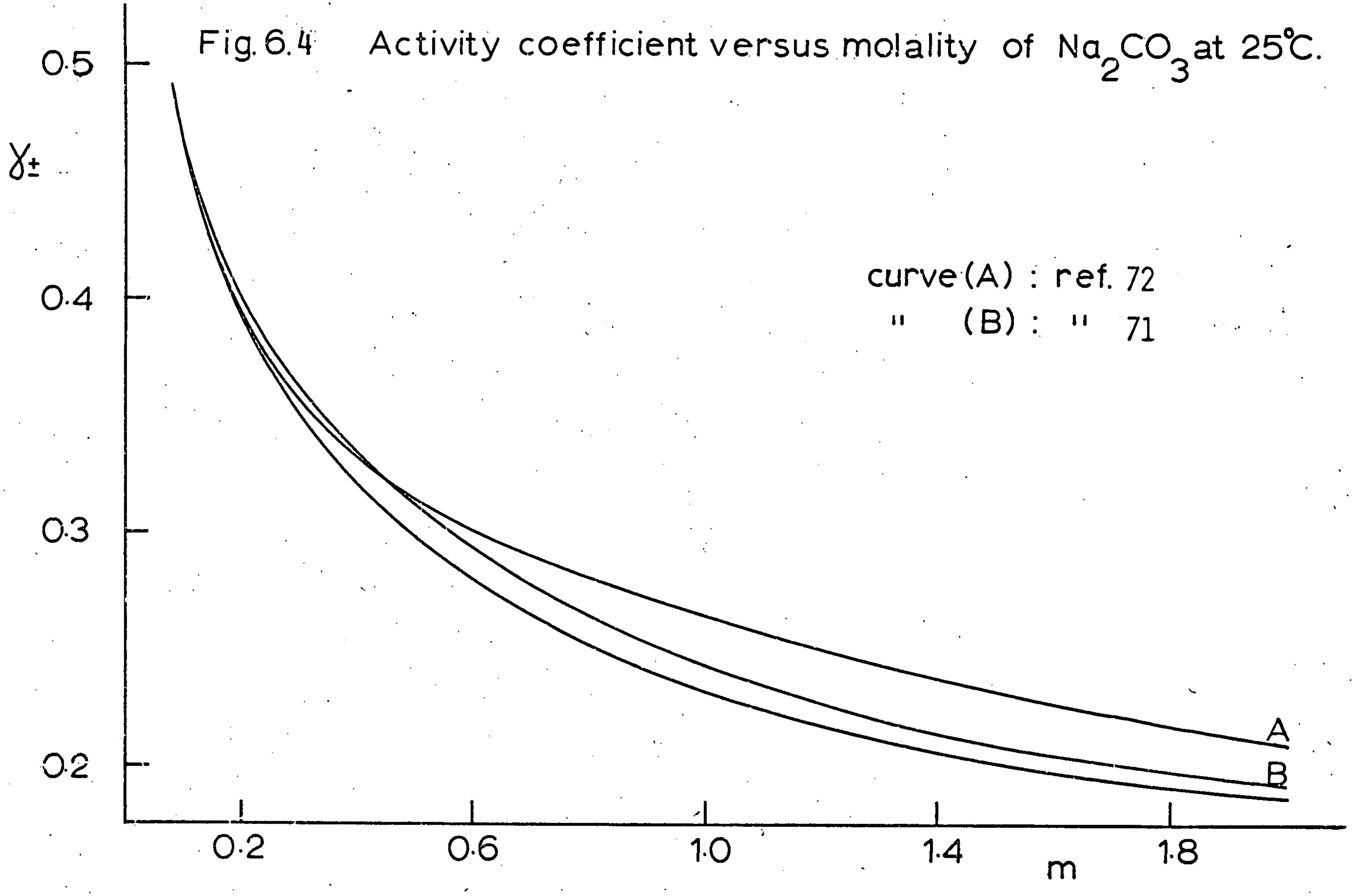
m	ϕ	ϕ Other Workers	$\gamma\pm$	$\gamma\pm$ Other Workers		a_w
0.1	0.8063	0.825[b]	0.4686	0.469[b]	0.466[c]	0.99565
0.2	0.7745	0.789	0.3926	0.405	0.394	0.99166
0.3	0.7541	0.770	0.3497	0.364	0.356	0.98785
0.4	0.7382	0.754	0.3199	0.334	0.332	0.98417
0.5	0.7250	0.740	0.2974	0.312	0.313	0.98060
0.6	0.7137	0.726	0.2794	0.293	0.301	0.97712
0.7	0.7040	0.714	0.2645	0.277	0.290	0.97372
0.8	0.6957	0.705	0.2520	0.264	0.281	0.97037
0.9	0.6887	0.698	0.2414	0.253	0.272	0.96706
1.0	0.6830	0.691	0.2322	0.243	0.264	0.96376
1.1	0.6785		0.2242			0.96047
1.2	0.6753	0.681	0.2173	0.228	0.250	0.95715
1.3	0.6732		0.2113			0.95380
1.4	0.6724	0.675	0.2060	0.215	0.238	0.95040
1.5	0.6727		0.2015			0.94693
1.6	0.6742	0.673	0.1976	0.205	0.227	0.94337
1.7	0.6770		0.1943			0.93970
1.8	0.6809	0.676	0.1915	0.198		0.93591
1.9	0.6861		0.1892			0.93198
2.0	0.6924	0.680	0.1874	0.192		0.92789

[a] Calculated from equations (6.8), (6.9) and (6.2). Parameters used in equations (6.8) and (6.9) were B = 1.4412, Z_1 = -0.064739, Z_2 = 0.006931

[b] ref 71 (Khvorostin et. al.)

[c] ref 72 (C. E. Taylor)

Fig. 6.4 Activity coefficient versus molality of Na_2CO_3 at 25°C.



shown in table 6.5 and are plotted against molality in figure 6.5. The initial impression is that the experimental points do not lie on a smooth curve like those of sodium carbonate (figure 6.3) particularly at concentrations less than 0.75 m. The values obtained at low concentrations seem too large and, at 0.1 m, $\phi > 1.0$, a value which one would expect to be attained only on extrapolation of values to infinite dilution. In addition, the osmotic coefficients obtained from successive measurements of the same set of solutions (see section 6.2.3) fall increasingly below the experimental curve, an effect particularly apparent with those solutions of lower concentration. Attempts to fit these results to equation (6.9) were, as expected, unsuccessful. However, by disregarding those results for concentrations < 0.75 m, and some rather suspect values from experiment I.P.10, a suitable agreement between calculated and experimental values was obtained as shown in table 6.5 and figure 6.5. Values of ϕ and $\gamma\pm$ calculated at rounded molalities by use of B, Z_1 and Z_2 from the curve-fit procedure are shown, along with values of the water activity, in table 6.6. However, since the curve-fit procedure was based only on points from concentrations 0.75 to 1.85 molal, the only use of values calculated out with this range is for comparison with the actual experimental values as shown in figure 6.5. Since the curve-fit is based only on this relatively narrow range of concentrations and on points which show some spread, the uncertainty associated with activity coefficients calculated from equation (6.10) is relatively large. By consideration of all the possible fitted curves it is estimated that, within the range 0.75 to 1.85 m, the values of ϕ and $\gamma\pm$ calculated at rounded concentrations and shown in table 6.6 are accurate to better than ± 0.3% and ± 5% respectively.

The only activity coefficient data available for solutions of

TABLE 6.5 OSMOTIC COEFFICIENTS (EXPERIMENTAL AND OBTAINED BY A LEAST-SQUARES CURVE FIT^a) AND ACTIVITY COEFFICIENTS FOR Na_2SiO_3 IN WATER AT 25°C.

Experiment Number	m	ϕ	$\phi_{C.F.}$ [b]	$\gamma\pm$ [b]
S2	1.8414	0.7457	0.7459	0.2614
	1.8416	0.7455	0.7459	0.2614
	1.8426	0.7451	0.7459	0.2614
	1.8430	0.7450	0.7459	0.2614
	1.8265	0.7446	0.7455	0.2618
	1.8262	0.7447	0.7455	0.2619
	1.6821	0.7456	0.7425	0.2664
	1.6834	0.7450	0.7425	0.2664
I.P.5	1.3626	0.7444	0.7429	0.2815
	1.3629	0.7442	0.7429	0.2814
	1.3593	0.7462	0.7430	0.2817
	1.3588	0.7464	0.7430	0.2817
	1.3687	0.7440	0.7428	0.2811
	1.3691	0.7438	0.7428	0.2811
	1.3658	0.7456	0.7429	0.2813
	1.3654	0.7458	0.7429	0.2813
	1.3174	0.7445	0.7438	0.2842
	1.3182	0.7440	0.7438	0.2841
	1.3149	0.7459	0.7439	0.2843
	1.3149	0.7459	0.7439	0.2843
	1.2734	0.7450	0.7449	0.2869
	1.2743	0.7445	0.7448	0.2869
	1.2712	0.7463	0.7449	0.2871
	1.2710	0.7464	0.7449	0.2871
	1.2131	0.7468	0.7466	0.2910
	1.2139	0.7463	0.7466	0.2909
	1.2112	0.7480	0.7466	0.2911
	1.2110	0.7481	0.7466	0.2911
	1.1577	0.7496	0.7485	0.2950
	1.1596	0.7486	0.7484	0.2949
	1.1529	0.7529	0.7487	0.2954
	1.1515	0.7539	0.7487	0.2955
	1.1086	0.7503	0.7504	0.2988
	1.1093	0.7498	0.7504	0.2988
	1.1069	0.7514	0.7505	0.2989
	1.1066	0.7517	0.7505	0.2990
	1.0636	0.7529	0.7524	0.3025
	1.0649	0.7520	0.7523	0.3024
	1.0632	0.7532	0.7524	0.3025
	1.0630	0.7534	0.7524	0.3025
	1.0235	0.7548	0.7543	0.3060
	1.0240	0.7545	0.7542	0.3059
	1.0224	0.7556	0.7543	0.3061
	1.0219	0.7560	0.7543	0.3061

TABLE 6.5 CONTINUED

Experiment Number	m	ϕ	$\phi_{C.F.}^{b}$	$\gamma_{\pm}^{b}$
I.P.6	1.7449	0.7428	0.7436	0.2642
	1.7444	0.7430	0.7436	0.2643
	1.7429	0.7436	0.7435	0.2643
	1.7425	0.7438	0.7435	0.2643
	1.6364	0.7421	0.7419	0.2682
	1.6364	0.7422	0.7419	0.2682
	1.6348	0.7429	0.7419	0.2683
	1.6347	0.7429	0.7419	0.2683
	1.5180	0.7408	0.7415	0.2733
	1.5186	0.7405	0.7415	0.2733
	1.5176	0.7410	0.7415	0.2733
	1.5171	0.7412	0.7415	0.2734
	1.4465	0.7410	0.7419	0.2769
	1.4473	0.7406	0.7418	0.2768
	1.4466	0.7410	0.7419	0.2769
	1.4462	0.7412	0.7419	0.2769
	1.3830	0.7415	0.7426	0.2803
	1.3839	0.7410	0.7426	0.2802
	1.3838	0.7411	0.7426	0.2803
	1.3832	0.7415	0.7426	0.2803
	1.3150	0.7424	0.7439	0.2843
	1.3168	0.7415	0.7438	0.2842
	1.3165	0.7416	0.7438	0.2842
	1.3154	0.7422	0.7439	0.2843
	1.2569	0.7442	0.7453	0.2880
	1.2598	0.7425	0.7452	0.2878
	1.2620	0.7412	0.7452	0.2877
	1.2606	0.7420	0.7452	0.2878
	1.2008	0.7453	0.7470	0.2919
	1.2042	0.7432	0.7469	0.2916
	1.2038	0.7434	0.7469	0.2917
I.P.7	1.0618	0.7543	0.7524	0.3026
	1.0611	0.7548	0.7525	0.3027
	1.0603	0.7553	0.7525	0.3028
	1.0585	0.7566	0.7526	0.3029
	0.9863	0.7550	0.7562	0.3093
	0.9828	0.7577	0.7564	0.3097
	0.9866	0.7548	0.7562	0.3093
	0.9802	0.7598	0.7565	0.3099
	0.9104	0.7561	0.7605	0.3167
	0.9065	0.7614	0.7607	0.3171
	0.9112	0.7574	0.7604	0.3167
	0.9046	0.7630	0.7608	0.3173
	0.8433	0.7642	0.7647	0.3239
	0.8395	0.7677	0.7650	0.3243
	0.8443	0.7634	0.7647	0.3238
	0.8374	0.7696	0.7651	0q3246

TABLE 6.5 CONTINUED

Experiment Number	m	ϕ	$\phi_{C.F.}$[b]	$\gamma_\pm$[b]
I.P.7 (Continued)	0.7666	0.7696	0.7701	0.3330
	0.7632	0.7730	0.7703	0.3334
	0.7675	0.7687	0.7700	0.3329
	0.7605	0.7757	0.7705	0.3337
I.P.10	1.1023	0.7492	0.7507	0.2993
	1.1021	0.7492	0.7507	0.2993
	1.1004	0.7504	0.7507	0.2995
	1.0090	0.7507	0.7550	0.3073
	1.0095	0.7503	0.7550	0.3072
	1.0065	0.7525	0.7551	0.3075
	0.9249	0.7536	0.7596	0.3153
	0.9264	0.7523	0.7595	0.3151
	0.9231	0.7550	0.7597	0.3154

[a] A satisfactory fit on m and ϕ to equation (6.8) can only be obtained with the results shown in columns 2 and 3. Reference to table 6.1 will show that all results below 0.75 m and the two lowest results from experiment I.P.10 have been omitted.

[b] Calculated from equation (6.8) and (6.9) respectively using $B = 2.0329$, $Z_1 = -0.059307$ and $Z_2 = 0.0058965$.

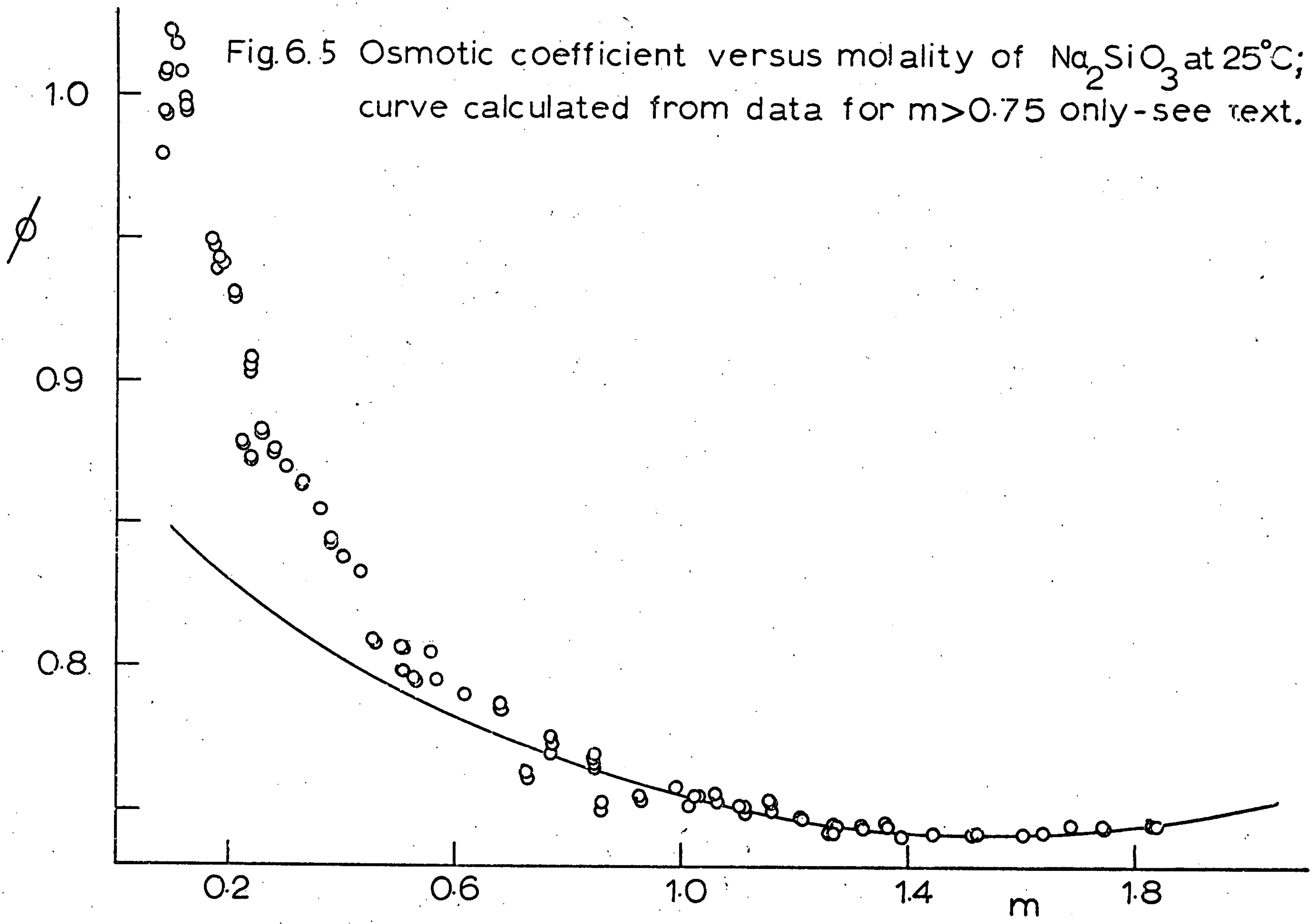


Fig. 6.5 Osmotic coefficient versus molality of Na_2SiO_3 at 25°C; curve calculated from data for m>0.75 only - see text.

TABLE 6.6 OSMOTIC COEFFICIENT, ACTIVITY COEFFICIENT AND WATER ACTIVITY FOR Na_2SiO_3 IN WATER AT $25^oC.^{a,b}$

m	ϕ	$\gamma\pm$	a_w
0.05	0.8673	0.5902	0.99766
0.10	0.8487	0.5250	0.99542
0.15	0.8375	0.4872	0.99323
0.20	0.8290	0.4604	0.99108
0.25	0.8217	0.4396	0.98896
0.30	0.8151	0.4225	0.98687
0.35	0.8091	0.4080	0.98481
0.40	0.8034	0.3953	0.98278
0.45	0.7981	0.3841	0.98078
0.50	0.7930	0.3740	0.97880
0.55	0.7882	0.3648	0.97684
0.60	0.7836	0.3565	0.97491
0.65	0.7793	0.3488	0.97300
0.70	0.7752	0.3417	0.97110
0.75	0.7713	0.3351	0.96922
0.80	0.7678	0.3289	0.96735
0.85	0.7643	0.3232	0.96550
0.90	0.7611	0.3178	0.96366
0.95	0.7582	0.3128	0.96182
1.00	0.7555	0.3081	0.95999
1.1	0.7508	0.2995	0.95635
1.2	0.7470	0.2919	0.95271
1.3	0.7442	0.0285	0.94906
1.4	0.7424	0.2794	0.94538
1.5	0.7415	0.2742	0.94166
1.6	0.7416	0.2697	0.93788
1.7	0.7428	0.2658	0.93404
1.8	0.7449	0.2625	0.93010
1.9	0.7480	0.2597	0.92607
2.0	0.7521	0.2575	0.92192

[a] Calculated from equations (6.8), (6.9) and (6.2) respectively. Parameters used in equations (6.8) and (5.9) were B = 2.0329, Z_1 = -0.059307 and Z_2 = 0.0058965.

[b] Values for molalities < 0.75 m have no real significance - see text.

Na_2SiO_3 are for γ_{Na^+} from work by Harman[73] and their reliability is uncertain. Osmotic coefficients for solutions of sodium metasilicate have not previously been reported.

6.4.3 SOME ADDITIONAL OBSERVATIONS ON THE Na_2SiO_3 RESULTS

In some early work, the use of anhydrous sodium metasilicate as a source of pure material of well defined water content was investigated and compared with nonahydrate. This material was prepared from pure nonahydrate as described in chapter 2, oven dried and stored in vacuo over P_2O_5. In theory, at least, the use of anhydrous metasilicate in isopiestic measurements was expected to overcome the problems of indefinite water content associated with the use of the nonahydrate. As in those measurements detailed in table 6.1, each solution was prepared in duplicate, at least, and it was observed that although concordance between molalities of solutions prepared from the same source of metasilicate was good, solutions prepared from nonahydrate were always in equilibrium with solutions of anhydrous material of lower molality i.e. the osmotic coefficients of the latter solutions were greater. Some crude conductivity measurements were made of the equilibrium solutions and it was found that the solutions prepared from anhydrous material had significantly higher conductivities than those of the nonahydrate.

During the viscosity and density studies which are described in chapter 5, damp nonahydrate batch H5 was used for preparation of most of the stock solutions of sodium metasilicate which were employed. As described earlier, experimental isopiestic solutions were prepared from concentrated stock solutions for molalities < 1.0 and some initial experiments were carried out using the stock solutions from the viscosity and density work. It was found that the osmotic coefficients obtained for solutions derived from nonahydrate H5 were very much higher than those from H8 nonahydrate. As described in section 5.3.3, differences were also observed in the values of ϕ_v and Bη obtained for solutions of these different sources of Na_2SiO_3. As shown in table 2.1, nonahydrate H5 was crystallised from highly caustic solution to remove colloidal material whereas H8 was clarified by ultrafiltration alone, without the use of additional sodium hydroxide. A similar effect was also observed in isopiestic measurements using nonahydrate batch H6 which was prepared similarly to batch H5. It seems likely that the low isopiestic molalities with consequently high osmotic coefficients observed with solutions prepared from nonahydrates H5 and H6 are simply the consequence of contamination with sodium hydroxide at low levels.

The similarity of the results obtained by use of anhydrous metasilicate to those of H5 and H6 nonahydrates tends to confirm the explanation proposed for the latter pair since it is known that the dissolution of anhydrous Na_2SiO_3 is slow and often associated with formation of silica particles. This requires an increase in the concentration of hydroxyl ions to achieve ion-charge balance in the solution. The magnitude of the effect which resulted from the use of anhydrous metasilicate was significantly greater than that observed with H5 and H6 nonahydrates and is consistent with the existence of a much smaller concentration of hydroxyl ions in the solutions of the latter.

6.4.4 AN INTERPRETATION OF THE FINAL RESULTS

When a plot of isopiestic ratio, R, against concentration is extrapolated to infinite dilution, R should tend to 1.0 as m ⟶ 0. A simple explanation is as follows :-

By equation (6.4),

$$R = (\nu_{ref}.m_{ref}) / (\nu_A.m_A)$$

for the isopiestic equilibrium between reference substance and solute, A. Consider a situation where Y particles of reference solute are present in one kg of solvent. For ideal solutions, isopiestic equilibrium is defined by,

$$R = \nu_{ref} \left(\frac{Y}{\nu_{ref}}\right) / \nu_A \left(\frac{Y}{\nu_A}\right) = 1 \qquad (6.11)$$

which, for real solutions, is only realised at infinite dilution. Consideration of figure 6.2 shows that the curves of R versus molality for sodium carbonate and for sodium metasilicate are significantly different, the latter lying at higher R for all solute concentrations. Extrapolation of the Na_2CO_3 curve suggests that R does tend to 1.0 as m tends to zero in complete contrast to the curve for Na_2SiO_3 which, instead of converging on the Na_2CO_3 curve as expected, actually diverges sharply at concentrations less than 0.75 m, attaining a value of R = 1.1 at m = 0.1. It is apparent that a possible reason for the behaviour of sodium metasilicate at the lower concentrations is that the value of ν_A used in equation (6.4) is incorrect and it was found that the experimental points could be made to lie on the smooth curve (dashed) in figure 6.2, by use of values of ν_A ranging from 3.0177 at 0.8 m to 3.410 at 0.1 m. This is consistent with a steady change in the number of ionic species formed per Na_2SiO_3 group, as solute concentration is reduced, and the most likely explanation of this is that extensive hydrolysis takes place. This odd behaviour of sodium metasilicate in dilute solution is similar to the anomalously high equivalent conductances observed by Harman[26] who attributed his results to hydrolysis of silicate species resulting in formation of hydroxyl ions which are well established as species of extremely high equivalent conductivity. The suggestion that hydrolysis is responsible for the anomalous isopiestic results obtained for Na_2SiO_3 is further supported by the observed increase in R and ϕ when materials containing hydroxide contaminant were used, as described in 6.4.3. The possibility that this behaviour is the result of a slow polymerisation of silicate species as proposed by Naumann and Debye[32] cannot be completely discounted, but, in face of the other evidence, this seems unlikely especially since no visible increase in turbidity was detected in any of the isopiestic solutions.

Several spectroscopic studies[36,37,42] have provided evidence consistent with the predominant silicate species in alkaline solution being $(HO)_2SiO_2^{2-}$. The hydrolysis of this species occurs in dilute solution :-

$$(HO)_2SiO_2^{2-} + H_2O \rightleftharpoons (HO)_3SiO^- + OH^- \qquad (6.12)$$

and the equilibrium constant is reported by Ingri[39] to be 1.023×10^{-1}. Calculation of the extent of hydrolysis of solutions of sodium metasilicate shows that, at 0.1 molal, the lowest concentration investigated in this work, approximately 60% of the monomeric silicate is present as $(HO)_3SiO^-$, rising to approximately 90% at 3×10^{-3} m. In contrast, the equilibrium constant for the hydrolysis of carbonate ion i.e. formation of bicarbonate ion,

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad (6.13)$$

is 2.148×10^{-4}.[59] This value is significantly smaller than that for hydrolysis of $(HO)_2SiO_2^{2-}$ (equation 6.12) and explains why at the concentrations investigated, the effects of hydrolysis in the carbonate system were insignificant in comparison with those in solutions of sodium metasilicate. Thus it seems likely that the observed deviation in R for Na_2SiO_3 at concentrations less than 0.75 m is the result of increasing hydrolysis of $(HO)_2SiO_2^{2-}$ to $(HO)_3SiO^-$ as in equation (6.12).

Since ϕ depends on R, it is not surprising that the curve of ϕ against molality for Na_2SiO_3 diverges increasingly from the expected curve at concentrations below 0.75 m although use of the corrected values of ν discussed earlier gives values which fall close to the curve calculated from data for concentrations greater than 0.75 m. Another effect shown in figure 6.5 is the tendency of successive results from the low concentration Na_2SiO_3 experiments to fall increasingly below the experimental curve. As shown in figure 6.3, this effect was also detected with the lowest concentration solutions of Na_2CO_3. A possible interpretation of this is that each time the experiment was disturbed for weighing of dish and contents, small amounts of atmospheric carbon dioxide dissolved in the alkaline solutions giving rise to small amounts of H_3O^+ which effectively neutralised some of the hydroxide ions shown in equations (6.12) and (6.13). The overall effect of contamination of either carbonate or silicate solutions with atmospheric carbon dioxide is replacement of $2OH^-$ ions with one CO_3^{2-} ion and would be expected to cause a reduction in osmotic coefficient of the contaminated solution since ϕ NaOH[74] is, at all concentrations, significantly greater than ϕ Na_2CO_3.[71] As discussed previously, the extent of hydrolysis is much less in solutions of Na_2CO_3 than in those of Na_2SiO_3 and explains why the effects of contamination were only detected at very low concentrations of Na_2CO_3.

Comparison of tables 6.4 and 6.6 at concentrations where the hydrolysis of $(HO)_2SiO_2^{2-}$ is less extensive shows that, within the range $0.8 < m < 1.6$, ϕ Na_2SiO_3 is greater than ϕ Na_2CO_3 by 0.071 ± 0.003. The fact that ϕ Na_2SiO_3 is greater than ϕ Na_2CO_3 may be explained qualitatively by consideration of the predominant species present, CO_3^{2-} and $(HO)_2SiO_2^{2-}$. The accepted structures of these species have, in the former case, the oxygens arranged with a planar, trigonal relationship to the central carbon and, in the latter case, oxygens tetrahedrally arranged around the silicon atom. Because of the three dimensional nature of the silicate monomer and the fact that it contains more groups capable of taking part in hydrogen bonding with the solvent water molecules, one would expect water activites for solutions of Na_2SiO_3 to be lower with consequently larger values of R and of ϕ. It has previously been suggested that the large positive deviation of R for Na_2SiO_3 at low concentrations can be interpreted simply in terms of an increase in the value of ν. However, it seems likely that a significant part of the effect may be attributed to the formation of hydroxyl ions since it is well known that ϕNaOH is greater than 0.9 at all concentrations.

It has for long been suggested that the solutions of sodium silicates contain not only monomeric species but also a range of small polymers and this has been confirmed by ^{29}Si n.m.r. measurements as described in chapter 7. In these isopiestic measurements, it was expected that some obvious difference between silicate and carbonate solutions would be detected which could be attributed to the presence of polymeric species in solutions of silicate but not of carbonate. As has been described in the preceding discussion, this evidence has not been found. However, from the similarity of the trends observed in the results for Na_2SiO_3 and Na_2CO_3 in regions where the formation of $(HO)_3SiO^-$ is relatively insignificant, it is possible to conclude that the distribution of the species known to exist in a solution of sodium metasilicate is not affected markedly by concentration. This view is supported by the observation described in chapter 7, that the ^{29}Si n.m.r. spectrum obtained from 0.35 m Na_2SiO_3 is very similar to that for a 1.35 m solution although overall peak intensities are reduced.

CHAPTER 7

NUCLEAR MAGNETIC RESONANCE SPECTRA OF AQUEOUS SOLUTIONS OF SODIUM METASILICATE AND SODIUM ALUMINATE BY ^{29}Si AND ^{27}Al F.T.n.m.r.

7.1 INTRODUCTION

A good understanding of the species present in solutions of sodium silicate is of importance to the interpretation of the results obtained by the viscosity, density, and vapour-pressure measurements described in chapters 5 and 6. Several workers have attempted to identify these silicate species by spectroscopic techniques, particularly Raman[36,37,42] spectroscopy, but information regarding the presence of polysilicates has remained indefinite. Therefore, the application of ^{29}Si F.T.n.m.r. spectroscopy to these systems is an obvious advance. As described in part II, zeolites are formed from systems which contain both soluble silicate and aluminate species and an investigation of the aluminate system is thus of value also.

In the work described here, aqueous solutions of sodium silicate and sodium aluminate of varying composition were examined at approximately 26°C using 10 mm outside diameter glass sample tubes and a Varian XL-100 spectrometer operating in the Fourier Transform (F.T.) mode. In addition, an aluminosilicate gel was examined by ^{29}Si and ^{27}Al n.m.r. and the ^{13}C spectra of aqueous sodium carbonate and bicarbonate were obtained. All chemical shifts are defined as positive to high frequency (low field) of the standard resonance i.e. anti-cartesian on the XL-100 traces.

7.2 AQUEOUS SOLUTIONS OF SODIUM SILICATE

7.2.1 EXPERIMENTAL DETAILS

Sodium metasilicate solutions ($r = SiO_2/Na_2O = 1$) were prepared from carefully recrystallised $Na_2SiO_3.9H_2O$ and those with $r \neq 1$ from the appropriate amounts of Analar sodium hydroxide and pure silica powder. In all cases, solutions were made up with distilled water to which was added D_2O (15%) for use as an internal lock, and were filtered through a 0.2 μm filter. Care was taken to exclude impurities such as carbon dioxide which would disturb the pH and possibly cause formation of colloidal silica. The magnetically active isotope of silicon, ^{29}Si, has a nuclear spin quantum number $I = \frac{1}{2}$ and is present at 4.7% natural abundance. It is, however, a difficult nucleus to observe and its relative sensitivity is approximately one half that of ^{13}C. Measurements were made at 19.9 MHz and the spectrum was recorded by use of a block-averaging technique in order to improve the signal to noise ratio. Typical conditions used were the accumulation of 130 blocks each of 511 transients by pulsing to give a 90^{o} tip angle at a repetition rate of 0.8s.

7.2.2 RESULTS AND DISCUSSION

Five groups of resonances were observed and these are shown in figure 7.1. All are to low frequency of the ^{29}Si resonance of Me_4Si (T.M.S.) which was used as the standard and have been labelled M, E, C, B and Q. The chemical shifts of the main resonances within these groups are listed in table 7.1 along with other experimental details.

This investigation showed that the relaxation of the silicate species present in such systems is very good with the result that many of the saturation problems commonly encountered with F.T.n.m.r. did not arise. Therefore, although a quantitative interpretation of the relative peak areas would be unjustified, it is possible to derive from them a qualitative picture of the species favoured by different ratios of

Fig. 7.1 ^{29}Si F.T. n.m.r. spectra of aqueous sodium silicates at 26 °C.

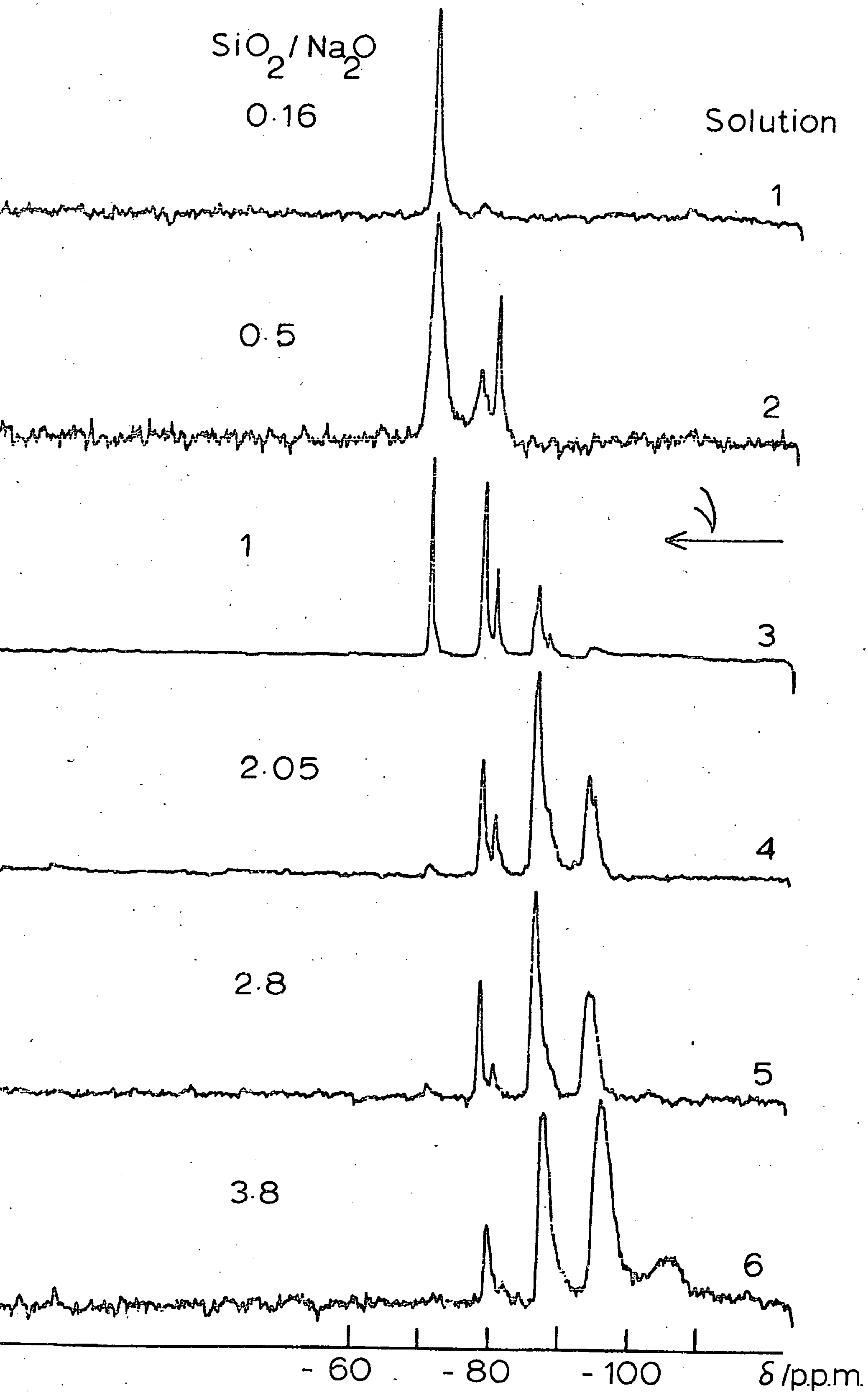


TABLE 7.1 DETAILS OF ^{29}Si SPECTRA SHOWN IN FIGURE 7.1

	Solution Details		Spectrum Observed $(-\delta/p.p.m.)^a$				
Number	Composition[b]	SiO_2/Na_2O	M	E	C	B	Q[c]
1	$6Na_2O.SiO_2$ conc.	0.16	69.81				
2	$2Na_2O.SiO_2$ conc.	0.5	70.12	77.20 78.12 79.81			
3	Na_2SiO_3 1.35M	1.0	70.43	78.41 80.44	86.73 88.35	94.66	
4	$Na_2O.2.05SiO_2.14H_2O$: waterglass type C100 see part II, 2.1	2.05	70.63	78.88 80.87	86.99 88.89	94.97 95.86	
5	$Na_2O.2.8SiO_2$ conc.	2.8		79.05 80.19	87.22	95.46	
6	$Na_2O.3.8SiO_2$ conc.	3.8		79.17	87.85	96.47	106.41

[a] All results obtained by ^{29}Si F.T.n.m.r. In all cases pulsing gave a 90° tip angle except for solution 6 where a 45° tip angle was used. A 0.8s repetition rate was employed throughout.

[b] As described in the text, water content did not have a marked effect on the spectrum observed and, in all cases highly concentrated solutions were used.

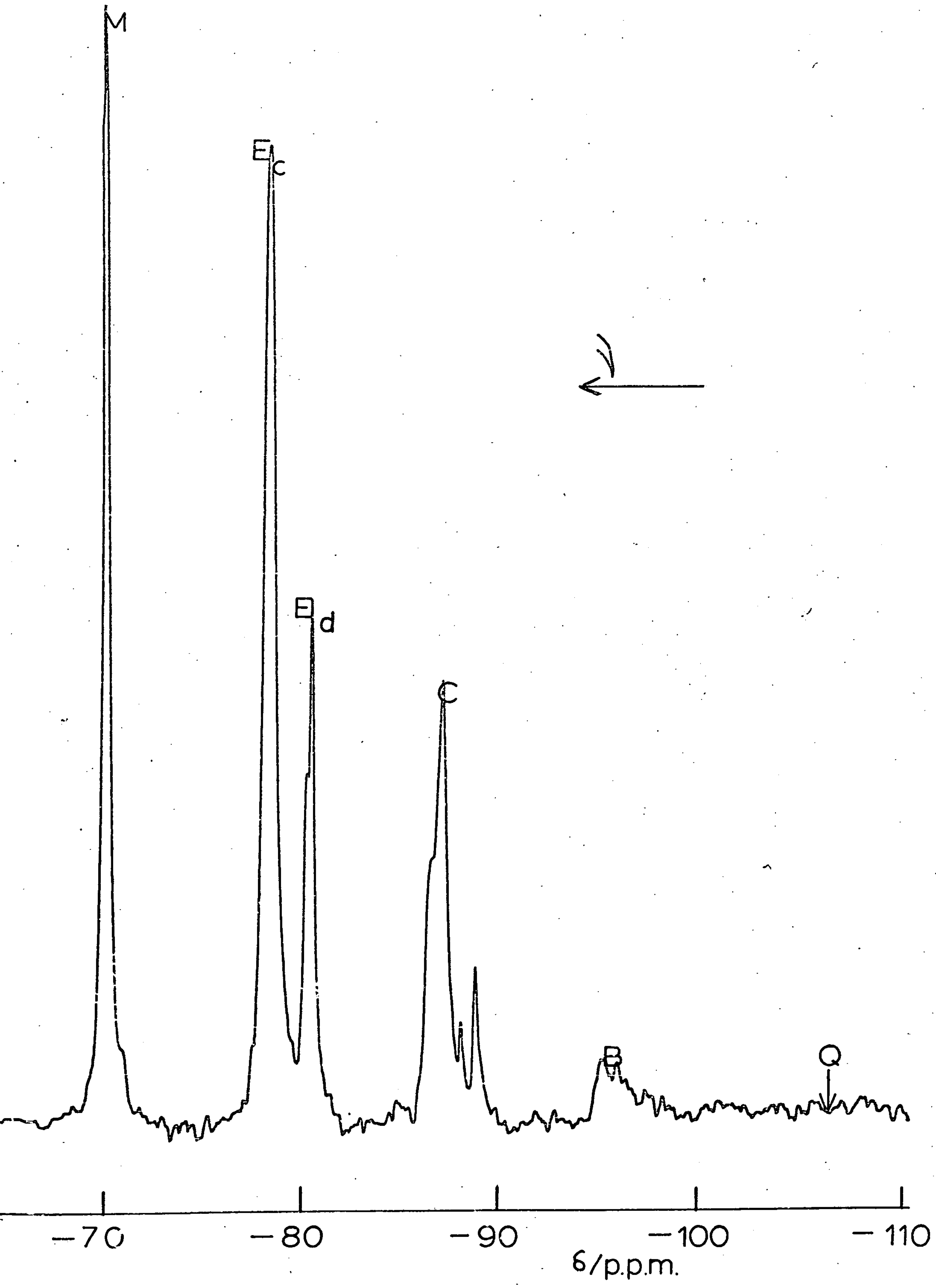
[c] For explanation of groups M, E, C, B, Q, see text.

SiO_2 to Na_2O. Preliminary investigations with sodium metasilicate solutions of differing concentrations showed that the variation of relative peak areas with concentration is almost insignificant in comparison with the effect of changes in r. Consequently, all subsequent measurements were made with concentrated solutions since this improves the signal to noise ratio of the observed spectra. The n.m.r. sample tubes and parts of the instrument probe were made from silicate glass, and, consequently, a broad baseline hump was observed to low frequency at - 110 p.p.m. in all ^{29}Si measurements. However, in most cases, this was removed from the trace produced, by use of the baseline levelling facility of the instrument.

As shown in figure 7.1, the spectrum obtained varies depending on the ratio of SiO_2 to Na_2O, and this suggests that these systems contain a range of silicate species, the exact distribution of which is mainly a function of r. This is consistent with previous studies by Raman spectroscopy [36,37,42] in which it is suggested that the basic unit of these species is a silicon atom bonded tetrahedrally to four oxygens, each of which can, in turn, form a bond with another Si atom. The origins of the various resonances will be discussed in relation to the spectrum of sodium metasilicate solution ($r = 1$), shown in figure 7.2.

The narrow, high frequency peak (M) is the only one which remains when r is reduced to 0.16 but is almost completely absent from solutions with $r > 3$ and it is considered, therefore, to arise from monomeric silicate species. Similar observations of the variation of relative peak areas with r show that peaks (E) belong to terminal Si atoms (i.e. those linked via oxygen to one other silicon) and that peak E_d is most probably that of the dimer whereas E_c is the end group of larger polymers. It

Fig. 7.2 ^{29}Si F.T. n.m.r. spectrum of 1·35M Na_2SiO_3.



seems likely that the group of peaks (C) is due to chain silicons (i.e. those linked by oxygens to two other silicons) and that the small group (B) is due to branching silicons (i.e. those linked by oxygens to three other Si atoms). The general pattern is similar to that observed in the ^{31}P n.m.r. spectra of the polyphosphates[75,76] in which the resonance of the chain group phosphorus lies 10 p.p.m. to low frequency of the end groups.

As shown in figure 7.1, increasing r results in increased proportions of those resonances assigned to chain and branching silicons relative to those assigned to end groups. In solution 6, (r = 3.8), the resonance assigned to branching silicons (B) is very large and is accompanied by a new low frequency resonance (Q) which is thought to arise from silicons bonded via oxygens to four other Si atoms. The chemical shift of resonance Q is -107 p.p.m., which is between that of silica (-113 p.p.m.) and that of the central atom of $(Me_3SiO)_4$ Si(-101 p.p.m.). This assignment is also consistent with the high viscosity and reduced solubility of these high silica systems. During this investigation, there was no indication of coupling between ^{29}Si nuclei and protons in bound hydroxyl groups, a result which is consistent with a very rapid exchange of protons between bulk water and bound groups as has been suggested.[77] This work, however, is only the beginning and a more extensive investigation is necessary to elucidate the fine structure which is apparent in these spectra.

Subsequent to this work, similar studies of silicate systems were published by Marsmann[78] and by Engelhardt and co-workers.[79] The general conclusions of these workers are in agreement with those described here and the chemical shifts of Engelhardt[79] are almost identical.

7.2.3 SOME RELATED STUDIES

An aluminosilicate gel of the type described in part II, experiments

8.1 and 8.2, was examined by ^{29}Si n.m.r. and the resonances observed were almost identical to those shown in figure 7.2 for sodium metasilicate except that they were slightly broadened, presumably by rapid relaxation through interaction with the gel structure. This suggests that such systems contain species of low molecular weight which are able to move relatively freely within the gel lattice. The gel was also examined by ^{27}Al n.m.r. as described in section 7.3.

Another interesting observation arising, also, from the work described in part II, was where the solution of an inactive sodium metasilicate was passed through an ion-exchange column (H^+) in an attempt to form $Si(OH)_4$ species. ^{29}Si n.m.r. of the resultant clear solution showed no detectable resonance at all. A possible interpretation of this is that no significant concentration of discrete $Si(OH)_4$ species is formed since polymerisation to colloidal silica proceeds rapidly. This explanation is compatible with the ^{29}Si n.m.r. results since relaxation of such particles would be expected to be extremely rapid. The resultant solution was found to be completely inactive when used in a zeolite X synthesis, behaviour which is compatible with the presence of colloidal silica particles in the reaction mixture as discussed in part II.

The ^{13}C n.m.r. spectra of concentrated solutions of sodium carbonate and sodium bicarbonate were obtained at 25.2 MHz using a 22.5^{o} pulse with a 0.66s delay. Solutions were prepared with distilled water to which 20% D_2O had been added for use as an internal lock. The proton decoupler was used and sharp resonances were obtained to high frequency of the standard (T.M.S.) at 169.75 p.p.m. for sodium carbonate and at 162.08 p.p.m. for sodium bicarbonate. This evidence justifies the use of sodium carbonate solution as an example of a simple electrolyte system when interpreting results obtained for solutions of sodium metasilicate which, as shown here, contain a range of solution species.

7.3 AQUEOUS SOLUTIONS OF SODIUM ALUMINATE

7.3.1 PREVIOUS WORK

As with the silicate systems, there have been several investigations of the solutions of sodium aluminate and aluminium salts. A review by Glastonbury[80] covers much of the early work. Some techniques which have been applied more recently include potentiometry[81], Raman and infra-red spectroscopy[82,83] and ^{27}Al n.m.r. spectroscopy.[84,85,86] The existence of two species is well established and these are the octahedral ion $Al(H_2O)_6^{3+}$ found in solutions of low pH and the tetrahedral ion $Al(OH)_4^-$ found in alkaline solutions.

Aluminium is a relatively convenient nucleus to observe since the common isotope, ^{27}Al, has a nuclear spin with quantum number $I = \frac{5}{2}$. Since I is $> \frac{1}{2}$, the nucleus of ^{27}Al has a quadrupole moment which can interact with unsymmetrical electric-field gradients, permitting very efficient nuclear relaxation with consequent n.m.r. line broadening. Thus, sharp ^{27}Al resonances are generally only observed when the nucleus is present in a symmetrical electrical field, and the width of resonances can give useful information about shapes of species.[84,85] In most ^{27}Al studies of these systems, the resonance assigned to $Al(H_2O)_6^{3+}$ has been taken as the standard. In solutions of high pH, Moolenaar and co-workers[83] observed a sharp resonance to high frequency of the standard at δ = 80 p.p.m. which broadened with increased concentration as previously reported by Haraguchi and Fujiwara[85]. They, likewise, assigned the sharp line to the tetrahedral species, $Al(OH)_4^-$, but interpreted the broadening as due to the formation of a dimeric species $(HO)_3AlOAl(OH)_3^{2-}$ rather than to a straightforward viscosity effect. Later work by Akitt and co-workers[86] detected a broad peak in solutions of low pH, to high frequency of the standard, at δ = 3.3 p.p.m., and a sharp resonance (δ = 62.5 p.p.m.) which become apparent at slightly higher pH. These peaks were attributed to a dimer, $Al_2(OH)_2(H_2O)_8^{4+}$, and to the central aluminium of a polynuclear species $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ respectively.

7.3.2. EXPERIMENTAL DETAILS

Conductivity and pH curves were obtained by the addition of small volumes of 5.0 mol dm^{-3} sodium hydroxide (AR) to 100 cm^3 of 0.25 mol dm^{-3} aluminium nitrate solution (AR). The solution was stirred magnetically and, after each addition, time was allowed for the pH - and conductivity - meter readings to reach a steady value. The results are displayed in figure 7.3 which demonstrates the large change in pH from 4 to 12 which accompanies the formation and then the dissolution of the aluminium hydroxide gel. Solutions corresponding to various regions of figure 7.3 were prepared from sodium hydroxide and aluminium nitrate, with appropriate volumes of 5M sodium nitrate solution added to keep the ionic strength constant, and then examined by ^{27}Al n.m.r.

Measurements were made at 14.9 MHz by use of the probe normally used for observation of ^{13}C spectra. D_2O which was contained in a concentric 5 mm tubs acted as the lock. The lock frequency was generated by the decoupler operated as described by Ellis and co-workers.[87]

7.3.3 RESULTS AND DISCUSSION

The results are shown in table 7.2. Resonances were detected in three areas : (A), (B) and (C) and in all cases peak width at half height was less than 7Hz. The differing results obtained from fresh and aged

Fig. 7.3 The addition of 5M NaOH to 100cm^3 0·25M Al$(NO_3)_3$.

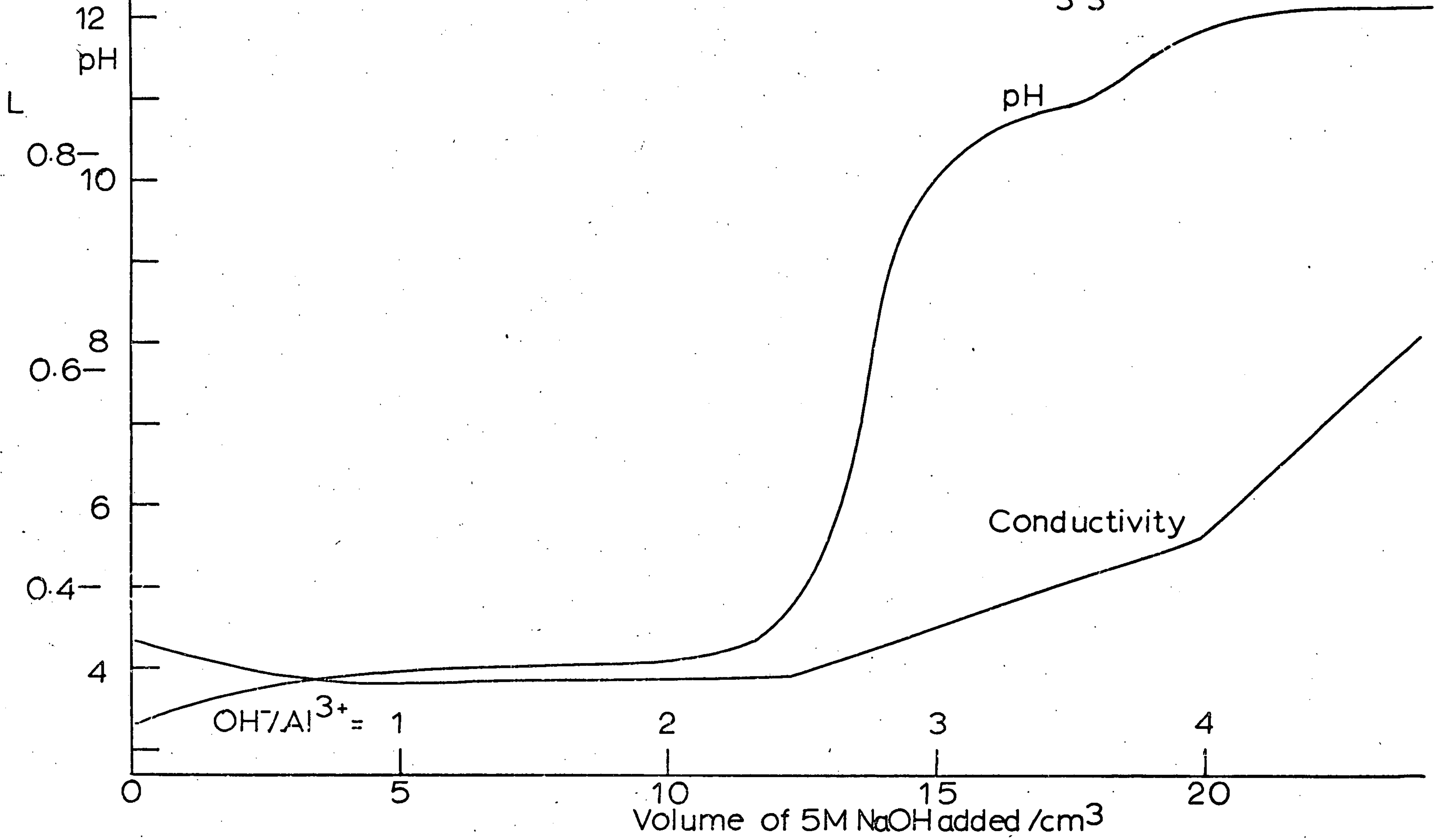


TABLE 7.2 THE EFFECT OF pH ON THE Al^{3+}(aq) ION - FOLLOWED BY ^{27}Al N.M.R.[a]

Solution Number	Preparation :- Volumes/cm^3			pH		Chemical Shifts of Resonances Observed, δ/p.p.m.[b]		
	$Al(NO_3)_3$(0.25M)	NaOH(5M)	$NaNO_3$(5M)	When Fresh	When used	A	B	C
a) Solutions aged for 2 days before use								
1	10	0.2	1.55	3.6	3.52	0.080 (100)		
2	10	0.5	1.25	3.95	3.75	0.186 (100)	62.789 (5)	
3	10	1.0	0.75	4.3	4.05	0.167 (100)	62.797 (90)	
4	10	1.35	0.40	6.15	6.05	No resonance observed : gel		
5	10	1.5	0.25	9.9	11.05			79.6 (95)
6	10	1.75	0	10.95	12.1			79.659 (100)
b) Solutions used when fresh								
7	10	1.0	0.75	-[c]	-	0.068 (100)	62.789 (15)	
8	10	1.1	0.65	-	-	0.072 (100)	62.781 (35)	
9	10	1.2	0.55	-	-	0.118 (100)	62.835 (70)	
9[d]	10	1.2	0.55	-	-	0.129 (47)	62.785 (100)	
10	10	1.3	0.45	-	-	No resonance observed : gel		

[a] Pulse width = 15μs ≡ 34° tip angle; Pulse frequency = 0.8s; observing frequency = 14.8 MHz; temperature = 26°C

[b] Chemical shifts measured relative to resonance of $Al(H_2O)_6^{3+}$ (Group A); δ is positive to high frequency of the standard. Machine always plots the largest peak at intensity = 100. Thus intensities shown in brackets give the relative heights of peaks in the same sample only.

[c] pH not measured. [d] solution 9 measured overnight

solutions is interpreted as due to incomplete mixing of solution components followed by slow equilibration. Resonance (A) has been observed previously[84,85,86] and is generally attributed to the octahedral species $Al(H_2O)_6^{3+}$. All chemical shifts are given relative to resonance (A) in accordance with other workers. Two other resonances were observed to high frequency of resonance (A) at 62.78 ± 0.05 p.p.m. (B) and at 79.65 ± 0.05 p.p.m. (C). Resonance (C) was observed in solutions of high pH (> 10) and corresponds to the resonance at 80 p.p.m. reported by Haraguchi and Fujiwara[85] and assigned by them to the tetrahedral species $Al(OH)_4^-$ favoured by most workers.

During this investigation, some measurements were made of highly concentrated, alkaline solutions and it was observed that, as the water content was reduced, the chemical shift (C) increased and the peak broadened considerably. In a solution of approximate composition $1.3\ Na_2O.Al_2O_3.8.76H_2O$, the resonance was observed at 88.8 p.p.m. and the half peak width was 2400 Hz. The solution was very viscous and it is possible that the observed peak broadening and up frequency change in δ are the result of the physical state of the system. However, when the overall water content is considered, it is apparent that many of the ions will have drastically reduced solvation shells. Under these circumstances, it is difficult to justify the existence of $Al(OH)_4^-$ and it seems quite feasible that dehydration occurs in such systems to form the species $OAl(OH)_2^-$. This species was proposed by Moolenaar et. al.[83] but discounted in favour of the dimer $(HO)_3AlOAl(OH)_3^{2-}$ although they state that monomeric, monovalent species are favoured for interpretation of other properties of these solutions. One would expect a species of the form $OAl(OH)_2^-$ to have an unsymmetrical electric field gradient around the aluminium nucleus and this is compatible with the observed line broadening, although the high viscosity of the system could possibly explain this on its own. In conclusion, it seems possible that the observed shift to high frequency of resonance (C) at high concentrations, with associated line broadening, may be attributed to formation of a dehydration product of $Al(OH)_4^-$, possibly $OAl(OH)_2^-$.

Resonance (B) corresponds to that at 62.5 p.p.m. reported by Akitt et. al.[86] who assigned this to the central aluminium of the polynuclear species $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$. An aluminosilicate gel of the type described in part II, experiments 8.1 and 8.2 was examined by ^{27}Al n.m.r. and the only resonance observed was a peak at δ = 64-65 p.p.m. with a half-peak width = 700 Hz. It seems likely that the broadening of this peak is due to interaction with the gel structure and that the species responsible is similar to, if not the same as, that which causes resonance (B). Overall, it seems unlikely that the polynuclear species proposed by Akitt[86] is responsible since, if this was so, one would expect to see some evidence of simpler polymeric species even if peaks were broadened by quadrupole relaxation. Measurements were made using spectral widths up to 10,000 Hz and no other resonances were detected. From consideration of the pH and conductimetric evidence, and from the results in table 7.2, it seems possible that a species of general form $Al(H_2O)_4(OH)_2^+$ could be responsible. This structure is compatible with the observed sharp resonance since the exchange of protons in such systems is very fast in relation to the n.m.r. process as shown by the absence of proton coupling to ^{27}Al and would result in charge averaging around the aluminium nucleus. If this species is present, then one might expect to detect the $Al(H_2O)_5OH^{2+}$ species at lower pH and this was not observed. However, this can be explained by assuming that the unipositive ion is much more stable than the dispositive species. No resonance was observed at 3.3 p.p.m. as has been reported by Akitt et. al.[86], who attributed this to the dimer $Al_2(OH)_2(H_2O)_5^{4+}$. In conclusion, this study has shown that the aluminate system is highly complex with many unexplained features and should be investigated in more detail.

CONCLUSION

The work described herein has confirmed previous reports[18] that the hydrates of sodium metasilicate which contain 5, 6, and 9 moles of water are easily prepared in comparison with the octahydrate. This is compatible with the observation that the octahydrate alone, is thermodynamically unstable with respect to disproportionation. These studies have also confirmed[18,19,20] that the sodium metasilicate hydrates contain discrete monomeric silicate species held in an extensive hydrogen bonded matrix in distinct contrast to the highly polymerised anhydrous phase.[17]

Solutions of the sodium silicates have been shown to contain a wide range of species, the distribution of which is largely dependent on pH. At high pH, the monomeric species $(HO)_2SiO_2^{2-}$ and $(HO)_3SiO^-$ become prevalent whereas a reduction in pH toward 9.5 results in extensive polymerisation. No evidence has been found for the species SiO_3^{2-} in solution. The underlying feeling from these studies is that solution species undergo interconversion easily and that equilibration of species following changes in pH, temperature, or water content, is rapid.

Undoubtedly, the ephemeral nature of silicate species in aqueous solution is the main reason why attempts to obtain quantitative data on these systems, have in the past proved frustrating, yet fascinating - and still do.

PART II

"THE USE OF SODIUM METASILICATE IN THE SYNTHESIS OF ZEOLITE X"

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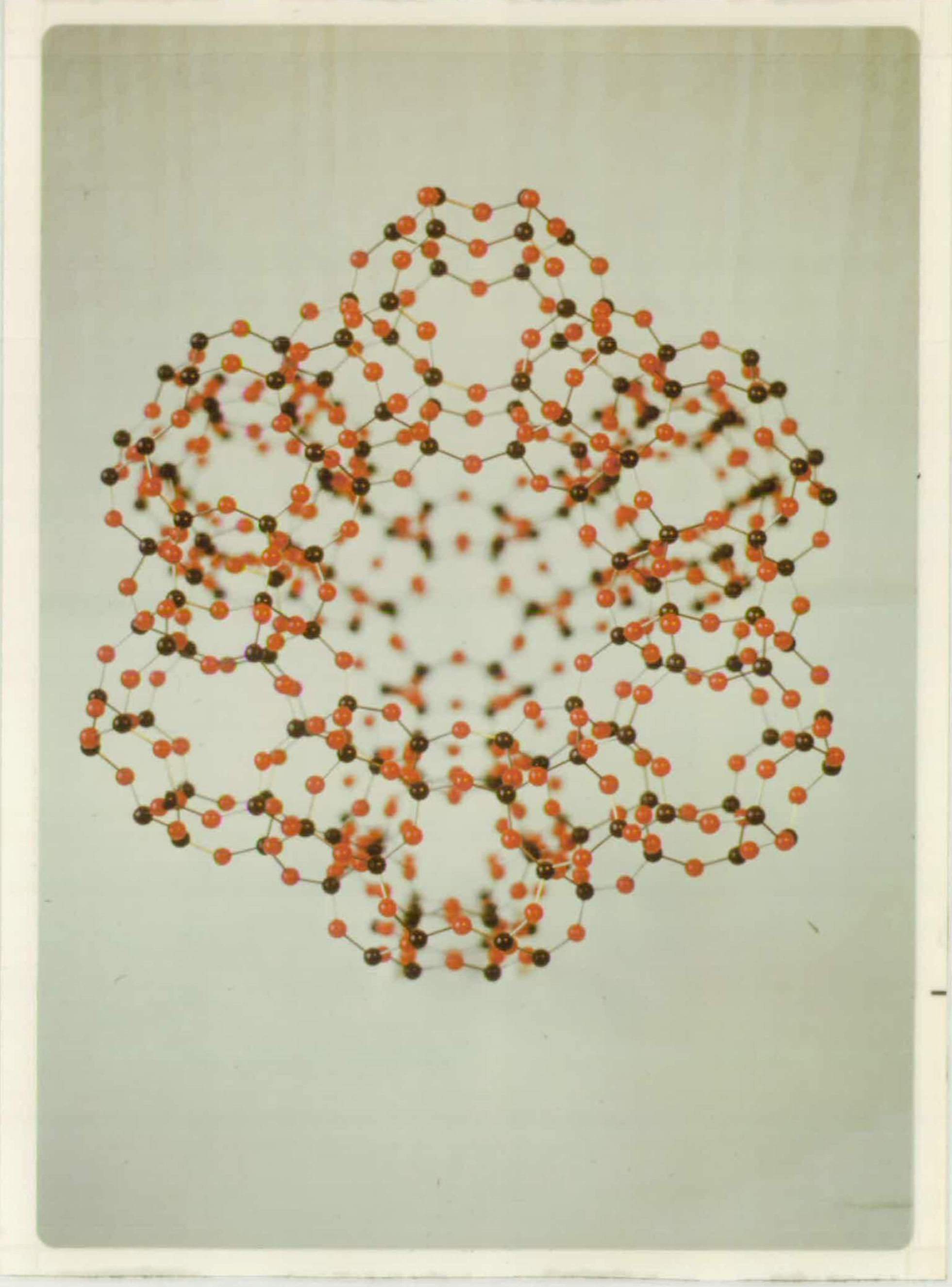
CHAPTER 4 : DISCUSSION

PLATE 1 : FAUJASITE SHOWING THE ENTRANCE TO THE "SUPERCAGE". (RED SPHERE ≡ O, BROWN SPHERE ≡ Al OR Si).



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CHAPTER 1

INTRODUCTION

1.1 ZEOLITES AS MOLECULAR SIEVES

Zeolites are crystalline hydrated aluminosilicate compounds of group I and II elements: in particular sodium, potassium, magnesium, strontium, calcium and barium. The zeolites are framework aluminosilicates and their structures are based on SiO_4 and AlO_4 tetrahedra which are linked to each other three-dimensionally by sharing all oxygens. Their compositions may be represented, in terms of oxides, by the empirical formula :-

$$M_{2/n}O.\ x\ SiO_2.\ Al_2O_3.\ y\ H_2O$$

The cation valency is n and x is generally greater than or equal to 2 since AlO_4 tetrahedra cannot be directly linked to one another.

In most zeolites, the cations can be exchanged and the water removed by reversible processes, although in some cases structural change may result. Within the framework, there are channels and voids, the dimensions and extent of which depend on the zeolite type. Thus, after dehydration, a particular zeolite is able to adsorb molecules or ions up to a particular cross-section and size and reject any which are larger.

In contrast, traditional adsorbents such as silica gel and activated alumina have very wide ranges of pore size. It is the uniformity or pore size and the resulting highly selective adsorptive characteristics which have earned the zeolites the title "Molecular Sieves".[88]

1.2 ZEOLITE SYNTHESIS - INTRODUCTION

Many zeolites are found as naturally occurring minerals and early workers attempted to synthesise them in the laboratory by simulation of the probable geological circumstances under which they had formed. This approach entailed reacting mixtures of composition corresponding to the desired product at high temperature (>200°C) and pressure, and was generally unsuccessful.

However, the synthesis of zeolites A and X[a] by R M Milton[89] in 1959 showed that it was possible to synthesise zeolites as non-equilibrium metastable phases from mixtures of reactive components at much lower temperatures (< 150°C). Since the zeolites thus formed are metastable, the nature of the reactant, rate of nucleation and reaction time are important in controlling the product formed. The great advantage, however, of this approach is that the general mildness of reaction conditions made large scale synthesis a possibility. Since 1959, very many more zeolites have been prepared by such hydrothermal synthesis, and the majority of these are formed as metastable phases.[90]

1.3 POSSIBLE PRODUCTS OF THE Na_2O-SiO_2-Al_2O_3-H_2O SYSTEM

In this work those zeolite phases which crystallise from the Na_2O-SiO_2-Al_2O_3-H_2O system have been investigated and particular attention has been given to the factors which influence the formation of zeolite X. Zeolite X, like zeolite Y is a synthetic analogue of the naturally occurring zeolite called Faujasite, a model of which is shown in plate 1. The basic unit in the aluminosilicate framework is the truncated octahedron or β-cage in which an aluminium or silicon

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[a] The structures of zeolites A and X are described in section 1.3.

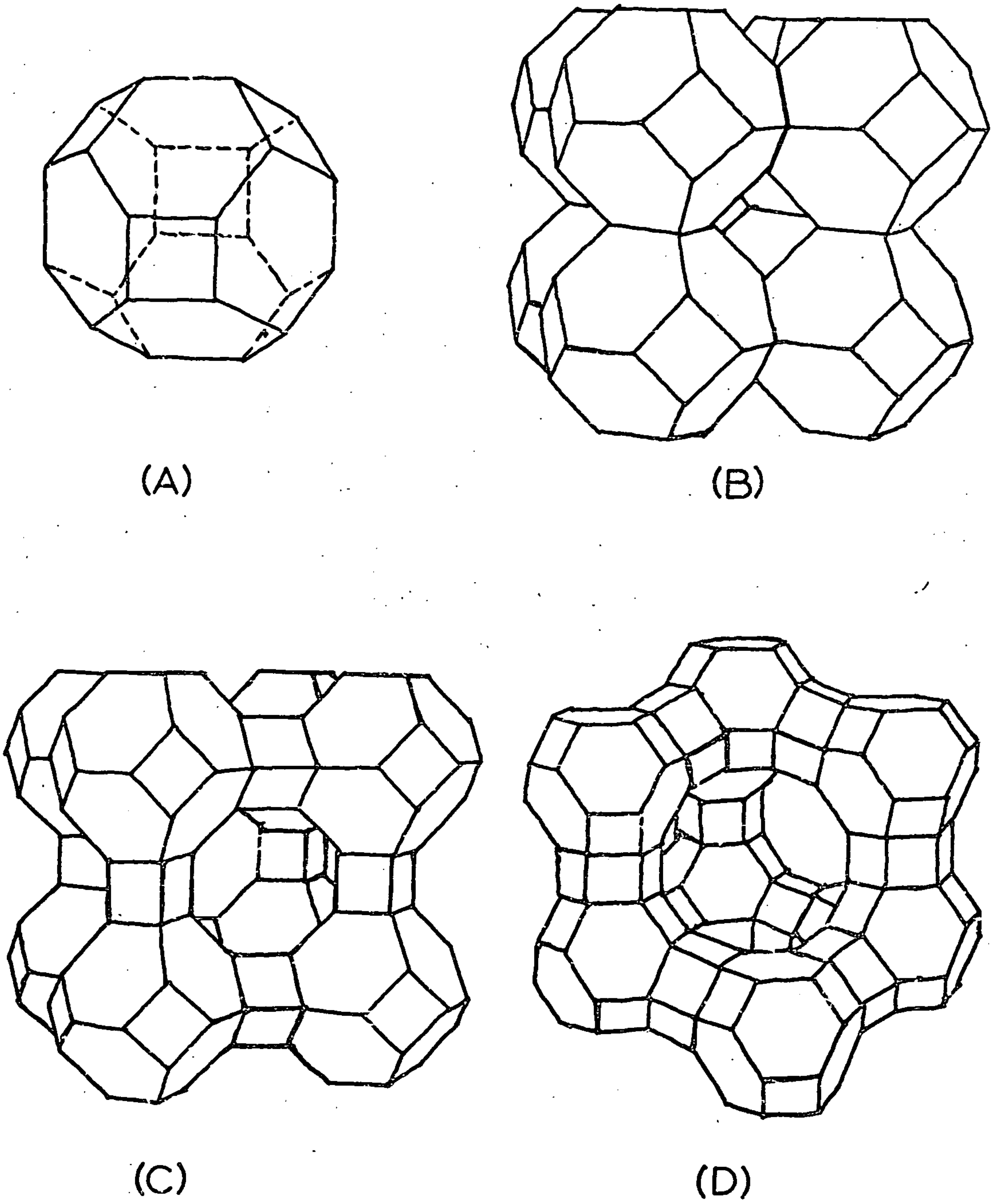
atom lies at each apex. A representation of a β-cage is shown in figure 1.1. The β-cages are joined tetrahedrally to one another by oxygen bridges across the six-unit rings. Thus the linking unit is a double six-unit ring or hexagonal prism containing twelve $(Si,Al)O_4$ tetrahedra. As shown in plate 1, the resulting framework contains large cavities or "supercages", each with a free diameter of ∿ 13 Å, which are interconnected by channels formed by distorted twelve-unit rings $[(Si,Al)O]_{12}$, with a free diameter of ∿ 8 Å. In contrast to the supercage, the free diameter of the β-cage is around 6 Å although the largest entrance, the six unit ring is only ∿ 2.2 Å in diameter.

Chemically, the difference between zeolites X and Y is that X has $2 < x < 3$ whereas Y has $3 < x < 6$ where x is the molar ratio SiO_2/Al_2O_3. In other words, the zeolite X framework contains more aluminium than does zeolite Y and this is the reason for their differing properties.

These synthetic faujasites are of great industrial importance because of their extremely large parts and cavities and their high thermal stability. For example, zeolite Y is stable in air up to 780°C. Their main uses are as adsorbents (the water adsorption capacity is 51% volume of the structure), ion-exchangers, and as catalysts in petrochemical processes where the high acidity of zeolite Y, in particular, is of great value.

The other phases which readily crystallise from the same system are zeolites A, B and hydroxysodalite (HS). Zeolite A has SiO_2/Al_2O_3 ∿ 2 and is similar to zeolite X in that the basic structural unit is the β-cage although the arrangement of the cages in the lattice is different as shown in figure 1.1. In zeolite A, the β-cages are linked

Fig.1.1 The relationship of the sodalite or β-cage (A) to the structures of hydroxysodalite (B), zeolite A (C) and faujasite (D).



(A)

(B)

(C)

(D)

by oxygen bridges across four-unit windows rather than across six-unit windows as in zeolite X. This different stacking of β-cages produces a void or α-cage, analogous to the supercage in zeolite X although smaller. The free aperture into the α-cage is in the order of 4 Å and, as a result, zeolite A is widely used as a highly selective desiccant and ion exchanger.

Hydroxysodalite (HS) has $SiO_2/Al_2O_3 = 2$ and has a structure which is again based on β-cages. The structure can be considered as built up from close packed β-cages, where the adjacent four-unit rings from six neighbouring cages have joined up to form what is in effect an interstitial β-cage. Because of this fusion of the cages, hydroxysodalite does not have any useful voids or channels and the largest molecule which it can adsorb is water.

Zeolite B is formed with a variable SiO_2/Al_2O_3 ratio and has a more dense structure than the other zeolites discussed. The structure of zeolite B differs from the other products of the system in that it does not involve any β-cages and can be visualised as having crankshaft-like chains built up from four-unit rings $[(Si,Al)O]_4$ joined edge to edge by oxygen bridges. Zeolite C is sometimes formed, but little is known about its structure except that it is a highly metastable phase and transforms to zeolite B with time at room temperature. In addition, zeolites S, Z21 and others may also form but these phases have not been considered here.

1.4 SYNTHESIS OF ZEOLITES IN THE Na_2O-SiO_2-Al_2O_3-H_2O FIELD

At the start of this work, a significant amount of empirical and theoretical information on the formation of the zeolites was already discussed[90] and, since most of these are metastable, a large part was on the subject of stability and interconversion of phases.

According to Goldsmith's "simplexity principle,"[91] low temperature crystallisation favours the more complex, more easily nucleated zeolites, X and Y, whereas zeolite B formation is favoured by an increase in temperature. At the higher temperatures (> 60°C), it was reported that the induction period for nucleation of zeolite B is longer than for zeolite X, although crystallisation proceeds at a greater rate once started.

There was experimental evidence[92] which suggested that zeolite B is a semi-equilibrium phase, at least in comparison with zeolites X and A. It was reported that if, during the crystallisation of zeolites X or A, the product is not removed but is left in contact with the mother liquor, then increasing amounts would transform to zeolite B, and complete conversion would occur within 3 days. In the limit, all of the zeolite B would itself transform to analcite which is recognised to be the terminal product of any synthesis in this field.

The discovery of "active silicates" in 1964 and their application to the crystallisation of zeolites X and Y was a major breakthrough.[93] Previous syntheses had been tedious and had proved extremely difficult to scale up to commercial production. In order to prepare a reasonably pure product, it was necessary to heat the appropriate reaction mixture for several hours without thermal or mechanical agitation. If the reaction mixture was aged at room temperature without agitation before it was heated, an improved product could be obtained. However, the necessity of non-agitated conditions throughout proved impossible to achieve on a commercial scale. As a result, large scale syntheses of zeolite X or Y usually produced material which contained significant quantities of zeolite B.

In contrast, a product of high purity could be obtained quickly from an agitated reaction without any ageing steps if an active silicate was used as part of the silicate component of the reaction mixture.[93] These reaction conditions were relatively easy to achieve on a plant scale.

1.5 ACTIVE SILICATES - ASSESSMENT OF ACTIVITY

The active silicates as originally defined were sodium metasilicate hydrates which were capable of yielding zeolite X of high purity after three hours reaction time when used in a test reaction. In the test reaction,[93] a mixture which contained sodium metasilicate, sodium hydroxide, sodium aluminate and water was heated with agitation at 95°C for three hours. The product was filtered, washed and dried before it was analysed by powder X-ray diffraction (X.r.d.). If an inactive sodium metasilicate was used in the test reaction, the product formed after three hours was substantially composed of zeolite B, possibly with some zeolite C. In order that metasilicates of differing activity could be assessed quantitatively, a technique was developed[93] whereby the amount of active metasilicate used in the test reaction was systematically reduced until the product formed in three hours ceased to be substantially pure zeolite X. This was achieved by dilution with inactive sodium disilicate waterglass, and the levels of water and sodium hydroxide were adjusted appropriately to retain the test reaction stoichiometry.

1.6 ACTIVE SILICATES - INFORMATION AVAILABLE

Initially, the following information was all that was available. Most of the details are described fully in the patent literature[93] and only the bare facts are given here.

The only known way to distinguish active from inactive metasilicates was by carrying out the test reaction described previously. Chemical analysis and powder X.r.d. investigations showed no significant difference between active and inactive samples of the same metasilicate hydrate. Infra-red analysis showed small differences, and suggested that active silicates might have stronger Si-O bonds more characteristic of solid silica than of silicates. An examination of a variety of commercial sodium metasilicate hydrates had shown that none of the commercial nonahydrates tested was active and that, of the pentahydrates, some were active to varying degrees, and others were completely inactive. Anhydrous sodium metasilicate was always found to be inactive. There was no apparent correlation between manufacturer and activity, and, as a result, various methods had been devised to prepare active material.

All these methods involved the treatment of sodium silicate with water, and active samples of composition $Na_2O.rSiO_2$, $0.5 < r < 1.5$ had been prepared, although useful levels of activity had only been achieved with the metasilicates (r = 1). The first two methods were a) by crystallisation of a supercooled melt of the desired sodium silicate hydrate and b) by mixing solid sodium silicate with insufficient water to dissolve it completely and inducing it to recrystallise as the desired hydrate. The temperature during each process was maintained above 15°C and below 15° below the melting point of the hydrate. In the third method, solid sodium silicate was hydrated by water vapour with the temperature kept between 0°C and 60°C.

In the first and second methods, it had been found necessary to keep the temperatures of crystallisation and recrystallisation respectively within the range specified, and ideally as low as possible; eg 20°C for sodium metasilicate pentahydrate (M.Pt = 73°C). It was reported that the activity of the silicate decreases as the temperature of crystallisation increases and that, in the limit, active material can be completely inactivated by being melted and then crystallised at its melting point. The crystallisation of the sodium metasilicate hydrates is very exothermic and, although the necessary cooling can be achieved in the laboratory, it was found to be very difficult on a commercial scale, and this limited the application of these two methods.

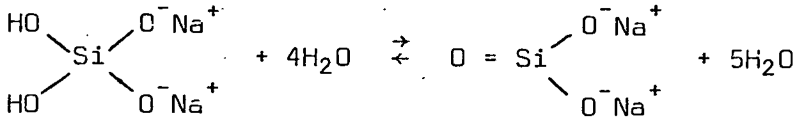
In the first case, the sodium silicate melt could be prepared in any manner and from any sources, although the use of colloidal or highly dispersed silica had been found to produce significantly less active material. The recommended method was to dissolve the silicate in sufficient water to ensure complete solution (eg 14 moles water per mole metasilicate), boil the solution down to the required water content and to supercool it before crystallisation was induced, by seeding if necessary. It was noted, however, that if the melt was supercooled with a lower water content than was required and was then adjusted by the addition of water before it was crystallised, the resulting material was especially active.

In the second recommended method, an anhydrous silicate or silicate hydrate was mixed with insufficient water to achieve complete solution and was allowed to recrystallise as any desired hydrate, within the temperature limitations. A convenient technique[94] was to spray the required amount of water slowly onto powdered anhydrous sodium metasilicate while the mixture was being stirred thoroughly. The rate of water addition was adjusted so that the mixture never became too wet and granulation of the fine powder was achieved. In a typical case 6 moles water was added to 1 mole anhydrous sodium metasilicate. Powder X.r.d. of the product showed sodium metasilicate nonahydrate with a few percent anhydrous metasilicate, but the intensities suggested that around fifty percent of the product was amorphous. While the activity of the material was initially poor, a marked improvement was noted after forty-eight hours at room temperature, although the X.r.d. analysis was unchanged. After a few months, the activity decreased and X.r.d. showed approximately 100% sodium metasilicate hexahydrate.

The third method which was recommended was the hydration of solid sodium silicate with water vapour in the temperature range 0 to 60°, 20 to 35°C being preferred. This was achieved by passing air of controlled humidity and temperature over or through a sample of solid sodium silicate which was contained in a stationary, moving or fluid bed. Samples with a much wider range of activity were prepared by this method, and a scale-up to a commercial process was thought to be possible. In one interesting experiment, very active amorphous sodium metasilicate was produced from anhydrous sodium metasilicate by hydration for 168 hours.

The original patent[93] concluded that, in the case of the sodium metasilicates, active forms of any hydrate, mixture of hydrates or mixture of hydrate(s) with anhydrous metasilicate could be prepared. It was proposed that activity was a consequence of an equilibrium which existed between "true" metasilicate and an acid orthosilicate and that the activation methods were freezing the equilibrium on one side or the other.

i.e.



Some additional information[94] was that inactive sodium metasilicate hydrates prepared by crystallisation, in particular pentahydrate, gained activity steadily if left at room temperature for several months. On the other hand, it had been noted that those hydrates prepared by the second and third hydration methods generally gain activity quickly, and then become less active on further ageing. It was also disclosed that inactive material was normally obtained when a metasilicate hydrate was crystallised from dilute aqueous solution rather than from an aqueous melt as described earlier.

With regard to solution preparation, an inactive solution was reported[94] to be the normal result when active material was dissolved in water at 90°C. In contrast, a solution of active material could be held at 90°C for 24 hours with loss of only 50% of the activity, provided the solution had been prepared at less than 40°C.

Finally, it was observed that activity was retained to a large extent in the mother liquor of the zeolite crystallisation mixture and that this could be recycled up to five times with the addition of inactive material each time and still produce good zeolite X.

Later work[95] showed that active silica could be prepared from a solution of an active silicate by precipitation with an acid while observing the same temperature limitations as had been defined for the crystallisation methods. In connection with this work, it was found[94] that, if the silica was precipitated in stages, the majority of the activity came down with the first portion of the precipitate.

1.7 THE AIM OF THIS WORK

As described in the preceding sections, the discovery of "active silicates" was a tremendous step forward in the advancement of zeolite synthesis, especially on a commercial scale. At the outset of the present work, methods for preparing "active" material were well established but the origins of "activity" and, in particular, the physical and chemical differences between "active" and "inactive" metasilicates were unknown. The only reliable way to test for "activity" was to carry out a zeolite X synthesis. The aims of this work were to establish the cause of "activity", to devise new methods for testing "activity" and to discover commercially viable methods for the preparation of "active" material.

CHAPTER 2

EXPERIMENTAL DETAILS

2.1 MATERIALS

SOURCE	MATERIAL SUPPLIED
Joseph Crosfield Ltd.	Technical grade $Na_2SiO_35H_2O$ Technical grade Na_2SiO_3 called "Metso"
B.D.H. Ltd.	Technical grade $Na_2SiO_35H_2O$ "Analar" grade NaOH Technical grade aluminium silicate, $Al_2(SiO_3)_3$ Dry sodium aluminate, $1.3Na_2O.Al_2O_3$
I.C.I. Ltd.	Dry sodium aluminate, $1.3Na_2O.Al_2O_3$
I.C.I. Ltd. (Mond division)	Commercial sodium silicate waterglasses, type C100, $Na_2O.2.05SiO_2.14.27H_2O$ and type Q79, $Na_2O.3.39SiO_2.23.9H_2O$
Akzo Ltd.	Pure silica, type KS300
Kaiser Inc.	Purified alumina trihydrate, $Al_2O_3.3H_2O$
Baco Ltd.	Technical grade $Al_2O_3.3H_2O$
Koch-Light Ltd.	Pure anhydrous alumina, Al_2O_3 Pinacyanol chloride (1,1'-diethyl-2,2' carbocyanine chloride).

As detailed in chapter I.2, two main routes were used in the preparation of purer sodium metasilicate. Material of high purity was obtained by the recrystallisation of the nonahydrate from a dilute aqueous solution prepared from technical grade pentahydrate and distilled water. The crystals were filtered in the absence of carbon dioxide and dried over sodium metasilicate pentahydrate until the material contained exactly 9 moles water per mole metasilicate. However, in much of this work, accurate stoichiometry of the metasilicate was relatively unimportant, and an easier method was by seeding a supercooled nonahydrate or pentahydrate melt prepared from pure silica, pure sodium hydroxide and distilled water. In those cases where a pure pentahydrate of accurate stoichiometry was required, nonahydrate from the former method was boiled down to pentahydrate water content and seeded as in the latter method. Pure anhydrous sodium metasilicate was prepared by the evaporation to dryness at 100°C of a pure sodium metasilicate solution.

2.2 APPARATUS

2.2.1 APPARATUS USED IN ZEOLITE SYNTHESIS

Reaction mixtures were prepared in a 600 cm^3 stainless steel or pyrex beaker and the resulting gel was homogenised by an electrically driven 5 cm diameter stainless steel paddle. The mixture was placed in a reactor which consisted of a 500 cm^3 three necked, round bottomed flask type FR500/3S/22P fitted with a reflux condenser and agitated by an electric stirrer with a teflon paddle. Two types of stirrer gland were used in the reactor and both had disadvantages. Quickfit type ST4/2 which used a ball race as the bearing, tended to corrode and ultimately seize. The type supplied by Jencons was a simple precision bore glass sleeve within which the stirrer rod fitted. The bearing surfaces were lubricated with vaseline, but tended to wear, particularly when in contact with zeolite product.

The apparatus was partly immersed in a water thermostat bath which maintained the temperature at 95 ± 2°C. Two types of bath equipped with constant-level devices were used. These were a Grant Instruments type SB3S with polypropylene spheres to reduce heat loss, and a conventional type of round bath supplied by Towers and equipped with a Jumo type GKT15 relay.

A 15 cm Buchner filter funnel fitted with Whatman No 1 paper was used for filtration and washing of the zeolite product. Powder X.r.d. analysis of the product was carried out with two models of Philips vertical diffractometer. The newer one (type 1050) was fitted with an automatic sample changer and operated at a scan speed of $\frac{1}{2}^{\circ}$ min^{-1} with 0.2 receiver slit and a 2 second time constant. The other was a type 1051 which was suitable for routine analyses. All quantitative measurements were made on the newer machine.

2.2.2 OTHER APPARATUS

A 350 cm^3 Gelman filter funnel No. 4371 fitted with 0.2 or 0.8 μm (200, 800 nm) pore size Metricel discs was used for ultrafiltration of silicate solutions.

The visible spectra of solutions containing pinacyanol chloride were obtained with a Unicam SP800D spectrophotometer fitted with a cell holder thermostatted at 23 ± 1°C.

2.3 PROCEDURE FOR ACTIVITY TESTING

In this work the synthesis of zeolite X was adopted as a routine, quantitative method for measurement of the activity of samples of sodium metasilicate hydrates. The overall reaction composition which was used for all activity testing was $5.15Na_2O.4SiO_2.Al_2O_3.242H_2O$, in which the molar component ratios agree well with those recommended[93] (shown in brackets) :-

SiO_2/Al_2O_3 = 4(3.85), Na_2O/SiO_2 = 1.29 (1.34), H_2O/Na_2O = 47.0 (47.0).

In the reaction, the metasilicate on test only contributed 1/9 of the total silica requirement, and the balance was supplied by an inactive sodium disilicate waterglass. Thus the molar ratio of active to inactive silicate was 1:8.

The test reaction, hereafter referred to as the Standard Reaction, was set up in the following way. 11.9g pure sodium hydroxide was dissolved in 11.9g distilled water and 7.8g technical alumina trihydrate was added. The mixture was boiled until a clear solution was obtained, then cooled to room temperature, and the lost water was replaced. Sodium metasilicate pentahydrate (4.7g) or the molar equivalent amount of another test metasilicate was dissolved in 50g distilled water with the temperature kept below 35°C. Sodium disilicate waterglass type C100 (28.4g) was added to the metasilicate solution and mixed thoroughly. This silicate solution was stirred rapidly with an electric mixer while the previously prepared aluminate solution was slowly added to form a stiff gel. Distilled water (126.2g) and any remaining aluminate solution were added and the mixture was stirred until a white homogeneous liquid was obtained. The mixture was placed in the reactor and stirred under reflux at 95°C for three hours. The resulting watery mixture was removed from the reactor, filtered, and the white residue was washed thoroughly with water.

The residue was dried in an oven at 100 - 130 °C, cooled and then ground finely. The product was left at room temperature and humidity for at least one hour before it was examined by powder X.r.d. The components of the product were identified by comparison of the trace obtained with published data.[90,93] An estimate of the percentage composition of the sample was normally obtained by comparison of the intensities of predominant peaks in traces of the sample and of pure standards run under identical machine conditions. For convenience, all results were classified on the scale shown in appendix A. Typical X.r.d. traces are shown in figure 2.1 and observed data for the commonly encountered zeolites is given in appendix B.

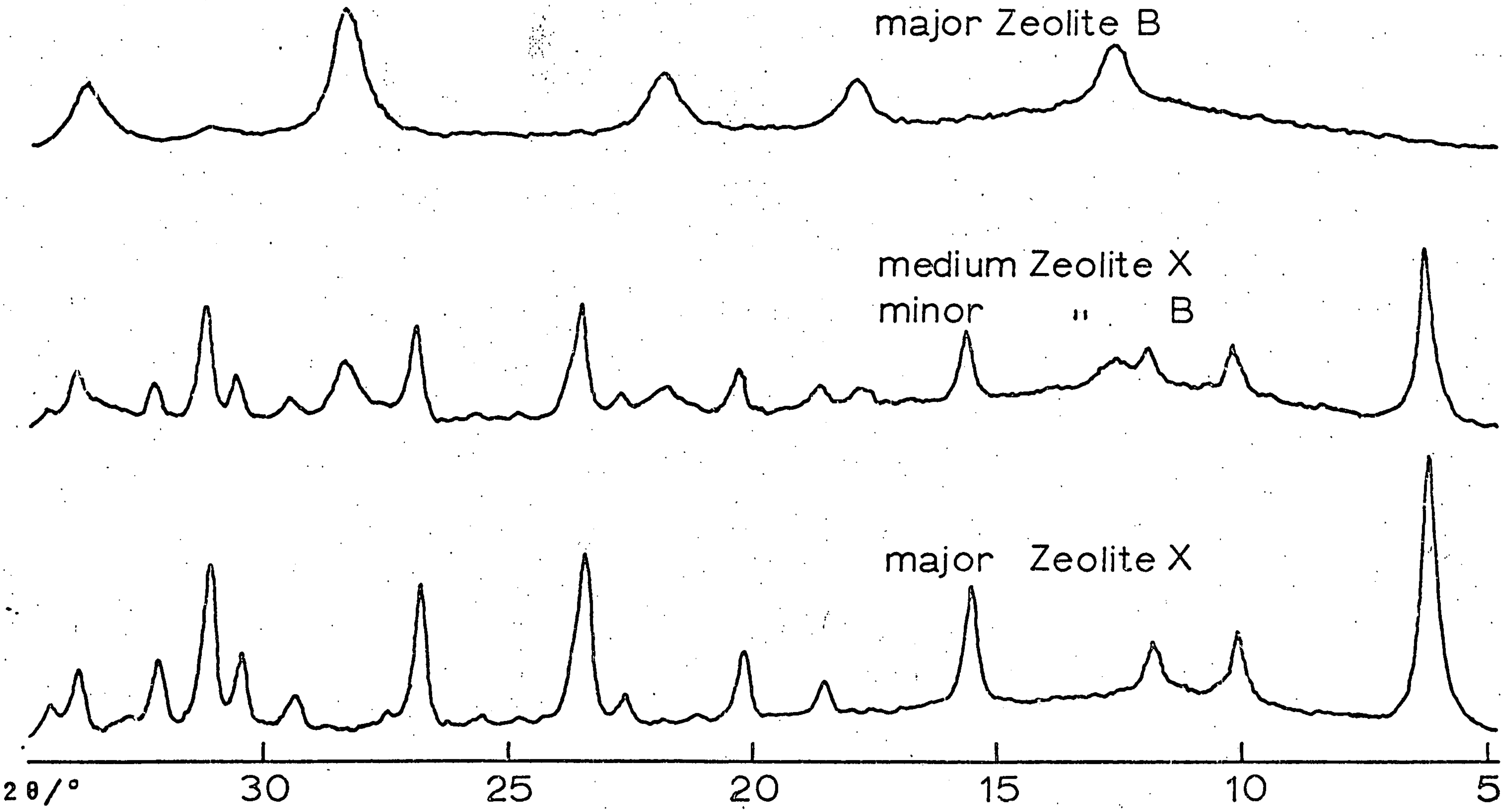


Fig. 2·1 Powder X.R.D. traces of typical products of the standard reaction.

CHAPTER 3

RESULTS

In an attempt to convey an impression of the way in which the conclusions evolved, experiments are presented in approximate chronological order. Full details of these experiments are given in tables which may be found at the end of this chapter along with a list of abbreviations used. Experiments have been numbered so as to relate to a particular table e.g. expt. 4.3 refers to the third experiment on table 4. A key which relates thesis and original experiment numbers is given in appendix E.

3.1 EARLY WORK

Much of the early effort was put into the detection of some reproducible difference between active and inactive material other than by the synthesis of zeolites.[93] An alternative approach was to attempt to remove the activity from active material by processes which did not involve the higher temperatures which previous work[93] had shown to be detrimental.

The examination of active and inactive commercial sodium metasilicate pentahydrate[a] by light microscope in the solid state and on fusion showed no significant difference between them. The Raman spectra of solutions of active and inactive pentahydrates were obtained using a Cary 83 laser Raman spectrometer, but the spectra were effectively

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[a] Hereafter sodium metasilicate pentahydrate and nonahydrate will be referred to as pentahydrate and nonahydrate respectively except where this could be ambiguous.

identical. It was observed that both active and inactive commercial pentahydrates produced cloudy solutions in water which could not be clarified by conventional grades of filter paper. When the solutions were boiled, the colloidal material flocculated and settled out in both cases and it seemed possible that this was significant since it was known that active solutions could be inactivated by heating.[94]

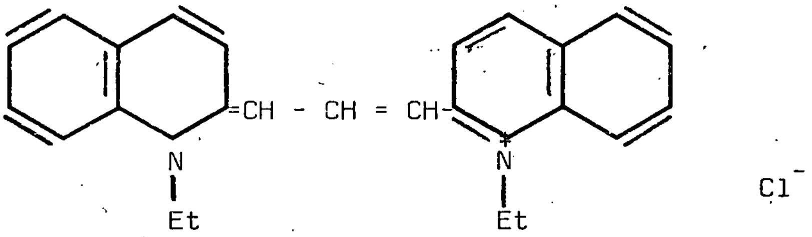
Therefore, attempts were made to modify or remove the visible colloidal material at room temperature to determine whether it had any connection with activity or inactivity. The details of these and subsequent experiments are given in table 1. Centrifuging was successful in taking down the visible particles, but the standard reaction showed no difference between cloudy and clarified active solutions. (1.1, 1.2). At that time, it was observed that the addition of 5% wt. of sodium hydroxide would dissolve the visible colloidal material in the solutions obtained from commercial silicates and it was decided to try this on active and inactive solutions before they were used in the standard reaction. This was achieved by redistributing some sodium hydroxide from the aluminate component to the silicate component before they were mixed (see section 2.3), thereby keeping the overall reaction stoichiometry unchanged. This experiment was carried out using active commercial pentahydrate and inactive purified nonahydrate, and the results showed that the activity was unaffected by the extra sodium hydroxide used. (1.1, 1.3, 1.4, 1.5).

Another aspect of the use of sodium hydroxide in silicate solutions was that a reddish-brown precipitate formed when solutions of commercial pentahydrate with added caustic were left at room temperature overnight. This precipitate was identified as ferric hydroxide ($Fe(OH)_3$) and raised the possibility that activity was a consequence of iron or some other impurity.

Experiments to measure the equilibrium pressures of several sodium metasilicate hydrate mixtures were carried out as described in chapter I.4. Two experiments were set up to observe the equilibrium between commercial pentahydrate and pure, inactive nonahydrate and it was found that the equilibrium pressure was the same whether active or inactive pentahydrate was used.

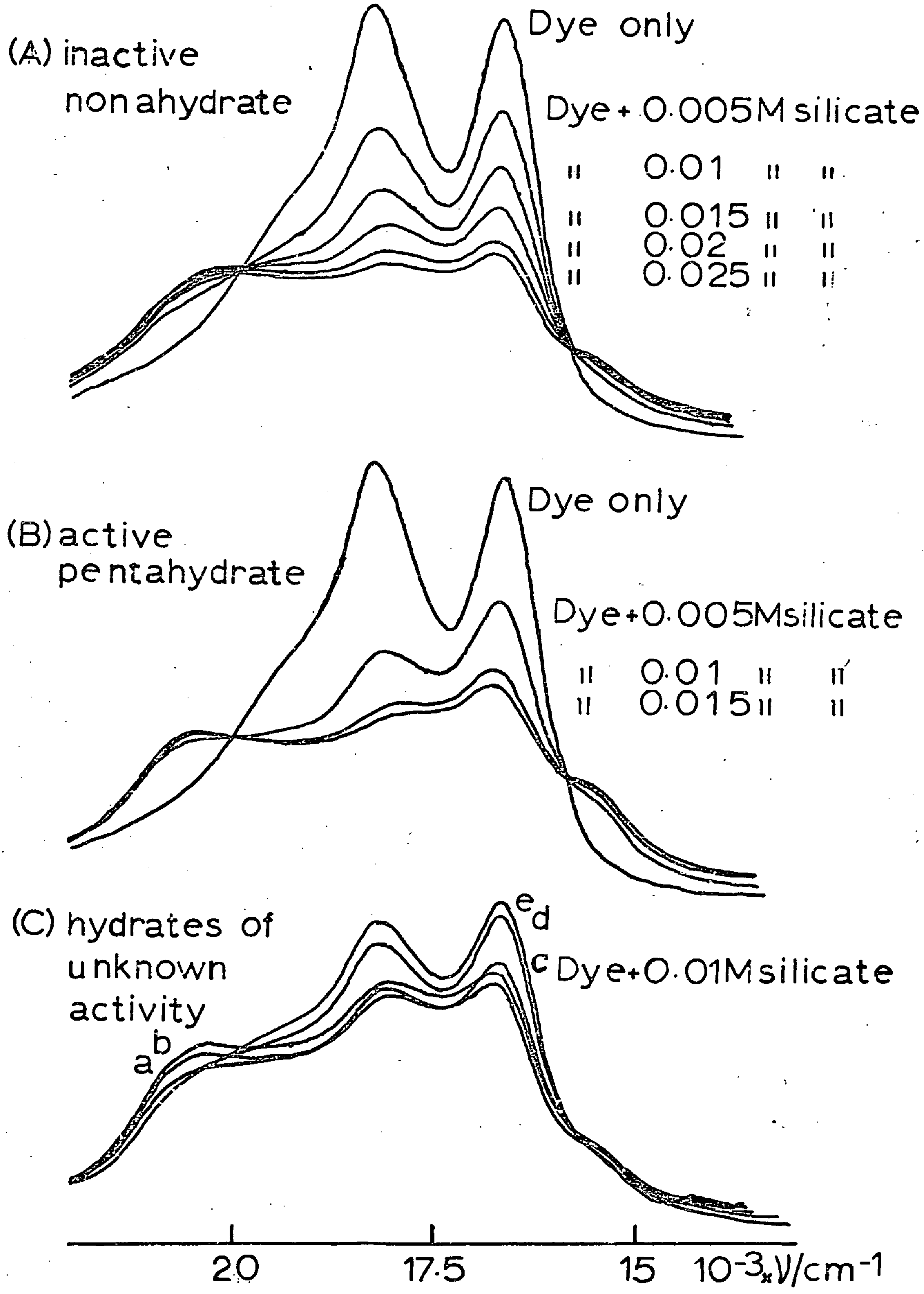
3.2 THE USE OF DYES IN SILICATE SYSTEMS

Several workers have studied the visible absorption spectra of dyes in silicate solutions.[96-99] Most of the work has been carried out with commercial polysilicates, and the most frequently used dye is pinacyanol chloride; 1,1'-diethyl-2,2'-carbocyanine chloride.



In this work, stock solutions of 0.5 mol dm^{-3} sodium metasilicate and 2×10^{-4} mol dm^{-3} pinacyanol chloride were prepared, and the visible spectra of solutions which contained varying concentrations of dye and silicate were obtained. The addition of sodium metasilicate to a solution of pinacyanol chloride reduced the visible absorbance and it was observed that this effect was much more marked for active metasilicate than for inactive metasilicate. This is shown in figure 3.1 where portions of 0.5 mol dm^{-3} sodium metasilicate solution were added successively to 10 cm^3 of 2×10^{-6} mol dm^{-3} pinacyanol chloride. After each addition of silicate, the solution was allowed to equilibrate for three minutes before the spectrum was obtained. As shown in the figure, the spectrum obtained after 0.2 cm^3 of active metasilicate solution

Fig.3.1 The visible absorption spectra of 2×10^{-6}M pinacyanol chloride in solutions of sodium metasilicate hydrates.



had been added was effectively the same as was obtained with 0.4 cm^3 of inactive metasilicate solution giving total concentrations of silicate = 0.01 and 0.02 mol dm^{-3} respectively. This suggested that, other things being equal, active solutions have a greater dye removal power than inactive solutions and that an activity test could be devised based on this observation. As a blind trial, this technique was applied to five sodium metasilicates of unknown activity by the measurement of the visible spectrum of a 2 x 10^{-6} mol dm^{-3} dye solution which contained 0.01 mol dm^{-3} metasilicate for each unknown. The spectra which were obtained are shown in figure 3.1 (c) and the unknowns were assessed as follows :-

Active $b \sim a > c > d > e$ Inactive

These results agreed well with activity testing carried out by the standard reaction.

The peaks observed for pure pinacyanol chloride solution at 16,300 cm^{-1} and 18,000 cm^{-1} are attributed[97,99] to monomeric and dimeric dye species respectively, while that which appears as a shoulder at around 19,000 cm^{-1} is thought to be due to the triple ion, dimer Cl^-. When silicate is present, well defined isosbestic points at 20,000 and 15,800 cm^{-1} are observed indicating the existence of equilibria involving silicate-dye complexes.

All of the pinacyanol chloride/silicate systems which were investigated were unstable and eventually flocculated and faded completely. Consequently, several other dyes were investigated in an attempt to find one which was more stable in silicate systems, yet enabled a distinction to be made between active and inactive solutions, and the results are shown in appendix C. Of those investigated, Bismarck Brown looked promising initially, but was found to fade in silicate solutions and was consequently discarded.

3.3 ULTRAFILTRATION EXPERIMENTS

Ultrafiltration was carried out using a Gelman filter equipped with Metricel filter discs which enabled particles larger than 0.2 µm (200 nm) to be removed from silicate solutions. The effect of ultrafiltration on the pinacyanol chloride activity test was investigated, and showed that the test was able to distinguish between active and inactive solutions, even after they had been filtered. The visible absorbance of pinacyanol chloride in filtered metasilicate solutions, was, however, greater than in unfiltered solutions, regardless of activity, and suggested that a significant amount of the dye added to silicate solutions was adsorbing on colloidal material larger than 200 nm. It was decided that all silicate solutions should be filtered thoroughly before the pinacyanol chloride test was applied since, in an extreme case, an inactive solution with a large amount of colloidal material could appear the same as a colloid-free active solution. The activity of metasilicate solutions as tested by the standard reaction was found to be unaffected by filtration through a 200 nm pore filter, and confirmed the evidence of the dye test that the species responsible for activity is smaller than 200 nm. (1.1, 1.6, 1.7, 1.8, 1.9). Samples of filtered and unfiltered active and inactive solutions were examined with an ultramicroscope and no significant differences could be observed between active and inactive solutions.

The conclusion drawn from these experiments was that the active species is probably much smaller than 200 nm, and it seemed likely that it is a very small particle of special size and structure, rather than an ionic species as had been suggested.[93] The possibility that a particular silica particle is responsible could not be discounted despite the insensitivity of active solutions to added sodium hydroxide (1.1, 1.3, 1.4, 1.5) which, as has been shown previously, is effective in dissolving colloidal silica.

Consequently, some experiments were carried out using ion exchange resins, in an attempt to prepare some such silica species in situ. Inactive sodium metasilicate solutions were shaken with protonated resin until the solution gave a satisfactory result with the dye test (see fig. 3.1 (B)). The solution pH was not changed significantly and showed that the response from the test was not a pH effect. The solutions were tested immediately by the standard reaction and were found to be completely inactive (1.10, 1.11). This result appeared to eliminate the possibility that a silica particle could be responsible for activity.

Subsequent work was based on the idea that active material probably contained some species which was able to be incorporated in the growing zeolite lattice. The obvious candidate was a small aluminosilicate species of particular structure, thereby able to promote crystallisation in a particular direction. If this was the case, then the question of the origin of the necessary aluminium could only be answered by assuming that it was present in a sufficient amount as an impurity. It had previously been observed that commercial pentahydrate contained iron impurity and, by the nature of the industrial processes involved in its preparation, it was quite conceivable that aluminium could also be present. Consequently experiments were carried out to investigate activation by the supercooled crystallisation process[a], and in particular, to see if it was effective when pure metasilicate was used. The results and experimental details are shown in table 2.

3.4 AN INVESTIGATION OF THE ACTIVATION PROCESS

It was observed that two sodium metasilicate hydrates which were previously inactive had increased in activity while left at room temperature for several months (cf 2.1 and 1.8, 2.2 and 1.3). This behaviour had been reported previously,[94] but what is significant here is that the nonahydrate had not increased in activity as much as the pentahydrate had done. Was this because the nonahydrate had been prepared from commercial material by recrystallisation and had thereby lost a significant part of an important impurity, or was it just because nonahydrates were inherently less active than pentahydrates? The latter possibility was supported by the report in the original patent[93] that, of a number of commercial metasilicate hydrates tested for activity, none of the nonahydrates was active. The mildly active nonahydrate was boiled down to pentahydrate composition and used in the activation process. The pentahydrate which was produced was found to be as active as the parent nonahydrate (2.3). This result suggested that activity was not a function of the hydrate concerned, and this was confirmed by experiments 2.4 and 2.5, in which equally active pentahydrate and nonahydrate were prepared by the activation process from the same inactive commercial anhydrous metasilicate.

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[a] The patented method of activation[93] by crystallisation of a supercooled sodium metasilicate hydrate melt at low temperatures will hereafter be referred to as "the activation process" except where this is ambiguous.

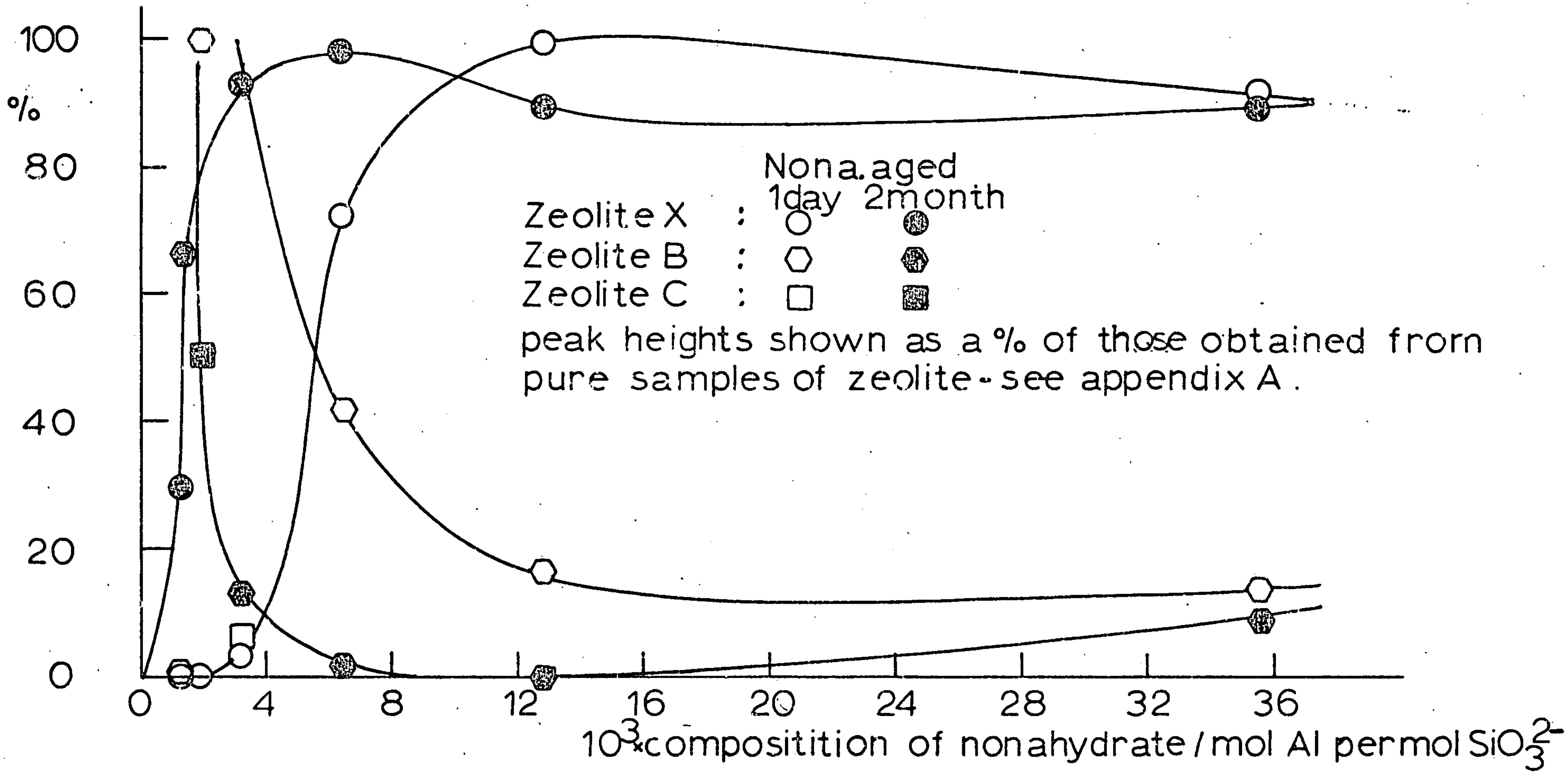
In an effort to confirm the suspicion that there was a correlation between the level of impurity, possibly aluminium, and the latent activity of metasilicate hydrates, some attempts at analysis for aluminium were undertaken. Samples of very active pentahydrate and of low activity nonahydrate as used in experiments 1.1 and 2.2 respectively were analysed by X-ray fluorescence spectroscopy (X.r.f.), but neither sample showed any detectable aluminium. Since the sensitivity of X.r.f. to aluminium is only in the order of percentage levels, wet analysis methods were used, and these showed that the very active pentahydrate contained 460 p.p.m. aluminium compared with 90 p.p.m. in the less active nonahydrate. This was a really important breakthrough, and in subsequent experiments attempts were made to dope pure metasilicate hydrates artificially with aluminium.

Experiments 2.6 to 2.9 showed conclusively the importance of aluminium impurity to the effectiveness of the activation process. When pure silica, pure sodium hydroxide and distilled water were used for preparation of the metasilicate hydrate melt, the patented activation process was totally ineffective, and the metasilicate formed produced only amorphous material when it was used in the standard reaction. This result was found to be unaffected by the metasilicate hydrate formed and the purity and activity of the seed used in the crystallisation (2.6, 2,9). On the other hand, where small amounts of hydrated alumina had been dissolved in the metasilicate melt before it was crystallised, then material was prepared which was active when tested within one day, regardless, as before, of the hydrate or of the seed used (2.7, 2.8).

A series of nonahydrates accurately doped with varying levels of sodium aluminate (sodium hydroxide plus alumina trihydrate) was prepared and the details are given in appendix D. The doped nonahydrates were crystallised from supercooled melts as in the activation process and the results obtained when they were tested in the standard reaction after ageing at room temperature for one day, and two months, are shown in figure 3.2. This shows that neither zeolite X nor zeolite B is formed, and an amorphous product results when no aluminium is present in the nonahydrate used. Figure 3.2 also demonstrates the previously reported observation[94] that impure metasilicate hydrates increase in activity with time when left at room temperature. A reassuring result of this work was the fact that the observed activities of the hydrates S9 (1) and S5 (1) which were analysed for aluminium corresponded well with the product/composition curve obtained for the two month old samples (2.2, 1.1). The results for the two month old nonahydrates showed that zeolite B formation tended to increase when the level of aluminium dope was reduced below 4×10^{-3} or increased above 1.6×10^{-2} mole Al per mole silicate.

The conclusion from this investigation of the activation process was that sodium metasilicate hydrates could only be activated by the supercooled crystallisation activation method[93] if they contained low levels of a soluble aluminium impurity and that, in the case of the nonahydrate, the optimum level is around 6×10^{-3} mole aluminium per mole silicate. Thus, the information[93] that the use of colloidal or finely dispersed silica in the preparation of active metasilicate hydrates usually resulted in material of low activity, can be explained by the fact that such silicas, by their mode of production, are probably relatively pure. These experiments demonstrated that a sodium metasilicate hydrate could be not only "active" or "inactive" but also

Fig.3.2 Product from the standard reaction using doped $Na_2SiO_3 9H_2O$, detailed in appendix D and aged at 22°C.



peak heights shown as a % of those obtained from pure samples of zeolite - see appendix A.

"non-active" i.e. have no directing effect at all on the zeolite synthesis. For the purpose of this work the terms "active", "inactive" and "non-active" will be applied to silicate materials which, when tested for activity in the standard reaction, give rise to substantially pure zeolite X, zeolite B or amorphous solid respectively.

In subsequent work, attempts were made to discover some alternative ways of introducing the aluminium which were not covered by existing patents and, in particular, to see if crystallisation is a necessary stage in an activation process.

3.5 LIQUID PHASE ACTIVATION EXPERIMENTS

Several attempts were made to activate impure liquid silicate systems without the use of the activation process and the details are shown in table 3. Inspection of experiments 3.1 to 3.10 will show how unsuccessful this work was. In several experiments activation was attempted by the introduction of sodium aluminate (sodium hydroxide plus alumina trihydrate) to pure sodium metasilicate hydrate melts which were then aged at room temperature without crystallisation (3.2, 3.7, 3.8, 3.9). Similar attempts were made using sodium disilicate waterglass but these were equally unsuccessful (3.4, 3.5, 3.6, 3.10). The remaining experiments attempted activation of an inactive solution by the introduction of aluminium metal (3.1), and activation of sodium aluminate solution by the addition of a small amount of sodium silicate (sodium hydroxide plus silica) (3.3). In an attempt to see if the addition of finely powdered zeolite could promote formation of the active species in doped pentahydrate melts, experiments 3.11 and 3.12 were carried out. These two experiments showed that the product of the standard reaction was predominantly zeolite B regardless of whether the added material was zeolite X or B.

3.6 SOME ADDITIONAL ACTIVATION EXPERIMENTS

Some additional miscellaneous experiments were carried out and these are detailed in table 4.

A small amount of technical grade aluminium silicate ($Al_2(SiO_3)_3$) was added to a pure sodium metasilicate solution before it was used in the standard reaction (4.1). The product was minor zeolite C which raised the possibility of some connection with the small amounts of zeolite C which were formed in the aluminium doped nonahydrate experiments (figure 3.2).

The failure of experiments 3.1 to 4.1 to produce any activation of impure silicate systems confirmed the suspicion that the solid state was somehow important in activation procedures. In experiment 4.2, a doped nonahydrate melt was prepared, crystallisation was induced, and then water was added to produce a partly crystallised solution. After one day at room temperature, this was found to be mildly active and produced minor zeolite X and zeolite C when it was used in the standard reaction. When the partially crystallised solution was tested 23 days later (4.3), the product was minor zeolite C which was in agreement with previous reports[94] that active solutions loose activity on standing.

In experiment 4.4 an active nonahydrate was dehydrated by evacuation over P_2O_5 without heating, until no more water could be removed. The composition was then 1.9 moles H_2O per mole metasilicate, and X.r.d. analysis showed it to be completely amorphous. When used in the standard reaction, the metasilicate was found to be as active as before, and this confirmed that the active species, once formed, can exist in an amorphous low water environment.

A pentahydrate was prepared by the hydration of technical anhydrous sodium metasilicate over saturated potassium carbonate dihydrate at 25°C for ten months. When the pentahydrate was used in the standard reaction, it was found to be inactive although it was expected to be active (4.5). It is possible that the activity had been destroyed during the long hydration and that, if the material had been tested earlier, it would have been found to be active.

3.7 SOLID STATE ACTIVATION EXPERIMENTS

A careful analysis of previous work showed that the solid state was involved in all those activation experiments which had proved successful. Consequently, some solid state activation experiments were carried out and the details are shown in table 5. Initial experiments showed that pure sodium metasilicate nonahydrate could be activated to a moderate extent by the addition of dry sodium aluminate (5.1, 5.2, 5.3). Intimate mixtures of finely ground nonahydrate and aluminate, containing aluminium in levels similar to the doped nonahydrate experiments (appendix D) were prepared and aged in sealed polythene bottles at 25°C. When the mixtures were used in the standard reaction, that which contained the larger amount of aluminium formed a greater amount of zeolite B (5.1, 5.3), a trend previously observed with doped nonahydrate experiments (figure 3.2).

On the assumption that this form of activation involved the incorporation of aluminate species into the metasilicate lattice by a solid-state process, some mixtures were prepared in which dry sodium aluminate was added to a mixture of nonahydrate and anhydrous sodium metasilicate (5.4, 5.5, 5.6). The ratios of aluminate to silicate were similar to the previous experiments and it was hoped that the resulting hydrate interconversion would increase the rate of activation. The results of 5.4, 5.5 and 5.6 were disappointing, possibly because the mixtures were too low in water overall. In the subsequent experiment (5.7), nonahydrate and sodium aluminate were used as in (5.1) except that the silicon to aluminium ratio of the mixture was 2.4 which is similar to that required for growth of zeolite X at 95°C. This mixture was found to be active when used in the standard reaction after it had aged for thirteen days at 25°C.

Experiment 5.7 was a most important development in this work, since it demonstrated for the first time, a route for the room temperature activation of pure nonahydrate without resorting to any previously patented methods.[93] Analysis of the activation mixture by powder X.r.d. after it had aged for ten days showed only pentahydrate peaks with a very slight trace of hydroxysodalite (HS). When the mixture was tested for activity after sixty days, however, it was found to have lost the majority of its previous activity, a tendency previously observed when active material was left in damp conditions. After eight months, the activation mixture was finally analysed by X.r.d. and showed nonahydrate and hydroxysodalite peaks only. The simplest explanation of these observations, which are summarised in table 10, is that the dry aluminate dissolved in the water which it obtained by dehydration of the nonahydrate to pentahydrate and produced a slurry of metasilicate pentahydrate crystals in a solution of sodium aluminate. The aluminate then took part in a reaction with metasilicate to produce some small zeolite precursors capable of seeding crystallisaton.

Crystallisation of hydroxysodalite began and continued until most of the aluminate had been used up. With the aluminate thus removed from solution, the pentahydrate was able to rehydrate to nonahydrate in the water which was made available.

This work showed that a room temperature slurry of sodium metasilicate hydrate crystals with sodium aluminate solution was conducive to the formation of active species. In subsequent experiments, attempts were made to reconstruct this situation and to see how it could be improved.

3.8 SOLID/LIQUID SLURRY ACTIVATION EXPERIMENTS

Initial experiments used solid sodium metasilicate nonahydrate and are detailed in table 6. The silicon to aluminium ratio, (Si:Al), was 2.2 in all experiments except for 6.4. Experiments 6.1, 6.2, 6.3 and 6.5 investigated how the degree of activation depended on water content and the direction in which the components were mixed i.e. solid metasilicate added to aluminate solution or vice versa. In experiment 6.6, solid nonahydrate and dry aluminate were thoroughly mixed before water was added, and in experiment 6.4, solid pentahydrate was mixed with a solution of sodium hydroxide and sodium aluminate in the same proportions as in the standard reaction. The only experiments which showed any significant activation after one day at room temperature were those with relatively low water content (6.1, 6.2) which were only moderately active although after four days (6.2) had become very active. Analyses of these mixtures by X.r.d. are shown in table 10.

A similar series of experiments in which solid sodium aluminate was used is shown in table 7. The first experiment was similar to 6.1, 6.2 in that it used the same silicon to aluminium ratio (=2.2) and a water level intermediate between them (7.1). In this case, however, solid aluminate was used and, when the mixture was used in the standard reaction after one day at room temperature, it was found to be active. Subsequent tests after two and then seven days at 22.5°C showed the activity to have diminished. The experiment was therefore repeated and samples were tested after much shorter periods at room temperature (7.5). This showed that the 7.1 type mixture was active after only a few hours at 22.5°C. The experiment was repeated at 36.5°C and at 60°C (7.6, 7.7 respectively), and this showed that by aging this mixture at these elevated temperatures, the time required to produce active material was reduced to 115 minutes and 45 minutes respectively.

Attempts were made to activate sodium disilicate waterglass type C100 by the addition of dry sodium aluminate (7.2, 7.3) but success was only achieved when sufficient sodium hydroxide had been added to the waterglass to give it metasilicate composition (7.4). A possible explanation of this is that the growth of the active species requires monomeric silicate which, as shown by ^{29}Si n.m.r. (chapter I.7), is present in significant concentrations in metasilicate but not in disilicate waterglass.

It was not clear which variables in the method of mixture preparation were important, and experiments were carried out to prepare a 7.1 type mixture using solid aluminate or solid silicate by mixing silicate into aluminate or vice versa (7.8, 7.9, 7.10, 7.11). All mixtures were aged for seventy minutes at 60°C before they were used in the standard reaction. Results showed that the direction in which the silicate and aluminate components were mixed was unimportant and that activation was more rapid when solid dry sodium aluminate was used (7.8, 7.11 cf 7.9, 7.10). The observation from previous work (table 6) that low water levels were preferable for solid/liquid slurry activation was confirmed at 60°C by experiments 7.8, 7.12 and 7.13.

The ratio of silicon to aluminium which was used in most of these activation mixtures (Si:Al = 2.2), was a result of the original success in this field (experiment 5.7), and some experiments were carried out with alternative ratios (7.14, 7.15, 7.16). All used solid sodium aluminate and the water content was as used in experiment 7.1. Samples were tested in the standard reaction after they had aged for seventy minutes at 60°C and the mixture which had Si:Al = 5 was found to be especially active (7.15).

In order to compare the performance of the activation processes discovered in this work with patented techniques, some mixtures of "nucleation centres" were prepared.[98] The mixture was prepared by the addition of a sodium silicate solution to a sodium aluminate solution with rapid stirring and formed a thin gel within several hours. Samples were used in the standard reaction after seventeen hours at room temperature and were found to be very active (8.1, 8.2). The compositions of some activation mixtures and the products obtained when samples of them were used in the standard reaction are shown in table 9. Similarly, table 10 lists the crystalline phases detected by X.r.d. in some activation mixtures and relates this to the product obtained when samples of the mixtures were used in the standard reaction.

3.9 EXPERIMENTS WITH ACTIVATION MIXTURES - SUMMARY

The investigation of activation mixtures which constituted a large part of this work demonstrates that the liquid phase ageing of aluminium doped silicate systems is very inefficient in comparison with solid-liquid slurries, especially where dry sodium aluminate is used in conjunction with sodium metasilicate solution. As had been reported[98], the time required for activity to reach a useful level was reduced remarkably if the mixture was aged at temperatures greater than 20°C and, in the case of experiment 7.15, a very active material was produced in seventy minutes at 60°C which compares favourably with patented methods of precursor formation[98] (8.1, 8.2).

For the solid-liquid slurry method, activation at room temperature was successful for mixtures whose compositions lie within the following ranges although optimum ratios which are shown in brackets were observed.

Na_2O/SiO_2	SiO_2/Al_2O_3	H_2O/Na_2O
1.0 to 1.3 (1.1)	3 to 12 (10)	7 to 18 (15)

3.10 THE USE OF PINACYANOL CHLORIDE IN THE STANDARD REACTION

Earlier work (section 3.2) with pinacyanol chloride had shown that the concentration of free dye in a silicate solution was reduced by silicate - dye complex formation and by adsorption of dye on colloidal material. In addition it had been shown that active solutions had a greater dye adsorption capacity than had inactive solutions even when colloidal material larger than 200 nm had been removed by ultrafiltration. This suggested that the addition of pinacyanol chloride to silicate solutions before they were used in zeolite syntheses could provide some useful results. Some such experiments were carried out using both active commercial pentahydrate and inactive commercial anhydrous metasilicate and the results are shown in table 11. In experiments using active metasilicate (11.1 to 11.6 inclusive), the addition of pinacyanol chloride up to a silicate to dye molar ratio of 1.6×10^3 produced no detectable effect on the product formed. On the other hand, in reactions using inactive material, the addition of pinacyanol chloride in the molar ratio of 2×10^4 (silicate : dye), suppressed the formation of zeolite B completely (11.7, 11.8).

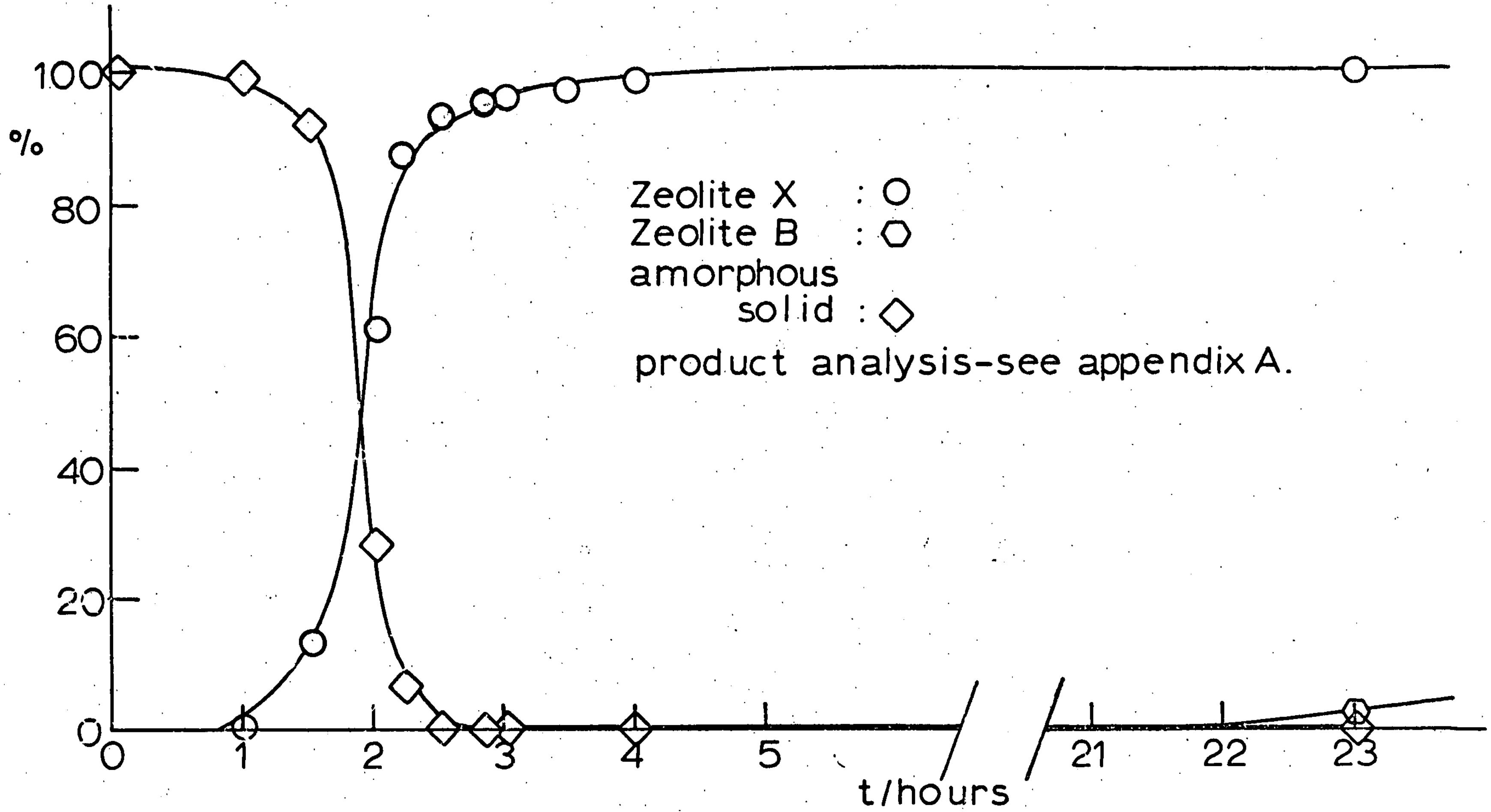
3.11 SOME VARIATIONS OF THE STANDARD REACTION PROCEDURE

Variations of the standard procedure were investigated, and the details are shown in table 12. A reaction using very active commercial pentahydrate was set up and samples of the product were taken at intervals over a 24 hour period (12.1). The samples were analysed by X.r.d., and the results are shown in figure 3.3. This experiment demonstrated that the induction period was short (1 - 1.5 hour), and that crystallisation was essentially complete after 2.5 hour when an active silicate was used in the standard reaction. The start of conversion to zeolite B was observed after 23 hours at 95°C.

In experiment 12.2, a standard reaction mixture was prepared using active metasilicate but the silicate and aluminate components were mixed in the reverse order i.e. in 12,2, the silicate solution was slowly added to the aluminate solution. The product was unchanged from that obtained from normal mixing.

For experiment 12.3, the standard reaction mixture was prepared using inactive anhydrous metasilicate as in 11.7 except that the aluminate solution was mixed into the silicate solution very quickly. X.r.d. of the product showed that no zeolite B had formed, as would have been expected from the materials used.

Fig. 3.3 Standard reaction using active pentahydrate; product sampled over 23hour period - expt. 12.1.



ABBREVIATIONS [a]

A	aluminate (Na)	
Al	alumina	
(1)	trihydrate $Al_2O_3.3H_2O$	- Kaiser
(2)		- Baco
(3)	anhydrous alumina Al_2O_3	- Koch-Light
(C)	commercial material	
crystn	crystallisation	
expt	experiment	
NaA	dry sodium aluminate 1.3 $Na_2O.Al_2O_3$	
(1)		- B.D.H.
(2)		- I.C.I.
PCl	pinacyanol chloride	- Koch-Light
rn	reaction	
S	metasilicate (Na)	
S0	anhydrous sodium metasilicate Na_2SiO_3	
(1)		- "Metso"
(2)	- prepared from batch H5 purified nonahydrate	
S5	sodium metasilicate pentahydrate $Na_2SiO_35H_2O$	
(1)	$Na_2SiO_35H_2O$ - commercial, batch 5J43	- Crosfield
(2)	8X52	- Crosfield
(3)		- B.D.H.
S9	sodium metasilicate nonahydrate $Na_2SiO_39H_2O$	
(1)	$Na_2SiO_39H_2O$ - batch H4 (recrystallised)	
(2)	H5 (recrystallised)	
(P)	after S, S0, S5 or S9, denotes "pure" - prepared from stoichiometric amounts of pure SiO_2 (KS300), ArNaOH and distilled water seeded with "pure" material where appropriate.	
SWG	sodium silicate waterglass	
(1)	$Na_2O.2.05SiO_2.14.27H_2O$: Type C100	- I.C.I.
(2)	$Na_2O.3.39SiO_2.23.96H_2O$: Type Q 79	- I.C.I.
Std	standard procedure	
Temp	temperature	
time :-		
mth	month	
d	day	
min	minute	
s	second	

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[a] Full details of all chemicals are given in section 2.1.

TABLE 1 - EARLY ATTEMPTS TO IDENTIFY THE ACTIVE SPECIES

Expt	Reaction Details	Product
1.1	Std, using S5 (1).[a]	Very Major X
1.2	S soln prepared from S5 (1) as in 1.1 and centrifuged to take down colloidal material. Clear soln decanted and used.	Very Major X
1.3	Std, using S9 (1).	Major B
1.4	S soln prepared from S9 (1) as in 1.3. 5.9g NaOH (dissolved in 20g H_2O and normally contained in A soln) was added and stirred at < 40°C for 10 min.	Major B
1.5	Similar to 1.4 but used S5 (1). Modified S stirred at 38°C for 90 min	Very Major X
1.6	S soln prepared from S5 (1) as in 1.1 and filtered through 0.2 μ filter. The resulting clear soln was used.	Very Major X
1.7	As in 1.6 but S soln filtered 4 times through 0.2 μ filter.	Very Major X
1.8	Std using S5 (2)	Major B
1.9	As 1.8 but S soln filtered through 0.2 μ filter	Major B
1.10	S soln prepared from S0 (1) and dissolved in 50g distilled H_2O. Shaken with 0.5 cm^3 protonated ion exchange resin (Amberlite IR 120(H)) and filtered through 0.2 μm. Checked by PC1 test before use.	Major C, Minor B
1.11	Repeat of 1.10, pH of resulting S soln = 11.45	Major B

[a] see previous page for abbreviations.

TABLE 2 - EXPERIMENTS TO INVESTIGATE ACTIVATION BY CRYSTALLISATION FROM SUPERCOOLED MELTS.

Expt	Metasilicate Details	H_2O	Seed	Age	Product of std rn
2.1	S5(2)	5	?	8 mth	Major X
2.2	S9(1) purified by recrystallisation from S5(3)	9	-	7 mth	Minor X
2.3	S9(1) boiled to $5H_2O$, supercooled to 26°C and seeded. Temp kept < 30°C.	5	S9(1)	3d	Minor X
2.4	S0(1) diss and boiled to $5H_2O$. Supercooled to 20°C and seeded, Temp kept < 40°C during crystn	5	S0(1)	4d	Med/Major X
2.5	As 2.4	9	S0(1)	6d	Med/Major X
2.6	S5(P) From pure SiO_2, ArNaOH and distilled H_2O. Supercooled to 20°C and seeded.	5	S0(1)	5d	Major Amorphous, v sl tr X
2.7	As 2.6 but with 1g Al(2) /mole S added before supercooling	5	S0(1)	few h 1d	Major Amorphous Major X, sl tr B
2.8	As 2.7	9	S0(2)	1d	Major X, sl tr B
2.9	As 2.8 without AL(2)	9	S0(2)	2d	Major Amorphous

TABLE 3 - EXPERIMENTS TO INVESTIGATE THE POSSIBILITY OF LIQUID PHASE ACTIVATION.

Expt	Reaction Details	Product of std rn
3.1	Al foil left in contact with soln of SO(2) (2.7g SO(2) in 52g H_2O) for 20 h at 22°C. Remains of foil removed and cloudy S soln used.	v. minor B
3.2	S5(P) melt doped by addition of 2.5g NaOH and 3g AL(2) per mole S. Cooled to 25°C, aged for 1 h and used without crystn.	Major Amorphous, v sl tr X
3.3	A. soln doped by addition of 0.4g NaOH and 0.3g SiO_2 to the correct amount for rn (11.9g NaOH, 11.9g H_2O + 7.8g AL(2). Cooled to 18°C, aged for 1 h and used. Other rn components SO(1) and SWG(1).	Major Amorphous, v minor X
3.4	38.4g SWG(1) doped by the addition of 0.1g AL(1) and 0.05g NaOH. Boiled, cooled to 20°C and aged 1 h before use. (Al:Si = 7.19×10^{-3}). Other rn components SO(2) and A.	Major B, tr X and C
3.5	100g SWG(1) + 0.5g NaOH and 1g AL(1). Boiled, H_2O replaced, cooled to 19°C and decanted soln used 1 h later. (Al:Si) = 27.9×10^{-3} Other rn components SO(1) and A.	Minor B, trace X
3.6	As in 3.5 but aged 7 d at room temp S9(P) used instead of SO(1).	Minor C, X
3.7	S prepared by adding 1g AL(1) and 0.5g NaOH per mole S9(2). Boiled to 1.95 H_2O/mol S, cooled and left overnight at 22°C. H_2O made up to 9H_2O/mol S keeping temp < 40°C.	Major C, Minor B, tr X

TABLE 3 CONTINUED

Expt	Reaction Details	Product of std rn
3.8	S prepared by adding 1g AL(3) + 0.5g NaOH/mole S to S5(P) melt. Boiled and left overnight at room temp with 3.8 H_2O/mole S. Made up to $9H_2O$ in cold.	Medium B, C, sl tr X
3.9	Doped S5 melt prepared by adding 2g AL(1) and 1g NaOH to 1 mole S5(P) melt. Boiled, cooled, H_2O made up and used after 4d at room temp. (non-cryst).	Major C
3.10	Doped SWG(1) prepared by adding 3g NaOH and 6g AL(1) to 1 mole SWG . Boiled, cooled, H_2O replaced and aged 4 d at room temp. Other rn components SO(2) & A.	Major B
3.11	Doped S5 melt prepared by adding 1g AL(1) and 0.5g NaOH to 1 mole S9(1) and boiling. Then 2g finely powdered product from 3.7 added (Major C, Min B, tr X). Aged 20 h at room temp.	Major B, Minor C
3.12	As 3.11 but with finely ground product of 2.7 added (Major X, sl tr B). Both 3.11 and 3.12 were aged uncrystallised.	Major B, sl tr X

TABLE 4 - SOME ADDITIONAL ACTIVATION EXPERIMENTS

Expt	Reaction Details	Product of std rn
4.1	S doped with $Al_2(SiO_3)_3$. i.e. 0.05g $Al_2(SiO_3)_3$ (B.D.H.) added to pure S soln (2.7g SO(2) in 52g H_2O) and mixed at < 40°C. Used within 1 h.	Minor C
4.2	S9(P) melt doped with 1g AL(1)/mole S, supercooled to 20°C and seeded with small amount S9(P). When crystn well established, H_2O added until partly cryst soln resulted. %H_2O determined by ignition and used after filtrn through 0.8 μ. 1d old.	Minor X,C
4.3	Using S soln as in 4.2, now 24 days old.	Minor C
4.4	S used was S9(doped) which had been dehydrated by pumping over P_2O_5 without heating until % H_2O_{wt}=22% (S5 = 42.4% H_2O)	Major X
4.5	S used was S5 obtained from SO(1) by hydration over satd $K_2CO_3.2H_2O$ soln at 25°C for 10 mth.	Major C, B, sl tr X

TABLE 5 - EXPERIMENTS TO INVESTIGATE THE POSSIBILITY OF SOLID STATE ACTIVATION.

Expt	Reaction Details Preparation	Age	Product of std rn
5.1	0.2g NaA(1) and 20g S9(P) ground intimately and aged in polythene bottle at 25^{o}C. Appropriate amount used in rn, (equiv to 2.4g AL and 1.2g NaOH/mole S) i.e. 31 x 10^{-3} mol AL (mol Silicate)$^{-1}$	7d 28d	Medium X, C Medium X, C (% X sl > 7d)
5.2	Using S9(P) as used in 5.1 prepn.		Major Amorphous, sl tr X
5.3	As in 5.1 but using 0.4g NaA(1) in 20g S9(P).	13d	Major B, Minor X
5.4	14.2g S9(P) + 3.1g S0(P) and 0.2g NaA(1) intimately ground and placed in sealed polythene bottle at 25^{o}C. Then appropriate amount used in rn. Molar ratio S9 : S0 = 2 (equiv to 2.3g AL and 1.15g NaOH/ mole S).	11d	tr X, C, Major Amorphous,
5.5	Materials as in 5.4 except freshly mixed together.	10 min	Major Amorphous
5.6	As in 5.4 but using 0.5g NaA(1)	18d	tr X, Minor B, C.
5.7	Similar to 5.1. 4.1g NaA(1) and 30.9g S9(P) ground intimately and sealed in polythene bottle at 25^{o}C Si : Al = 2.4	13d 60d	Major X, Minor B tr HS traces X, HS

TABLE 6 EXPERIMENTS TO INVESTIGATE THE POSSIBILITY OF SOLID/ LIQUID ACTIVATION (1) USING SOLID SODIUM METASILICATE

Expt	Composition	Direction of mixing	Temp of ageing °C	Age at test	Product of std rn
6.1	28.4g S9(P);	S → A soln	25	1d	Medium X
	41g NaA(1) +			4d	Major X,
	4.6g H_2O		"		Minor B
	Si:Al = 2.2			6d	As at 4d
			"	13d	Major X,
			"		trace HS
6.2	28.4g S9(P);	S → A soln	"	1d	Medium X
	4.1g NaA(1) +			4d	Very Major X
	23.25g H_2O			6d	Very Major X
6.3	28.4g S9(P);	A soln → S	22.5	1d	Major Amorphous,
	4.1g NaA(2)				trace X
	+ 50g H_2O				
6.4	23.7g S5(P);	A soln → S	22.5	1d	Major Amorphous,
	60g NaOH +				sl tr X
	39.3g NaA(2)				
	+ 60g H_2O				
	(In 6.4, mixture contained S, NaOH and AL in correct ratio for test rn i.e. only SWG(1) and H_2O needed to be added)				
6.5	28.4g S9(P);	A soln → S	22.5	1d	Major Amorphous,
	4.1g NaA(2)				tr X
	+ 35g H_2O				
6.6	28.4g S9(P)	Mixed dry	22.5	1d	Major Amorphous,
	+ 4.1g NaA(2)	then 10 cm^3			tr X, A
		H_2O added			

TABLE 7 EXPERIMENTS TO INVESTIGATE THE POSSIBILITY OF SOLID/ LIQUID ACTIVATION (2) USING SOLID SODIUM ALUMINATE

Expt	Composition	Direction of mixing	Temp of Ageing °C	Age at test	Product of std rn
7.1	4.1g NaA(2);	A → S soln	22.5	1d	Major X
	28.4g S9(P)		"	2d	Medium X
	+ 17g H_2O		"	7d	Medium X
	(Si:Al = 2.2)				
7.2	0.9g NaA(2)	A → S soln	22.5	1d	Major Amorphous
	38.4g SWG(1)				
	(T < 35°C)	(Used in test as normal SWG(1); S9(P) as metasilicate)			
	(Si:Al = 18)				
7.3	2.5g NaA(2);	A → S soln	22.5	1d	Major Amorphous, tr X
	38.4g SWG(1)				
	(T < 35°C)	(Used as in 7.2)			
	(Si:Al = 6.5)				
7.4	4.1g NaA(2)	A → S Soln	22.5	1d	Medium X
	21.6g SWG(1)			2d	Major/Med X
	+ 20g H_2O				
	+ 4.0g NaOH i.e. SWG(1) made up to metasilicate by addition of NaOH. Overall ratios as in 7.1 and used as if normal metasilicate.				
7.5	4.1g NaA(2);	A → S soln	22.5	1.5 h	Medium/Min X
	28.4g S9(P)				
	+ 17g H_2O i.e. As 7.1		"	4 h	Major X
			"	24 h	Major X
7.6	4.1g NaA(2);	A → S soln	36.5	52 min	Medium X
	28.4g S9(P)		"	115 min	Major X
	+ 17g H_2O				
7.7	4.1g NaA(2);	A → S soln	60	15 min	Minor X
	21.2g S5(P)			45 min	Major X
	+ 24.2g H_2O				
7.8	4.1g NaA(2);	S soln → A	60	70 min	Major X
	21.2g S5(P)				
	+ 24.2g H_2O (Same overall composition as 7.1)				

TABLE 7 CONTINUED

Expt	Composition	Direction of mixing	Temp of ageing °C	Age at test	Product of std rn
7.9	21.2g S5(P); 4.1g NaA(2) + 24.2g H_2O	S → A soln	60	70 min	Major X
7.10	21.2g S5(P); 4.1g NaA(2) + 24.2g H_2O	A soln → S	60	70 min	Medium X
7.11	4.1g NaA(2); 21.2g S5(P) + 24.2g H_2O	A → S soln	60	70 min	Major X
7.12	4.1g NaA(2); 21.2g S5(P) + 53.8g H_2O	S soln → A	60	60 min	Major Amorphous, sl tr X
7.13	4.1g NaA(2); 21.2g S5(P) + 100g H_2O	S soln → A	60	60 min	Major Amorphous, sl tr X
7.14	9.1g NaA(2); 28.4g S9(P) + 17g H_2O (Si:Al = 1)	S soln → A	60	70 min	Medium X, Minor A, trace HS
7.15	As 7.14 but with 1.82g NaA(2) (Si:Al = 5)	S soln → A	60	70 min	Very Major X
7.16	As 7.14 but with 1.3g NaA(2) (Si:Al = 7)	S soln → A	60	70 min	Medium X

TABLE 8 - SOME OTHER ACTIVATION METHODS FOR COMPARISON

Expt	Composition	Direction of mixing	Temp of ageing °C	Age at test	Product of std rn
8.1	Gel prepared as in patent G.B. 1,318,157 (Grace) 26g AL(1) + 153g NaOH + 279g H_2O; 52g SWG(2) + 310g H_2O	S soln → A soln 150 $cm^3 min^{-1}$	22	20 h	Very Major X
8.2	As in 8.1 but cooled after mixing to keep temp < 35^oC	S soln → A soln	22	17 h	Very Major X

TABLE 9 - MOLAR COMPOSITIONS OF SOME ACTIVATION MIXTURES AND THE PRODUCTS WHEN USED IN THE STANDARD REACTION.

Expt	Na_2O	SiO_2	Al_2O_3	H_2O	Ageing Temp °C	Ageing Time	Product of std rn
5.7	6.14	4.84	1	43.6	25	13d	Major X, Minor B. trace HS
6.1	5.75	4.45	1	51.5	25	1d	Medium X
6.2	5.75	4.45	1	97.6	25	1d	Medium X
7.1	5.75	4.45	1	82.1	22.5	1d	Major X
(same ratios for 7.5, .6, .7, .8, .9, .10, .11)							
7.11	5.75	4.45	1	82.1	60	70 min	Major X
7.12	5.75	4.45	1	115.4	60	60 min	Major Amorphous, sl tr X
7.14	3.3	2.0	1	37.0	60	70 min	Medium X, Minor A, trace HS
7.15	11.29	10.0	1	184.4	60	70 min	Very Major X
7.16	15.35	14.1	1	259	60	70 min	Medium X
8.1	15.9	15.3	1	318	22	20 h	Very Major X
	5.15	4.0	1	242 : std reaction mixture			

TABLE 10 - RESIDUES DETECTED IN SOME ACTIVATION MIXTURES

Expt	Ageing		X.r.d. Analysis of activation mixture	Product of std rn
	Temp ^{o}C	Time		
5.7	25	0	S9 and NaA	
	"	10d	S5 + HS (v sl tr)	
	"	13d		Major X, Minor B, trace Sodalite
	"	20d	S5 + HS (sl tr)	
	"	60d		traces X, HS
	"	8 mth	S9 + HS (minor)	
6.1	25	1d	S9	Medium X
	"	4d	S9 + HS (v sl tr)	Major X, Minor B
	"	6d	S9 + Sodalite (trace)	Major X, Minor B
	"	13d		Major X, tr HS
6.2	25	1d	S9	Medium X
	"	4d		Very Major X
	"	5d	S9 + X (sl trace)	
	"	6d	S9 + X (trace)	Very Major X
			washed and dried residue[a]	
7.1	22.5	1d	Zeolite X 300 Å[b] Zeolite A 200 Å	Major X
7.11	60	70 min	(then left at room temp)	Major X
	22	15 h	Zeolite X 60 Å HS 100 Å Zeolite A 200 Å	
7.12	60	60 min		Major Amorphous, sl tr X
	22	15 h	Major Amorphous	
7.14	60	70 min		Medium X, Minor A, trace HS
	60	20 h	Major HS, sl tr A	
8.1	22	20 h		Very Major X
	22	8d	Zeolite X 40 - 50 Å	

[a] The activation mixtures of experiments 5.7 to 6.2 inclusive were examined by X.r.d. as finely ground pastes. In the case of experiments 7.1 to 8.1 inclusive, the activation mixture was dispersed in water and the insoluble residue was filtered and dried before X.r.d. examination was carried out.

[b] Mean crystallite size was estimated by comparison of measured X.r.d. peak width at half height with a calibration curve for the machine in question. Peak width increases as the mean particle size decreases.

TABLE 11 - EXPERIMENTS TO SHOW THE INFLUENCE OF PINACYANOL CHLORIDE ON ACTIVE AND INACTIVE METASILICATES.

Expt	Reaction Details	Product
11.1	Std using S5(1)	Very Major X
11.2	As in .1 but with S5(1) dissolved in soln containing 6.67×10^{-7} mol PCl keeping temp < 35°C. S soln then used normally.	Major X
11.3	As in .2 but with 26.7×10^{-7} mol PCl.	Major X
11.4	As in .2 but with 133.5×10^{-7} mol PCl.	Major X
11.5	As in .2 but with 477×10^{-7} mol PCl.	Major X
11.6	As in .2 but with 1220×10^{-7} mol PCl.	Major X
11.7	Std using S0(1)	Medium B, trace X
11.8	Similar to .2 but using S0(1) and 97.5×10^{-7} mol PCl (Sample A at 2 hrs, B at 3 hrs)	A 100% Amorphous B Major Amorphous, trace X

TABLE 12 - AN INVESTIGATION OF THE STANDARD REACTION PROCEDURE

Expt	Reaction Details	Product
12.1	Std using S5(1) Sampled frequently over 24 h period - see FIG 3.3 sample (A) at 3 h.	(A) Very Major X
12.2	Using S5(1) but silicate component added slowly to A soln (Normally A soln mixed slowly into silicate component).	Very Major X
12.3	Using S0(1) as in 11.7 but adding the A soln to silicate component as quickly as possible (< 2 s for complete addition).	Major Amorphous

CHAPTER 4

DISCUSSION

There have been several publications on the subject of hydrothermal synthesis of zeolites and, in particular, on possible mechanisms for the crystallisation process.[100-109] Although it has not been possible to undertake detailed mechanistic studies, it is impossible to discuss activity and active silicates without some consideration of the possible mechanisms of zeolite crystallisation.

4.1 MECHANISM OF ZEOLITE CRYSTALLISATION - INTRODUCTION

It is widely accepted[90,100,102] that the crystallisation of a zeolite from the appropriate reaction mixture proceeds by a series of nucleation steps which involve the growth of appropriate seeds, until sufficient such seeds have been formed for crystallisation to proceed at a significant rate. If, however, it is possible to provide the reaction mixture with some appropriate seed precursors then the induction period of the crystallisation could be reduced, and that the reaction would have less critical initial conditions, since the important primary nucleation steps would not be necessary. This is undoubtedly the manner in which the active silicates and the other activation mixtures described in this thesis promote the crystallisation of zeolites, particularly X, Y, A and HS from the Na_2O-SiO_2-Al_2O_3-H_2O system.

It is thought that the distribution of polymeric species which are present during the initial stages of a zeolite synthesis has a major influence on the product which will be formed.[90,103,110] It is clear that the relationship between the activity and inactivity of silicate materials in the present context is complex and finely balanced, but fundamentally dependent on aluminate which is present either fortuitously or by design. This was demonstrated by the fact that the use of aluminate-free sodium metasilicate in the standard reaction always resulted in a completely amorphous product i.e. non-active.

A likely explanation is that particular aluminosilicate species or groups of species which are of use in the initial stages of nucleation of the promoted zeolite are present in the active material as a result of its composition and the conditions of its preparation and storage. These desirable species are absent from inactive materials, the use of which invariably results in the formation of the more stable product, zeolite B. The situation which must therefore be explained is why the treatment of such silicate/aluminate systems by one of the activation procedures described in this work or in the patent literature[93] can produce material which has the ability to promote the crystallisation of specific metastable zeolite phases whereas the untreated material cannot. It must also be explained why aluminate-free metasilicate gives rise to amorphous products in the standard reaction.

4.2 PROPOSED STRUCTURE OF THE ACTIVE SPECIES

As described previously, active material has a directing effect on the crystallisation of several zeolite phases. Thus, a distinct possibility is that such material contains some small building unit which is common to all their structures. One such building unit is the β-cage which, as described in section 1.3, is fundamental to all of the promoted structures but does not feature in the structure of zeolite B, the product invariably formed when inactive material is used. It seems reasonable, therefore, that the addition of material which contains free β-cages to an appropriate reaction mixture will enhance the rate of nucleation of a product whose structure can be constructed from them.

As mentioned earlier, this work has shown that inactive material, likewise, relies on low levels of aluminate impurity for its ability to promote the formation of zeolite B in the standard reaction. In contrast to the other promoted zeolites, all the available information suggests that, in this case, no specific aluminosilicate species is particularly important and that the nucleation of zeolite B occurs in the presence of aluminosilicate particles regardless of their structure.

4.3 PROPOSED MECHANISM OF FORMATION OF THE ACTIVE SPECIES

Other work has shown that a wide range of polymeric species exists in aqueous solutions of sodium silicate[13] and that pH, concentration and temperature influence the actual distribution of species. This is discussed in chapter I.7. All the available evidence from this and other work suggests that a similar situation exists in systems which contain mobile aluminate and silicate ions, and that some likely aluminosilicate species are single four- and six-unit rings i.e. $[(\mathrm{Al}, \mathrm{Si})\mathrm{O}]_{4,6}$. Under appropriate conditions, it is possible to propose the growth of larger aluminosilicate species, and it is undoubtedly the distribution of these growth products which determines the activity or inactivity of the resultant material.

A possible mechanism for the formation of the β-cage, proposed to be the active species, is that rings of four or six units as described above, cluster around a solvated sodium ion and link up to each other by the condensation polymerisation of hydroxyl groups. The proposal that the hydrated sodium ion acts as the template for formation of the active species is supported by reports[94] that activity in this sense has only been observed with the sodium silicates. In conditions where sufficient building units are present, one would expect growth to continue, and this was observed in some of the activation mixtures which were studied, as shown in table 10. For example, powder X.r.d. of the activation mixture of experiment 7.11 showed the presence of small crystallites of zeolites X, A and HS only, all of which have structures based on the β-cage. This work showed that, in mixtures of acceptable composition, the formation of the β-cage and growth products based on it were the preferred processes at room temperature. Zeolite B crystallites were never observed in any of the activation mixtures examined, in agreement with reports[92] that nucleation of zeolite B becomes increasingly favoured at higher temperatures. It was shown that the rate of activation could be increased mainly by aging the system at higher temperatures or by increasing the concentration of aluminate, both of which are compatible with an enhanced rate of β-cage formation. In many cases it was found that continued high growth conditions resulted in the formation of increased levels of β-cage growth products with an associated increase in the inactivity of the material. This is compatible with the formation of larger aluminosilicate particles which, as discussed earler, seem to enhance the nucleation of zeolite B in the standard reaction. However, in the limit of time and under conditions where extensive growth of the aluminosilicate species in the material could take place, it was found that both inactivity and activity diminished to insignificant levels i.e. the material became non-active. This was exemplified by experiment 5.7, as shown in table 10 and suggests that the formation of both zeolite X and zeolite B in the standard reaction is fundamentally reliant on the provision of basic building species, such as the four- and six-unit rings, in the initial reaction mixture by the sodium metasilicate component.

Thus it is proposed that both active and inactive silicates contain a range of aluminosilicate species which can extend from discrete aluminate and silicate ions through oligomers, cyclic species such as four- and six-unit rings $[(Al, Si)O]_{4,6}$ and single β-cages to larger aggregates such as small zeolite crystallites and amorphous aluminosilicate particles. The effect of such silicates when used in zeolite syntheses of the type described in this work, is dependent largely on the distribution of the species present. Activity is favoured by a significant concentration of discrete β-cages, whereas inactivity is favoured by the presence of large aluminosilicate particles of any structure and neither effect is observed when the material is devoid of simple aluminosilicate species, possibly four- or six-unit rings, which experiment suggests are the fundamental growth units of the nucleation process.

4.4 PROPOSED ROLE OF THE ACTIVE SPECIES IN ZEOLITE CRYSTALLISATIO

A likely mechanism for the nucleation of zeolites X, Y and A is that preformed β-cages come together and are linked by oxygen bridges between the atoms of appropriate rings, depending on the reaction conditions and mixture composition. The nucleation of hydroxysodalite is favoured by an increased level of sodium ions in a zeolite X type of reaction mixture (e.g. standard reaction). It is possible that this is because hydrated sodium ions act as templates for the growing HS structure in a similar manner to that proposed for formation of β-cages, except that the ion is now eclosed by the four-unit faces of six separate β-cages rather than by single six- or four-unit rings.

In all cases, it is possible that further growth could occur by a continuation of these proposed nucleation mechanisms, but it seems more likely that much of the subsequent growth takes place by formation of β-cage or of other building units directly on the growing sites of the crystallite.

Other possible structures of the active species are double six- or four- unit rings, or larger aggregates of β-cages, but none of these could, on its own, explain the versatility of active material in different syntheses. It is, however, quite possible that the true situation is not so simple as is proposed here, and that two or more of the alternatives mentioned operate concurrently.

As discussed earlier, there is no evidence that any particular aluminosilicate species, comparable with the β-cage, is uniquely important in the nucleation of zeolite B. All the available results suggest that nucleation could involve the formation of double aluminosilicate chains by polymerisation of the four-unit rings proposed earlier, in a side to side manner. The fact that the formation of zeolite B is favoured by increased reaction temperature and has a longer induction period but faster growth than zeolite X suggests that nucleation is kinetically hindered which is compatible with the proposed mechanism. The observation that the formation of zeolite B is favoured by an increase in the number and size of aluminosilicate particles in the reaction mixture, whether by growth or by seeding[94], can be explained by the fact that these particles probably provide anchors from which the double chains are able to grow. In other words, crystallisation is seeded in a conventional fashion.

4.5 DISCUSSION OF SOME EXPERIMENTAL OBSERVATIONS IN RELATION TO THE PROPOSED THEORIES

4.5.1 ACTIVATION MIXTURES

This work has shown that the activation of systems which contain silicate and aluminate species is most effective when some solid or gel phase is present, and this is epitomised by the inactivity of uncrystallised melts of technical sodium metasilicate in comparison with the activity of the same materials after crystallisation. It seems likely that the reasons for this are that saturated systems favour crystallisation, and that the necessary polymerisation of aluminosilicate species, which is required in the formation of the active species, can occur more readily in the interphase region, where the hydration of the reacting species would be expected to be less complete. The necessity of a supersaturated system to the stability of the active species is confirmed by the steady loss of activity which is observed when dilute aqueous solutions of active materials are aged at room temperature. This can be interpreted as the hydrolysis of β-cages into simpler aluminosilicate ions.

4.5.2 ACTIVITY OF COMMERCIAL SODIUM METASILICATES

Aluminium is one of several impurities which are present in commercial silicates as a result of the use of sand as a major raw material. Thus, the phenomena of activity and inactivity which were originally observed in commercial sodium metasilicate pentahydrates[93] were the consequences of a fortuitous accident - or was it intended? In the industrial preparation of sodium metasilicate hydrates, a melt of the desired composition is seeded with up to 20% wt of a metasilicate hydrate and then poured onto a cooled steel conveyer belt to crystallise. Consequently, the temperature of the crystallising material is not controlled and, as confirmed by published data[93], this variation in temperature is undoubtedly responsible for the wide range of activities which is observed in the hydrates produced. The activity of all the impure sodium metasilicate hydrates which were studied[93] was low immediately after preparation, but improved to an optimum value after a few days at room temperature in the case of those which had been crystallised at the lower temperatures. On the other hand, those formed at higher temperatures, were inactive for several months although they also became active eventually. The most reasonable explanation of these facts is that crystallisation at or near the melting point of the hydrate is slow and, as a result, the aluminium impurity is largely excluded from the silicate lattice. In contrast, those melts which are crystallised at low temperatures, when supercooled, retain the impurity within the silicate lattice since solidification of the melt is rapid. The impurity which is locked within the silicate lattice is much more accessible for use in the formation of β-cages or other species and thus activation is more rapid.

The observation that commercial anhydrous sodium metasilicate is invariably inactive can be explained by the fact that the environment of the aluminate impurity is highly polymeric, with no discrete, mobile silicate species, as is the case in the metasilicate hydrates. It seems unlikely that β-cages or other small aluminosilicate species could form in such an environment.

4.5.3 THE DOPED SODIUM METASILICATE HYDRATES

The results from the doped nonahydrate experiments (figure 3.2) showed that those aged materials which contained aluminate up to an aluminium to silicon molar ratio of 2×10^{-3} formed products in the standard reaction which contained significant amounts of zeolite B whereas those which contained higher levels of aluminate produced mainly zeolite X. In addition, those which had Al:Si molar ratios of greater than 1.2×10^{-2}, while still effective at producing significantly pure zeolite X, tended also to form small but increasing amounts of zeolite B as the aluminate content was increased.

A likely explanation of these facts is that at the lower levels of aluminium, there were insufficient aluminosilicate species present to form significant numbers of active species, whereas at the higher levels, increasing numbers of active species and related growth products were formed. As the size and concentration of these growth products increased, the nucleation of zeolite B in the standard reaction became increasingly significant.

4.5.4 THE PINACYANOL CHLORIDE ACTIVITY TEST

The pinacyanol chloride test for activity resulted from the observation that the visible absorbance of 2×10^{-6} mol dm^{-3} dye in 0.01 mol dm^{-3} solutions of commercial sodium metasilicate pentahydrate was less if the silicate was active than if it was inactive, even after the silicate solutions had been filtered through a 200 nm pore filter. From this, it was deduced that the active material had a greater dye adsorptive power than the inactive material.

It was shown that pinacyanol chloride has a strong affinity for solid aluminosilicates, and, as proposed earlier, active materials have, in general, higher levels of β-cage growth products such as crystallites of zeolites A, X, and HS than do inactive materials. These growth products have structures of high surface area, and thus solutions of active silicates have a greater capacity for dye removal than do inactive solutions of the same concentration.

As discussed in section 4.3, an active material can, with extended growth of the active species, become inactive and eventually neither active nor inactive i.e. "non-active" since no simple aluminosilicate building species remain. This situation was often encountered with those products which were activated by one of the hydration methods[93], probably because the material was very inhomogeneous and, as such, contained regions where extended growth could occur. The dye test was found to be less effective in such materials than it had been with the silicates prepared by the crystallisation of supercooled melts. It seems likely that, as continued growth takes place, then overall dye adsorptive capacity increases steadily although in reality, activity may be decreasing.

4.5.5 PINACYANOL CHLORIDE IN THE STANDARD REACTION

The use of pinacyanol chloride in the standard reaction showed that the performance of the active silicates is unaffected, while the formation of zeolite B from inactive silicates is completely suppressed in most cases. This is consistent with the observation that pinacyanol chloride adsorbs strongly on all aluminosilicate particles and confirms that nucleation of zeolite B is favoured by the presence of aluminosilicate particles in the reaction mixture. It is likely that the surfaces of such particles are blocked by adsorption of the pinacyanol chloride and are thus made ineffective as nucleation sites for zeolite B. The observation that the active species is unaffected by dye addition is consistent with the proposal that discrete β-cages, which one would expect to be too small to adsorb pinacyanol ions, are responsible for activity.

4.6 CONCLUSIONS

This work has demonstrated convincingly that the reason for the activity which was originally observed in commercial sodium metasilicate pentahydrates is that these materials contain discrete zeolite nucleation precursors, probably β-cages, in addition to other aluminosilicate species. These form within the silicate lattice under suitable conditions as a result of an aluminate impurity. It has been shown that active material can be prepared in various systems which contain mobile silicate and aluminate species and that this is most effective in supersaturated conditions in the presence of a solid or gel phase. It seems likely that the effect of active material on the crystallisation of zeolites X, Y, A and HS from the Na_2O-SiO_2-Al_2O_3-H_2O field is mainly by the provision of advanced building units to the reaction mixture at an early stage. Experiment has also shown that the nucleation of zeolite B is favoured by the presence of aluminosilicate particles and that, in most cases, this can be suppressed by the addition of pinacyanol chloride to the reaction mixture.

It is very likely that the nucleation of other, possibly new, zeolites in different reactant fields could be promoted in a similar manner by the addition of small amounts of carefully grown building units to the reaction mixture.

A thorough investigation of the application of this concept should be carried out.

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APPENDIX A CLASSIFICATION OF THE COMPOSITION OF ZEOLITE SAMPLES.

$\left(\frac{\text{Sample peak height}}{\text{Standard peak height}}\right) \times 100 = R^{a}$	Classification of composition (with abbreviations)[b]
$95 < R < 100$	Very Major (v Maj)
$75 < R < 95$	Major (Maj)
$25 < R < 75$	Medium (Med)
$7 < R < 25$	Minor (Min)
$2.5 < R < 7$	trace (tr)
detectable $< R < 2.5$	slight trace (sl tr)
only detectable	Very slight trace (v sl tr)

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[a] Some convenient peaks are :- Zeolite X $2\theta = 23.4^{\circ}$
Zeolite B $2\theta = 28.05^{\circ}$
Zeolite C $2\theta = 13.27^{\circ}$

Amorphous solid is assessed by the baseline height at $2\theta = 26\text{-}28^{\circ}$

[b] In the tables of results, only the crystalline phases are mentioned except where some special importance is attached to the presence of amorphous material. For example; if the product is stated to be Minor X, then the balance of the sample is amorphous material i.e. Medium or Major Amorphous.

APPENDIX B USEFUL POWDER X.R.D. DATA[a,b]

Zeolite X

$2\theta/^{o}$	$(I/I_o)100$
6.2	100
10.1	31
11.8	24
15.53	44
18.52	15
20.2	25
21.15	3
22.6	10
23.4	61
23.75	11
24.8	3
25.55	3
26.78	51
27.5	3
29.35	12
30.45	26
31.1	61
32.15	26
32.76	6
33.76	23
34.35	10
35.3	4
36.8	2
37.55	13
38.9	1
40.2	3
40.95	10
41.5	8
42.8	6
43.6	3
46.7	4
47.28	4
48.85	2
50.05	3

Zeolite B[c]

$2\theta/^{o}$	$(I/I_o)100$
12.45	65
17.7	38
21.7	21
28.1	100
33.45	21

Zeolite C[c]

$2\theta/^{o}$	$(I/I_o)100$
13.4	100
18.6	44
23.0	76
29.8	75

Zeolite A[c]

$2\theta/^{o}$	$(I/I_o)100$
7.4	96
10.3	71
12.65	46
16.3	45
20.5	12
21.8	55
24.1	92
26.2	27
27.2	88
30.05	100

Hydroxysodalite (HS)[c]

$2\theta/^{o}$	$(I/I_o)100$
14.1	77
20.0	8
24.5	100
28.4	10
31.8	28
34.95	42
37.85	10

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[a] All measurements were made with a vertical diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å). Interplanar (d) spacings can be obtained from the equation $d = \lambda/2 \sin\theta$.

[b] All samples were equilibrated at room temperature and humidity for at least one hour before examination.

[c] Only the main peaks are listed

APPENDIX C SUMMARY OF RESULTS FROM THE VISIBLE SPECTRA OF SOME DYE-SILICATE SYSTEMS.

Dye	Observations[a]
Crystal Violet	Colour fades very rapidly
Malachite Green	"
Methyl Violet	"
Nuclear Fast Red	Does not discriminate active from inactive
Methylene Blue	"
Methyl Orange	"
Fuchsin	"
Rhodamine 6G	"
Toluidine Blue	Active solutions paler than inactive but peak very broad
Bismarck Brown	Active solutions paler than inactive

---

[a] All solutions contained 0.01 mol dm^{-3} sodium metasilicate and were run four minutes after preparation.

APPENDIX C COMPOSITION AND PREPARATION OF NONAHYDRATES ACCURATELY DOPED WITH Al. TEST RESULTS ARE SHOWN IN FIGURE 3.2.

Nona No.	Preparation	Composition 10^3 mol Al (mol Si)$^{-1}$
D.1	S(P) soln doped by addition of 0.1g AL(1) and 0.05g NaOH per mole S. Dissolved by heating and H_2O adjusted to $9H_2O$ mol S^{-1}. Supercooled to 25°C and seeded with a small amount S9(P). During crystallisation temp kept < 30°C.	1.28
D.2	As .1 with 0.15g AL(1) and 0.075g NaOH	1.92
D.3	As .1 with 0.25g AL(1) and 0.125g NaOH	3.2
D.4	As .1 with 0.5g AL(1) and 0.25g NaOH	6.4
D.5	As .1 with 1.0g AL(1) and 0.5g NaOH	12.8
D.6	As .1 with 3.0g AL(1) and 1.5g NaOH	35.5
	For comparison :- S9(1) as in 2.2	0.95
	S5(1) as in 1.1	3.6

APPENDIX E KEY RELATING THESIS AND ORIGINAL EXPERIMENTAL NUMBER

Thesis	Original Work	Thesis		Original Work	Thesis	Original Work
1.1	N 16[a]	5.1		5.18, 5.30	11.1	7.1
1.2	15	5.2		5.19	11.2	7.3
1.3	2.2	5.3		5.26	11.3	7.4
1.4	2.1	5.4		5.27	11.4	7.2
1.5	2.4	5.5		5.28	11.5	7.7
1.6	3.2	5.6		5.29	11.6	7.5
1.7	3.4	5.7		5.31, 5.32	11.7	7.11
1.8	3.5				11.8	7.6
1.9	3.6	Thesis	Mixture Code	Reaction Code	12.1	7.9
1.10	3.10				12.2	7.8
1.11	3.11	6.1	SA1	6.1, 6.3, 6.7, 6.12	12.3	7.10
2.1	4.1					
2.2	4.3	6.2	SA2	6.2, 6.4, 6.8		
2.3	4.5					
2.4	4.6	6.3	SA3	6.9		
2.5	4.7	6.4	SA4	6.10		
2.6	4.10	6.5	SA5	6.12B		
2.7	4.8, 4.9	6.6	SA6	6.14		
2.8	4.11	7.1	SA7	6.15, 6.18, 6.24		
2.9	4.12A					
3.1	4.12B	7.2	SA8	6.16		
3.2	4.15	7.3	SA9	6.17		
3.3	4.18	7.4	SA10	6.19, 6.24		
3.4	4.20	7.5	SA11	6.20, 6.21, 6.22		
3.5	5.1					
3.6	5.5	7.6	SA12	6.27, 6.28		
3.7	5.2	7.7	SA12B	6.29, 6.30		
3.8	5.4	7.8	SA14	6.31		
3.9	5.10	7.9	SA15	6.32		
3.10	5.9	7.10	SA16	6.33		
3.11	5.3	7.11	SA17	6.34		
3.12	5.7	7.12	SA18	6.35		
4.1	5.8	7.13	SA19	6.36		
4.2	5.14	7.14	SA20	6.37		
4.3	5.16	7.15	SA21	6.38		
4.4	5.17	7.16	SA22	6.39		
4.5	5.15	8.1	GA1	6.26		
		8.2	GA2	6.25		

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[a] In the original work all experiment and reaction codes were preceded by the letter N which has been omitted in this table

APPENDIX F PUBLISHED WORK

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THERMAL PROPERTIES OF SODIUM METASILICATE HYDRATES

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ABSTRACT

The heats of fusion and heat capacities at 298.2 K of $Na_2SiO_3 \cdot 5H_2O$, $Na_2SiO_3 \cdot 6H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ have been measured by DSC. The enthalpies and entropies of fusion increase with the water content of the hydrate and the entropy of fusion per mole of water is almost constant. The application of DSC/DTA to the analysis of metasilicate hydrate mixtures is discussed.

INTRODUCTION

Sodium metasilicate forms hydrates with 5, 6, 8 and 9 molecules of water per metasilicate group[1,2]. Their structures have been investigated by X-ray[3–6] and neutron diffraction[7] and it appears that almost all of the hydrogen atoms are involved in hydrogen bonds. All of the hydrates are known[2] to melt below 75 °C but apart from some estimations by McCready[8] there have been few studies of their thermal properties[9], and no direct measurements of their heats of fusion. We now report values for their heat capacities at 25 °C and their heats of fusion obtained by DSC, and we also discuss the use of DSC/DTA for the analysis of their mixtures. Although DTA has been used to investigate hydrated sodium polysilicates[10] its application to metasilicate hydrates has not been previously reported.

EXPERIMENTAL

Sodium metasilicate nonahydrate was prepared by recrystallisation at room temperature from an aqueous solution which contains 30% by weight of Na_2SiO_3 (ref. 2). The crystals were filtered in the absence of CO_2 and dried over $Na_2SiO_3 \cdot 5H_2O$ to give a product with nine moles of water per mole of silicate.

Preparation of the octahydrate by crystallisation from aqueous solution proved to be extremely difficult (cf., ref. 3), and it was never obtained completely free from other hydrates.

The hexahydrate was prepared by isothermal crystallisation at 52 °C from a 45% by weight solution of Na_2SiO_3 after the addition of a small quantity of seed crystals.

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The pentahydrate was prepared by crystallisation of a pure supercooled melt and required approximately 10% of a metasilicate hydrate as seed. Technical grade material (BDH Ltd.) was also used for comparison; its thermal behaviour did not differ significantly from that of the pure material.

All of the materials were carefully analysed by powder X-ray diffraction[3] and weight loss on ignition at 1000°C.

Measurements were made with a DuPont Instruments Ltd. 990 thermal analyzer used with a cell base Module II and differential scanning calorimeter (DSC) cell. The temperature scale was calibrated with ice, $Ca(NO_3)_2 \cdot 4H_2O$, stearic acid, naphthalene, benzoic acid and indium, and in all cases the onset of fusion (obtained by extrapolation of the leading edge of the endotherms) agreed to within ±1.5°C with the melting points reported in the literature. The energy calibration was based on the heat capacity of synthetic sapphire[11] and confirmed to within ±1% by the heats of fusion of ice, indium and stearic acid.

The sodium metasilicate hydrates were found to react with the aluminium sample pans normally used with the DSC cell and it was therefore essential to use copper pan bases and lids. Accurate enthalpy and heat capacity measurements could only be obtained when the samples were tightly sealed to prevent the loss of water, but good qualitative analyses could be made with samples in pans with crimped on lids. For quantitative heat measurements water loss was kept below 0.1% of the sample weight; this was particularly difficult to achieve with the pentahydrate which has a relatively high melting point.

RESULTS AND DISCUSSION

Thermodynamic properties

The experimental results and their estimated errors are given in Table 1 along with the values of other workers. The melting points of the three lower hydrates agree within experimental error with the literature values[2] whilst that of the nonahydrate is slightly higher.

The enthalpies of fusion given in Table 1 are in each case the mean of at least 4 observations. The value obtained for the nonahydrate lies between the indirect experimental value of Lange and Stackelberg[9] and the estimated value of McCready[8], whilst that of the pentahydrate is higher than both earlier values[8,9]. The heat of fusion of the hexahydrate has not been previously reported. Our value lies between those of the penta- and nonahydrates, and as might be expected it is somewhat closer to the pentahydrate value.

The entropies of fusion calculated from our ΔH_f values increase with the water content of the salt and the entropy of fusion per mole of water (Table 1) is almost constant. It is thus easy to estimate a value for the entropy of fusion of the octahydrate and hence to obtain an approximate value for its heat of fusion. These estimates, which are the only available values for the octahydrate, are shown in Table 1. The mean value of the entropy of fusion per mole of water based on the results for the 9-, 6- and

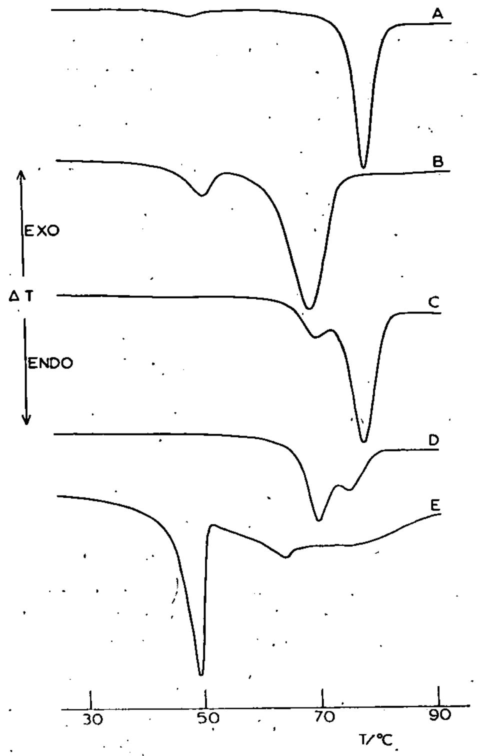

Fig. 1. Typical DSC curves obtained for sodium metasilicate hydrate mixtures. Powdered samples (1–4 mg) in Cu pans with crimped on Cu lids. Heating rate: 10°C min^{-1} (A–D); 5°C min^{-1} (E). Approximate molar compositions: (A) 1% 9, 99% 5; (B) 20% 9, 80% 6; (C) 25% 6, 75% 5; (D) 35% 5, 65% 6; (E) 5% 6, 95% 9.

hydrate are indistinguishable. Quantitative measurements have not been made although it is clear that provided the equipment is calibrated with known standards, exact analyses could be obtained more rapidly and easily than by other methods.

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TABLE 1

THERMAL PROPERTIES OF SODIUM METASILICATE HYDRATES $Na_2SiO_3 \cdot xH_2O$

Hydrate, x	T_f *(°C)*	ΔH_f *(kJ mol⁻¹)*	ΔS_f *(J mol⁻¹ K⁻¹)*	$(\Delta S_f/x)$ *(J mol⁻¹ K⁻¹)*	$10^2 C_p$ *(J mol⁻¹ K⁻¹) (solid, 25 °C)*
9	49.8 ± 1.5 47.8^a	59.6 ± 2.5 67.6^d 55.4^e	184.5	20.48	5.3 ± 0.5 4.75^g
8	49.5 ± 1.5 48.4^a	53.1^f	164.8^f	20.6^f	
6	63.2 ± 1.5 62.9^a	42.0 ± 2.5	124.9	20.82	3.3 ± 0.3 3.53^g
5	73.0 ± 1.5 72.2^a	37.3 ± 3.5 30.7^d 31.5^e	107.6	21.52	3.1 ± 0.3 3.15^g
0	$1088^{b,c}$	52.0^c	38.2^c		1.11 ± 0.05 1.13^g 1.12^c

[a] Ref. 2. [b] Ref. 12. [c] JANAF Thermochemical Tables, 2nd ed., 1970. [d] Ref. 8, [e] Ref. 9, obtained indirectly from heats of solution. [f] Estimated, see text. [g] Ref. 8, estimates based on Kopp's law.

5-hydrates (20.9 ± 0.5 J mol^{-1} K^{-1}) is only slightly less than the entropy of fusion of water (22.0 J mol^{-1} K^{-1})[13]. This behaviour is similar to that observed for other inorganic hydrates, many of which have entropies of fusion per mole of water within ± 4 J mol^{-1} K^{-1} of the pure water value. The fact that sodium metasilicate solutions contain substantial amounts of polymeric silicates[14] does not appear to have a marked effect on the entropies of fusion of the hydrates.

Within experimental error the heat capacities obtained at 25 °C for the solid hydrates agree with those estimated by McCready[8]. Those of the melts were found to be approximately twice as large as those of the solids, but because of the experimental difficulties it was impossible to obtain accurate values[15].

Analytical applications

During this work it was found that DSC/DTA provides an excellent method for the qualitative analysis of metasilicate hydrate mixtures and that in most cases it is much quicker, requires much smaller samples, and is at least as sensitive as the powder X-ray diffraction methods which are usually used. Typical curves obtained with prepared mixtures are shown in Fig. 1 and the operating conditions are given in the caption. The method is particularly suitable for the detection of small quantities of higher hydrates present as impurities in the lower hydrates, thus for example 1% by weight of the nonahydrate in the pentahydrate is detected much more easily than by X-ray diffraction. As can be seen from the figure the method is applicable to a wide range of mixtures. However, it should be noted that the octahydrate and the nona-

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and seeded with a small quantity of nonahydrate crystals. The crystals were filtered and dried over the pentahydrate until their composition was exactly that of the nonahydrate.

Sodium metasilicate octahydrate (S8) is difficult to obtain pure.(3) It was prepared by crystallization from a solution of pure metasilicate, but was contaminated with pentahydrate.

Sodium metasilicate hexahydrate (S6) was prepared by isothermal crystallization at 325 K from an aqueous solution which contained 47 per cent by mass of purified sodium metasilicate, seeded with a small amount of hexahydrate.

Sodium metasilicate pentahydrate (S5) was prepared from its melt which was made by careful evaporation of a nonahydrate melt. The crystallization was induced at approximately 303 K by the addition of pure pentahydrate seed to the extent of 20 per cent of the mass of the melt.

Anhydrous sodium metasilicate (S0) was obtained by crystallization from an aqueous metasilicate solution which was slowly evaporated at temperatures above 350 K.

Care was taken to avoid contamination of the metasilicates by atmospheric carbon dioxide during and after the preparation. All of the hydrates were assayed by powder X-ray diffraction(3) before preparation of the mixtures.

APPARATUS AND PROCEDURE

Vapour pressures were measured with U-tube mercury manometers made from Veridia precision bore tubing of 20 mm internal diameter. One side of the manometer was sealed and the other was joined to a 25 cm^3 bulb which was half-filled with an intimate mixture of two of the salts. Before use the manometer and bulb were cleaned with Analar nitric acid, washed with distilled water, and oven dried. The manometer was then filled under vacuum with clean mercury and the salt mixture was placed in the bulb and degassed by repeated freezing and pumping. The sealed apparatus was mounted vertically in a Townson and Mercer Ltd. E270 water thermostat which kept the temperature constant to within ±0.01 K. Temperatures were measured with a calibrated mercury-in-glass thermometer and are accurate to ±0.02 K. The vertical distances between the two menisci were observed with a Precision Tool and Instrument Co. Ltd. cathetometer.

The metasilicate mixtures $Na_2SiO_3 \cdot 9H_2O + Na_2SiO_3 \cdot 6H_2O$ (S9+S6), $Na_2SiO_3 \cdot 6H_2O + Na_2SiO_3 \cdot 5H_2O$ (S6+S5), and $Na_2SiO_3 \cdot 5H_2O + Na_2SiO_3$ (S5+S0) were prepared in duplicate from independent samples of the pure materials, and single preparations of the mixtures $Na_2SiO_3 \cdot 8H_2O + Na_2SiO_3 \cdot 5H_2O$ (S8+S5) and $Na_2SiO_3 \cdot 9H_2O + Na_2SiO_3$ (S9+S0) were also investigated. All of these mixtures were allowed to equilibrate in the sealed apparatus at 298.15 K for 60 d. The equilibrium vapour pressures were then measured in turn at 303.15, 298.15, 293.15, 290.15, 308.15, and 298.15 K allowing approximately 14 d at each temperature. The vapour pressures at 298.15 K were then observed after a further 480 d. The apparatus was then dismantled and the mixtures were analysed by powder X-ray diffraction and d.t.a.(8)

3. Results

By the end of the initial 60 d equilibration at 298.15 K the vapour pressures of the mixtures (S9+S6), (S6+S5), and (S8+S5) were completely steady and those of the (S5+S0) and (S9+S0) mixtures were changing by less than 0.0007 Torr/d; 600 d later the vapour pressures at 298.15 K of the (S9+S6), (S6+S5), and (S8+S5) mixtures were in exact agreement with the original values whereas those of the (S5+S0) mixtures had decreased by 0.36 Torr and that of the (S9+S0) mixtures had increased by 0.19 Torr but appeared to be constant.† Analysis of the final mixtures confirmed the original compositions in all cases except that of the (S9+S0) mixture which was found to contain S9+S5. No crystalline S0 could be detected and it appears that in this case the systematic drift in vapour pressure arose from the conversion of S0 to S5. Although the overall stoichiometry of the mixture corresponded to that of a heptahydrate the presence of S6 could not be detected. The failure of the (S5+S0) mixture to reach equilibrium in the first few months is not readily explained.

TABLE 1. Vapour pressures of sodium metasilicate hydrate mixtures
[Torr = (101.325/760) kPa]

T/K	289.84	293.07	298.07	303.04	308.09
Mixture			p/Torr		
S5+S0	3.59 [a]	4.50 [a]	6.53±0.08 [b] 6.17±0.08 [b, c]	9.17 [a]	12.85 [a]
S6+S5	5.96	7.44	10.68±0.04 [d]	15.11	21.14
S9+S6	7.13	8.86	12.71±0.10 [d]	18.06	25.77
S9+S5 [d]	6.53	8.17	11.73±0.20 [e] 11.92±0.20 [c, e]	16.77	24.06
S8+S5	6.73	8.45	12.22±0.20 [e]	17.45	24.71

[a] Errors in vapour pressures are unlikely to exceed twice those given for 298.07 K.
[b] Estimate of error based on differences between duplicates.
[c] Final equilibrium value, see text.
[d] Originally (S9+S0), see text.
[e] Error estimated by analogy with those for other mixtures.

It could, as was found with anhydrous sodium carbonate,(9) be due to the physical state of the anhydrous sodium metasilicate. It seems more likely, however, to have arisen from slow equilibration between the two solids, related to the fact that S0, unlike the hydrates, does not contain discrete silicate ions.(10-13)

The observed vapour pressures are given together with estimated errors in table 1. In the case of the (S5+S0) and (S9+S5) mixtures the values given at temperatures other than 298.07 K are believed to be systematically high by about 0.36 Torr and low by about 0.19 Torr respectively.

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† Throughout this paper Torr = (101.325/760) kPa.

4. Discussion

The only vapour pressures with which those given in table 1 may be compared are the estimates of McCready(4) whose values for the S5, S6, and S9 hydrates at 298.2 K (10, 11, and 16 Torr) are in fair agreement with ours (6.2, 10.7, and 12.7 Torr). The vapour pressure of the octahydrate $p_{8/6}$ was not measured directly in our experiments, but by means of the relation:

$$p_{8/6}^2 = p_{8/5}^3/p_{6/5}, \tag{6}$$

a value of 13.07 Torr in poor agreement with McCready's estimate (9 Torr) is obtained. The internal consistency of our values may be partially confirmed by calculation of the vapour pressure of the S9+S5 mixture from those of the S9+S6 and S6+S5 mixtures with the equation:

$$p_{9/5}^4 = p_{9/6}^3 p_{6/5}. \tag{7}$$

The calculated value (12.17 ± 0.06) Torr at 298.15 K is within experimental error of the final equilibrium value (11.92 ± 0.20) Torr given in table 1 but not with that (11.73 ± 0.20) Torr observed after equilibration for only 60 d.

Equilibrium constants K for the reactions (1) to (5) calculated from the vapour pressures in table 1 can be fitted to within their experimental error to the equation:

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R, \tag{8}$$

with temperature-independent values of ΔH° and ΔS°. The values of ΔH° and ΔS° obtained by a least-squares procedure are given along with their standard errors in table 2. For reactions (2), (3), (4), and (5) the errors in ΔH° and ΔS° from all sources are unlikely to exceed twice those obtained from the curve-fitting procedure and given in table 2. This is also likely to be true for reaction (1), since the known uncertainty in the "60 d value" of ΔG° (0.71 kJ mol^{-1}) corresponds to an error in ΔH° or ΔS° much less than those given in table 2. Best-fit values for the parameters α and β in the equation,

$$\ln(p/760\ \text{Torr}) = \beta - \alpha/T, \tag{9}$$

are also given in table 2 together with the average deviation δp between the observed and calculated vapour pressures.

Values of ΔH° and ΔS° for reactions (1) to (5) have not been previously reported. The values divided by the stoichiometric number x of H_2O are almost constant and approximately the same as those observed for other hydrates and for the sublimation of ice.(14) A further check on the experimental results is given by the agreement between the values of ΔH° and ΔS° observed for reaction (4) and those calculated from the values obtained for reactions (2) and (3) shown in table 2.

Also given in table 2 are calculated values for the (S9+S8) and (S8+S6) equilibria which we were not able to study. These were obtained from reactions (4) and (5), and (2) and (5), respectively. Combinations of the equations also give the following values for disproportionation of hydrates:

$$3\text{S8} = \text{S6}+2\text{S9}; \quad \Delta G^\circ = -0.7\ \text{kJ mol}^{-1},$$

$$4\text{S6} = 3\text{S5}+\text{S9}; \quad \Delta G^\circ = +1.4\ \text{kJ mol}^{-1},$$

$$6\text{S5} = 5\text{S6}+\text{S0}; \quad \Delta G^\circ = +6.6\ \text{kJ mol}^{-1},$$

TABLE 2. Standard thermodynamic functions at 298.15 K for sodium metasilicate hydrate equilibria [Torr = (101.325/760) kPa]

Reaction	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}	$10^{-2}\alpha$/K	β	δp/Torr
$S5 = S0 + 5H_2O$	59.6±0.2	260.6±1.6	677±5	62.68±0.38	16.27±0.13	0.02
$S6 = S5 + H_2O$	10.6±0.1	51.8±0.3	138±1	62.28±0.39	16.63±0.13	0.03
$S9 = S6 + 3H_2O$	30.4±0.1	157.4±1.9	426±6	63.10±0.75	17.09±0.25	0.13
$S9 = S5 + 4H_2O$	41.1±0.2	212.7±2.4	575±8	63.96±0.74	17.30±0.25	0.12
	41.0±0.2 [a]	209.2±2.2	564±7			
$S8 = S5 + 3H_2O$	30.7±0.2	159.5±1.1	432±4	63.94±0.42	17.33±0.14	0.05
$S9 = S8 + H_2O$	10.4±0.3 [a]	53.2±2.6	143±9			
$S8 = S6 + 2H_2O$	20.1±0.2 [a]	107.7±1.1	294±4			

[a] Calculated values, see text.

from which it may be seen that only S8 is thermodynamically unstable under experimental conditions.

For comparison with the values in table 2, values of ΔH° for reactions (1) and (4) may be calculated from the enthalpies of solution of Lange and von Stackelberg,(5) and the enthalpy of vaporization of water at 298.15 K (44.02 kJ mol^{-1}).(14) These values are 284.5 and 212.7 kJ mol^{-1} respectively. The value for reaction (4) is in

TABLE 3. Standard Gibbs free energy and enthalpy of formation and entropy of sodium metasilicates at 298.2 K [a]

Hydrate	ΔG_f°/kJ mol^{-1}	ΔH_f°/kJ mol^{-1}	S°/J K^{-1} mol^{-1}
S0	−1467±5 [b] −1432 [c]	−1561±4 [b] −1526 [c]	113.8±1.3 [b] 113.8 [c]
S5	−2670±5 −2642 [d]	−3031±7 −3021 [d] −3006 [e]	381±12 322.2 [d]
S6	−2909±5 −2879 [d]	−3325±8 −3316 [d]	431±14 364.0 [d]
S8	−3387±5 −3361 [d]	−3916±10 −3911 [d]	515±20 447.7 [d]
S9	−3626±5 −3598 [d]	−4207±12 −4205 [d] −4158 [e]	571±27 489.5 [d]

[a] Calculated from the results in table 2 using $\Delta H_f^\circ(H_2O, g, 298.15\ K) = -241.8$ kJ mol^{-1}, $\Delta G_f^\circ(H_2O, g, 298.15\ K) = -228.6$ kJ mol^{-1}, $S^\circ(H_2O, g, 298.15\ K) = 188.7$ J K^{-1} mol^{-1} and the values for anhydrous sodium metasilicate given in the table; all taken from reference 7.

[b] Reference 7.

[c] Reference 6.

[d] Estimated by McCready, reference 4.

[e] Calculated from enthalpies of solution (reference 5) using $\Delta H_f^\circ(Na_2SiO_3, s, 298.15\ K) = -1561$ kJ mol^{-1} and $\Delta H_f^\circ(H_2O, l, 298.15\ K) = -285.8$ kJ mol^{-1}.

excellent agreement with ours, while that for reaction (1) is not. A possible explanation of this is that their⁽⁵⁾ anhydrous silicate contained some amorphous material.

Values of the standard Gibbs free energies and enthalpies of formation and the standard entropies at 298.15 K of the sodium metasilicate hydrates calculated from the results in table 2 are given in table 3. The standard enthalpies of formation are in good agreement with the estimates of McCready⁽⁴⁾ but the standard Gibbs free energies of formation and the standard entropies are not. McCready estimated the molar increase in entropy per H_2O to be 42 J K^{-1} mol^{-1} whereas the experimental value is approximately 50 J K^{-1} mol^{-1}.

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Investigation of Aqueous Sodium Metasilicate Solutions by ^{29}Si N.m.r. Spectroscopy

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Summary The presence of a variety of polysilicates, including branched chain species, in aqueous sodium metasilicate solutions has been shown by ^{29}Si n.m.r.

MOST of the early work on aqueous sodium metasilicate ($SiO_2/Na_2O = r = 1$) solutions[1] leads to the conclusion[2] that the silicate species is entirely monomeric. However their Raman spectra show a band which has been attributed to a polymeric species,[3] and trimethylsilation experiments[4] indicate that besides the monomer there are substantial amounts of the dimer, linear trimer, cyclic tetramer, and other unidentified polymers. We now report ^{29}Si n.m.r. spectra which provide new information about the nature of the polymeric species in metasilicate solutions.

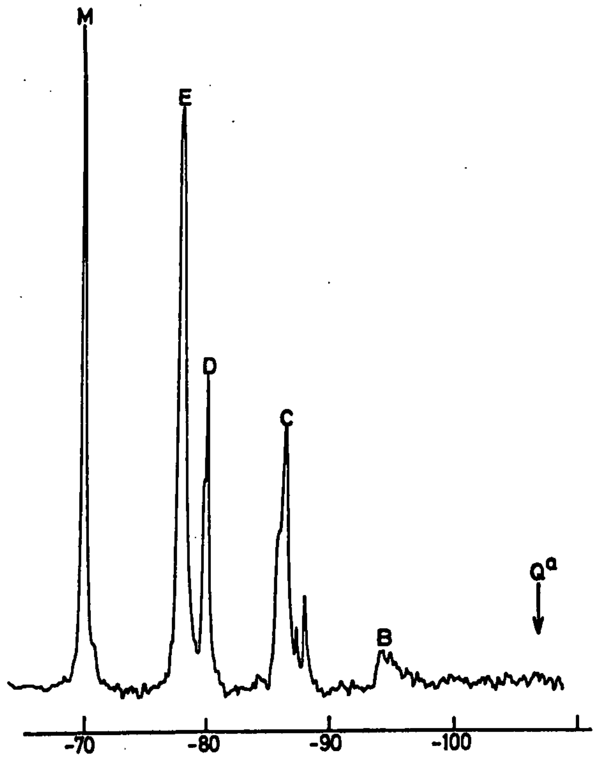

FIGURE. ^{29}Si F.T. n.m.r. spectrum at 19·9 MHz of 1·35 mol dm^{-3} Na$_2$SiO$_3$ (r = 1) at 26° (66430 transients, $\pi/2$ pulse, repetition rate 0·8 s). For identification of resonances see text. The relative peak areas are not proportional to Si concentrations.
[a] Position of resonance observed for solutions with high SiO$_2$/Na$_2$O ratios, e.g. r = 3·8 (see text), but not for metasilicate (r = 1) solutions.

Measurements were made at 26° using 10 mm outside diameter n.m.r. tubes and a Varian XL-100 spectrometer operating in the Fourier Transform mode at 19·9 MHz. Sodium metasilicate solutions (r = 1) were prepared from carefully recrystallised Na$_2$SiO$_3$9H$_2$O and those with $r \neq 1$ from the appropriate amounts of Analar NaOH and pure SiO$_2$ powder In all cases the solutions were made up with distilled water to which was added D$_2$O(15%) for use as an internal lock and were filtered through a 0·2 μm filter. Care was taken to prevent the ingress of impurities such as CO$_2$ which would disturb the pH and possibly cause formation of colloidal silica.

A typical sodium metasilicate solution spectrum is shown in the Figure. The relative magnitudes of the peaks show a small variation with concentration and it follows that these solutions contain a variety of silicate species. The spectra are consistent with previous work[4] which suggests that these species are polysilicates in which each Si atom is bound tetrahedrally to four oxygen atoms each of which can form a bond with another Si atom. The narrow low field peak (M) is the only one which remains when the SiO$_2$/Na$_2$O ratio r is reduced to 0·16 but it is almost completely absent from solutions with $r > 3$ and it is therefore considered to arise from monomeric species. Similar observations of the variation of relative peak areas with r show that peaks (E) and (D) belong to end group Si atoms (*i.e.* those linked *via* oxygen to one other silicon) and that peak (D) is most probably that of the dimer; that the cluster of peaks (C) is due to chain silicons (*i.e.* those linked by oxygens to two other silicon atoms) and that the small group (B) is due to branching silicons (*i.e.* those linked by oxygens to three other Si atoms). The resonances all lie upfield of that for Me$_4$Si and the shifts of (M), (E), and (D) relative to Me$_4$Si are −70·4, −78·4, and −80·4 p.p.m. respectively. The shifts of the three resonances in cluster (C) are −86·7, −87·6, and −88·4 p.p.m. and that of the main peak in cluster (B) is −94·4 p.p.m. The general pattern is similar to that observed in the ^{31}P n.m.r. spectra of polyphosphates[5] in which the resonance of the chain group phosphorus lies 10 p.p.m. upfield of that of the end groups.

These observations show that ^{29}Si n.m.r. provides a powerful new method for the investigation of soluble silicate solutions and suggest that its use to elucidate the structures present in water glasses should prove worthwhile. Preliminary measurements on a solution with r = 3·8 suggest that the polymeric species in water glasses have fewer end groups and more branching and chain silicons than those found in solutions with lower SiO$_2$/Na$_2$O ratios. Especially important is the detection of a broad peak (Q) with a chemical shift of −107 p.p.m., which is believed to be due to Si atoms linked to four others since its shift lies between those[6] for silica (−113 p.p.m.) and the central atom of (Me$_3$SiO)$_4$Si (−101 p.p.m.).

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