

CRYSTALLISATION PROPERTIES OF
PENTAERYTHRITOL

by

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S U M M A R Y.

The results of measurements of density, solubility and refractive index of aqueous solutions of purified pentaerythritol are presented. The density was measured over the range of concentration from zero to saturation over the temperature range 20 - 80°C by the Principle of Archimedes. The refractive index was measured over the same range of conditions with an Abbé refractometer.

The preparative methods of pentaerythritol synthesis are briefly reviewed with a view to explaining the possible sources of impurity which occur in the commercial product and which have significant effects on the crystal growth rate.

The problem of identifying one of the impurities was tackled. Although this impurity was probably present to an extent of less than 0.1% it had a drastic effect in reducing the rate of crystal growth.

A preliminary literature survey of the work done so far on surface energy is presented along with some proposed methods of measurement.

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INTRODUCTION.

Pentaerythritol ($C(CH_2OH)_4$) [2,2-bis(hydroxymethyl)-1,3-propane diol, hereafter called "Pe"] was initially discovered accidentally by Tollens⁽¹⁾ in 1882 as a by-product of the reaction between impure formaldehyde and barium hydroxide. Subsequent investigation led Tollens and his co-workers⁽²⁾ to the conclusion that Pe was the product of the reaction between formaldehyde and acetaldehyde, the latter being present as an impurity in the formaldehyde.

The main use of Pe is as an ester with various poly-functional organic acids for the production of paints and varnishes. It reacts with nitric acid to form the tetranitrate ("PETN") which has some medical uses but is also used as a primary explosive.

Considering the rising industrial importance of Pe the physical properties of its aqueous solutions do not appear to be well reported in the literature, apart from data of Rogers⁽⁴⁾ and Cooke⁽¹⁷⁾.

This thesis forms part of a larger programme of work and is in three principal sections:

- (1) Sections 1,2 and 4 deal with an attempt to identify an unknown trace impurity which appears to critically affect the crystal growth rate;
- (2) Section 3 covers the physical properties of Pe aqueous solutions;
- (3) Section 5 is concerned with a proposed method for determining the surface energy of the crystals.

SECTION ONE

PREPARATION AND PURIFICATION OF
PENTAERYTHRITOL

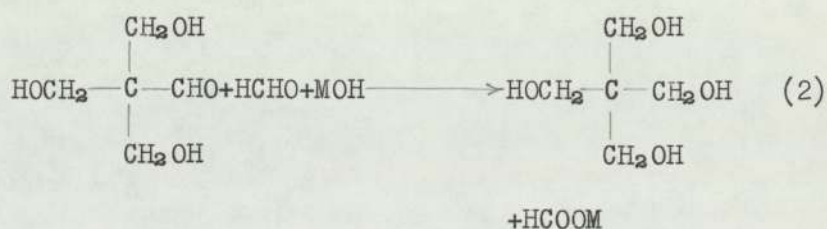
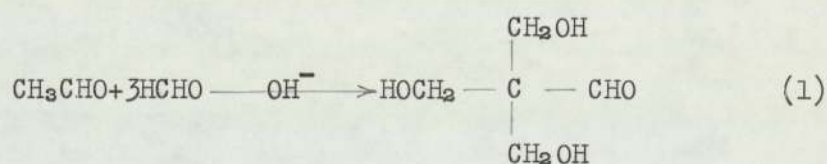
1.1) Synthesis.

The synthesis of Pe is described in the chemical literature and in numerous patents. However, the measures taken to obtain a good yield are very different and often controversial and the problem of eliminating impurities is not clearly understood. As a result the problem of chemical purity is still rather acute despite the substantial literature on Pe manufacture.

1.1.1) Method of preparation.

This can be described in concise form as follows:

Pe is prepared from a mixture of acetaldehyde and formaldehyde in the presence of an alkaline condensing agent according to the following equations, viz:



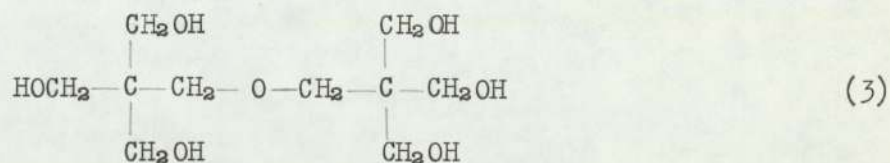
where M represents an alkali or alkaline earth metal.

Although the reaction is shown as a two-step process, i.e. an aldol condensation of three molecules of formaldehyde and one molecule of acetaldehyde to form one molecule of pentaerythrose followed by a crossed-Cannizzaro reaction between pentaerythrose and formaldehyde to give Pe, it is essentially one step in that there is no isolation of the intermediate product.

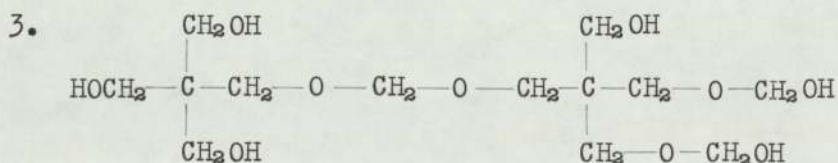
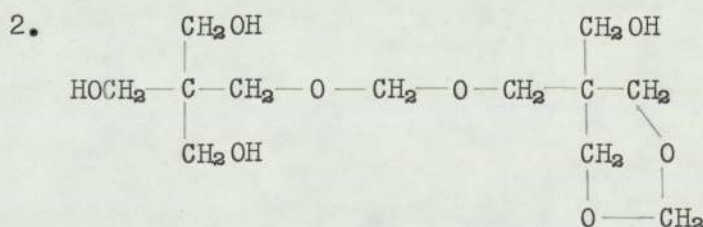
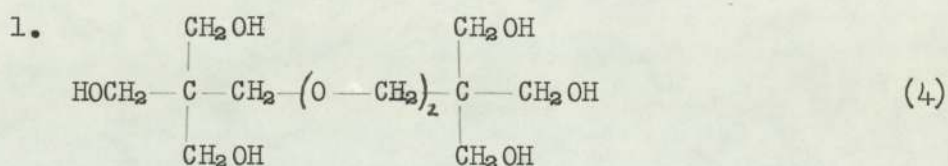
The main impurities normally appearing with the

1.1.1) contd.

Pe are the poly-Pes, particularly di-Pe⁽²⁶⁾ (normally present to approximately 1%) which has the formula



and also a formal (present to approximately 5%) which has been given several possible formulae:-⁽¹⁰⁾



The side reactions suggested in the literature are mainly the self-aldol and self-Cannizzaro of the reactant aldehydes and these, without any doubt, influence the reaction yield. Therefore in most processes the conditions were chosen so as to minimize these side-reactions. It should be pointed out, however, that the yield and the purity of Pe are, to a large extent, unrelated problems and should be analysed separately.

1.1.2) Reaction conditions.

In general it can be said of the Pe reaction that:

- (i) The optimum aldehyde ratio of approximately 3:1 for maximum yield of di-Pe was reported by Friedrich⁽²⁵⁾ and his findings were supported by many others;
- (ii) High concentration of formaldehyde leads to high formal content⁽¹⁰⁾;
- (iii) Increasing the time of the first part of the reaction leads to higher di-Pe content^(4,27);
- (iv) There is evidence to show that the aldol reaction can be completed before the Cannizzaro reaction starts⁽²⁸⁾;
- (v) In order to obtain reasonable yields of Pe it is necessary to allow for the "second reaction" as the final step before the neutralization and separation procedures^(28,29);
- (vi) In most earlier works the need for very low temperature during the first part of the reaction was stressed. In other words, lower temperature, during the aldol stage, can be expected to lead to less di-Pe and formal⁽¹⁰⁾;
- (vii) No significant yields can be obtained if methanol is present in amounts over 7%⁽³⁰⁾;
- (viii) The influence of initial concentrations upon yield is dependent on the aldehyde ratio⁽³¹⁾;
- (ix) The control of the pH during the reaction is important although the values given by different authors are not very consistent. Several investigations stress the advantages of amphoteric additives

1.1.2) contd.

and most probably their purpose is to keep the pH within some close range due to their buffer action^(26,30);

- (x) The catalyst (base) type influences the yields and purity of Pe⁽¹⁰⁾;
- (xi) The order of addition of reactants influences the yield and purity⁽⁵⁾;
- (xii) The influence of free radicals on the yield and purity of Pe, and the reaction velocity is important⁽³²⁾.

1.2) Reaction Methods.

The reaction of formaldehyde, acetaldehyde, and calcium or sodium hydroxide has been carried out in many ways and some controversial literature has been written on this topic. The latter aspect is summarised well in the book by Berlow et al.⁽⁵⁾. Most investigators prefer to add acetaldehyde to formaldehyde, having obviously in mind the minimising of the local concentration of acetaldehyde, and hence its self-condensation.

One of the best studies of the reaction has been done by Kudssus⁽⁶⁾ where formaldehyde was added to an acetaldehyde calcium hydroxide mixture. However, the yield was low and Luke⁽⁷⁾ has claimed the results would have been better if all the reactants were fed together by rapid mixing in order to minimize side reactions.

The conditions under which the reaction is carried out have an important effect in determining the yield and the quality of the Pe. Wide variations in the molar ratio of formaldehyde to acetaldehyde have been reported. In most of

1.2) contd.

the works that have been published molar ratios of 4:1 to 5:1 have been used. It has been shown that the di-Pe content of the product varies inversely with the molar ratio of the formaldehyde to acetaldehyde with maximum quantities obtained at a molar ratio of 3:1⁽⁸⁾. The use of ratios of 5:1 to 10:1, or higher, results in products containing up to 99% of Pe⁽¹¹⁾.

The number of equivalents of alkaline reagent per mole of acetaldehyde reported in the literature ranges from 0.5⁽⁸⁾ to 3.65⁽⁹⁾. A slight excess of alkali is not a problem, since it requires only a small amount of extra acid for neutralization.

1.3) Purification and Extraction.

The preparation of Pe is followed by its isolation and in this country the only grade available on the market also contains di-Pe, formal, other impurities and other by-products of the reaction. In order to obtain a reference datum for measurements a very pure material was required and procedures for the purification of the commercial material have been developed. In most of the published work on purification of Pe on the laboratory scale, the recrystalliation method has been chosen. Kuznetsova et al.⁽¹⁴⁾ after 25 recrystallisations were able to improve the purity indicated by the increase in melting point from 150 to 200°C. This is still 60 degrees below some published data and suggests the presence of impurities. Due to the low latent heat of fusion and high molecular weight of Pe it is calculated that a 0.002 mass fraction of formaldehyde in the Pe would be sufficient to

1.3) contd.

depress the melting point by 4°C . This indicates the difficulty of obtaining an accurate value for the melting point of the pure material since it tends to decompose at its melting point and regenerate formaldehyde.

Chromatographic separation has been reported and the recovery of Pe amounted to 85 per cent⁽¹²⁾ but the quantities available by this process are far too small to be useful.

1.4) Practical Purification Procedure.

In the original purification method developed by Rogers⁽⁴⁾ commercially obtained Pe containing the two main impurities di-Pe (1%) and formal (5%) was dissolved in sufficient 10% (W/V) hydrochloric acid to form a saturated solution at its boiling point. The solution was refluxed for two hours and then cooled to 0°C to crystallise the product which was then filtered off and washed in ice cold water. This procedure was then repeated and the resulting Pe recrystallised from distilled water. The product was then washed successively with quantities of ice cold water and dried in an oven at 100°C . The gas chromatographic analysis (Section 3) showed no detectable impurities to be present. However, growth rate experiments on batches of Pe obtained at different times suggested that sometimes one or more trace impurities must be present which seriously reduced the crystal growth rate⁽¹³⁾. Since this

1.4) contd.

impurity was not detectable by the gas chromatographic method used, it was either below the detection threshold limit or was not a by-product impurity and did not form a volatile product in the sample preparation. Therefore a further step was taken in order to obtain Pe containing impurities below the threshold at which their presence had measurable effect on the crystal growth rate. In other words there would result, not ideally but effectively, pure Pe. To this end extensive research was carried out first by Rogers⁽⁴⁾ and later Rehmatullah⁽¹³⁾ and active charcoal extraction was proposed as the most efficient method.

The procedure for preparing purified extracted Pe was to prepare a 10% solution of hydrolysed Pe (that is, free of di-Pe and formal) and add 10 g of activated charcoal per litre of solution. This gives a Pe:C ratio of 10:1. The mixture was stirred at 40°C for two hours and was then filtered while still warm. This procedure was repeated twice more. The filtration was carried out using a 0.45 μm membrane filter and finally the filtrate was recrystallised and dried in an oven at 100°C. Since the crystal growth rate appeared to be particularly sensitive to the impurities it was used as a measure of their effective removal. It was found⁽¹³⁾ that after the second extraction there was no further improvement in the crystal growth rate and three extractions were therefore used in the standard purification procedure. It should be stated that it was not conclusively proved that the improvement in growth rate was not due to a further impurity entering the solution from the charcoal which "neutralised" the unknown trace impurity but in view of the earlier work of Rogers⁽⁴⁾ this seems unlikely. It was

1.4) contd.

found necessary to use grade Norit SXL (Hopkin and Williams) since poorer grades (e.g. Norit S1 from Hopkin and Williams, not acid washed) did not give such an improvement in growth rate. The growth rate of the extracted Pe was higher than reported values in the literature by about two orders of magnitude.

SECTION TWO

ANALYSIS METHODS

2.1) Introduction.

The analysis of Pe involves the assay of Pe content as well as the measurement and characterisation of the impurities present. The analysis of commercial Pe generally includes the following determinations: Pe content, melting range, hydroxyl content, ash content, acidity, moisture content, water solubility, colour and physical state.

2.2) Benzyl Derivative.

Most of the work that has been published for determining Pe content has used the benzyl method for accuracy and reliability. This procedure is based on the reaction of Pe with benzaldehyde to form its dibenzylidene acetal which is specific for Pe only and is a well defined crystalline compound. It is almost insoluble in dilute aqueous methanolic solution of hydrochloric acid containing excess benzaldehyde and is thus determined gravimetrically.

2.3) Paper Chromatography.

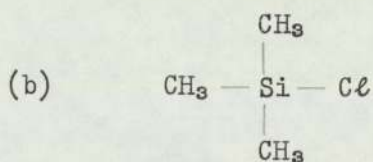
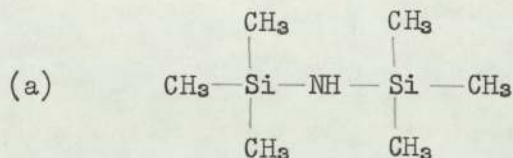
During an investigation⁽³⁶⁾ of the course of Pe synthesis, portions of the reaction solution were examined by paper chromatography. The products were identified by spraying the paper chromatograms with potassium periodatocuprate⁽³⁷⁾. Unchanged starting materials were too volatile to be retained by this treatment. Other products, i.e. formals and di-Pe, were probably not detectable by the technique used but Pe was found to be present.

2.4) Gas Chromatography.

The benzyl method is tedious and the paper chromatographic method lacks quantitative accuracy. The

2.4) contd.

method finally used therefore was that described by Suchanec⁽¹⁵⁾ which has been further developed in practical detail by Simons⁽¹⁶⁾. It consisted of forming volatile silane ethers from the solid hydroxyl containing materials and this was done by reacting the dried solid with a mixture of (a) hexamethyl-disilazane and (b) trimethylchlorosilane (or TMS) in pyridine solution.



The ethers of the form $\text{R}-\text{O}-\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ were formed rapidly

and completely with some heating, whilst the precipitated $\text{NH}_4 \text{Cl}$ did not interfere with the subsequent analysis.

The TMS ethers have been found to be very suitable for gas-chromatographic analysis in the temperature range 150-350°C and with proper temperature programming gave very good resolution of the peaks.

The gas-chromatograph used for analysing the Pe in this work was a Pye series 104. It was equipped with a flame-ionization detector attached to a double-column comparative amplified and controlled by a programmer. A Kent Mark 3 potentiometric recorder was used to produce the

2.4) contd.

graph⁽¹⁰⁾.

2.5) Hydroxyl Content.

The hydroxyl content of Pe, which serves as an indication of reactivity, is determined by acetylating the product with an excess of acetic anhydride in pyridine containing a small amount of water. The amount of unreacted anhydride is then measured by titration with sodium hydroxide solution.

SECTION THREE

PHYSICAL PROPERTIES

3.1) Properties of Solid State.

Pe is an odourless, white, crystalline compound and it usually crystallises in the form of near perfect tetragonal bipyramids^(3,4) and a common habit is shown diagrammatically in Figure 4. It is nonhygroscopic, practically non-volatile, and stable in air with a theoretical density of 1.396 g/cm^3 . The properties published in the literature are not generally in good agreement probably due to the difficulty of obtaining pure Pe. It is surprising to see even different values for molecular weight of Pe. Various melting points ranging from $256\text{--}265.5^\circ\text{C}$ have been recorded for pure Pe with $261\text{--}262^\circ\text{C}$ most often mentioned⁽⁵⁾, and a boiling point of $276^\circ\text{C}/30\text{mm.Hg}$.

Other thermodynamic properties of Pe have been reported⁽⁸⁵⁾:

heat of solution	-4.77 - -5.28 kcal/mole
heat of combustion	660.8 - 661.4 kcal/mole
heat of transition	8.4 - 10.5 kcal/mole
heat of fusion	1.3 - 1.7 kcal /mole
heat of formation	226.6 kcal/mole
heat of vaporisation	22 kcal/mole
heat of sublimation	31.4 kcal/mole
heat of hydration	26.6 kcal/mole
specific heat	{ 60.8 cal/mole at 100°C 103.3 cal/mole at 190°C

Refractive index in sodium light is 1.5559 along the a crystal axis and 1.5146 along the c axis⁽¹⁹⁾.

3.2) Properties of Aqueous Solution.

The physical properties of the aqueous solutions of Pe do not appear to be well reported in the literature apart from the data of Cooke⁽¹⁷⁾, Kuznetsova and Gavrilova⁽¹⁴⁾ on solubility and also two spot values of density and refractive index^(18,20).

As it was pointed out, the lack of published data on the physical properties of the aqueous solutions was the main incentive to measure the density, solubility and refractive index of them and obtain correlation formulae⁽³³⁾.

3.3) Density of Aqueous Solution of Pe.

3.3.1) Method

In general, the density of liquids may be determined by the measurement of the mass of the liquid occupying a known volume (pycnometric methods) or by buoyancy methods based on the principle of Archimedes.

In this work the second method was chosen due to its higher degree of accuracy, although the errors produced by a pycnometer can be reduced to a great extent. These errors can be summarised as: due to the difficulties of handling concentrated solutions in capillary tubes at temperatures far above ambient, and the adsorption of an unknown amount of moisture by the glass. It is also necessary to make a correction for the buoyancy of the air and its variation due to changes of temperature, barometric pressure, and relative humidity which in practice are not simple factors.

3.3.2) Apparatus.

The apparatus used for measuring the density of solutions of Pe consisted essentially of a glass globe of about 20 cm³ and containing ca.50 g lead shot, a Stanton Unimatic balance, a double walled pyrex glass beaker with internal volume of 500 cm³, the outer cylinder acting as a water jacket, a Churchill "Thermocirculator" and a calibrated thermometer graduated to 0.1 deg. C.

A disc of expanded polystyrene was fitted above the solution level and was drilled with a hole to take the fine wire connecting the glass globe to the balance beam. The general arrangement of the apparatus is shown in Figure 1.

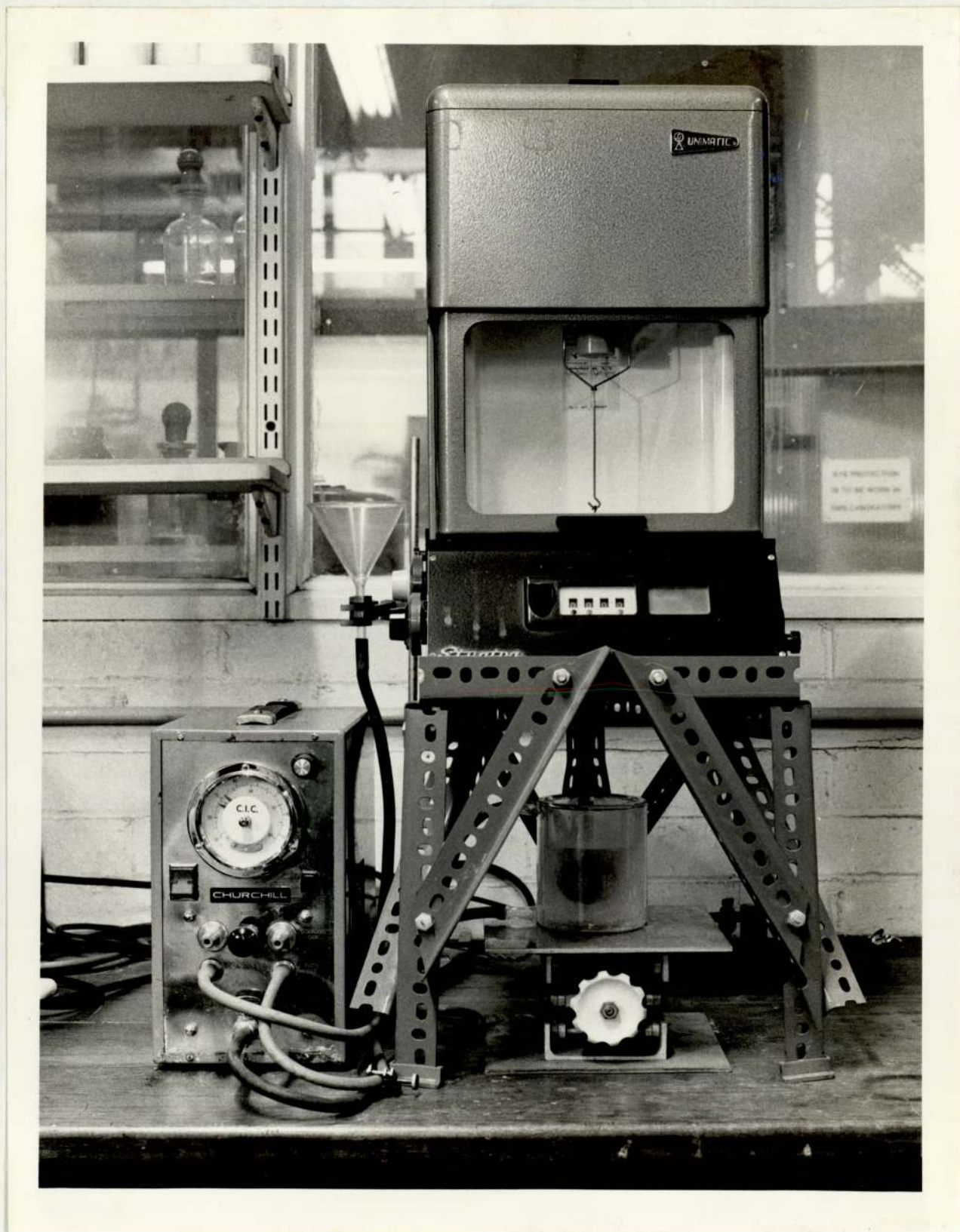
3.3.3) Practical procedure.

The thermometer was calibrated and during the calibration of the glass globe in water it was found that after 20 minutes from a temperature change the effect of convection currents on the globe could be neglected since the temperature and upthrust remained constant thereafter.

A solution of known concentration was prepared on the basis of mass fraction by weighing purified Pe, dissolving it in distilled water and then weighing the solution. The concentrated solutions had to be weighed hot as the solubility at ambient temperature was low (about 5g/100g water). In such cases the necessary precautions were taken to prevent any evaporation.

The solution was placed in the inner cylindrical vessel and sealed to prevent any evaporation except for the small hole to allow the fine wire to pass through counterpoising the glass globe on the balance.

FIGURE 1.



Density Measurement Apparatus

3.3.3) contd.

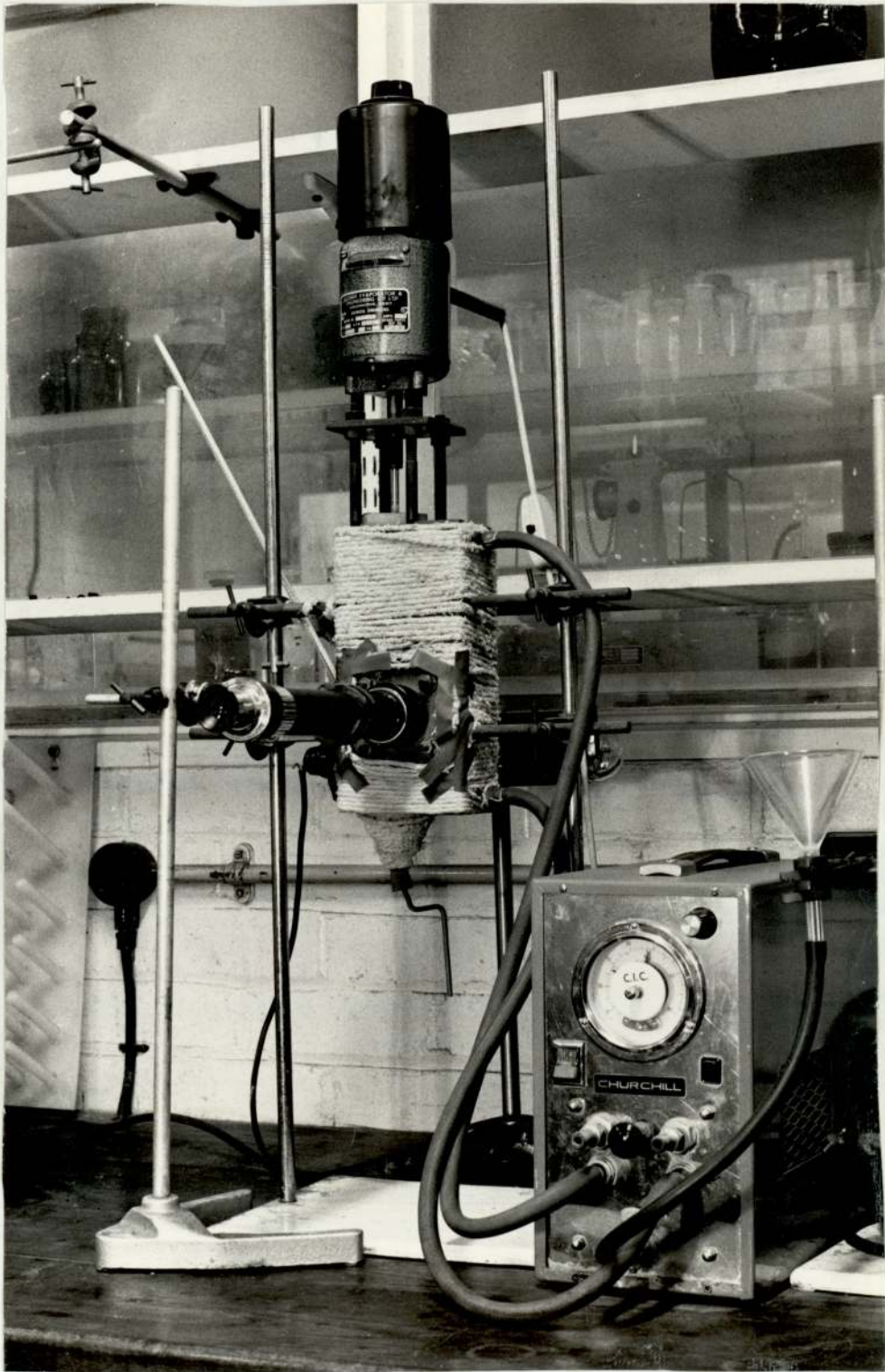
The net weight of the globe was measured over the temperature range 20-80°C relative to a concentration range of 0-0.2 mass fraction. The density of the solution was calculated by knowing the density of water at the corresponding temperature⁽³⁴⁾ and the calibration weight of the globe in water. The results are shown in Table I and are graphically represented in Figure 5.

3.4) Refractive Index and Solubility.3.4.1) Methods.

Rogers⁽⁴⁾ measured the refractive index of stirred solutions of Pe with an Abbé refractometer over the temperature range 30-70°C. He found that this was an accurate method for determining the solubility (both from dissolution and growth) and measuring the refractive index of the solution.

3.4.2) Apparatus.

The apparatus for measuring refractive index and solubility, Figure 2, was constructed from a solid block of brass with a two inch diameter hole bored through it. It had an overall length of 12 inches. The water jacket consisted of a slot about 2 in x 1 in bored down one side of the cell through which water was circulated from a Churchill (515-642) "Thermocirculator" unit. A thermometer pocket was sealed into the side of the cell as also was the refractometer and illuminated window at about 3 inches from the base so as to be immersed when 250 cm³ of the solution was used. A conical copper base with a draining plug was soldered to the cell base. A rubber

FIGURE 2.

Refractive Index Measurement Apparatus

3.4.2) contd.

bung was placed in the top with a Teflon bush to accommodate a stirrer with a three blade marine type impeller of about one inch diameter. The stirrer motor was fixed rigidly to the cell housing. A Bellingham and Stanley immersion refractometer was used with a 1B prism and arbitrary scale from -5 to 105 graduated in intervals of 0.1 divisions (range $n_D = 1.3254$ to 1.3664) which made it possible to read solution concentrations to ca. 0.025% without the need for estimation. The refractometer was screwed into a circular brass plate bolted to the front of the cell and designed so that the prism was off-centre in the cell. The light source from the illuminating window at the back of the cell was incident to the plane of the prism face. The cell was lagged with asbestos rope to minimize heat losses.

3.4.3) Practical procedure.

The thermometer used was graduated in 0.1°C and could be estimated to about 0.05°C which was sufficiently accurate compared with the refractometer accuracy.

After spot checks on the calibration of the refractometer, the approximate amount of Pe required for the concentration to be tested was accurately weighed out and was dissolved in about 250cm^3 distilled water by raising the temperature to ca. 70°C (or higher for more concentrated solutions). The solution was weighed and, the necessary precautions being taken to prevent evaporation, was poured into the cell which was at about the same temperature and the stirrer started. The temperature was then raised at least 20°C above the expected solubility value for 30

3.4.3) contd.

minutes to ensure solution of any nuclei formed during the transfer operation. Cooling was then commenced at a rate of about 1°C/min.

Readings of the refractive index and temperature were taken every 5°C and a plot of some of these points is shown in Figure 6 for the temperature range 30-70°C and the concentration range of 0-0.3 mass fraction. The actual results are shown in Table II.

The solubility was determined by adding excess solid to the solution in the cell at the given temperature and hence the solubility was obtained from the refractometer calibration.

3.5) Experimental Results and Calculations.3.5.1) Density refractive index and solubility.

For practical utility the experimental results are plotted in the form of density and refractive index versus concentration, Figure 5 and Figure 6 respectively.

For a given temperature it was found that the density could be expressed as a linear function of the composition with standard deviation of $\pm 4 \times 10^{-5}$ (g/cm³) and no useful improvement was obtained by using a second order equation. Over the temperature range considered the slopes of the correlation lines were almost the same, having a range of only $\pm 2 \times 10^{-3}$ (g/cm³ mass fraction) and were therefore assumed parallel for the purpose of correlation which resulted in the equation:

$$\rho_{12} = 1.0024 + 0.2573x_1 - 1.3004 \times 10^{-4}t - 3.1692 \times 10^{-6}t^2 \quad (5)$$

where ρ_{12} is the solution density (g/cm³), t is the temperature (°C) and x_1 is the concentration of Pe (mass fraction). The standard deviation of equation (5) is

3.5.1) contd.

$$\pm 1.5 \times 10^{-5} (\text{g/cm}^3).$$

The refractive index of the solutions was found to be correlated by the equation:

$$N_{D_{12}} = 1.3340 + 1.336 \times 10^{-1} x_1 + 2.406 \times 10^{-2} x_1^2 - 5.670 \times 10^{-5} t - 1.127 \times 10^{-6} t^2 \quad (6)$$

with a standard deviation of $\pm 9 \times 10^{-5}$ refractive index units.

For concentrations greater than $x_1 = 0.0494$ the refractive index is adequately correlated by linear equations for each temperature for which the standard deviation does not exceed $\pm 2 \times 10^{-5}$. Again, the slopes of these correlation lines were similar, within the range $\pm 5 \times 10^{-4}$ ($\Delta n_D / \text{mass fraction}$) and thereafter again assumed to be parallel, hence the simplified correlation becomes:

$$N_{D_{12}} = 1.3349 + 1.361 \times 10^{-1} x_1 + 1.698 \times 10^{-2} x_1^2 - 7.213 \times 10^{-5} t - 1.148 \times 10^{-6} t^2 \quad (7)$$

($x_1 > 0.0494$) with a standard deviation of $\pm 2.4 \times 10^{-5}$.

The solubility data agree well with those of Cooke⁽¹⁷⁾ except below 40°C where Cooke gives equilibrium concentrations about 3% greater than those found in this work. The solubility data of Kuznetsova et al.⁽¹⁴⁾ is as much as 30% too high at 90°C and this is almost certainly due to the impure Pe used as indicated by the low melting point of their material (200°C). When the solubility data were plotted on a basis of $\ln(n_1)$ versus $(1/T)$, a distinct curve resulted indicating a heat of solution of 6.1 kcal/mole at 30°C and 7.3 kcal/mole at 75°C (endothermic) for $n_1 = 0.0110$ and 0.0453 respectively. The value obtained by Bright and Carson⁽²¹⁾

3.5.1) contd.

was 5.28 kcal/mole at infinite dilution and was based on direct calorimetric measurement at 29°C.

3.5.2) The partial molar volume and refractive indices of pure (hypothetical) liquid Pe.

By definition the solution molar volume is given by

$$V_{12} = (M_1 n_1 + M_2 n_2) / \rho_{12} \quad (8)$$

and Table III consists of the data to this basis.

The partial molar volume has been evaluated graphically by plotting the molar volume of the mixture (V_{12}) versus the mole fraction of Pe (n_1). A linear interdependence proved to be quite accurate in the range 0-25% mass fraction, thus rendering it unnecessary to construct tangents to find the partial molar volume at various concentrations, i.e. the partial molar volume is independent of concentration over the range of conditions studied. Hence, by extrapolating this graph for each temperature the partial molar volume of Pe (\bar{V}_1) was obtained. By the method of least squares the values of \bar{V}_1 were found to be well correlated by:

$$\bar{V}_1 = 103.198 + 0.0274t \quad (9)$$

with a standard deviation of $\pm 3 \times 10^{-5}$ cm³/mol.

Assuming the ideal relation for an extensive property:

$$n_{D_{12}} = Z_1 n_{D_1} + Z_2 n_{D_2} \quad (10)$$

where the volume fraction, Z_i is defined by

$$Z_i = (n_i \bar{V}_i) / \sum (n_i \bar{V}_i) \quad (11)$$

the refractive index of pure hypothetical liquid Pe (n_{D_1})

3.5.2) contd.

was calculated over the range of experimental temperatures. The results, Table IV, are shown graphically in Figure 8, which can be represented by equation:

$$n_{D_1} = 1.51320 - 3.55559 \times 10^{-5}t - 1.15594 \times 10^{-6}t^2 \quad (12)$$

with a standard deviation of $\pm 1.0 \times 10^{-6}$ refractive index units.

The apparent molal volumes⁽²²⁾ at $X_1 = 0.03$ and 0.05 and 25°C are 101.61 and $101.78 \text{ cm}^3/\text{mol}$ respectively which compare favourably with the values of Kelly et al. of 101.7 and 101.8 ⁽²³⁾, and Woolf's⁽¹⁸⁾ value of 101.86 .

The reliability of equation 12 was checked by calculating the original data points (from equation (10)) and it was found that the standard deviation of the calculated points from the original data points ($n_{D_{12}}$) was $\pm 3.4 \times 10^{-5}$ refractive index units.

SECTION FOUR

UNKNOWN IMPURITY

4.1) Impurities of Pe.

It has been found (Section 1.3) that after hydrolysing commercial Pe, although gas chromatography has not detected the presence of any remaining impurity, it was not pure Pe and must still contain an unknown impurity. This impurity is called "unknown" as further analysis has shown that it was neither di-Pe nor formal, and its effect on the rate of growth of Pe crystals was not comparable with either di-Pe or formal.

The possibility of the addition of further counteracting impurities from the activated charcoal during the extraction was checked by taking powder X-ray spectra which confirmed the presence of an unknown impurity in the unextracted material.

4.2) Identification of Unknown Impurity.

There are two possibilities for the unknown impurity in Pe which can be classified as extraneous addition and/or by-product impurity.

4.2.1) Extraneous addition.

At first it was thought that the presence of the unknown impurity may be due to the addition of extraneous chemicals which have been used during the industrial manufacture of Pe such as oil or grease from stirrer shafts and pump bearings, etc. or any intentional chemical additives used to carry out the reaction and production of Pe.

A series of tests was carried out by Rehmatullah⁽¹⁵⁾ measuring the effect of a number of selected chemicals on the growth rate of a Pe crystal in a solution prepared from

4.2.1) contd.

purified and extracted Pe. None of the results were comparable with the effect of the unknown impurity.

4.2.2) By-product impurity.

The second possibility for the unknown impurity was that a side reaction produced a product or products in minute amounts (judged by the absence of obvious peaks on the GC) in addition to the di-Pe and formal already noted. Work is being planned to prepare Pe from pure raw materials: even the use of "Analar" sodium hydroxide pellets as alkali catalyst is being avoided due to the possibility of extraneous impurity introduction. The alkali is being prepared by reaction of pure sodium metal and deionised water.

4.3) Identification Methods Attempted.

As has been explained in Section 1, the unknown impurity was thought to be extracted from Pe by activated charcoal. In order to concentrate this impurity the contaminated charcoal used in the extraction process was back extracted. For this purpose a column was set up with a draining tap at the lower end, Figure 3. The column had an internal diameter of $1\frac{1}{2}$ in. and the height was 33 inches. The first 3 inches above the draining tap was packed with glass wool. Contaminated charcoal, containing the unknown impurity, was placed in the column as a packed bed. The column was heated and kept at 60°C with an isomantle heating tape. In the hope of back extracting the unknown impurity from activated charcoal, a series of solvents was made from distilled water and ethanol to cover the entire concentration

4.3) contd.

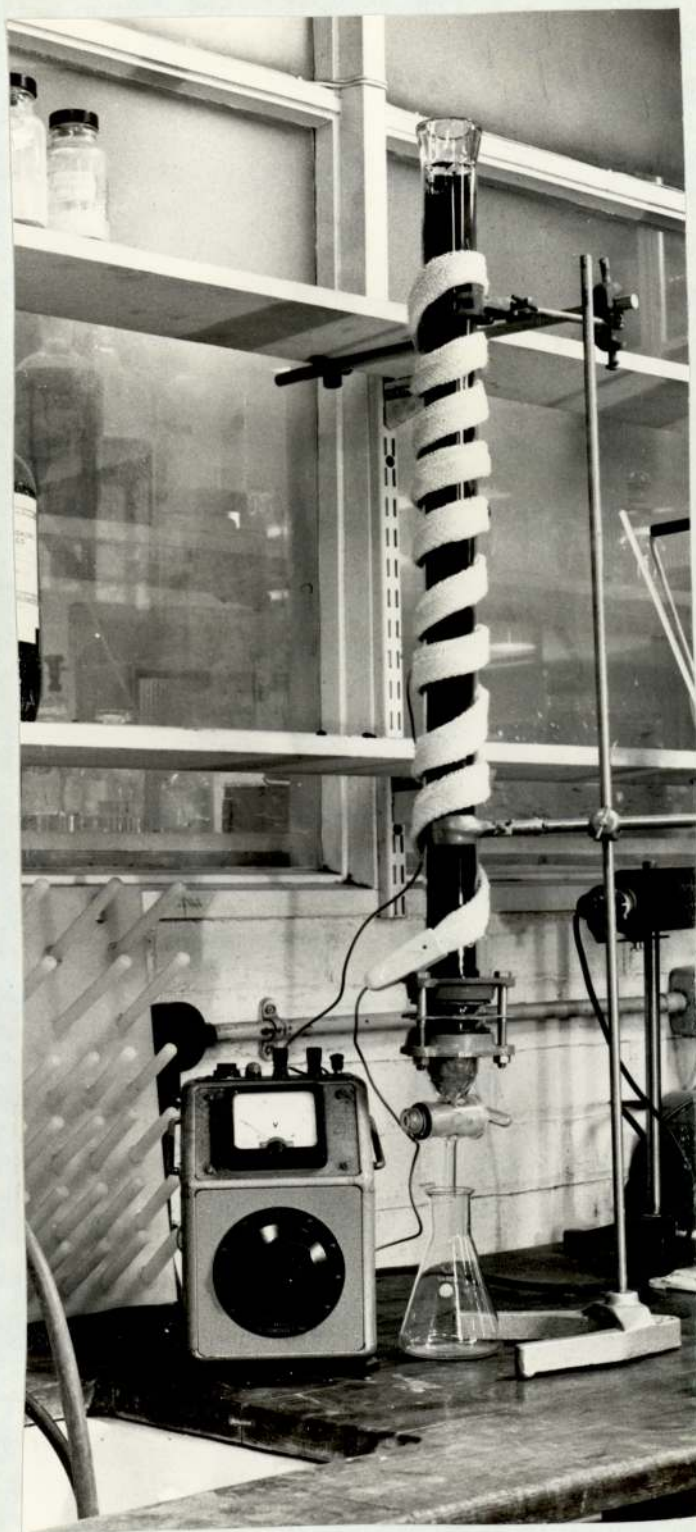
range at 20% intervals. These were heated up to 70-80°C for pouring down the column hot. Unfortunately, due to the fineness of charcoal, it was found to be completely impervious to the solvent. The contaminated charcoal was therefore transferred to a beaker and treated with each of the solutions consecutively by heating near their boiling point for one hour and filtering hot. The six filtrates were evaporated to dryness. The reason for using different concentrations of alcohol was that the solubility of the unknown impurity may have differed and in certain concentrations may have had a maximum value.

A number of infra-red spectra on a KBr disc was obtained in the range 600-2000 cm^{-1} from the six samples above mentioned and also an hydrolysed and extracted Pe sample.

The sensitivity of the infra-red system was not sufficient to show any noticeable difference in spectra, except for slight increases in absorption 9.5 and 10 μm due to the unknown impurity (Figures 9 and 10). The spectra were further examined up to 4000 cm^{-1} but no further difference was detectable.

The results of these spectra can be summarised as:-

1. Absence of C = O groups
2. Branched C skeleton
3. The skeleton with similar complexity to Pe
4. Presence of OH' group
5. Fewer OH' groups than Pe
6. Presence of CH_3 radicals
7. Presence of CH_2 radicals



Re-Extraction Column

4.3) contd.

It was suggested that for more useful results a differential infra-red spectra be obtained. This required a solution of Pe and the solvent should not contain any OH' group to prevent overlapping of the spectra peaks. The solvents tried are listed below together with the solubilities at ambient temperature in g Pe/100 g solvent:

Hexa methylphosphoric triamide	< 0.5
Carbon tetrachloride	< 0.5
Carbon disulphide	< 0.5
Benzene	< 0.5
Chloroform	< 0.5
Acetone	< 0.5
Amylacetate	< 0.5
Formamide	1.5
Diethyl ether	< 0.5
Dioxane	< 0.5
Nitrobenzene	< 0.5
Sulpholane	< 0.5
n-butylamine	16

The last one was the only solvent for high solubility but unfortunately the amine radical's spectra peaks overlapped those of the Pe. A differential spectra for Pe dissolved in carbon tetrachloride was attempted but did not show any specific peak.

For Mass Spectrum analysis two samples were chosen: one of contaminated charcoal from the hydrolysed and extracted Pe, and the other a mixture of the original charcoal (Norit SX1) and hydrolysed and extracted Pe. The reason for choosing these samples was that they could be compared and any difference would then indicate the presence of the unknown impurity and

4.3) contd.

possibly give some information as to its identification.

The conclusions from the comparison of the spectra were as follows:

- 1) Peaks above the molecular weight of Pe (136.15) in both pairs of samples strongly implied the presence of impurities of molecular weight greater than Pe. While these could also have arisen from the contamination of the mass spectrum system, it was suggested that the peaks were too strong for this and could only be due to the presence of di-Pe and formal which were not completely destroyed by hydrolysis. Although gas chromatography showed no trace of these impurities it should be admitted that the sensitivity of the gas chromatography system is considerably less than that of mass spectroscopy.
- 2) Peaks above 272 indicate the possible presence of impurities of a higher molecular weight than di-Pe. However, these peaks were rather small.
- 3) There was a strong peak on all spectra at 15. The main possible sources for this are CH_3^{\cdot} and NH^{\cdot} radicals. It is suggested that the latter be initially discarded as there is no reason for suspecting the presence of such a radical.
- 4) There were very small peaks at 284 and 267 which could be ascribed to the molecular ion peaks of formal.
- 5) A peak representing silicon was also noted.

A nuclear-magnetic resonance (N.M.R.) spectra was prepared with a sample of hydrolysed Pe, but there were no effective peaks of CH_3^{\cdot} and CHO^{\cdot} or silicon groups.

4.3) contd.

All the peaks were ascribable to H_2O and Pe. The N.M.R. spectra was repeated with a more sensitive system, Figure 11, from which strong peaks of CH_3^{\cdot} and Si radicals were visible. Between the peaks of these two radicals there were some peaks suggesting the presence of CH_2^{\cdot} radicals but due to overlapping with the CH_3^{\cdot} peaks it was not possible to identify them with certainty.

As has been previously stated (Section 4.1) the powder X-ray pattern has been obtained from a hydrolysed and extracted Pe, Figure 12. By comparison, the powder X-ray pattern of the sample of hydrolysed Pe (which has not been extracted and contains the unknown impurity) had two lines at distances of 1.825 \AA° and 1.865 \AA° which did not occur in the extracted sample. The two peaks were not classified on the reference card of $Pe^{(38)}$. The possibility of these being theoretical peaks of Pe existed and therefore the theoretical values of the positions of the Pe peaks were calculated⁽³⁹⁾. The two visible peaks did not coincide with any theoretical value. It was therefore suggested that the peaks were due to the presence of the unknown impurity which was extracted by active charcoal. Unfortunately the presence of two peaks was not sufficient to identify the nature of the unknown impurity and anyway the majority of its peaks were probably overlapped by Pe peaks.

To obtain more information on identification of the unknown impurity a Laser Raman spectra of hydrolysed Pe crystals (i.e. Pe containing unknown impurity) Figure 13, was prepared. However, the resulting spectrum was swamped by fluorescence. Since pure Pe does not fluoresce this suggests the possibility of double bonding to the unknown impurity or

4.3) contd.

the impurity and Pe form double bonds in the crystal state.

For confirmation (or denial) of the existence of double bonding in the unknown impurity a UV spectrum was attempted. The UV spectrum of a 16% solution of hydrolysed Pe (containing the unknown impurity) in distilled water is shown in Figure 14. This did not show fluorescence and therefore presumably the double bond did not exist in solution and therefore the impurity does not contain double bonds.

The results of Rehmatullah's tests with added impurities and the inferences from the series of spectra (infra-red, mass, N.M.R., X-ray, Laser Raman and ultra-violet) can be summarised as follows:

- 1) The increase in growth rate of charcoal extracted Pe crystals was not due to the addition of further counter-acting impurities from the activated charcoal.
- 2) The presence of the unknown impurity in commercial Pe was probably not due to addition of extraneous chemicals which have been used during the manufacturing process of Pe such as oil or chemical additives or corrosion products⁽¹³⁾.
- 3) The unknown impurity is a by-product in the Pe process.

The following suggestions may be made concerning its identifications:

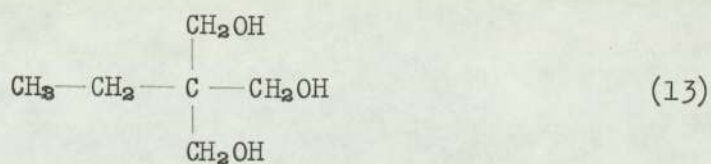
- 1) Absence of double bond
- 2) Branch C skeleton
- 3) Presence of OH' groups
- 4) Fewer OH' groups than Pe
- 5) Presence of CH₃' radicals
- 6) Presence of CH₂" radicals
- 7) The skeleton with similar complexity to Pe
- 8) A retrospective study of the gas chromatographs of the original Pe material revealed that of the six batches

4.3) contd.

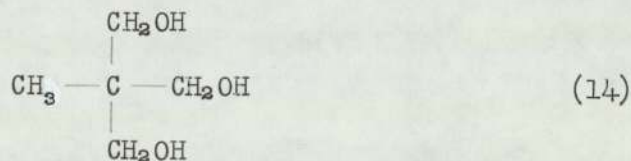
obtained the two which showed no growth rate at all had very small peaks which appeared just before the Pe peak at a position suggesting a molecular weight of approximately 144. To ascribe a molecular weight of course presupposes that the behaviour is the same as for that of Pe homologues.

Considering the above results two possible formulae have been suggested:

a) 1,1,1 Trimethylolpropane, MW = 134



b) 1,1,1 Trimethylolmethane, MW = 120



SECTION FIVE

LITERATURE SURVEY: SURFACE ENERGY

5.1) Introduction.

The surface plays a very important part in the science of solids. Most phenomena involving solids are related to their surfaces. The growth of crystals from solution or melt occurs at the surface and demonstrates these phenomena. The principal property of the surface of a solid is what is known as the surface energy and in this section the concept of surface energy of solids will be considered.

Internal particles in a solid are surrounded on all sides by similar particles but on the surface of a solid particles adjoin similar particles on one side only; therefore their state differs from that of the internal particles. In other words, a particle of crystalline lattice inside the crystal is subjected to forces exerted by all the particles surrounding it and is in a state of equilibrium, the resultant of these forces being equal to zero⁽³⁹⁾. A particle at the surface of a crystal is in a different position, since the particles acting on it are disposed only on one side; the case considered here is that of a single crystal in vacuum, therefore more potential energy is stored in the surface layers. In general this potential energy is called surface energy and in fact is the work required to transfer particles from the body of solid to its surface. To be more precise, specific surface energy or or simply surface energy is the work required for the formation of a unit surface area. The surfaces of liquids possess surface energy but it is only when the surface is mobile that its effects become apparent.

Young^(40,41) and Laplace⁽⁴²⁾ were the first to attempt an explanation of "energy of surface" and formed

5.1) contd.

a relationship for a curved surface as follows:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

where ΔP is a pressure gradient, R_1 and R_2 are the radii of curvature and the surface stress is denoted by γ .

From the thermodynamic definition of specific surface energy, it follows that this energy is equal to the work of isothermal and reversible formation of 1 cm² of the surface layer. The work required is in fact the sum of two quantities - a "mechanical" part (γ) known as Surface Tension and a "thermal" part (η). If σ is the surface energy we have

$$\sigma = \gamma + \eta \quad (15)$$

Helmholtz called the mechanical part of the surface energy the free energy surface or the surface free energy and is in fact the surface tension. For liquids this nomenclature is true and it would be the same for a solid if the change in area could occur slowly, or in general, in such a way that an equilibrium surface configuration was always maintained. But in the case of a solid whose surface is not in equilibrium, which it usually is not, surface tension has not the same value as surface free energy. It is helpful to imagine that the process of forming a fresh surface is divided into two steps: first the solid is cleaned so as to expose a new surface, keeping the atoms fixed in the same position that they occupy when in the bulk phase, and secondly, the atoms in the surface region are allowed to rearrange to their final equilibrium position. If these two steps were to occur as one, surface tension and free energy would be equal (which

5.1) contd.

happens in a liquid) but in the case of solids, the second step may occur only slowly because of the immobility of the surface. Shuttleworth⁽⁴³⁾ gives a relation between surface free energy and surface tension as follows:

$$\gamma = d(\Delta F_s)/dA = F_s + A dF_s/dA \quad (16)$$

where γ is surface tension, F_s is total increase in free energy and dA is the increase in area. For liquids, the last term of equation 16 is zero, so that $\gamma = F_s$.

5.2) Important Effects of Surface Energy.

Frank⁽⁴⁴⁾ and Jackson⁽⁴⁵⁾ have pointed out that surface energy is important when the crystals are microscopic or submicroscopic in size, for example, during nucleation, during the growth of eutectics, during dendritic growth or in determining the structure of the interface on a small scale as in cellular growth. In the usual case, temperature and compositional inhomogeneities in the system will be much larger than the effects of surface energy. The equilibrium shape is never observed on macroscopic crystals (anything larger than a few microns).

Therefore measuring the surface energy of a crystal larger than a few microns would have no significance. Unfortunately, only a few papers are known in which this quantity is measured using the crystals less than two microns in size (mostly by the method of heat of solution which experimentally is not accurate).

5.3) Theory of Surface Energy of Solids.

The nature of the theoretical approach to the

5.3) contd.

calculation of surface energy necessarily varies with the type of solid considered. Since cohesive forces fall off very steeply with distance, one can consider as a first approximation interactions between neighbouring molecules. Unfortunately not many papers have been published in which surface energy is calculated theoretically and those which are known are not in a good agreement with practical values that internationally are accepted, for example, Lennard-Jones et al.^(46,47) obtained positive values of several thousand dynes per centimeter for alkali halide crystals while Shuttleworth^(48,48) found negative values of several hundred dynes per centimeter. The following theory developed by Skapski⁽⁴⁹⁾ for calculation of surface energy of nonionic solids (metals and nonmetals) is in satisfactory agreement with experimental results. The thermodynamic relation,

$$\Delta F = \sigma_M = \Delta U - T_m \Delta S \quad (17)$$

where σ_M is molar surface energy, ΔU is the change of internal energy and ΔS is the change of entropy. From the arrangement of next neighbours:

$$\Delta U = Z_i U - Z_a U = U(Z_i - Z_a) \quad (18)$$

where U is the energy of interaction between the chosen molecule and its next neighbours, Z_i denotes the number of next neighbour in the bulk and Z_a , on the surface. Therefore equation 17 becomes

$$\sigma_M = U(Z_i - Z_a) - T_m \Delta S \quad (19)$$

Skapski has calculated the value of the surface energy from the heat of fusion, the surface energy of the liquid at its freezing point and the arrangement of next neighbours from the following formulae:

5.3) contd.

$$\sigma_s = \frac{Z_i - Z_a}{Z_i} \cdot \frac{Q_f}{A_s} + \left(\frac{\rho_s}{\rho_L} \right)^{\frac{2}{3}} \sigma_L + \frac{T_m}{A_s} (\Delta S_L - \Delta S_s) \quad (20)$$

where ρ_s and ρ_L are density of solid and liquid and A_s is molar area of solid. Also, for nonmetallic solids, a relation between the surface energy and the heat of sublimation L_s has been shown to exist⁽⁵⁰⁾.

$$\sigma_s A_s + T_m \Delta S = \frac{Z_i - Z_a}{Z_i} L_s \quad (21)$$

Hence

$$\sigma_s = \frac{L_s}{A_s} \left(\frac{Z_i - Z_a}{Z_i} \right) - \frac{T_m \Delta S}{A_s} \quad (22)$$

5.4) Measurement of the Surface Energy.

5.4.1) The method of splitting.

The energy required for splitting a crystal into two parts where two new surfaces are produced each with an area S is

$$U = 2\sigma S$$

where σ is the surface energy of the fracture plane. Hence, by determining the energy U required for splitting the crystal, it is possible to calculate σ .

Attempts at experimental determination of the surface energy of rock salt crystals has been made by a number of scientists. Ioffe and Levitskaya⁽⁵⁾ split rock salt crystals with a knife attached to a scale; a weight was dropped on to the scale (from the shortest distance at which the crystal was split) and the work required for splitting

5.4.1) contd.

was considered to be the product of the value of the weight and the distance of fall. The experimental results for the cube (100) face of the rock salt crystal was approximately 10^4 times the theoretical value of Born⁽⁵⁶⁾. Frenkel⁽⁵²⁾ describes some other experiments made by Ioffe and Levitskaya in which the rock salt crystal was split by a knife but there is no mention of a scale and the experimental value of $\sigma^{(100)}$ is about 100 times higher than the theoretical value. Kuznetsov and Ambroz⁽⁵³⁾, and later on Kuznetsov and Kudryavtseva⁽⁵⁴⁾ have tried several methods to determine the surface energy of rock salt crystals by splitting, but the results relative to theoretical calculation were in poor accord. Many objections may be raised against experiments based on methods of splitting such as the energy content transformed into heat which occurs during experiments.

5.4.2) Hardness and surface energy.

An attempt has been made to show that the hardness of brittle solids determined by certain methods is related to surface energy and tensile strength. According to Polanyi⁽⁵⁵⁾, strength Z is related to surface energy σ by the equation

$$\sigma = \frac{Z^2}{2Ea} \quad (23)$$

where E is the modulus of elasticity and a is the inter-atomic distance. The experimental methods can be classified as: scratching method, hardness scale, Hertz' method, the method of damped oscillations, drilling method and grinding method. It will be assumed that all these methods are used for the determination of the hardness of solids for which

5.4.2) contd.

the ultimate tensile strength is below the yield point and which are fractured without plastic deformation.

5.4.2.1) Degree of accuracy of hardness and surface energy.Methods:

It should, however, be remembered that in all the methods of hardness and its relation to surface energy, the problem is complicated by the fact that the main portion of the energy employed for comminution is lost in elastic deformation, friction and other phenomena which are irreversibly converted into heat. Therefore, methods of hardness in general cannot be counted as an accurate experimental or theoretical determination of surface energy. Moreover, hardness methods do not determine the surface energy but a relative surface energy, which in itself increases the degree of inaccuracy. One point which has been overlooked by a number of authors in methods of hardness measurement and surface energy is the interatomic (molecule or ions) energy. In all these methods two different kinds of atoms (molecules or ions) are in contact and interface surface tension has not been taken into account.

5.4.3) Investigation of the method of scratching.

The scratching of brittle materials by tools of any kind results in fragmentation; a portion of the solid is converted into powder, the particles of which have a large surface area and this work lost should be taken into account. Grdina and Kuznetsov⁽⁵⁶⁾ have investigated the method of scratching on rock salt crystals. The crystals

5.4.3) contd.

were not subjected to preliminary annealing and although in some cases they split along regular planes, in the majority of cases it was impossible to talk about any definite volume of the scratch or to calculate the specific work in scratching per unit volume as the fraction was stepped or along a curved face indicating a deformation had occurred. Blakely and Mykura⁽⁵⁷⁾ have measured the surface energy of platinum by the multiple scratch method. Mills and Leak⁽⁵⁸⁾ measured the surface energy of iron -3% silicon by the same method. However, this technique for surface energy measurement is not accurate because it was difficult to maintain standard conditions when polishing mechanically as was mentioned in both of the above cases. This made it difficult to produce surface layers with reproducible properties. Moreover, after polishing the hardness measured by scratching will be equal in all directions so that there will be no hardness rosettes.

5.4.4) The method of damped oscillation.

The method of damped oscillation or, as it is otherwise called, the "pendulum sclerometer" method of hardness determination, was proposed by Kuznetsov⁽⁵⁹⁾. It consists of supporting a horizontal surface on a sharp point made of a hard material. When this pendulum is displaced from the position of equilibrium it will start to perform a damped oscillation motion. The relative value of surface energy can be determined by measuring depth of penetration, the degree of disintegration and the time or

5.4.4) contd.

number of oscillations. Rehbinder⁽⁶⁰⁾ proposed that hardness, H , is proportional to the decrease of the energy of oscillations of the pendulum in a unit time $-\frac{du}{dt}$, this energy being used up in the fragmentation of the specimen and in increasing its free surface energy:

$$-\frac{du}{dt} = \sigma \frac{ds}{dt} + w \frac{ds}{dt} = H \frac{ds}{dt} \quad (24)$$

where w is the work going into the fragmentation and hence

$$H = \sigma + w. \quad (25)$$

5.4.5) Hertz' method.

Hertz' method consists in pressing a ball against a plate, both made of the material under test, until the formation of cracks at the surface of contact. The pressure at the surface of contact is a measure of energy.

5.4.6) Grinding and drilling methods.

Grinding and drilling methods are most closely related to each other from the characteristic point of view. The bulk of the energy input is expended on elastic deformation and transformed into heat. A number of scientists have proposed a theoretical foundation for the process and the experimental work has been carried out by Savitsku and Kuznetsov⁽⁶¹⁾, Bessonov⁽⁶²⁾, and other authors, but none of the numerical results were in good agreement.

5.4.7) Determination of the surface energy by method of cracks.

A crack in a homogeneous brittle solid grows

5.4.7) contd.

when a tensile force is applied to the solid perpendicularly to the crack and a new free surface is formed in the process. Griffith⁽⁶³⁾ solved the problem of the origin of a crack. According to Griffith's theory a brittle solid can deform up to a definite limit, beyond which a crack begins to grow and failure occurs. When cracks are present the energy of the solids consists of three parts:

- I) Energy of the elastic deformation of the entire solid with the exception of the portion adjoining the crack;
- II) Surface energy of the crack. This energy can be considered to be approximately proportional to the surface area of the crack;
- III) Energy of elastic deformation related to the crack and caused by its presence.

The surface energy of glass was determined by the method of cracks (glass in water, alcohol, benzene, mixed media, vaseline oil, air and vacuum), and the numerical results were much higher than was expected⁽⁶⁴⁾.

5.4.8) Surface energy and heat of solution.

This method was used by Lipsett et al.^(65,66) to determine the surface energy of rock salt crystals. Finely and coarsely ground powder of rock salt was dissolved in water and the heat of solution was measured. The difference in the heat of solution was assumed to be due to different surface area and so the surface energy was determined. For determination of surface energy by this method, the experimental and theoretical results have proved that the size of the particles should be less than 2 μm . Giaque and Archibald⁽⁶⁷⁾ used the same method for determination of surface energy

5.4.8) contd.

of magnesium oxide and later Jura and Garland⁽⁶⁸⁾ repeated it to calculate surface entropy and free energy as well as surface energy.

Due to inaccuracies involved in calculating the heat capacities of the medium, the parts of apparatus in contact with the powder (which is not practical) and accurate measurement of particle size⁽⁶⁹⁾, the error in determining surface energy is relatively large. In this method the point which has been overlooked is that small particles of colloidal dimensions frequently have a highly distorted lattice. Consequently, their heat content apart from their surface energy is considerably greater than that of large particles⁽⁷⁰⁾.

5.4.9) Angle of contact.

This method, which is one of the most popular methods of measuring surface energy is only applicable to those substances where very reliable theoretical and experimental values of interfacial and liquid surface energy are available e.g. copper and a number of other metals, sodium chloride, etc.,

Experimental techniques are based on:

- I - placing a drop of liquid on a smooth surface of solid,
- II - the tilting plate,
- III - rise or descent of a liquid in a capillary tube.

I - Droplet method.

If a small drop of liquid is placed on a uniform, chemically clean, flat, solid surface, it will, in general, not spread completely over the surface, but the tangent to the surface of separation between the liquid drop

5.4.9) contd.

and the air (vapour) at the intersection of all three surfaces forms a definite angle with the solid surface, called the angle of contact, which depends on the properties of the three phases.

From the well-known relation of Newman

$$\gamma_s = \gamma_{sl} + \gamma_l \cos \theta \quad (26)$$

where θ is the angle of contact, surface tension can be determined. Gorsku and Mikulich⁽⁷¹⁾, Strel'tsyn⁽⁷²⁾ and some other authors have measured angle of contact, normally by means of photographing the drop of liquid lying on the solid surface. This method is commonly used for determination of the crystal-melt interphase energy rather than surface energy. Harkins and Livingston⁽⁷³⁾ have corrected Newman's relation as it was doubtful whether γ_s was ever the correct quantity since this would imply a perfectly clean solid surface immediately adjacent to the liquid or a solid surface which has come to equilibrium with the saturated vapour of the liquid. Harkins et al.⁽⁷³⁾ have written the equation as follows:

$$\gamma_s = \gamma_{sl} + \gamma_l \cos \theta + \pi \quad (27)$$

where γ_{sl} denotes the surface tension of solid-liquid interface,

$$\pi = - \int dy = \gamma_{sl} - \gamma_{sv}, \quad \gamma_s \text{ denotes the surface tension of}$$

the clean solid surface and γ_{sv} that of the solid-gas interface. If the contact angle is large, the adsorption of vapour on the solid is usually small so that, unless contamination is present, π is small and negligible relative to other values. If the contact angle is zero, then the

5.4.9) contd.

liquid spreads on the solid and π would be equivalent to the spreading coefficient or:

$$\pi = S_{lv^o/s^o} = \gamma_s - \gamma_{lv^o} - S_{sl} \quad (28)$$

The above discussion concerns the treatment of the solid-liquid-gas contact angle; it is possible to have a solid-liquid-liquid contact angle where the liquids are immiscible.

II - The tilting plate method.

Adam et al.⁽⁷⁴⁾ used an apparatus for measuring the angle of contact which has given the most reproducible and possibly the most accurate contact angle value and is known as the tilting plate method. The method is based on dipping a several centimeter wide plate of solid in the liquid. The plate is rotated to a position where the liquid surface appears to remain perfectly flat right up to its surface. The angle of contact is the angle between the plane of the plate and the undistorted surface of the liquid. In actual practice it is found that the angle of contact depends on whether the plate is being pushed into the liquid or raised. Therefore the actual contact angle is taken as the mean value of advancing and receding angles of contact. Ablet⁽⁷⁵⁾ has used a cylinder of solid instead of a plate and his method was to raise or lower the cylinder until the liquid surface appears to continue undistorted right up to the surface of the solid. The contact angle is then given by the equation

$$\cos\theta = 2h/d - 1 \quad (29)$$

where h is the distance from the bottom of the cylinder to the surface of the liquid and d is the diameter of the cylinder. Both the tilting plate and the cylinder methods suffer from the disadvantage that a large and uniform solid

5.4.9) contd.

surface is needed.

III - Capillary rise or descent.

The capillary rise method is generally considered to be the most accurate of all methods of contact angle measurement, partly because the theory has been worked out in considerable exactitude and partly because the experimental variables can be closely controlled.

If a liquid wets the wall of the capillary, the liquid will rise in the tube and its surface must therefore be concave in shape while a liquid which completely fails to wet the walls would descend and its surface is convex. The theory and practical statements are similar.

If the capillary is circular in cross section and not too large in radius, the meniscus will be approximately hemispherical and by assuming the angle of contact is zero, it can be written

$$\Delta p = 2\gamma/r \quad (30)$$

where r is the radius of capillary. If h denotes the height of the meniscus above the flat surface of the liquid then Δp would be equal to the hydrostatic pressure drop in the column of liquid in the capillary or

$$\Delta p = \rho gh \quad (31)$$

where ρ is density of liquid. Therefore

$$2\gamma/r = \rho gh \quad (32)$$

Now supposing the angle of contact is θ , the above formula becomes:

$$\frac{2\gamma \cos \theta}{r} = \rho gh \quad (33)$$

Adamson⁽⁷⁶⁾ elaborated the above theory by

5.4.9) contd.

means of analytical geometry. Antonov^(77,78) has stated that the surface energy of a solid is equal to the surface energy of a liquid which does not rise or descend in a capillary tube made of the solid, forming a flat meniscus. This is based on the hypothesis that if a liquid wets a capillary and rises in it, this means that the forces between the particles of the material from which the tube is made and liquid particles are greater than the forces between liquid particles. Conversely, if the forces between liquid particles are greater than the forces between the particles of the solids and liquids, the liquid descends in the capillary forming a convex meniscus. Antonov considers that when the surface energy of a liquid is higher than the surface energy at the liquid solid interface the liquid does not wet the solid and vice versa. When these two surface energies are equal, there will be a transition between the wetting and non-wetting cases, the liquid will not move up or down in the capillary and will form a flat meniscus. Adam⁽⁷⁹⁾ shows that Antonov's statement is incorrect as the quantity measured is not surface energy of the solid but is the work of molecular attraction or adhesion of the liquid on the solid. It should be noted that the measurement of angle of contact is generally used for determination of interfacial surface energy rather than surface energy of solid.

5.4.10) The undercooling method.

Because of the simple relation given by equation

$$\sigma_s = \sigma_{sL} + \sigma_L \quad (34)$$

any method which can measure the interface tension of the

5.4.10) contd.

solid with its own liquid can be used for the determination of the solid surface energy. The undercooling method, combined with the theory of nucleation can therefore be considered as a legitimate method for the solid-surface tension measurement. The value obtained represents most likely the minimal surface tension of solid.

The undercooling method has been found to be, theoretically and experimentally more accurate than the methods discussed previously. Therefore this method is proposed for measuring the surface energy of Pe from its nucleation characteristics. Unfortunately there is no general agreement on the application of the classical theory of homogeneous nucleation⁽⁸⁰⁾ to real systems. For this reason, it has been suggested^(81,82) that empirical relationships such as

$$J = k_n \Delta C^m_{(Max)} \quad (35)$$

where J is nucleation rate, $\Delta C_{(Max)}$ is maximum allowable supersaturation and k_n denotes nucleation rate constant, are the only ones that can be justified in industrial crystallisation describing the kinetics of nucleation.

The nucleation rate may also be expressed⁽⁸³⁾ by the following definition

$$J = qb \quad (36)$$

where the cooling rate $b = - \frac{dt}{dr}$ and q is the mass of solid deposited per unit mass of free solvent present when the solution is cooled by 1°C , which is a function of the slope of the solubility curve. In general,

$$q = \frac{\epsilon dc}{dt} \quad (37)$$

In the case of crystalliation in an anhydrous form (such as Pe) $\epsilon = 1$.

5.4.10) contd.

The maximum allowable supersaturation, ΔC_{Max} , may be expressed in terms of the maximum allowable undercooling, Δt_{Max} :

$$\Delta C_{\text{Max}} = \left(\frac{dc}{dt} \right) \Delta t_{\text{Max}} \quad (38)$$

Substituting and taking logarithms equation (35) becomes:

$$\log b = (m-1) \log \left(\frac{dc}{dt} \right) - \log \epsilon + \log k_n + m \log \Delta t_{\text{Max}} \quad (39)$$

which indicates that the dependence of $\log b$ on $\log \Delta t_{\text{Max}}$ is linear, and the slope of the line (m) is the "order" of nucleation process. Hence rate of nucleation can be determined and by using the following reaction⁽⁸⁴⁾

$$\ln J = \ln \Omega - \frac{16}{3} \cdot \frac{\pi \sigma^3 v^2}{K^3 T^3 \ln^2 s^*} \quad (40)$$

where Ω is the kinetic constant, s^* is degree of supersaturation, T is temperature, v is volume, and σ is surface energy. A plot of $\log J$ versus $(1/\ln s^*)^2$ for various supersaturation ratios close to s^* can be made and the interfacial energy is determined from the slope. The kinetic constants are often in quite good accord with theoretical expectations.

- 1) Density of aqueous solutions was determined and the experimental data were correlated by the equation:

$$\rho_{12} = 1.0024 + 0.2573x_1 - 1.3004 \times 10^{-4}t - 3.1692 \times 10^{-6}t^2 \quad (41)$$

- 2) The refractive index of the aqueous solutions was measured and found to be correlated by the equation:

$$n_{D_{12}} = 1.3349 + 1.361 \times 10^{-4}x_1 + 1.698 \times 10^{-2}x_1^2 - 7.213 \times 10^{-5}t - 1.148 \times 10^{-6}t^2 \quad (42)$$

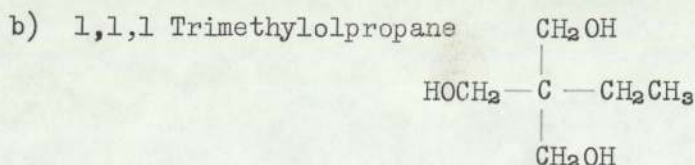
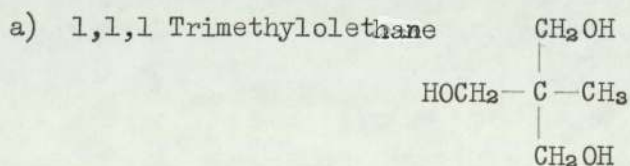
- 3) The partial molar volumes were calculated and were found not to vary with concentration but their variation with temperature was found to be linear and correlated by:

$$\bar{V}_1 = 103.198 + 0.0274t \quad (43)$$

and the refractive index of pure (hypothetical) liquid Pe was calculated over the range of experimental temperatures and correlated by the equation

$$n_{D_1} = 1.5132 - 3.5556 \times 10^{-5}t - 1.1559 \times 10^{-6}t^2 \quad (44)$$

- 4) The presence of an unknown impurity in commercial grades of Pe was confirmed. This impurity is capable of almost complete inhibition of growth even at a concentration of 0.1%. This impurity is in addition to the formal and di-Pe already known to be present.
- 5) An attempt was made to identify this unknown impurity and allocate a formula. The following possibilities are proposed:



CONCLUSIONS

- 6) As a result of surveying the literature on the work done so far about surface energy, the most appropriate method for determining surface energy of Pe should be the undercooling method.

APPENDIX A (referring to Section 3)

TABLE 1
Density of Pe Aqueous Solution at Various Concentrations

conc. = %wt/wt

t °C	2.5%	5%	7%	9%	11%	13%	15%	17%
21	1.0042	1.0104	1.0159	-	-	-	-	-
23	-	-	-	1.0206	-	-	-	-
25	1.0035	1.0098	1.0150	-	-	-	-	-
26	-	-	-	1.0192	-	-	-	-
28	1.0016	1.0086	1.0138	-	-	-	-	-
30	1.0014	1.0075	1.0133	1.0184	-	-	-	-
31	-	-	-	-	1.0236	-	-	-
34	1.0004	1.0068	1.0117	1.0171	1.0223	1.0272	-	-
38	0.9988	1.0051	1.0103	1.0151	1.0206	1.0257	1.0312	-
40	0.9980	1.0041	1.0095	1.0144	1.0196	1.0247	1.0284	1.0342
44	0.9955	1.0022	1.0071	1.0122	1.0173	1.0225	1.0279	1.0339
48	0.9947	1.0008	1.0060	1.0114	1.0163	1.0211	1.0266	1.0320
50	0.9938	1.0002	1.0051	1.0102	1.0154	1.0186	1.0257	1.0311
54	0.9922	0.9983	1.0032	1.0083	1.0135	1.0175	1.0238	1.0295
58	0.9905	0.9961	1.0013	1.0061	1.0113	1.0164	1.0218	1.0270
60	0.9893	0.9954	1.0003	1.0054	1.0106	1.0157	1.0214	1.0263
64	0.9880	0.9940	0.9989	1.0040	1.0092	1.0142	1.0195	1.0249
68	0.9865	0.9910	0.9960	1.0013	1.0065	1.0112	1.0165	1.0219
70	0.9841	0.9899	0.9952	1.0002	1.0054	1.0104	1.0157	1.0205
74	0.9821	0.9882	0.9934	0.9982	1.0029	1.0078	1.0137	1.0188
78	0.9803	0.9860	0.9911	0.9966	1.0012	1.0053	1.0115	1.0169
80	0.9766	0.9854	0.9905	0.9951	1.0006	1.0045	1.0106	1.0160

Mass fraction x_1 $t(^{\circ}\text{C})$	0.0494	0.0736	0.0974	0.1209	0.1447	0.1670	0.1896	0.2118	0.2332	0.2555
25	1.3390	1.3458	1.3458	1.3489	1.3523	1.3556	1.3590	-	-	-
30	1.3383	1.3417	1.3452	1.3483	1.3516	1.3549	1.3583	-	-	-
35	1.3377	1.3410	1.3444	1.3476	1.3509	1.3541	1.3575	1.3606		
40	1.3370	1.3403	1.3437	1.3468	1.3501	1.3533	1.3567	1.3598	1.3631	-
45	1.3362	1.3395	1.3428	1.3460	1.3494	1.3525	1.3558	1.3589	1.3615	-
50	1.3353	1.3386	1.3420	1.3452	1.3473	1.3516	1.3459	1.3580	1.3614	1.3645
55	-	1.3377	1.3411	1.3434	1.3467	1.3506	1.3539	1.3570	1.3603	1.3635
60	-	1.3368	1.3401	1.3422	1.3464	1.3496	1.3529	1.3569	1.3592	1.3625
65	-	1.3357	1.3390	1.3421	1.3454	1.3485	1.3519	1.3549	1.3581	1.3610
70	-	-	1.3379	1.3411	1.3443	1.3471	1.3503	1.3538	1.3567	1.3602
75	-	-	1.3363	1.3399	1.3421	1.3462	1.3496	1.3526	1.3558	1.3602
80	-	-	1.3356	1.3386	1.3418	1.3451	1.3483	1.3506	1.3546	1.3574

Refractive Index of Fe Aqueous Solution at Various Concentrations - Temperature $^{\circ}\text{C}$

TABLE II

Table III - Molar Volume of Solution.

T = 30°C

Mass Fraction x_1	Mole Fraction n_1	Molar Volume V_{12}
0	0	18.0795
.1E-01	.133364E-02	18.191
.2E-01	.269084E-02	18.3047
.3E-01	.407223E-02	18.4207
.4E-01	.547845E-02	18.539
.5E-01	.691019E-02	18.6597
.6E-01	.836814E-02	18.7829
.7E-01	.985303E-02	18.9086
.8E-01	.113656E-01	19.0369
.9E-01	.129067E-01	19.1678
.1	.14477E-01	19.3015
.11	.160775E-01	19.4379
.12	.17709E-01	19.5773
.13	.193724E-01	19.7196
.14	.210687E-01	19.865
.15	.227988E-01	20.0136
.16	.245637E-01	20.1653
.17	.263646E-01	20.3205
.18	.282026E-01	20.479
.19	.300788E-01	20.6411
.2	.319943E-01	20.8069
.21	.339505E-01	20.9764
.22	.359487E-01	21.1498
.23	.379902E-01	21.3273
.24	.400764E-01	21.5088

T = 40°C

0	0	18.1401
.1E-01	.133364E-02	18.2531
.2E-01	.269084E-02	18.3683
.3E-01	.407223E-02	18.4858
.4E-01	.547845E-02	18.6056
.5E-01	.691019E-02	18.7279
.6E-01	.836814E-02	18.8526
.7E-01	.985303E-02	18.9799
.8E-01	.113656E-01	19.1097
.9E-01	.129067E-01	19.2423
.1	.14477E-01	19.3776
.11	.160775E-01	19.5157
.12	.17709E-01	19.6568
.13	.193724E-01	19.8008
.14	.210687E-01	19.9479
.15	.227988E-01	20.0982
.16	.245637E-01	20.2518
.17	.263646E-01	20.4087
.18	.282026E-01	20.5691
.19	.300788E-01	20.733
.2	.319943E-01	20.9007
.21	.339505E-01	21.0721
.22	.359487E-01	21.2475
.23	.379902E-01	21.4269
.24	.400764E-01	21.6105

Table III (continued)

X_1	n_1	V_{12}
0	0	18.2124
.1E-01	.133364E-02	18.332
.2E-01	.269084E-02	18.4468
.3E-01	.407223E-02	18.564
.4E-01	.547845E-02	18.6835
.5E-01	.691019E-02	18.8054
.6E-01	.836814E-02	18.9297
.7E-01	.985303E-02	19.0566
.8E-01	.113656E-01	19.1862
.9E-01	.129067E-01	19.3184
.1	.14477E-01	19.4533
.11	.160775E-01	19.5911
.12	.17709E-01	19.7318
.13	.193724E-01	19.8755
.14	.210687E-01	20.0223
.15	.227988E-01	20.1723
.16	.245637E-01	20.3255
.17	.263646E-01	20.4821
.18	.282026E-01	20.6422
.19	.300788E-01	20.8058
.2	.319943E-01	20.9732
.21	.339505E-01	21.1443
.22	.359487E-01	21.3194
.23	.379902E-01	21.4985
.24	.400764E-01	21.6818

T = 60°C

0	0	18.3069
.1E-01	.133364E-02	18.4195
.2E-01	.269084E-02	18.5344
.3E-01	.407223E-02	18.6515
.4E-01	.547845E-02	18.7709
.5E-01	.691019E-02	18.8928
.6E-01	.836814E-02	19.0172
.7E-01	.985303E-02	19.1441
.8E-01	.113656E-01	19.2737
.9E-01	.129067E-01	19.4059
.1	.14477E-01	19.5409
.11	.160775E-01	19.6787
.12	.17709E-01	19.8195
.13	.193724E-01	19.9632
.14	.210687E-01	20.1101
.15	.227988E-01	20.2601
.16	.245637E-01	20.4134
.17	.263646E-01	20.5701
.18	.282026E-01	20.7303
.19	.300788E-01	20.894
.2	.319943E-01	21.0615
.21	.339505E-01	21.2327
.22	.359487E-01	21.4079
.23	.379902E-01	21.5872
.24	.400764E-01	21.7706

Table III (continued)

X_1	$T = 70^\circ\text{C}$	
	n_1	V_{12}
0	0	18.4109
.1E-01	.133364E-02	18.5243
.2E-01	.269084E-02	18.64
.3E-01	.407223E-02	18.7579
.4E-01	.547845E-02	18.8763
.5E-01	.691019E-02	19.001
.6E-01	.836814E-02	19.1263
.7E-01	.985303E-02	19.2541
.8E-01	.113656E-01	19.3846
.9E-01	.129067E-01	19.5177
.1	.14477E-01	19.6537
.11	.160775E-01	19.7925
.12	.17709E-01	19.9342
.13	.193724E-01	20.079
.14	.210687E-01	20.2269
.15	.227988E-01	20.378
.16	.245637E-01	20.5323
.17	.263646E-01	20.6901
.18	.282026E-01	20.8514
.19	.300788E-01	21.0163
.2	.319943E-01	21.1849
.21	.339505E-01	21.3574
.22	.359487E-01	21.5338
.23	.379902E-01	21.7142
.24	.400764E-01	21.8989

 $T = 80^\circ\text{C}$

X_1	n_1	V_{12}
0	0	18.5184
.1E-01	.133364E-02	18.6311
.2E-01	.269084E-02	18.746
.3E-01	.407223E-02	18.8632
.4E-01	.547845E-02	18.9823
.5E-01	.691019E-02	19.1043
.6E-01	.836814E-02	19.2293
.7E-01	.985303E-02	19.3564
.8E-01	.113656E-01	19.4861
.9E-01	.129067E-01	19.6186
.1	.14477E-01	19.7538
.11	.160775E-01	19.8918
.12	.17709E-01	20.0329
.13	.193724E-01	20.1769
.14	.210687E-01	20.3241
.15	.227988E-01	20.4744
.16	.245637E-01	20.6281
.17	.263646E-01	20.7851
.18	.282026E-01	20.9457
.19	.300788E-01	21.1099
.2	.319943E-01	21.2778
.21	.339505E-01	21.4495
.22	.359487E-01	21.6252
.23	.379902E-01	21.805
.24	.400764E-01	21.989

TABLE IV

Refractive Index of Pure (Hypothetical) Liquid Pe

Volume Fraction of Pure Liq. Pe	Volume Fraction of Water	Refractive Index of Pure Liq. Pe	Refractive Index of Water	Experimental Refractive Index of Solution
T = 30°C				
Z ₁	Z ₂	N _{D1}	N _{D2}	N _{D12}
.763329E-02	.992362	1.51636	1.33167	1.33303
.230247E-01	.976976	1.51543	1.33167	1.333591
.385594E-01	.961441	1.51461	1.33163	1.33373
.542445E-01	.945756	1.51373	1.33163	1.34156
.700321E-01	.929918	1.51285	1.33169	1.34433
.860746E-01	.913926	1.51197	1.33169	1.34721
.102224	.897776	1.5111	1.3317	1.35003
.118533	.881467	1.51022	1.3317	1.35236
.135004	.864996	1.50934	1.3317	1.35569
.151639	.848361	1.50847	1.33171	1.35851
.163441	.831559	1.50759	1.33171	1.36134
.185412	.814539	1.50672	1.33172	1.36417
.202554	.797446	1.50584	1.33173	1.36699

T = 40°C

.762131E-02	.992379	1.51523	1.33015	1.33156
.229743E-01	.977026	1.51436	1.33015	1.33438
.384763E-01	.961524	1.51348	1.33015	1.33721
.541295E-01	.945871	1.51259	1.33016	1.34003
.699361E-01	.930064	1.5117	1.33016	1.34286
.853933E-01	.914102	1.51082	1.33017	1.34568
.102013	.897932	1.50993	1.33017	1.34851
.113299	.881701	1.50905	1.33017	1.35134
.134742	.865253	1.50816	1.33018	1.35416
.151351	.848649	1.50723	1.33018	1.35699
.163127	.831373	1.50639	1.33019	1.35981
.185073	.814927	1.50551	1.3302	1.36264
.202192	.797808	1.50463	1.3302	1.36547

T = 50°C

.760449E-02	.992396	1.51391	1.32339	1.3293
.229244E-01	.977076	1.51301	1.32339	1.33263
.383941E-01	.961606	1.51212	1.3234	1.33545
.540156E-01	.945935	1.51122	1.3234	1.33823
.697914E-01	.930209	1.51032	1.32341	1.3411
.857237E-01	.914277	1.50943	1.32341	1.34393
.101315	.898185	1.50854	1.32342	1.34675
.113067	.881933	1.50764	1.32342	1.34953
.134433	.865517	1.50675	1.32342	1.35241
.151065	.848935	1.50586	1.32343	1.35523
.167316	.832184	1.50497	1.32343	1.35806
.184733	.815263	1.50407	1.32344	1.36089
.201833	.798167	1.50313	1.32345	1.36371

TABLE IV (contd.)

T = 60°C

Z_1	Z_2	N_{D_1}	N_{D_2}	$N_{D_{12}}$
.753733E-02	.992412	1.51233	1.32641	1.32732
.22375E-01	.977125	1.51143	1.32641	1.33064
.333125E-01	.961633	1.51052	1.32641	1.33347
.539023E-01	.946097	1.50961	1.32642	1.33629
.696431E-01	.930352	1.50871	1.32642	1.33912
.855506E-01	.91445	1.50731	1.32643	1.34194
.101613	.898337	1.50691	1.32643	1.34477
.117337	.882163	1.50601	1.32644	1.3476
.134226	.865774	1.50511	1.32644	1.35042
.150732	.849218	1.50421	1.32645	1.35325
.167507	.832493	1.50331	1.32645	1.35603
.184405	.815595	1.50241	1.32646	1.3589
.201478	.798522	1.50151	1.32646	1.36173

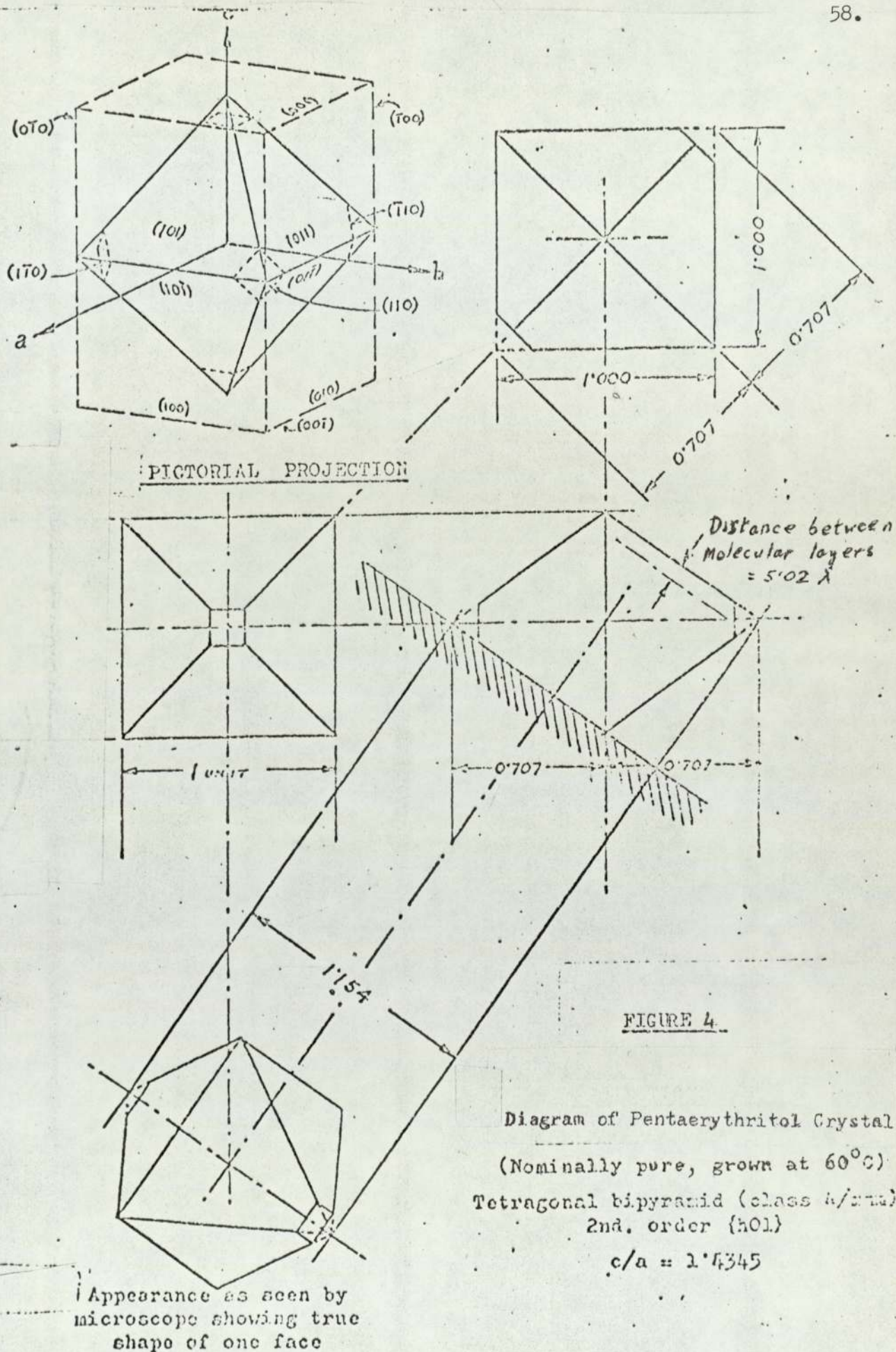
T = 70°C

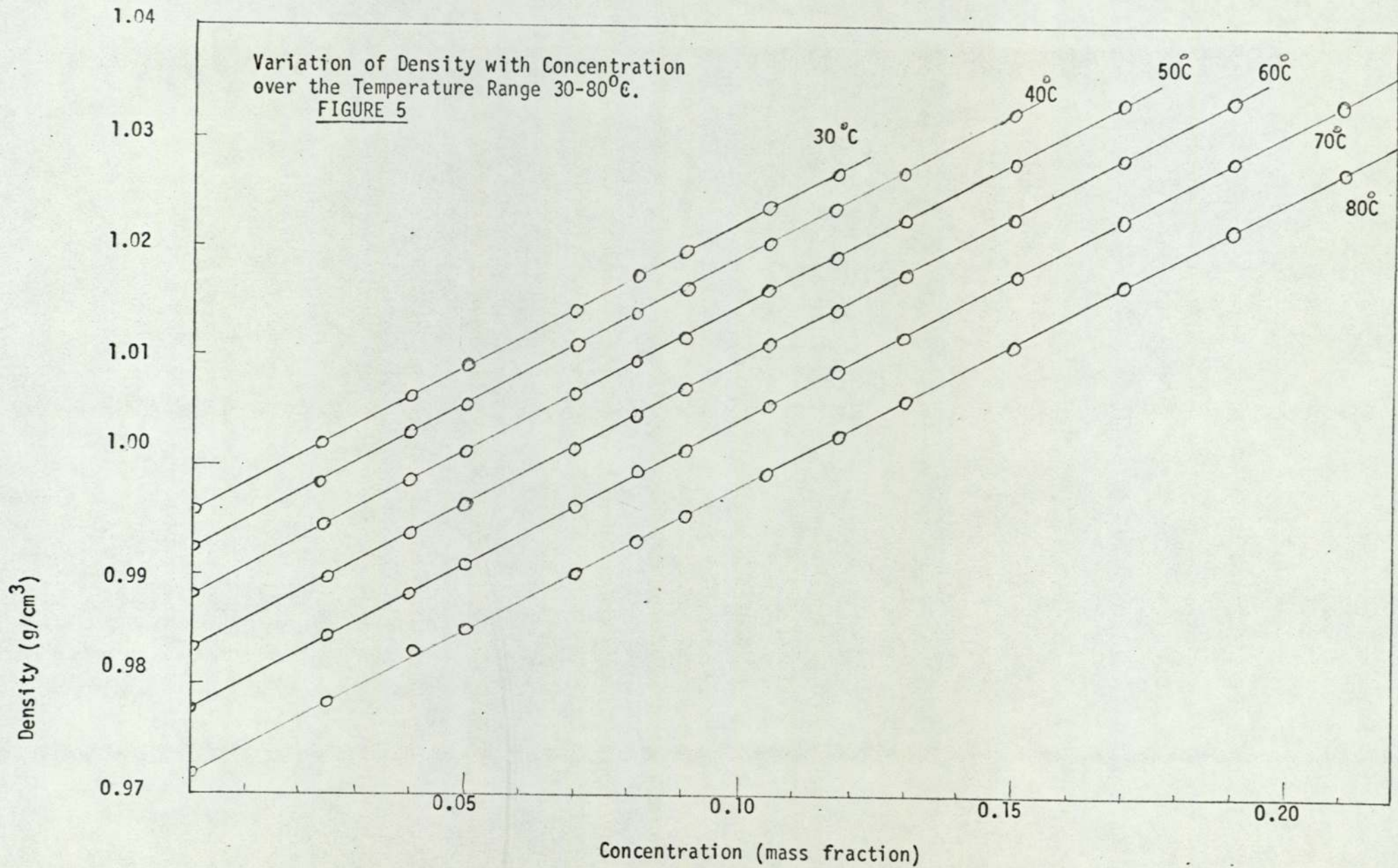
.757133E-02	.992429	1.51053	1.32419	1.3256
.22326E-01	.977174	1.5096	1.3242	1.32343
.332313E-01	.961768	1.50869	1.3242	1.33125
.537911E-01	.946209	1.50773	1.3242	1.33403
.695061E-01	.930494	1.50687	1.32421	1.3369
.853792E-01	.914621	1.50596	1.32421	1.33973
.101413	.898537	1.50505	1.32422	1.34256
.117609	.882391	1.50414	1.32422	1.34533
.133971	.866029	1.50323	1.32423	1.34821
.150501	.849499	1.50232	1.32423	1.35103
.167202	.832799	1.50142	1.32424	1.35386
.184075	.815925	1.50051	1.32424	1.35669
.201125	.798875	1.4996	1.32425	1.35952

T = 80°C

.755499E-02	.992445	1.50349	1.32175	1.32316
.227775E-01	.977223	1.50755	1.32175	1.32593
.331513E-01	.961843	1.50664	1.32176	1.32831
.536304E-01	.94632	1.50571	1.32176	1.33163
.693654E-01	.930535	1.5048	1.32176	1.33446
.852093E-01	.914791	1.50333	1.32177	1.33729
.101214	.898736	1.50296	1.32177	1.34011
.117333	.882617	1.50205	1.32173	1.34294
.133719	.866231	1.50113	1.32173	1.34576
.150223	.849777	1.50021	1.32179	1.34859
.166399	.833102	1.49929	1.32179	1.35142
.183743	.816252	1.49833	1.3213	1.35424
.200775	.799225	1.49746	1.3213	1.35707

APPENDIX B (referring to Section 4)





Variation of Refractive Index with
Concentration over the Temperature
Range 30-80°C

FIGURE 6

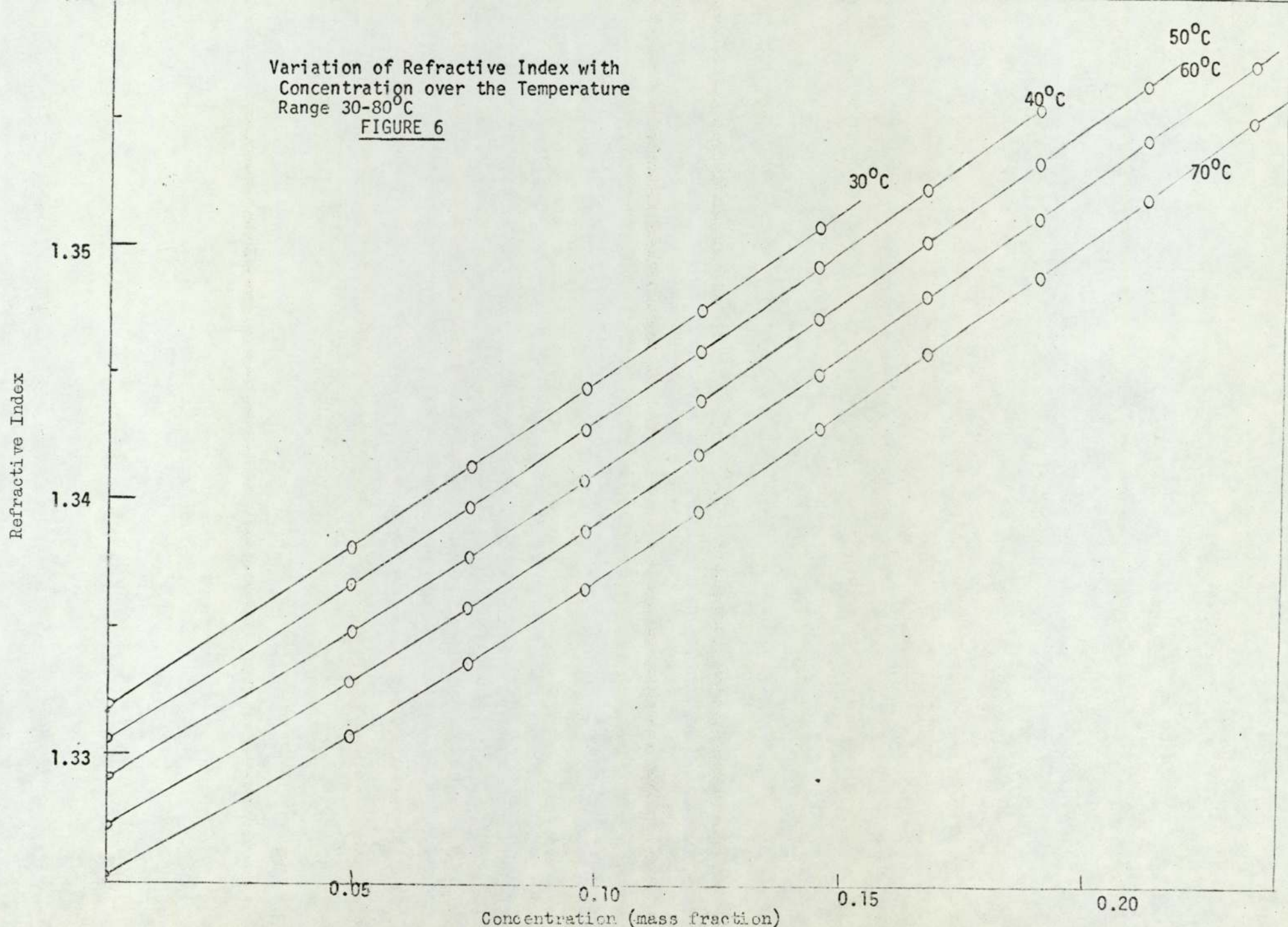
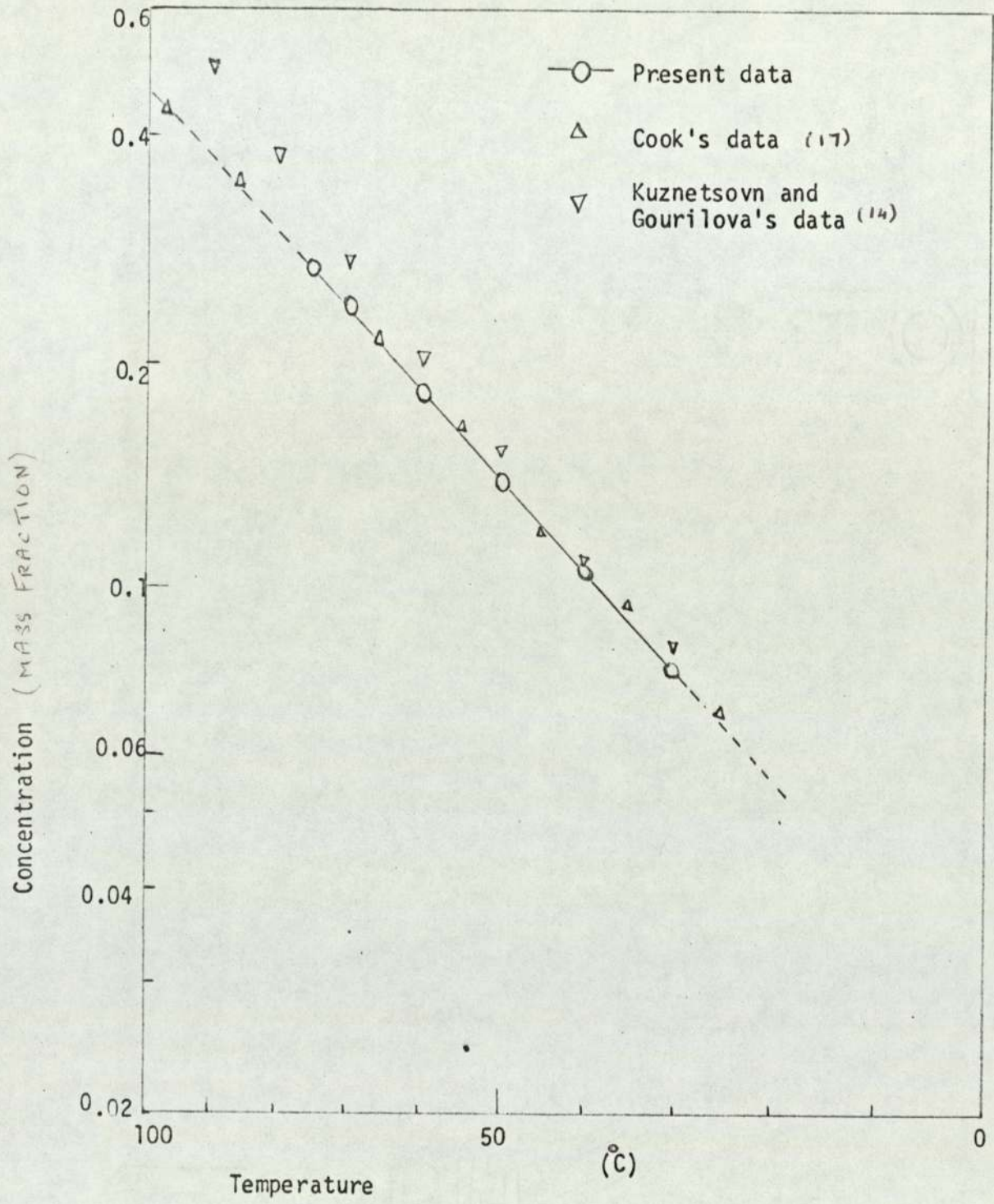


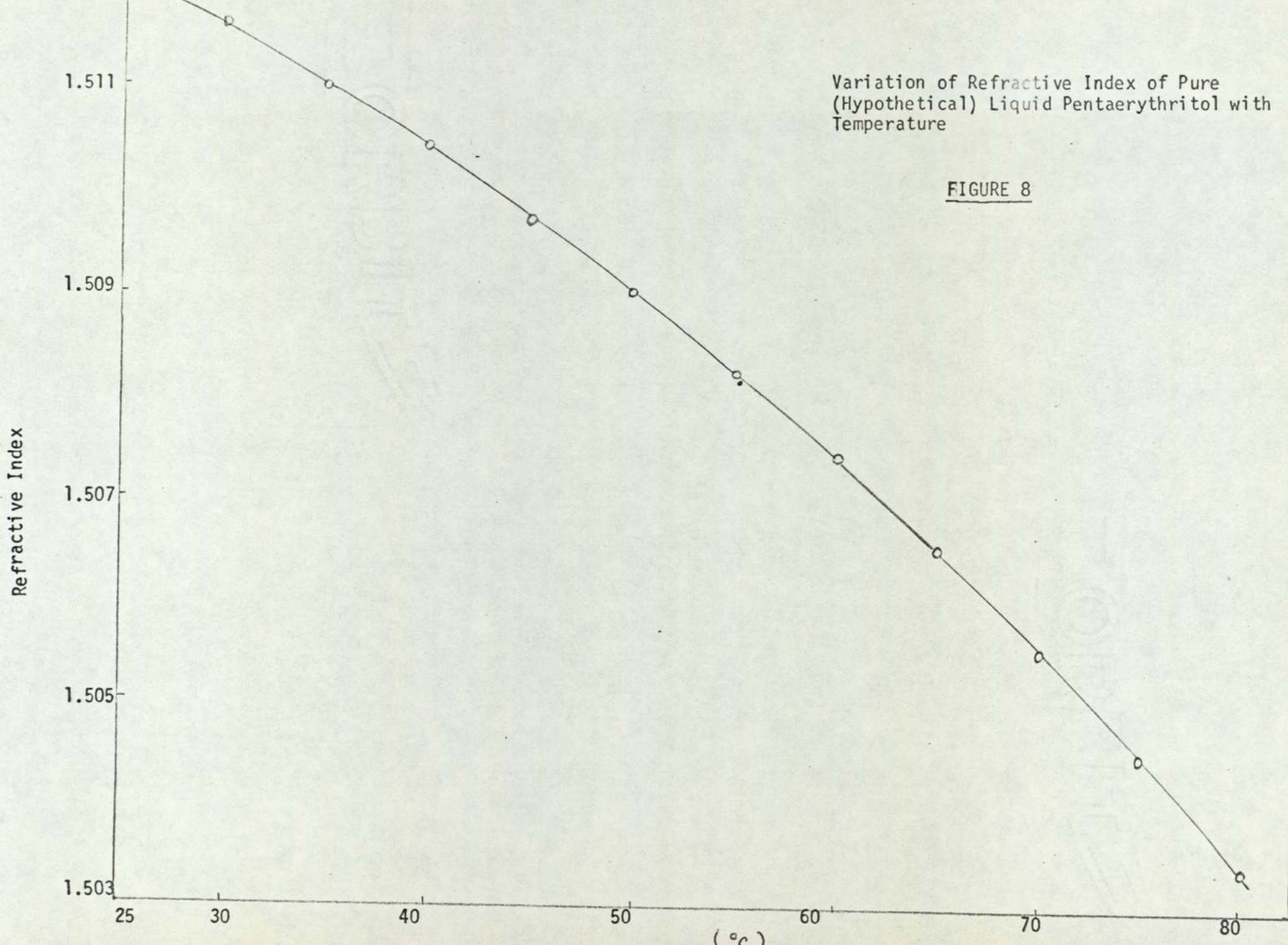
FIGURE 7

Solubility curve of Pentaerythritol



Variation of Refractive Index of Pure
(Hypothetical) Liquid Pentaerythritol with
Temperature

FIGURE 8



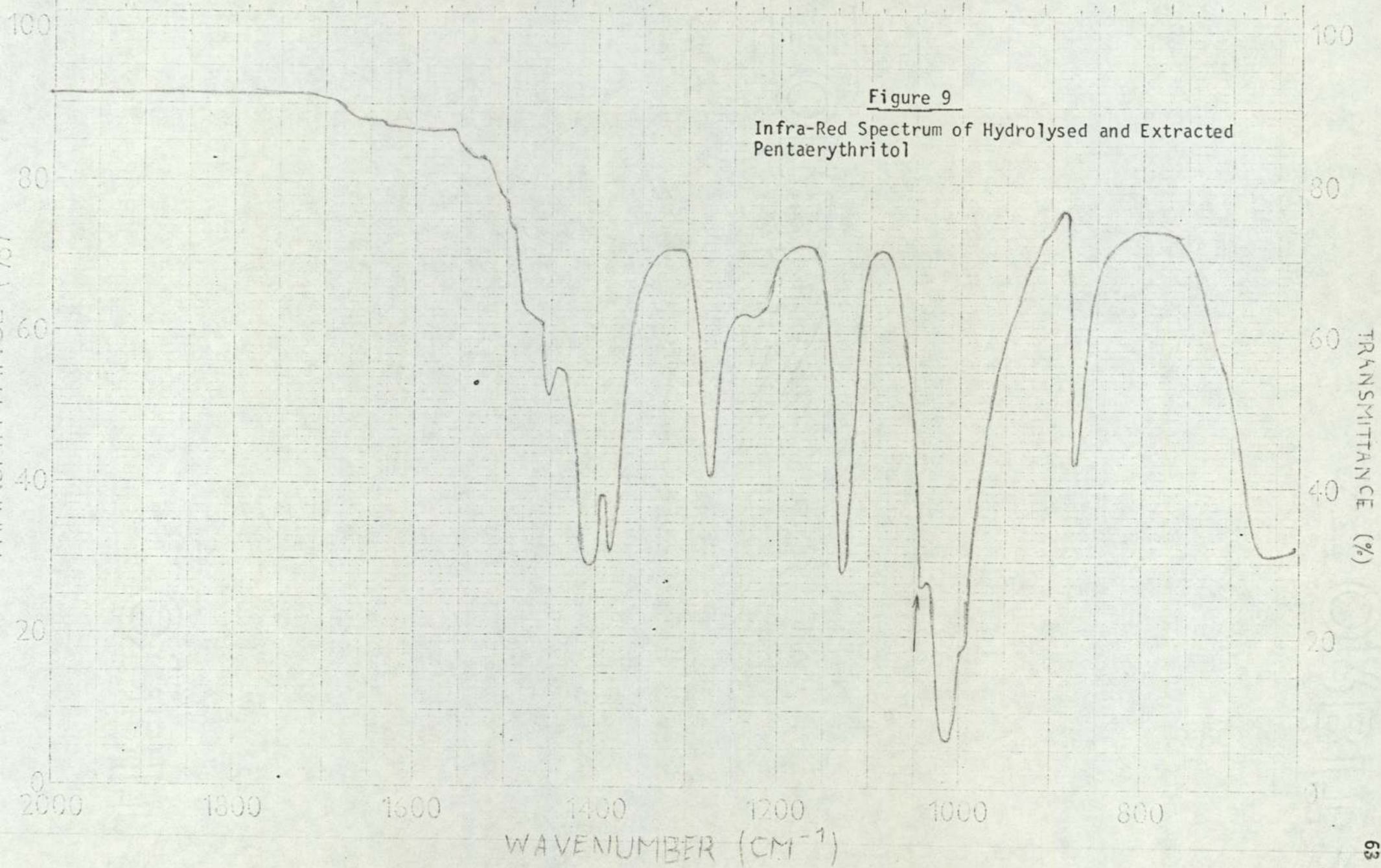


FIGURE 10

Infra-Red Spectrum of Hydrolysed Pentaerythritol
(Not Extracted with charcoal) showing Greater
Adsorption at 1045 cm^{-1} than for the Extracted
Material

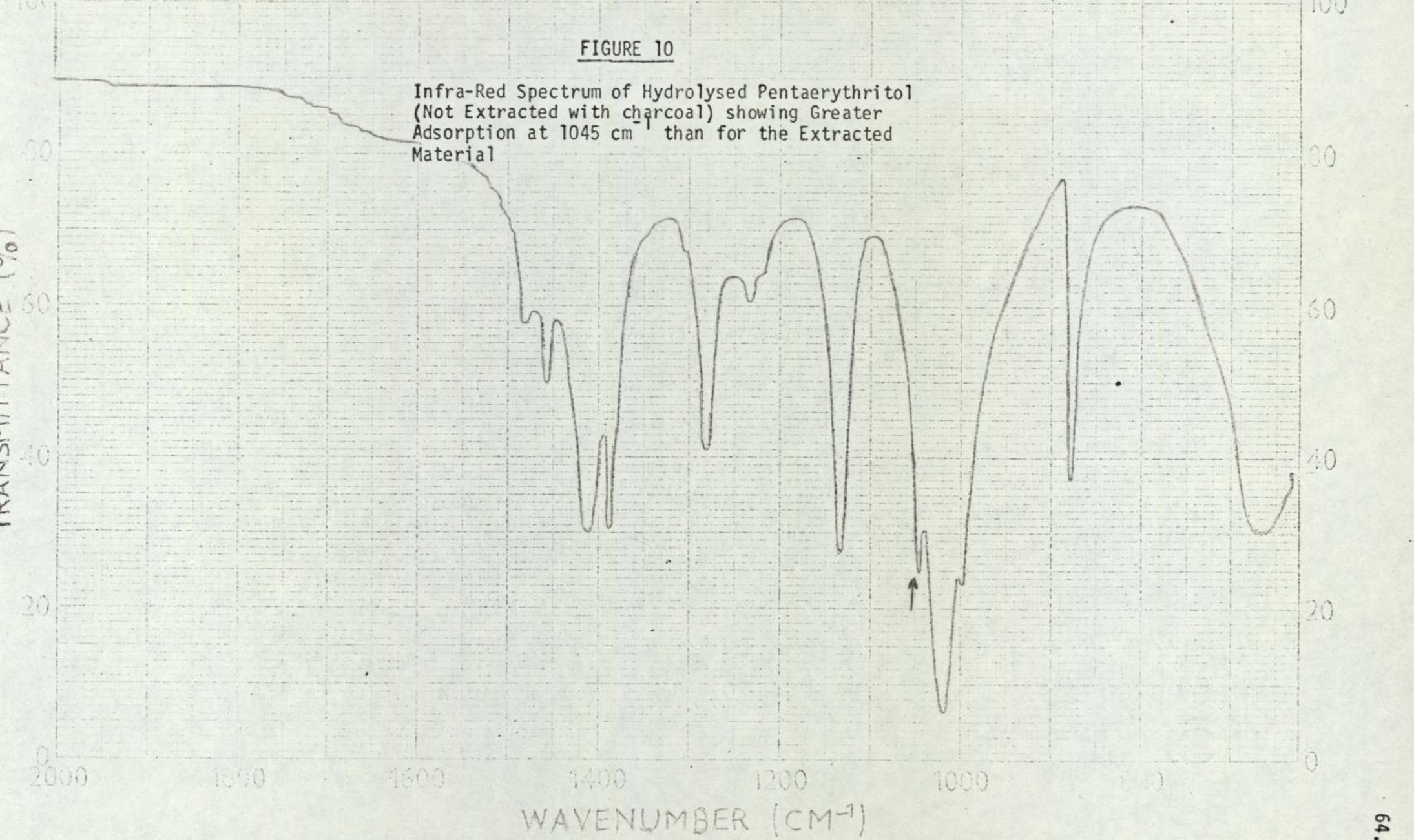


FIGURE 11

Nuclear-Magnetic Resonance (N.M.R.) Spectrum of
Hydrolysed Pentserythritol (Not Extracted with
charcoal) showing Presence of CH_3 Radicals

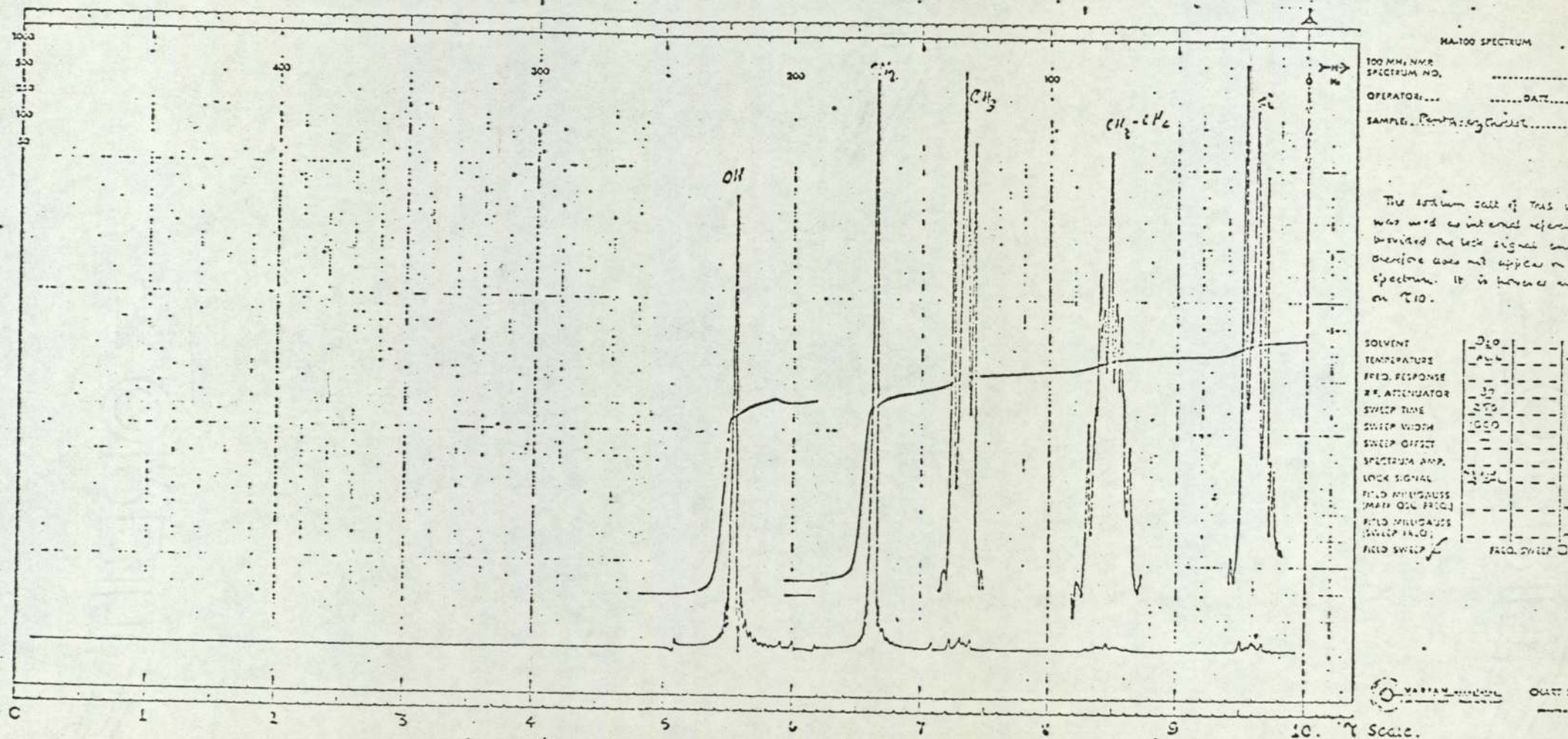
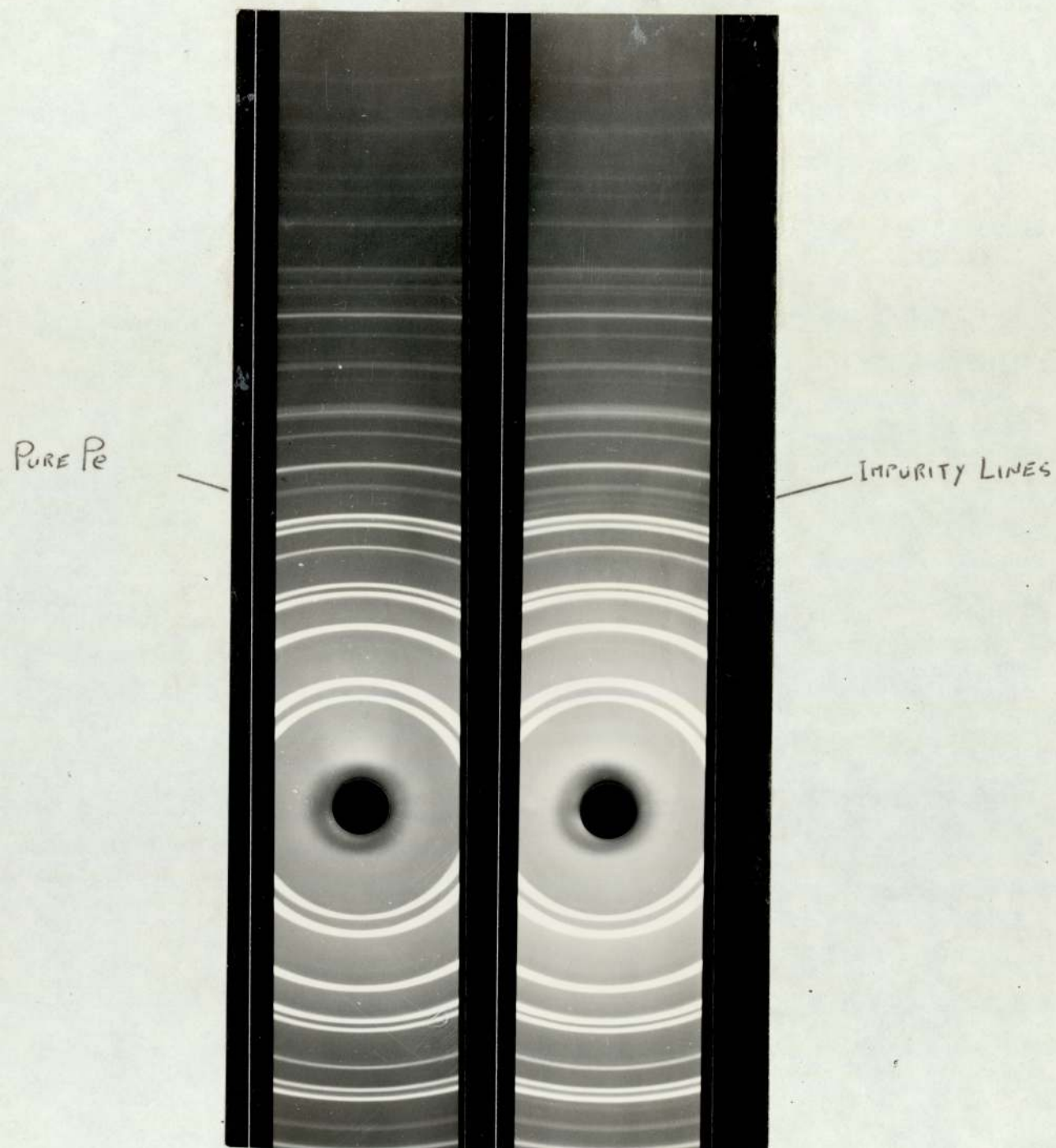


FIGURE 12

X-Ray Spectrum of Hydrolysed and Extracted
Pentaerythritol compared with Hydrolysed but
not Extracted Material showing the Extra Lines
due to the Unknown Impurity

SPECTRUM No. 2

DATE 11/12/72

COMPOUND Hydrolysed Pentaerythritol
STATE powder
SOLVENT
SLIT 0.8 cm⁻¹ 12 MM
SCAN SPEED 1 X 100
SENSITIVITY PA 100 X 25
LASER Ar⁺ 5145 Å

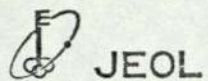
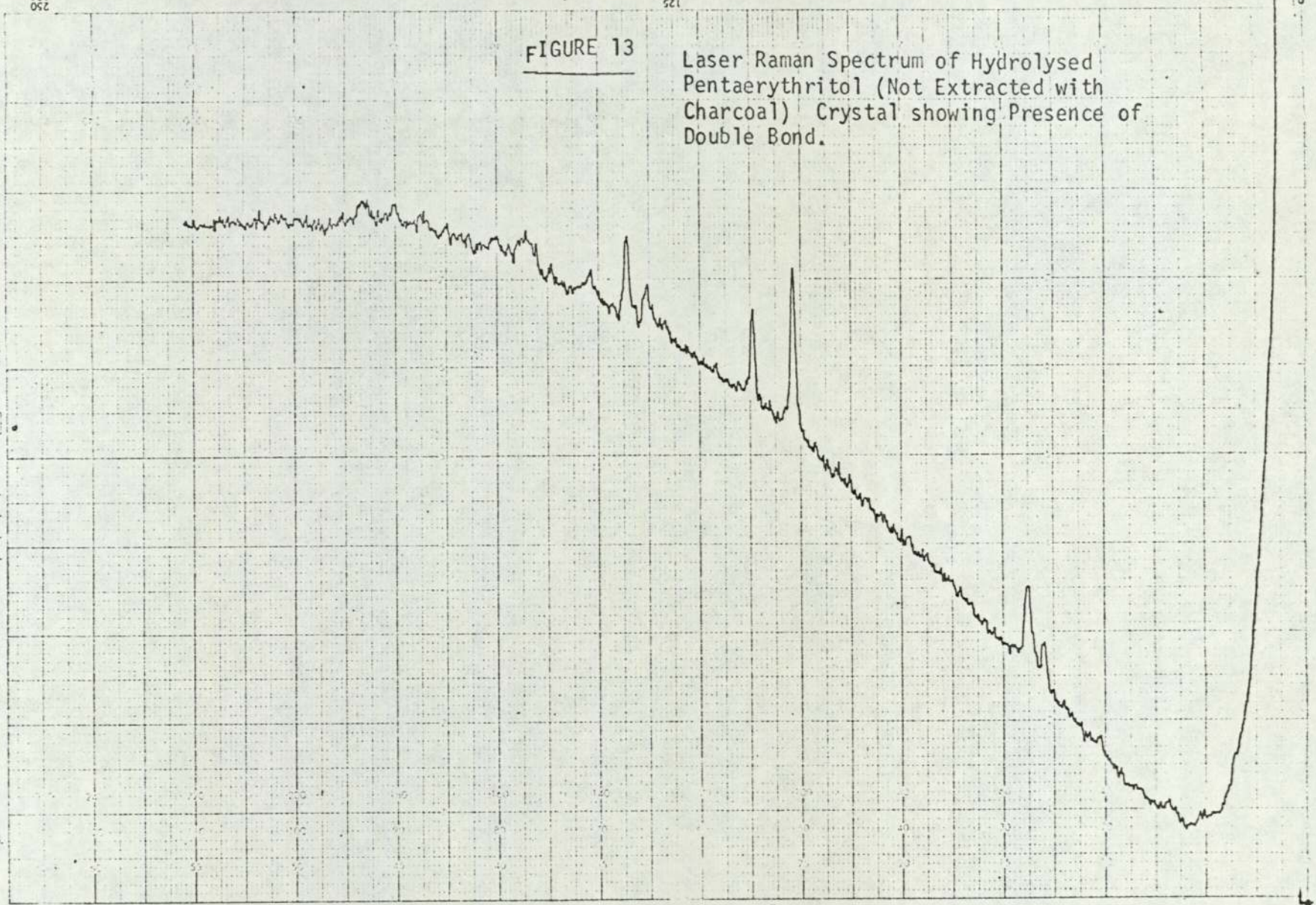
DETECTION METHOD:
POLARIZATION ON/OFF
REPEAT ON/OFF

WAVENUMBER EXPANSION
62.5 125 250
2500

OPERATOR SLB
REMARKS 2F
capillary

FIGURE 13

Laser Raman Spectrum of Hydrolysed Pentaerythritol (Not Extracted with Charcoal) Crystal showing Presence of Double Bond.

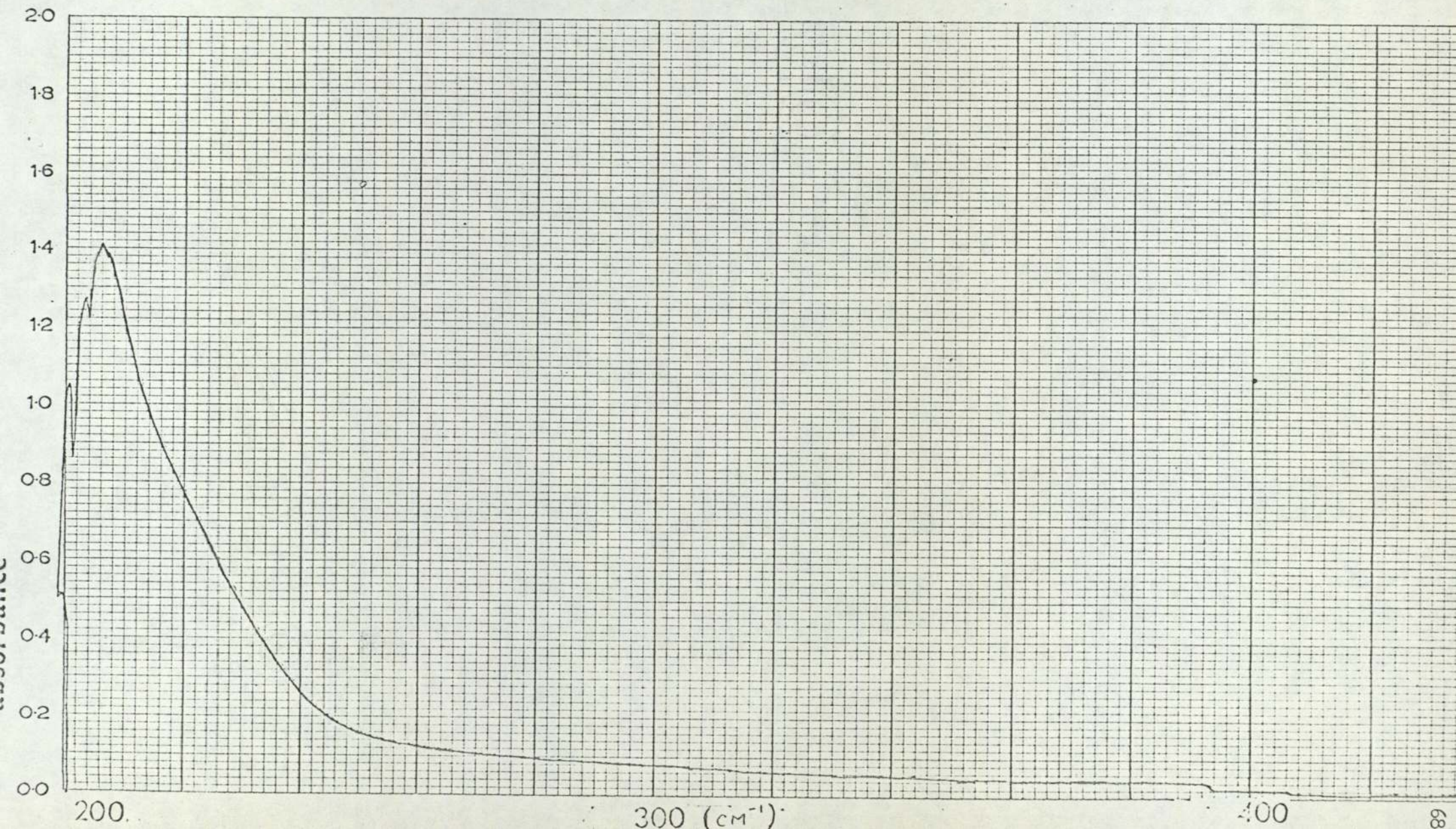


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2000

1000 (CM⁻¹)



REFERENCES.

- 1) TOLLENS, B., U.S. Pat. 2,882,287 (April 14, 1959)
- 2) TOLLENS, B. et al., U.S. Pat. 2,798,885 (July 9 1945)
- 3) WELLS, A. F., *Phi. Mag.*, 37, 184, 217 (1946)
- 4) ROGERS, J. F., Ph.D. thesis, University of Aston in Birmingham, 1969.
- 5) BERLOW, E. et al., "The Pentaerythritols," ACS Monograph, Reinhold, N.Y., 1958.
- 6) KUDSSUS, H. PB 73507 Fr. No. 4723-4937 (14th August 1939).
- 7) LUKE, O. V. et al., U.S. Pat. 2,951,095 (August 14 1960).
- 8) BRIED, E. A., U.S. Pat. 2,325,589 (August 3 1943).
- 9) BLUDWORTH, J. E., U.S. Pat. 2,333,696 (November 9 1943).
- 10) WACHS, R., M.Sc. thesis, University of Aston in Birmingham, 1970.
- 11) I. C. I., British Pat. 599,357 (March 10 1948).
- 12) WOLFROM, M. L., et al., *J. Am. Chem. Soc.*, 68, 1449, (1946).
- 13) REHMATULLAH, S., Ph.D. thesis (to be published 1973), University of Aston in Birmingham.
- 14) KUZNETSOV, L. I. et al., "Growth of crystals" 3; 20, 1962).
- 15) SUCHANEC, R., *Anal. Chem.*, 37; 11; 1361-5 (1965).
- 16) SIMONS, T., Ph.D. thesis (to be published 1973), University of Aston in Birmingham.
- 17) COOKE, E. G., *Paint Manuf.*; 18, 125 (1948).
- 18) WOOLF, L. A., *J. Phys. Chem.*, 67; 273 (1963).
- 19) KIRIYAMA, R. et al., *J. Chem. Soc.*, 140, 883 (1937).
- 20) KELLEY, F. J., Ph.D. thesis, University of New England, (1961).
- 21) BRIGHT, N. F. H. et al., *Can. J. Technol.*, 31, 221 (1953).
- 22) HARNED, H. S. and OWEN, B. B., "Physical chemistry of electrolyte solutions", 3rd Ed., (Reinhold, 1958) p. 358.
- 23) KELLEY, F. J. et al., *J. Phys. Chem.*, 64, 1448 (1960).
- 24) EDWARDS, A., University of Aston, Chemical Engineering Dept., Private communication.
- 25) FRIEDRICH, W., BRUEN, W., *Ber.* 63, 2681, (1930).
- 26) SHERWOOD, P. W., *Petroleum Refiner* 35 (1956), No. 1, 171-179.
- 27) MEISSNER, F., B. Pat. 958654, 21 May 1964.

REFERENCES (contd)

- 28) PETERS, M.S., CUPIT, C.R., Chem. Eng. Sci. 10 (1959) 57.
- 29) ELDERFELD, R.C. "The preparation of pentaerythritol", OSRD, No. 1804, P.B. 30748, Sept. 1, 1943.
- 30) PALTIN, E., TEODORN, E., Rev. Chim. (Bucharest) 15(a) 546-50 (1964).
- 31) HOLECKE, S., DURAS, S., Chemické Zvesti 18, 867-871 (1964).
- 32) PRINS, H.J., Rec. Trav. Chim., 71, 1131-6 (1952).
- 33) ROGERS, J.F., FARAZMAND, H., CREASY, D.E., J. Chem. Eng. Data, to be published.
- 34) WEAST, "Handbook of Chem. Phys.", 53 Ed., 1972-1973.
- 35) MULLIN, J.W., J. Appl. Chem., 1970, Vol. 20.
- 36) BOURNE, E.J., et al., Chem. and Ind. (1961), 750.
- 37) BONNER, T.G., Chem. and Ind. (1960), 345.
- 38) A.S.T.M. The powder Diffraction File 1973.
- 39) IOFFE, A.F., "The phys. crystals", Gosisdats, Mos.-Len., (1929).
- 40) YOUNG, T., Miscellaneous work, Peacock G., Ed. J. Maray, (London), 1, 418 (1855).
- 41) YOUNG, T., Phil. Trans., 95, 65, 82 (1805).
- 42) LAPLACE, P.S. de, "Mechanique Celest," supplements to book 10, (1806).
- 43) SHUTTLEWORTH, R., Proc. Phys. Soc., (London) 63A, 444 (1950).
- 44) FRANK, F.C., "Growth and Perfection of crystals", Ed. Doremus et al., Wiley, (New York) (1958).
- 45) JACKSON, "Crystal growth", Ed. Peiser, 2A, (1966).
- 46) LENNARD-JONES, J.E. et al., Proc. Roy. Soc. A109, 476 (1925).
- 47) LENNARD-JONES, J.E. et al., Proc. Roy. Soc. A121, 247, (1928).
- 48) SHUTTLEWORTH, R., Proc. Phys. Soc., (London) 62A, 167, (1949)
- 49) SKAPSKI, A.S., Acta. Met., 4, 576 (1956).
- 50) SKAPSKI, A.S., J. Chem. Phys., 16, 389 (1948).
- 51) IOFFE, A.F., LEVITSKAYA, M.A., "The mech. of residual deformation", Soobshch., O., Nauchno-Tekhn. Rabotakh v Respublike., 13, 12 (1924).
- 52) FRENKEL ya. I., "Electrical theory of solids", 195 (1924).
- 53) KUZNETSOV, V.D., "Surface energy of solids", Dept. Sci. Ind. R., 32 (1957)
- 54) KUZNETSOV, V.D., KUDRYAVTSOVA, V.M., Zhur. Russ. Fiz. Khim. Obshch., 57
413 (1925)

REFERENCES (contd)

- 55) POLANYI, M., Zeits. F. Phys., 7, 323 (1921).
- 56) GRDINA Yu V., KUZNETSOV, V. D., Zhur. Prikl. Fiz., 6(5), 87 (1929).
- 57) BLAKELY, J. M., MYKURA, H., Acta Met. 10, 565, (1962).
- 58) MILLS, B., LEAK, G. M., Acta. Met., 16, 303 (1968).
- 59) KUZNETSOV, V. D., Zhur. Prikl. Fiz., 6(1), 33, (1929).
- 60) REHBINDER, P., Zeits, F. Phys., 72, 191, (1931).
- 61) SAVITSKU, K. V. et al., Tomdy Sih., Fiziko-Tekhm. Inst., 5(3), 175 (1939).
- 62) BESSONOV, N., "The physics of solids", Vol. 3, 413 (1941).
- 63) GRIFFITH, A. A., Phil. Trans. Roy. Soc. (London) 221, 163 (1921).
- 64) BERDENNIKOV, V. P., Zhur. Fiz. Khim., 5(2-3), 358 (1934).
- 65) LIPSETT, S. G. et al., J. Am. Chem. Soc., 49, 925, 1940 (1927).
- 66) LIPSETT, S. G. et al., J. Am. Chem. Soc., 50, 2701, (1928).
- 67) GIAUQUE, W. F. ARCHIBALD, R. C., J. Am. Chem. Soc., 59, 561, (1937).
- 68) JURA, G., GARLAND, C. W., J. Am. Chem. Soc., 74, 6033, (1952).
- 69) JURA, G., HARKINS, W. D., J. Chem. Phys., 11, 430, (1943).
- 70) HÜTTIG, G. F., KOLLOID-Z., 124, 160 (1951).
- 71) GORSKU, F. K., MIKULICH, A. S., Cryst. Proc. 3, (1966).
- 72) STREL'TSYN, G. S., Znev. V. V. (U.S.S.R) Ohogashch. Rud., 15(6), 52 (1970).
- 73) HARKINS, W. D., LIVINGSTON, H. K., J. Chem. Phys., 10, 342 (1942).
- 74) ADAM, N. K., et al., J. Chem. Soc., 1863, (1925).
- 75) ABLET, R., Phil. Mag., 46, 244, (1923).
- 76) ADAMSON, A. W., "Phys. Chem. of Surfaces", 11 (1960).
- 77) ANTONOV, G. N., Phil. Mag., 1(7), 1258, (1926).
- 78) ANTONOV, G. N., Phil. Mag., 4(7), 792, (1927).
- 79) ADAM, N. K., Phil. Mag., 3(16), 863, (1927),
- 80) MULLIN, J. W., "Crystallisation", (London, Butterworth) (1961).
- 81) BRANSON, S. H., Chem. Proc. Eng., 46, 647, (1965).
- 82) NIELSON, A. E., "Kinetics of precipitation", (London) Pergamon Press (1964).
- 83) HYVLT, J., J. Cryst. Growth, 3/4, 377, (1968).

REFERENCES (contd)

- 84) WALTON,A.G., "Nucleation", Zettlemyer, chap.5, (1969).
- 85) KIRK-OTHMER, Encycl.Chem.Tech., 2nd Ed., Vol.1.
- 86) BORN,M., "Atomic Theory of the Solid State", (1923)

NOMENCLATURE.

a	Interatomic Distance (cm)
A	Area (cm ²)
dA	Change of Area (cm ²)
b	Cooling Rate (deg h ⁻¹)
$\Delta C_{(Max)}$	Maximum allowable supersaturation (kg m ⁻³)
dC	Change of concentration (kg m ⁻³)
d	Diameter of cylinder (cm)
E	Modulus of Elasticity (dynes cm ⁻²)
F _s	Total increase in Free Energy (dynes cm ⁻¹)
g	Acceleration due to Gravity (cm s ⁻²)
h	Height of the Meniscus (cm)
J	Nucleation Rate (kg m ⁻³ h ⁻¹)
k _n	Nucleation Rate Constant (kg ^{1-m} m ^{3m-3} h ⁻¹)
m	Nucleation Order
M _{1,2}	Mol wt. Pe, Water (g mole ⁻¹)
n _D	Refractive Index
n _{D12}	Refractive Index of Pe solution
n _{D1,2}	Refractive Index Pe, Water
ΔP	Hydrostatic Pressure Drop (kg cm ⁻²)
q	Mass of Solid deposited per unit volume Mass of Free Solvent per Degree (kg m ⁻³ deg ⁻¹)
Q _f	Heat of Fusion (cal g ⁻¹ mole ⁻¹)
r	Radius of cylinder (cm)
R _{1,2}	Radius of Curvature (cm)
s*	Degree of Supersaturation
ΔS	Change of Entropy (cal mole ⁻¹ deg ⁻¹)
t	Temperature (°C)
T	Temperature (°K)
u	Energy of Interaction (dynes cm)
ΔU	Change of Internal Energy (dynes cm mole ⁻¹)

NOMENCLATURE (contd)

V_{12}	Molar Volume of Solution ($\text{cm}^3 \text{ mole}^{-1}$)
$\bar{V}_{1,2}$	Partial Molar Volume of Pe, Water ($\text{cm}^3 \text{ mole}^{-1}$)
v	Molecular Volume ($\text{cm}^3 \text{ mole}^{-1}$)
$X_{1,2}$	Mass Fraction of Pe, Water
Z	Strength (dynes cm^{-2})
$Z_{1,2}$	Volume Fraction of Pe, Water
Z_i	Number of next neighbours in the bulk
Z_a	Number of next neighbours on the surface
γ	Surface Tension (stress) (dynes cm^{-1})
ϵ	Factor
σ	Surface Energy (dynes cm^{-1})
σ_M	Molar Surface Energy ($\text{dynes cm} \text{ mole}^{-1}$)
η	Thermal Energy (dynes cm)
Ω	Kinetic Constant ($\text{kg m}^{-3} \text{ h}^{-1}$)
π	Specific Coefficient (dynes cm^{-1})
τ	Time (h)
θ	Angle of Contact (deg)
ρ	Density (g cm^{-3})
ρ_{12}	Solution Density (g cm^{-3})
ρ_s	Density of Solid (g cm^{-3})
ρ_L	Density of Liquid (g cm^{-3})