# MOLECULAR WEIGHT MEASUREMENTS OF MACROMOLECULES WITH AN IMPROVED OSMOMETER

# A Thesis

by

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9.7. Junanni

Chemistry

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A source of error was found in osmometers described in the literature which used treated cellulose sheets which acted both as a membrane and gasket to seal the osmometer. This error was discovered to be caused by diffusion of solvent through the periphery of the cellulose membrane. A new osmometer was developed to permit the use of "composition" foil gaskets to seal the membrane from the thermostating media.

For the first time osmotic measurements were made employing copper ferrocyanide membranes impregnated on sintered glass for use in organic solvents.

Adsorption on Carter and Record type of membranes was confirmed with the improved osmometer.

Viscometric and osmometric measurements on aged polymethyl methacrylate indicated that oxygen is responsible for major changes in molecular weight, but dispersion in a solvent is not necessary. A change in shape of the molecule takes place in the ageing process.

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#### INTRODUCTION

An essential measurement for the exact comprehension of the physical properties of macromolecular substances, as well as for the study of the rules through which their polymerization reactions occur, is the determination of the molecular weight.

A theoretically unquestionable method for the determination of the molecular weight of high polymers, in the ranges between  $10^4$  and  $10^6$ , is the application of osmotic pressure measurements, or measurements of the sedimentation equilibrium (1) using a Svedberg ultracentrifuge. The importance of these methods depends upon the fact that in the case of their evaluation, only the gas constant R is assumed (2). Besides these methods, because of its extreme simplicity, the viscometric determination of the molecular weight has been used extensively, particularly in industry. However, the inherent uncertainty associated with the interpretation of the results limits its value considerably. In the present work viscosity and osmotic measurements have been undertaken.

The investigation carried out here falls into several related parts. The first part was based upon the studies of Morrison (3), Grummitt (4) and Holmes (5) on the ageing of solutions of high polymers. For a more complete understanding of their results, it was decided to study the ageing of high polymers by oxygen in the absence of solvents at a higher temperature. The original study by Morrison et al was made exclusively by viscometric measurements. McIntosh and Morrison (6) attempted to determine the molecular weights on the samples using a modified van Campen type of dynamic osmometer (7). This osmometer does not yield very accurate results, especially in the ranges of low concentration, where a small hydrostatic head of solvent is involved. It was decided to attempt the development of an osmometer of greater accuracy for the low pressure range.

The final portion of the problem arose out of studies by Robertson (7) on the behaviour of caustic and Carter and Record type of cellophane membranes, since the molecular weights found with these two types appeared to differ when measured in the van Campen cell. The planned osmometer was to be used in developing these studies more fully. In constructing the new osmometer, deficiencies were found in the designs used by many workers. The corrections of these deficiencies constituted an appreciable portion of the problem.

## THEORETICAL BACKGROUND

# 1. General

It is generally assumed on the basis of experimental evidence (8) that high polymers consist of large molecules. Each molecule consists of groups of atoms held together by homopolar chemical covalencies (9) in such a way that a line representing covalencies can be drawn from each individual atom to any other atom of the molecule (10). In almost all cases, both naturally occurring and synthetically prepared polymers contain a mixture of polymer homologues differing markedly in molecular weight. They can, however, be separated by careful fractional precipitation. In addition, predominantly straight chained molecules may have a small amount of branching or cross linkage. Therefore the polymer may be described as being heterogeneous with respect to molecular weight and to shape.

There are two groups of filament molecules. The first group forms (or is believed to form) relatively rigid elongated filament molecules in solution such as cellulose and its derivatives. The second group comprises the synthetic polyvinyl compounds which contain more or less coiled filament molecules in solution.

Branched molecules may be regarded as giving rise to a three dimensional net work. These polymers are very poorly soluble and their molecular weight cannot be determined (11). However, deviations from linearity will have a marked influence on viscometric determinations but will not alter the absolute osmotic value which depends on the number of particles present for a known concentration.

Heterogeneity arising from the presence of molecules of varied chain lengths is by far the most important type. Lack of homogeneity in this sense not only complicates the comparison of average molecular weights obtained by various methods, but casts a doubt on existing values where this factor has been neglected.

On account of the tremendous viscosity of even dilute solutions of high polymers, these solutions were originally believed to be colloidal suspensions, each particle of which was an aggregate of several large molecules, along with any attached liquid (12). However, Staudinger (13) demonstrated that in dilute solutions the viscosity imparted to a liquid by dissolved polymer depended essentially on the molecular weight of the polymer and only slightly on the nature of the solvent. The physical proof was difficult to obtain, but the logic of the conclusion was shown more clearly by Kraemer (1, 14). He pointed out that the intrinsic viscosity, defined as

$$\left[ \begin{array}{c} \gamma \\ \end{array} \right] = \left( \begin{array}{c} \frac{\gamma_{sp}}{c} \end{array} \right)_{c = 0} = \left( \begin{array}{c} \frac{\ln \gamma_{r}}{c} \end{array} \right)_{c = 0}$$

**7** sp = the specific viscosity which is a measure of the increase in viscosity due to the suspended solute and defined mathematically as

$$\int \mathbf{r} - \mathbf{1} = \frac{\sqrt{2}}{\sqrt{2}} - \mathbf{1} = \int \mathbf{sb}$$

where ?r = relative viscosity
?s = viscosity of solution
?o = viscosity of pure solvent
c = concentration of solute in grams per 100 c.c.
(?) = intrinsic viscosity

was approximately constant (15) for a given polymer when dissolved in solvents of widely different nature and mixtures of solvents. Kraemer (14) also demonstrated that sec-cellulose acetate could be put through various chemical conversions without appreciably altering the particle size. In addition, Gee (16) and Staudinger and Warth (17) have shown that the molecular weight of a given polymer, determined osmotically in various solvents, is approximately constant. If the liquid is considered as a colloidal suspension, the obvious conclusion arises that different solvents produce colloidal particles of equal average size, containing equal amounts of solvated liquid and bound in some way which resists chemical attack. A much simpler conclusion is that particles of uniform average size are produced by dispersion of the solute to individual molecules. Consequently, a true solution is formed.

According to Mark and Raff (8) this picture becomes too simple in the case of less dilute solutions and secondary valence forces do cause the formation of aggregates. Therefore, investigation of molecular weight phenomena is limited to the region of very low concentrations.

The original conception of chain molecules as straight, stiff rods has likewise given way to a conception of a more

or less randomly kinked molecule. Whether the molecules are rigid is not definitely known. Experimental evidence by Kemp and Pitzer (18), Kistiaskowsky and Nazmi (19) and others has proved the existence of potential energy barriers in the case of paraffins. These may analogously be considered probable for other chain polymers. Rotation about the carbon-carbon bond is therefore limited to a few degrees. Only partial flexibility may be assumed. It appears probable, therefore, that portions of a molecule behave as semi-independent kinetic units, and, in solution, the molecule executes internal Brownian motion. Kauzmann and Eyring (20) decided that viscous flow of molten polymers takes place in segments, and Powell et al (21) attempted to show that polymers also act in segments in producing other phenomena, such as osmotic pressure.

The present problem arose out of observations by various workers on the instability of high polymers during preparation, and purification, and in some cases even on standing. Blaikie and Crozier (22) found that polyvinyl acetate increased in viscosity when purified by steam distillation, whereas heating it in acetic acid produced a drop in viscosity, occasionally followed by a rise. Mead and Fuoss (23) found that the viscosity of solutions of polyvinyl chloride in cyclohexanone slowly decreased on standing, while it increased in methyl amyl ketone. Similar degradations have been noted by Jirginson (24) for solutions of gelatin in water, by Bartell and Cowling (25) for alkali cellulose and by Ott (26) for pure cellulose.

It has been noted in most cases (22, 25, 26) that the presence of oxygen accelerates the rate of degradation. Impurities (22, 23, 25) may affect both the rate and direction of the changes. Rubber solutions exposed to light and oxygen (27) slowly absorbed oxygen. The viscosity of the solution decreased. Tobolsky et al (28) noted a two-fold ageing reaction for rubber samples at high temperatures. The rubber underwent two changes, softening or tackefying, which was considered due to scission of the chains, and hardening or embrittlement, which was related to cross-linking. Both of these reactions were shown to be dependent on the presence of oxygen.

Simha (29), Jellinek (30) and others have given a quantitative treatment of the degradation of long-chain polymers for simple cases. Mark and Simha (31) developed the distribution curve for the simplified case of the degradation of an initially homogeneous polymer. Jellinek (30) obtained better agreement with experiment by assuming a number of weak links distributed over each polymer chain.

Morrison (3), Grummitt (4) and Holmes (5) carried out a detailed investigation of the viscosity changes of polyvinyl acetate, polystyrene and polymethyl methacrylate in various solvents over long periods of time. Morrison, Grummitt and Holmes found that solutions of polyvinyl acetate and polymethyl methacrylate in solvents such as B-B'-dichlorodiethyl ether, acetone and nitrobenzene decreased in viscosity over long periods of time. The presence of oxygen and impurities, especially ferric salts, affected the rate of degradation and in some cases an increase in viscosity occurred. As in the results of Tobolsky et al (28), these effects were interpreted as the result of two opposing processes. The first was a decrease in viscosity due to rupture of the polymer chain by oxygen. The second consisted in the formation of cross links between polymer molecules through atoms of iron. Thus the solvent was immobilized and gels formed. In extreme cases the polymer separated out on the walls of the glass.

Morrison (3) showed that changing the solvent could alter not only the rate, but also the direction of the viscosity change. This effect was not due to solvation because the addition of 1-chloro-1-nitropropane - a highly polar substance was without effect. Naunton (27) has also observed similar dependence on solvent. Morrison (3) felt, however, that the effect of solvent was more apparent than real, since the amount of oxygen reaching the solute depends on the solubility of oxygen in the particular solvent in use.

It was felt that the ageing of polymers in the absence of solvent should be investigated. The ageing of a polymer homologous series of polymethyl methacrylate was undertaken as a portion of the present problem. The changes were followed by viscometric and osmometric measurements.

Methacrylates are prepared from acetone (32). The acetone is first converted to acetone cyanohydrin by the addition of hydrocyanic acid.

$$(CH_3)_2 C = 0 + HCN --> (CH_3)_2 COH$$
  
i  
CN

The acetone cyanohydrin is treated with methyl alcohol and sulfuric acid to form the monomer. After purification it is polymerized by the action of heat, light, air or by oxygenproducing substances which are used as catalysts (33, 34). In the absence of oxygen and light at temperatures up to 100°C, the polymerization of methyl methacrylate practically stops (32) after a small fraction of the monomer has polymerized. The recurring unit in polymethyl methacrylate is

Staudinger and Warth (17) degraded the polymer quantitatively to the monomer at 300°C. They concluded on this basis that polymethyl methacrylate was unbranched.

# 2. Viscosity of dilute polymeric solutions

Much has been written in the past 40 years concerning the classification and characterization of solutions by viscometric measurements. Two methods of approach have been used, namely, the theoretical method based on suspensions, begun by Einstein (35), and the empirical, based on solutions, begun by Staudinger (13, 36). Einstein's calculation of the viscosity was based upon an idealized suspension of rigid spheres at extremely low concentrations. The spheres are

large compared with solvent molecules, and are completely wet by them. The solvent is incompressible and flow rates are so gradual that turbulence is excluded.

For such a suspension Einstein's viscosity law,

 $\eta_c = \eta_o (1 + 2.5 c)$ where  $\eta_c$  is the viscosity at concentration c

 $\eta$  o is the viscosity of pure solvent, and

c is the concentration of the suspension in cc/100 c.c. predicts that the coefficient of viscosity will increase by a fraction corresponding to 2.5 times the volume fraction of the suspended spheres. The subsequent experimental verification of this law has been reviewed thoroughly by Mark (37).

Attempts were made to use Einstein's law for solutions of high polymers. In the course of these investigations Berl (38) and Biltz (39) observed wide variations from Einstein's law for systems containing solutions of starch and cellulose derivatives. Biltz recognized that there is a relationship between the molecular weight and the viscosity in solutions of high polymers. Staudinger (13, 36) formulated this relationship quantitatively in the empirical equation

$$\gamma_{sp} = \frac{\gamma_s - \gamma_o}{\gamma_o} = Km MC$$

M = the weight average molecular weight of the solute.

To explain the disagreement with Einstein's calculations, Staudinger suggested that the molecules could be represented by straight, stiff rods, each of which vibrates in such a way as to occupy, for viscosity purposes, a flat cylinder of height equal to the diameter of the molecule and base equal to  $\Pi \left(\frac{L}{2}\right)^2$ 

where L is the length of the molecule.

Staudinger (17) and Schulz and Husemann (41) showed that in the range between 1,000 and 10,000 the rule gave good agreement with absolute methods for straight paraffins, esters and amines, for cellulose and cellulose derivatives (42). Thus finding that his rule gave good agreement with cryoscopic and osmotic measurements, Staudinger immediately assumed its validity far above this range of molecular size.

As osmotic pressure methods were refined and measurements extended to higher molecular weights and a greater variety of polymers, it soon became evident that many exceptions to Staudinger's rule existed (43, 44). Wide variations were observed for long flexible molecules such as the polyvinyl polymers. For these Staudinger and Werth (17) found the value of Km to decrease as the molecular weight in a given species increased. Staudinger suggested that this was either due to branching of the molecules or to an exceptional chain configuration. Dinglinger (2) showed that the Km for polymethyl methacrylate was independent of the method of preparation

and decreased with increasing molecular weight, but became constant between the degrees of polymerization of 1500 to 6000. Fractionated samples were employed. Nevertheless, in spite of the fact that Staudinger's rule was only a rough approximation, it stimulated further work along similar lines which proved to be very fruitful indeed.

The mathematical treatment of the increase in viscosity due to the presence of non-spherical particles introduces many difficulties. Jefferey (45), by the application of hydrodynamic principles, extended Einstein's theory to the case of ellipsoids. Retaining Einstein's original concepts of dilute solution and gradual flow (35), he showed that as a result of the presence of a velocity gradient, the molecules rotate in the solution, with a preferential orientation in the direction of flow - an orientation which is opposed by Brownian motion. The resultant degree of orientation depends on the relative magnitudes of the two superposed forces.

Using these concepts, Eisenschitz (46, 47) derived an expression for suspensions of long, ellipsoidal particles with large Brownian motion, and, finally, Kuhn (48) and Boeder (49) applied them to two cases of high polymers - the case of a long, straight chain and a highly simplified picture of a branched polymer. The influence on the viscosity of a small section of a chain was separated into two parts, one due to its presence in the liquid, as calculated by Einstein (35) and the other due to its rotational motion as a part of the complete molecule. For the case of a long, stiff, rod-like particle with large Brownian motion and no solvation, Kuhn (48) obtained the following expression:

$$\gamma_{\circ} = \gamma_{\circ} \left(1 + 2.5 \ \mathrm{G} + \frac{\mathrm{G}}{16} \left(\frac{\mathrm{S}}{\mathrm{d}}\right)^{2}\right)$$

where G is the volume of solute per c.c. of solution

S is the length of the particle, and

d is the diameter of the particle.

It can be readily seen that the relation reduces to Einstein's formula provided the particles are spherical as the rotational part is negligible. As the molecule elongates, the rotational part begins to predominate, and Einstein's portion decreases in magnitude. Consequently, the viscosity becomes proportional to  $\left(\frac{S}{d}\right)^2$  and thus to  $M^2$ .

Huggins (50) showed that none of the equations previously developed agreed well with experiment. Kuhn (51) suggested that this was due to an improper picture of the molecule. For a more or less coiled chain he found

$$\left(\frac{\gamma_{\rm sp}}{c}\right)_{\rm c = 0} = \operatorname{Km} M^{\rm v}$$

where o < v < 2

Huggins (50,52,53,54,55) extended Kuhn's treatment to the case of kinked molecules, a concept first suggested by Haller (56). Like Kuhn, Huggins calculated the energy loss due to the presence of solute molecules and obtained, as an approximation, for thread-like molecules and large Brownian motion,  $\frac{\gamma_{sp}}{c} \propto M^2$ 

for randomly kinked molecules

$$\frac{\eta_{sp}}{c} \propto M$$

While for spherical molecules, the expression reduces to Einstein's formula

$$\frac{\gamma_{sp}}{c} = constant$$

The general viscosity law now became

$$\{\gamma\} = \operatorname{Km} M^{v}$$

where v equals 0, 1 or 2 if the chain molecules are coiled into a ball, kinked in a purely random manner, or extended in a rod-like configuration.

Obviously, v may have fractional values corresponding to intermediate cases.

For lower molecular weights (up to 30,000), Hibbert and co-workers (57, 58) and Flory and Stickney (28) obtained better agreement, using

 $\{\gamma\} = KM + I$ 

where I is a secondary constant.

The revised viscosity relation  $(?) = \text{Km M}^{v}$ , in which Staudinger had empirically set the exponent of M as 1, was probably first used in its modified form by Mark (60, 61). It has been repeatedly verified by Houwink (62) from data of Staudinger and Warth (17) on heterogeneous samples, by Flory (63) and Mark et al (64, 65) for fractionated polymers. The hydrodynamic theory, thus developed, was based on the assumption that there was no interaction between solvent and solute particles, and that the monomolecules were so separated that the solvent could flow freely about each one, so that Stoke's law could be applied to compute frictional forces (66, 67). That this was not the case was quickly demonstrated when it was found that a given polymer in different solvents had different specific viscosities (17, 68). Such dependency could only be explained as interaction between solute and solvent. Huggins (54) proposed that this interaction, which was a distinctive property of a given solutesolvent system, might be used to define the nature of the polymer in that solvent. For the ideal case Huggins (54) had derived

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} (1 + \eta_{sp})$$
$$= (\eta)(1 + \eta_{sp})$$

At low concentrations

 $\frac{\eta_{sp}}{c} = (\eta) + (\eta)^2 c$ 

In developing these expressions, Huggins started by using a modified form of Stoke's law for computing the frictional force acting on each submolecule in order to correct for the deviation from the ideal case,

where  $\eta$  is the viscosity of the solution

"a" is the effective diameter of the submolecule

Thus the new viscosity equation according to Huggins led to

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} \quad (1 + k' \eta_{sp})$$
or 
$$\frac{\eta_{sp}}{c} = (\eta) \left[1 + k' \eta_{sp}\right]$$

This equation, in expanded form, is equivalent to the empirical equation of Schulz and Blaschke (34), who proved experimentally that k' was independent of molecular weight for various samples of fractionated and unfractionated polymethyl methacrylate in chloroform. McIntosh et al (69) have found that for solutions of polyvinyl acetate in acetone, the value of k' decreases slightly with decreasing molecular weight.

Not only has Huggins elucidated the initial problem, but also provided in the k' factor a means of investigating the shapes of the molecules. It is to be noted that the introduction of the shape factor does not completely account for the effect of solvent, because Huggin's equation (54) predicts that  $(\mathcal{N})$  shall be independent of solvent type. This prediction has been disproved by Mark et al (70), Flory (63) and others. Both Huggins (55) and Flory (71) agree that solvation of the chains causes steric hindrance which would make it impossible for a more coiled configuration. Consequently, the average length of the molecule increases, simultaneously the value of the exponent " $\vee$ " and the intrinsic viscosity [ $\gamma$ ].

According to Mark (70) for any given polymer solvents may be roughly classified as "good" solvents and "bad" solvents. Good solvents are characterized by an exothermic solution process which tends to solvate and thus elongate the molecule; whereas "bad" solvents are characterized by an endothermic solution process, where the molecules tend to squeeze out the solvent as a result of intromolecular attractions, and now favour an unusually coiled configuration. Simha (72) suggests that no special significance is to be assigned to the case (v = 1) (expression reduces to Staudinger's equation) because the exponent "v" is not merely a function of the normal shape of the molecule.

Results from viscosity measurements on the polymer-liquid interaction have led different investigators to conflicting conclusions (73). In attempts to correlate  $\frac{\gamma_{sp}}{c}$  versus c, Frith (74) has shown in the case of polyvinyl chloride solutions that the steeper slope corresponds to the better solvent, whereas Spurlin (75) has shown the opposite to hold in the case of solutions of cellulose derivatives. The lack of generality of any conclusions is emphasized by Huggins' statement that the molecular weight determined from viscosity measurements should be strictly defined as the Viscosity Molecular weight "for a certain polymer in a certain solvent at a certain temperature".

## 3. Osmotic Pressure of high polymers

As mentioned earlier, there are two absolute methods of determining the molecular weight of long chain polymers dispersed in dilute solution, namely, the sedimentation equilibrium method using a Svedberg ultracentrifuge, and by direct measurement of the osmotic pressure. The advantages of the ultracentrifuge have been stressed by Svedberg (77) and Kraemer (14), but owing to the large initial expense it has not been adopted into general use. The measurement of osmotic pressures has the advantage of requiring relatively simple equipment. Other methods of measuring the colligative properties of solutions of small molecules are inapplicable for molecular weights above 5000. The osmotic method in this range is also difficult owing to incomplete semi-permeability of the membranes.

Although the phenomenon of osmosis had been known for a long time previously, in 1886, van't Hoff showed the analogy between gases and solutions. For the first time thermodynamic methods were applied to the colligative properties of solutions. Experimental confirmation of this generalization was carried out by Morse and Frazer (78), Lord Berkley and Hartley (79) and many others. Experimentalists have proven ven't Hoff's limiting law without a doubt, but at present ven't Hoff's original concept of osmotic pressure arising from "the impact of the dissolved molecules on the semi-permeable membrane" is false on the basis of thermodynamic reasoning.

Thermodynamic states that when two phases (80) are separated by a membrane perfectly permeable to one component and quite impermeable to all others, the condition for equilibrium is that the partial molal free energy of the component which can pass through the membrane should be the same in both phases. There is no condition for the molecules which cannot pass the membrane. The nature of the membrane such as its thickness, chemical composition, physical state, have no effect at equilibrium (81).

The component which is common to both phases is the solvent, component 1; the other component is the solute.

If the system is under the same pressure at constant temperature, and the solvent is separated from a solution by a semi-permeable membrane, the chemical potential  $\mathcal{M}_i''$  of the solvent in the solution will be less than  $\mathcal{M}_i''$ , the chemical potential of the pure solvent, if both phases are under the same pressure p'. If the system is to be in equilibrium, the chemical potential of the solvent in the solution must be increased by a suitable change in the pressure on the solution (82). This can be effected by solvent flowing into the solution, thus increasing the pressure from p' to the greater pressure p''. Therefore at steady state

 $(\mu_{i}')_{p'} = (\mu_{i}'')_{p''} = (\mu_{i}'')_{p'} + \int_{p'}^{p''} \overline{v}_{1} dP$ 

Hence

or 
$$\int_{p'}^{p''} \overline{v}_{1} dP = \left( (\mathcal{M}_{1'})_{p'} - (\mathcal{M}_{1''})_{p'} \right)$$
$$\int_{p'}^{p''} \overline{v}_{1} dP = - \left( (\mathcal{M}_{1'})_{p'} - (\mathcal{M}_{1'})_{p'} \right) = - \Delta \overline{F}_{1}$$

where  $\overline{F}_1$  is the partial molal free energy

$$\overline{V}_1$$
 (P'' - P') =  $-\Delta \overline{F}_1$ 

The difference (P'' - P') is called the osmotic pressure  $\overline{''}$  of the solution when the latter is under pressure P''.

For dilute solutions in which the osmotic pressure is small,  $\overline{V}_1$  may be regarded as constant and equal to  $V_1$ , the molal volume of pure solvent.

Hence

 $v_1 \pi = -\rho \overline{F}_1 = -RT \ln a_1$ or  $-v_1 \pi = \rho \overline{F}_1 = RT \ln a_1$ 

where  $a_1$  is the activity of the solvent in the solution. In very dilute solutions where Raoult's law is applicable,  $x_1$  the mole fraction may replace  $a_1$ , the activity of the solvent in the solution. Since  $x_1 = 1 - x_2$  and  $\ln (1-x_2) = -x_2$ the above equilibrium conditions may be written as  $\pi V_1 = RTx_2$ . This equation in the limiting case is equivalent to van't Hoff's law.

For the determination of molecular weights, this equation may be restated as

$$M_2 = \frac{W_2 RT}{T V}$$

where w<sub>2</sub> is the number of grams of solute in volume V

M<sub>2</sub> is the molecular weight of solute

R is the gas constant in appropriate units

and T is the absolute temperature

The application of this equation to the determination of molecular weights of high polymers is much less simple and necessitates certain restrictions and modifications.

Since M<sub>2</sub> is very large,  $\Pi$  will be very small, the resulting experimental necessity arises that measurements be carried out on only moderately dilute solutions, in order that the resulting osmotic pressure may be determined with a high degree of accuracy.

Very large deviations from ideality occur even in moderately dilute solutions and as a result the limiting law will no longer apply. This concentration effect, analogous to that in connection with viscosity due to the strong interaction between solvent and solute molecules, suggested the expansion of the osmotic pressure as a series in powers of C<sub>2</sub> (concentration). Thus the expression for osmotic pressure becomes

 $TT = AC_2 + BC_2^2 + CC_2^3 + \dots$ 

At very low concentration ranges all terms in  $C_2^3$  and higher are negligible and the equation reduces to

$$TT = AC_2 + BC_2^2$$

In dilute solutions, therefore, the plot  $\frac{\overline{\Pi}}{C_2}$  versus  $C_2$  should be a straight line. This fact has been empirically verified by Mark (83), Meyer et al (84) and many others. However, Flory (63) and Mark (64) and Schulz (2) have obtained curved lines at concentrations as low as 3 gm. per litre. As will be discussed shortly, a linear relationship between  $\frac{\Pi}{C_2}$  vs.  $C_2$ has been deduced on theoretical grounds by Huggins and Flory.

From the classical kinetic point of view, A, the first coefficient of the power expansion, is directly connected with the number of particles which move independently in the solution. As Mark notes (37), A represents the pure gain in entropy for ideal mixing. Subsequent coefficients will represent the entropy anomalies and energy terms due to intermolecular and intramolecular interaction as a result of chemical attraction and the unusual shape and size of the chain-like solute.

The equation can therefore be rearranged in the form

$$\frac{\Pi}{C_2} = \frac{RT}{M_2} + BC_2$$

In dilute solutions it is still possible to evaluate M<sub>2</sub> by extrapolating the  $\frac{TT}{C_2}$  versus C<sub>2</sub> curve to infinite dilution (85), therefore,

$$\lim_{C_2 \to 0} \frac{\pi}{C_2} = \frac{RT}{M_2}$$
  
or 
$$M_2 = \frac{RT}{\left(\frac{\pi}{C_2}\right)}_{C_2=0}$$

In order to explain deviations from van't Hoff's law, early attempts were made by Schulz (86), Stamberger (87) and others. By analogy with van der Waal's theory of real gases, they introduced a co-volume, b, caused by solvation and wrote

$$\Pi = \frac{\mathrm{RT}}{\mathrm{M}_2} \left( \frac{1}{\mathrm{V-b}} \right) = \mathrm{RT} \left( \frac{\mathrm{C}_2}{\mathrm{M}_2} + \mathrm{bC}_2^2 \right)$$

Ostwold (13), on the other hand, ascribes the deviation to a swelling pressure, thus writes

$$TT = \frac{C_2 RT}{M_2} + KC_2^n.$$

As mentioned earlier, Powell, Clark and Eyring (21) in order to explain exceptionally large osmotic pressures, assumed that a long-chain molecule acts in segments. This theory has been severely criticized on various bases. Flory (71) and Huggins (88) do not believe the statement that a polymer molecule becomes stiffer as the solution is diluted. Huckel (89) questions their assumption of the primary validity of the ideal solution laws when applied to mixtures of molecules differing greatly in size.

In the past several years a statistical-thermodynamic attack on the problem has been more advantageous. It consists generally in an extension of the method developed by Guggenheim (90, 91) and applied to perfect and nearly perfect solutions. Essentially the total possible number of configurations is determined for a mixture of NA molecules of type A and NB molecules of type B. This is related to the thermodynamic functions of the mixture, from which Guggenheim obtains the expression

$$\mathcal{\Pi} = \frac{kT}{VA^{\perp}} \log \frac{NA + NB}{NA}$$

where  $V_A^{\perp}$  is the volume of liquid A under very low pressure.

Guggenheim (91) attempted to extend these concepts to slightly imperfect solutions, which he defined as "Regular Solutions". It was difficult, however, to evaluate some of the new terms introduced.

It was Fowler and Rushbrooke (92) who tried a rigorous attempt to extend the theory to the case of markedly dissimilar molecules. They treated the case where one molecule was a dumbbell exactly twice the size of the other. Retaining the essential Guggenheim concepts, they calculated the number of configurations by considering the liquid as a crystal upon the lattice points of which the large molecules are arranged. Obviously, a given molecule must occupy adjacent lattice points. Subsequently, the blank spaces are then filled with small molecules whose addition does not affect the number of configurations. If the number of configurations are known, the thermodynamic functions of the mixture can be calculated.

It is to be noted, however, that the behaviour of a mixture depends on two factors, the decrease in free energy and the increase in entropy. As a result of intermolecular forces, the former represents a tendency toward a minimum potential energy, whereas the latter represents a striving toward the most probable state as a result of the kinetic notions of the particles (93).

Fowler and Rushbrooke's work demonstrated that unusually large entropies of mixing, resulting from the difference in size of the molecules, may be sufficiently great to cause

deviations from ideality, apart from intermolecular forces. For polymers of very high molecular weight, the entropy of mixing becomes the predominating factor.

The extension to really long-chain molecules was first discussed qualitatively by Meyer (94) and Haller (56), using a quasi-solid lattice, each point of which may be occupied either by a solvent molecule or a polymer segment. Assuming flexibility at each chain linkage, there will be many alternative positions for each succeeding segment. Owing to the great number of possible configurations, an unusually large entropy arises, on the basis of the well-known Boltzmann equation

## $S = k \ln W$

where S is the entropy

W is the number of possible configurations and k is Boltzmann's constant

Simultaneously Flory (71,95) and Huggins (88,96,97) gave a quantitative elucidation of the problem using the quasisolid lattice of Meyer (94) and Haller (56) and obtained equivalent results. Although a heat of mixing term was introduced, based on the work of van Laar (98), Hildebrand (99) and Scatchard (100), it was assumed small enough not to interfere appreciably with entropy changes.

In this fashion Huggins (101) obtains

$$\ln a_{1} = \ln \overline{\nabla}_{1} + (1 - \frac{\overline{\nabla}_{1}}{\overline{\nabla}_{2}}) \overline{\nabla}_{2} + \underline{\mathcal{M}}_{1} \overline{\nabla}_{2}^{2}$$
  
and 
$$\ln a_{2} = \ln \overline{\nabla}_{2} + (1 - \frac{\overline{\nabla}_{2}}{\overline{\nabla}_{1}}) \overline{\nabla}_{1} + \frac{\overline{\nabla}_{2}}{\overline{\nabla}_{1}} \underline{\mathcal{M}}_{1} \overline{\nabla}_{1}^{2}$$

where al and ag are the activities of solvent and solute respectively,

 $\bigvee_1$  and  $\bigvee_2$  and the volume fractions of solvent and solute respectively,

 $\overline{V}_1$  and  $\overline{V}_2$  are the partial molal volumes, and for the present purposes assumed equal to the actual molal volumes, and  $\mathcal{M}_1$  is a term which includes

- Ŧ
  - (a) the heat of mixing
  - (b) the difference in entropy of mixing between that for infinite co-ordination number and for a small effective co-ordination number
  - (c) deviations from complete random distribution on account of association, solvation, etc.

Consequently,  $\mathcal{M}_1$ , like k', is dependent upon the polymer solvent type, but not greatly on molecular weight. Similarly to k',  $\mathcal{M}_1$  can be used to investigate changes in molecular shape. Qualitatively  $\mathcal{M}_1$  "is a measure of the preference of each molecule (or submolecule) to have like molecules (or submolecules) rather than units of the other kind for immediate neighbors". Its value will be specific for a given system. Its quantitative interpretation is, however, complicated and possibly prevented by the fact that  $\mathcal{M}_1$  combines the heat of mixing with unpredicted entropy effects. This is reflected in recent papers by Mark et al (64,65) where  $\mathcal{M}_1$  is evaluated, but it has not been given quantitative interpretation.

From the preceding equations

$$\frac{\ln a_1 - \ln \sqrt{1}}{\sqrt{2}} - 1 = -\frac{\sqrt{2}}{\sqrt{2}} + \frac{\sqrt{1}}{\sqrt{2}}$$
  
where  $\ln a_1 \approx -\frac{\pi \sqrt{2}}{RT}$ 

Hence,  $M_1$  can be evaluated as the slope of a plot

$$\frac{\ln a_1 - \ln \sqrt{1}}{\sqrt{2}} - 1 \quad vs \quad \sqrt{2}$$

By expanding  $\ln \nabla_1$  as

$$\ln \sqrt{1} = \ln (1 - \sqrt{2})$$
  
=  $-\sqrt{2} - \frac{\sqrt{2}}{2} - \frac{\sqrt{2}}{3} - \cdots -$ 

Huggins (102) writes

$$\frac{\pi}{\sqrt{2}} - \frac{RT}{3V_1} = \frac{RT}{V_2} + \frac{RT}{V_1} \left(\frac{1}{2} - \frac{1}{1}\right) \sqrt{2}$$

If the concentration is expressed in grams of solute per 100 c.c. of solution, the expression became, according to Huggins,

$$\frac{\pi}{C_2} - \frac{\mathrm{RTd}_1 \mathrm{C_2}^2}{\mathrm{3M}_1 \mathrm{d}_2^3} - \cdots = \frac{\mathrm{RT}}{\mathrm{M}_2} + \frac{\mathrm{RTd}_1}{\mathrm{M}_1 \mathrm{d}_2^2} \left(\frac{1}{2} - \mathcal{M}_1\right)^{C_2}$$

where  $d_1$  and  $d_2$  are the densities of solvent and solute respectively.

 $M_1$  and  $M_2$  are the molecular weights of the solvent and solute respectively.

It is to be noted, however, that the negative term on the left is negligible for many osmotic pressure studies, but its omission or inclusion should be tested empirically. Weissberger (103) and Huggins (76) have shown that errors are introduced in the molecular weight when this term is neglected.

Nith reference to 
$$\frac{TT}{C_2} = A + BC_2$$

Huggin's expression

$$\left[\frac{\pi}{c_2} - \frac{RTd_1c_2^2}{3M_1d_2^3}\right] = \frac{\pi}{c_2}$$

$$A = \frac{RT}{M_2}$$

$$B = \frac{RTd_1}{M_1d_2^2} \left(\frac{1}{2} - \frac{\mu}{1}\right)$$

should yield a straight line for a plot of  $\frac{77}{C_2}$  versus  $C_2$ . M<sub>2</sub> can be determined and the slope should be independent of molecular weight for a given polymer-solvent system. The constancy of slope has been demonstrated approximately by Robertson, Grummitt and McIntosh (69) and by Wise (104) for the system polyvinyl acetate in acetone. Exceptions have been noted by Mark (65). Schulz (2), however, obtained curved lines concave downward for fractionated polymethyl methacrylate in acetone of low molecular weights, and concave upwards for high molecular weights (about 600,000).

The straightness of the  $\frac{7}{C_2}$  versus  $\mathbf{6}_2$  line is still debatable. McIntosh et al (69) and Gee (105) obtain straight lines as predicted, while others (63,64,106,107) report both straight and curved lines. Gee and Treloar (108) report curved lines for the system rubber-benzene. In support of Huggin's work, Bartovics and Mark (65) and Dobry (109) have shown that for a given polymer sample the solvent, and even the chemical characteristics of the polymer, may be altered sufficiently to affect the values of k',  $[\gamma]$  and  $\mu_1$  without altering appreciably the  $\frac{\pi}{c_2}$  intercept or the molecular weight determined from it.

Flory (110), however, has demonstrated that the equations for the partial entropy and partial heat of mixing do not agree well with experiment. He ascribes this to the fact that the randomness of distribution is less than calculated by Huggins. Each molecule occupies a "cluster" of lattice points, and the intervening spaces contain only solvent molecules. The deviation of a dilute polymer solution from ideality is then found to be a function of the

On this assumption, Flory predicted that  $\mathcal{M}_1$  should decrease slightly with increasing molecular weight, in the case of high polymeric solutions at low concentrations.

# 4. Average Molecular Weights

In the process of polymerization a mixture of chain lengths is obtained. The polymers thus obtained are heterogeneous in respect to molecular weight. The chain lengths are distributed over a wide range, and will approximate symmetrical distribution about a single maximum analogous to the Gaussian error curve. The conventional methods of determining molecular

weights will yield average values. The thermodynamic relations deduced for homogeneous samples are not affected by the heterogeneity (110). It is necessary, however, to distinguish at least two different average molecular weights. Cryoscopic, chemical methods and osmotic methods, etc., which "count" the number of molecules present in a given concentration, will yield for a heterogeneous material a number average molecular weight. This is defined by Kraemer and Lansing (2) as

$$Mn = \frac{\sum_{i=0}^{i=\infty} niMi}{\sum_{i=0}^{i=\infty} ni} = \frac{\sum_{i=0}^{i=\infty} niMi}{N}$$

where Mi is the molecular weight of the i<sup>th</sup> species; ni is the number of molecules of molecular weight Mi and N is the total number of molecules present.

For any given concentration of a heterogeneous material, however, it is evident that a small amount of low molecular weight molecules will have a much greater effect on the osmotic pressure than an equal amount of high molecular weight substance. On the other hand, the intrinsic viscosity for a heterogeneous mixture, depends on the molecular weight of each species. Consequently a high molecular weight material has a disproportionate influence on the viscosity. The intrinsic viscosity for such systems is given by

where  $[\gamma_i]$  is the intrinsic viscosity of the species of molecular weight Mi

and wi is the weight of the ith species.
As has been pointed out by Mark (112), Lansing and Kraemer (1), if the Staudinger Rule is applicable

$$\left[ \mathcal{N} \right]_{1} = KsT Mi$$
 iii

where Mi = molecular weight of the i<sup>th</sup> species

KsT = Staudinger's constant.

Recently, however, the Staudinger Rule has been replaced by the relationship

$$\left[ \mathcal{N} \right] \mathbf{i} = \mathbf{K} \mathbf{M} \mathbf{i}^{\mathbf{V}} \qquad \mathbf{i} \mathbf{v}$$

where K and v are viscosity constants described in a previous section.

. substituting equation iv in ii

$$\left( \gamma \right) = \Sigma \frac{K \operatorname{Mi}^{v} \operatorname{Wi}}{\Sigma \operatorname{Wi}} \qquad v(a)$$

$$= \frac{K \sum Mi^{l+v} ni}{\sum ni Mi}$$
 v(c)

The "Viscosity Average Molecular Weight" is defined as

$$[\gamma] = KM_v^v$$
 vi

Substituting the value of  $\gamma$  in equation vi to equation v(c)

$$KM_{v}^{v} = \frac{K \sum Mi^{1+v} ni}{\sum ni Mi}$$

$$M_{v} = \sqrt{\frac{\sum Mi^{(1+v)} ni}{\sum ni mi}}$$
vii

Thus it can be seen that Number Average and Viscosity Average Molecular Weights are entirely different. The two averages become identical, however, in the case of homogeneous samples. It is for this reason that the number average molecular weight must not be used directly to determine the viscosity constants unless the distribution is known.

To evaluate the two averages a distribution function relating the number of molecules of given molecular weight to the molecular weight must be assumed. In so doing, the summations are replaced by integrations, but since the increments of molecular weight are small compared with the molecular weight, the error introduced is probably very small. It is desirable to choose a distribution function which has a single maximum and represents substantially zero numbers of molecules of very low molecular weight and of very high molecular weight. Theoretically there are probably several functions which could be used, but the one adopted here is the logarithmic distribution which has been used by Lansing and Kraemer (2) in the form

$$\frac{dN}{N} = \frac{1}{\sqrt{\pi}} \mathcal{L}^{-y^2} dy$$
where  $y = \frac{1}{B} \ln \frac{M}{Mo}$   
 $dN$  = number of molecules between y and y + dy  
 $N$  = total number of molecules .

Mo and B may be considered parameters of the distribution function. Mo is the molecular weight at the maximum value of  $\frac{dN}{dM}$  and B is defined as the non-uniformity coefficient.

This is illustrated in the curve of the form:



For homogeneous materials  $\beta$  is zero, and for heterogeneous samples it has a positive value.

Since the curve is a continuous function

$$Mn = 2 \int_{0}^{\infty} \frac{MdN}{\int_{0}^{\infty} dN} = \frac{2N}{\sqrt{\pi}} \frac{\int_{0}^{\infty} Me^{-y^{2}} dy}{N}$$

But

 $M = Moe^{\beta y}$ 

Mn

Hence

$$= \frac{2}{\sqrt{\pi \tau}} \int_{0}^{\infty} Mo e^{\beta y - y^2} dy$$

completing the square, and since

$$2 \int_{0}^{\infty} e^{-(y-\beta/2)^2} dy = \frac{\sqrt{77}}{2}$$

This method has been applied by McIntosh and Morrison (6) to the relation for the average intrinsic viscosity and they obtained

$$\left[\gamma\right] = KM_{o}^{V} e^{\beta^{2}\left(\left(\frac{j+\nu}{2}\right)^{2}-\frac{j}{4}\right)}$$

Combining this with the expression for the number average molecular weight,

$$[7] = Mn^{\vee} K e^{\frac{B^{2}}{4}(1+\nu)\nu}$$
 was ob:

was obtained.

or

 $\ln \left[ \gamma \right] = \sqrt{\ln Mn} + \ln K + \frac{B^2}{4} (1+\nu)\nu$ 

It is evident from this expression that a plot of  $\ln Mn$  versus  $\ln [\gamma]$  should give a straight line of slope "V", provided that the samples have the same degree of heterogeneity or have been rendered homogeneous by careful fractional precipitation. The intercept,  $\ln K'$ , will depend on  $\beta^2$ , and therefore heterogeneous samples cannot be employed to determine K. However, with "V" known and an arbitrary chosen value of K,  $\beta^2$  may be evaluated.

#### Experimental

#### 1. Materials

Two different polyvinyl derivatives were used in this investigation, polyvinyl acetate (Gelva) and polymethyl methacrylate. The polyvinyl acetate (Gelva 45) used in this investigation was a commercial product, supplied by Shawinigan Chemicals Limited. The polymer was graded on the basis of the viscosity at 20°C of a benzene solution of one monomolecular weight (86 grams) of polyvinyl acetate per litre. Thus, a solution of Gelva V 45 has a viscosity of 45 centipoises. This terminology was retained as a convenient method of naming the polymers examined.

The polymethyl methacrylate polymers used in this investigation were commercial samples. They were supplied by E. I. du Pont de Nemours and Co. and were identified by the code numbers

NDR	474
NDR	471
NDR	359

The polymers were in the form of very fine snow-white powder of about -200 mesh. All of these commercial samples contained small amounts (usually less than 1%) of insoluble polymer and other foreign material. Two procedures were adopted, one for polyvinyl acetate and another for polymethyl methacrylate, in order to remove the above impurities.

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Procedure for Polyvinyl Acetate (Gelva V 45)

A sample large enough for all tests was dissolved in acetone and filtered under suction through two thicknesses of Kleenex paper and a No. 1 Whatman filter paper supported on a six-inch Büchner funnel. The clear filtrate was made up to 5-6% concentration with acetone and precipitated by pouring slowly into distilled water with stirring. The sticky polymer collected on the stirring rod and was removed periodically instead of being permitted to accumulate into a large mass. The bulk water was permitted to drain off, and the wet polymer was then placed in a vacuum desiccator over anhydrous calcium chloride under a vacuum of 5 mm. overnight. The partially dry. porous mass was sliced manually with a sharp razor blade into small pieces for further drying. Scrupulously clean blades and forceps were used in handling the polymer. The drying of the polymer was completed under vacuum at room temperature (25°C) in two or three days. Heating of the polymer was avoided.

#### Procedure for Polymethyl Methacrylate

In order to remove impurities such as insoluble polymer, foreign substances, benzene solutions were filtered in the same fashion described in the case of Gelva. Due to difficulties in filtering, however, less concentrated solutions were used. It was extremely difficult to filter NDR 359 above 1% concentration; NDR 471 and NDR 474 above 2% concentration. After filtration, the clear liquid was precipitated by means of petroleum ether B. P. 30 - 60°C. The petroleum ether

was stirred and the somewhat sticky polymer gathered around the stirrer from which it was removed at regular intervals. The precipitated polymer was placed in fresh petroleum ether and after several such rinses, the polymer was free from benzene. This required about 16 hours. The product, after the solvent exchange with petroleum ether, was dried under vacuum at room temperature (25°C) to constant weight. This required about 24 hours. A very brittle, snow-white, porous material was obtained. Enough polymer was precipitated to last for the entire investigation. The samples were stored over CaCl<sub>2</sub> when not in use and evacuated again for several hours when solutions were to be made up from them.

#### Solvents

#### Chloroform

The chloroform used in all phases of this work was Merck's Reagent grade. The chloroform was dried over calcium chloride for 24 hours, distilled over fresh calcium chloride and stored over "Drierite" until used.

#### Benzene

The benzene used in this work was Mallinckrodt's Reagent grade (thiophene free). The benzene was dried over calcium chloride and stored over clear sodium wire.

#### Acetone

The acetone used was Merck's Reagent grade. It was treated in the same manner as chloroform.

#### Ethanol

The ethenol used in the preparation of membranes was

Standard Chemical Co. 95% ethanol.

#### Petroleum Ether

Mallinckrodt's Reagent grade B.P. 30-60°C petroleum ether was used to flocculate polymethyl methacrylate polymer.

#### 2. Solutions

The accurate knowledge of concentrations of polymer in acetone, benzene and chloroform solutions was important. In both osmotic and viscometric determinations, values at zero concentrations were required, and these were obtained by extrapolating the concentration function of the observed phenomena from the range of finite concentration to an ideal value at infinite dilution (C=O). The accuracy of such extrapolation depended to a large degree on a precise knowledge of the concentration.

Two general methods for determining concentrations of such solutions have been reported. The more satisfactory method and the one adopted in this investigation, was to dissolve a known weight of polymer in the solvent and make up to any desired concentration by weight. In the relatively dilute solutions used it is permissible to assume no change in density from that of pure solvent when expressing such concentrations in terms of grams per 100 c.c. of solution. The second method depends upon the evaporation of the solvent from a weighed sample of solution taken from the apparatus immediately after a measurement has been made. Such a method, if accurate, would have two important advantages for osmotic investigations. It would overcome the uncertainty concerning the real concentration in the cell after indeterminate amounts of adsorption have taken place on the membrane and at the walls. Besides, such a method would eliminate the wasteful procedures involving numerous washes - an important consideration where molecular weight determination must be made on a limited sample.

The direct method of determining the amount of polymer in a weighed sample of solution by evaporation was found unsatisfactory for the system polyvinyl acetate - acetone by Robertson (7) and Wise (104).

A similar method was attempted to determine the concentration of polymer in a solution in this work, since the polymer and solvents differed from those employed by Robertson and Wise. The solutions were evaporated directly, in addition, by the aid of a flocculating agent. The results obtained are shown in TABLE I. This method of determining concentrations was abandoned owing to the erratic results obtained.

Two tests for semi-permeability of membranes used in osmotic pressure determinations were employed. In the first the contents of the solvent half-cell were pipetted into a tared weighing bottle and the thimble and contents quickly weighed. The sample was then evaporated to dryness and the container again weighed. Blank determinations permitted correction for any corrosion of the brass osmotic cell.

The second test was found to be somewhat more sensitive and, to be sure, more convenient. In this case the contents of the solvent half-cell (about 10 c.c.) were run into a small

rorymennyr Mounderyrate - Denzene.					
Calculated Residue	I Temperature (°C)	Time in Hours (% Error)	Flocculating		
		24 48 72	Agents		
0.0482 0.0978 0.1495 0.0935	100 100 100 100	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$			
0.0338 0.0286 0.1096 0.0915 0.0302 0.1354 0.0180 0.0233 0.0490 0.0521	90 90 60 60 60 90 90 90 90	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Water Pet. Ether * Pet. Ether * Water Pet. Ether * Pet. Ether * Cyclohexane "		

Showing Errors in Evaporation Methods for the System Polymethyl Methacrylate - Benzene.

TABLE I

Glass weighing bottles were used in all cases.

\* These samples were flogculated in petroleum ether B.P. 30-60, and the clear supernatant liquid was carefully pipetted out. The precipitate was carefully rinsed several times with petroleum ether. The per cent error was based on the calculated residue.

beaker containing about 25 c.c. of water. The appearance of turbidity indicated that polymer was present. Tests with this procedure, in the case of Gelva V 45, showed that a solution of 0.11% concentration could be detected with certainty on a Fisher A.C. Model Electrophotometer. In the case of the system polymethyl methacrylate - chloroform or benzene the contents of the solvent half-cell (about 10 c.c.) were poured into 25 c.c. of petroleum ether. Tests carried on known concentrations showed that a solution of 0.0018% could be tested with certainty visually.

#### 3. Ageing of Polymethyl Methacrylate

As previously mentioned Morrison (3), Grummitt (4) and Holmes (5) aged the majority of their polymer solutions in various solvents at 60°C. It was expected, however, that the changes in the solid state would proceed more slowly. Therefore, in order to magnify these changes the polymethyl methacrylate samples were aged at 100°C.

An air bath was constructed for this purpose large enough to hold a large number of glass bombs. The bath consisted of an insulated metal container, 15 inches in diameter and 18 inches deep. The outside portion of the vat was wound with two parallel layers of nichrome wire heating element, insulated from one another, and regulated by a De Khotinsky bi-metallic thermoregulator. This bath could be maintained at  $100^{\circ}$  1°C without difficulty.

#### Bombs

The polymers were aged in this work both in the presence and absence of oxygen. For this purpose, bombs of the sort shown in Fig. IA were constructed. These consisted of 500 - ml. Erlenmeyer flasks to which two tubes were attached as shown. The larger tube (C) served the purpose for filling and then sealed off. The male part of a 10/30 ground glass joint was attached to the other. Thereby, connection could be made to the vacuum system.

A second type of bomb (Fig. IB) was used to investigate pressure changes above the polymer to detect the possible evolution or absorption of gases. This was constructed with two 250 - ml. Erlenmeyer flasks, connected first through a small mercury manometer and secondly, by means of a common tube, to the vacuum system. One flask was partially filled with polymer, the other was left empty. After evacuation and filling to a pressure of  $\frac{1}{2}$  atmosphere of oxygen, the two upper tubes were sealed off simultaneously at "D", leaving the only connection through the manometer. By so doing, the heat required to seal off the upper tubes did not cause a large differential to be set up in the mercury manometer.

#### Method of Evacuation and Filling

The system used in this investigation for evacuating and filling the bombs is shown in Fig. 2. The bomb was connected to the system by means of the ground glass joint C. In order to fill the bomb with oxygen, stop cocks A and H were opened



Figs. 1A and 1B

Bombs in which Polymer was Aged

(Following page 46)



## Fig. 2

System for Filling and Evacuating

Glass Bombs

(Following page 46)

and the system  $ev_acuated$  by means of a mercury diffusion pump backed by a Hyvac pump to a pressure of about  $10^{-4}$  MM. as read on the McLeod Gauge. The liquid air trap, D, was flushed by means of a stream of oxygen entering at stopcock E and escaping through stopcock B to the open air. By reversing stopcock B, oxygen was admitted into the system to a pressure of about  $\frac{1}{2}$  atmosphere as read on mercury manometer F. Stopcock H was then closed and the polymer left in contact with the oxygen for at least two hours, in order to flush the polymer thoroughly. Stopcock H was then opened, the system again  $ev_acuated$  to the previous pressure and the bomb refilled with oxygen in the same fashion to a pressure of  $\frac{1}{2}$  atmosphere. The bomb was then sealed at the constriction.

During the preliminary trials, bombs to be aged in vacuum were merely pumped down to  $4 \times 10^{-4}$  mm. of Hg. and sealed off. Meanwhile, Tobolsky et al (28) showed that very small amounts of oxygen were sufficient to cause definite deterioration of rubber. Consequently, later samples, the ones reported in this work, were flushed with carbon dioxide. This was achieved by condensing gaseous carbon dioxide in the trap D with stopcock B closed and E connected to vacuum. The condensed carbon dioxide was purified by being allowed partially to vaporize and the gases being pumped off. The purified fraction was then admitted through stopcock B to the evacuated system, to a pressure of 3/4 atmosphere and permitted to remain in contact with the polymer for at least two hours. Finally the

bomb was evacuated to a pressure of  $10^{-4}$  mm. and sealed off at the constriction. The amount of polymer aged in each bomb was about 12 grams.

Physical appearance of polymer after ageing

The polymer samples as viewed visually did not fuse together. There was also no change in color. They remained snow-white during the entire ageing process ranging from two weeks to six and one-half months.

#### 4. Viscosity Measurements

#### Apparatus

Viscosities were measured in a modified Ostwald type of viscometer, having an outflow time of 136 seconds for 2.5 c.c. of benzene and about 72 seconds for chloroform. The capillary was 10 cm. long and had a radius of 0.038 cm. Other dimensions are included in pamphlet No. 188 of the British Engineering Standards.

The viscometer was mounted on a brass frame which fitted snugly into grooves in a second frame clamped to hold the viscometer vertically in the water bath. A standard mercury thermoregulator relay system controlled the temperature at  $20 \pm 0.02^{\circ}$ C. Accurate temperature control is of particular importance in specific viscosity measurements since a variation of as little as  $0.01^{\circ}$ C will cause a calculated (105) variation of 1% in a specific viscosity determination of 0.05.

#### Procedure and calculation of viscosities

To determine the intrinsic viscosity of a polymer, a series of 4 to 6 solutions varying from 0.1 to 0.35% was made up by weight in 125 c.c. glass stoppered Erlenmeyer flasks. About 50 c.c. of solution was made for concentrations above 0.1%, and 100 c.c. for solutions of 0.1% and lower. Intrinsic viscosities were carried out with benzene and chloroform solutions of polymethyl methacrylate.

Just before the determination the viscometer, which had been in contact with chrome-sulfuric acid mixture, was thoroughly rinsed with distilled water, dry acetone, then followed by dry benzene or chloroform. The viscosity of the solvent used in making up the solutions was determined since small deviations in the viscosity of the solvent can cause appreciable errors in the specific viscosity.

The solutions were allowed to reach approximate temperature equilibrium by having them partially immersed in the water bath for at least 10 minutes. In order to reduce errors due to evaporation and suspended foreign matter, the solutions were blown into the viscometer by filtering through a fine sintered glass disc by slight pressure applied through a drying tube. The viscometer was rinsed twice and in the final filling the solution level was adjusted to the graduated line above the lower bulb with a fine glass pipette. After the solution had reached thermal equilibrium. usually less than five minutes, it was blown to the upper bulb and the outflow time noted with a stop watch. Three or four determinations of the same solutions were made. The solutions were measured in the order of increasing concentrations. The average deviation was about 0.1 to 0.3 seconds in an outflow time of at least 110 seconds in the worst cases. The average deviation from the mean, however, was much less. Such accuracy is none too great since an error of 0.05 seconds in the flow time can introduce an error of 1% in a specific viscosity of 0.05.

Viscosities were calculated from the flow times by the formula

# $\eta = c p t - c' p_{t}$

where C and C' are constants of the instrument. They are calculated according to Bingham (113) by determining the outflow times for freshly boiled distilled water, dry benzene, chloroform and acetone.

> ρ = density of solution - assumed to be the same as the solvent in such dilute solutions
> t = the time of flow

The kinetic energy correction term was of the order of 1.9% of the viscosity of the solution in the worst cases.

From a series of such measurements on any sample, the intrinsic viscosity  $[\gamma]$  is obtained by means of a plot of

$$\frac{\ln \frac{\gamma}{\gamma_o}}{\frac{1}{C}}$$
 versus C

or  $\frac{\gamma_{SP}}{C}$  versus  $\gamma_{SP}$ 

also from  $\frac{\gamma_{sP}}{c}$  versus C, as previously described.

The value of the characteristic constant k' is obtained in the first plot by the slope

$$\left(k'-\frac{1}{2}\right)\left[\gamma\right]^2$$
 = -slope

In the second plot

$$k' = \frac{\text{slope}}{(\gamma)}$$
  
and in the last plot  
$$k' = \frac{\text{slope}}{(\gamma)^2}$$

#### 5. The Osmometer

Osmotic pressure measuring devices fall generally into two classes, static and dynamic. In the dynamic type, first used by Berkeley and Hartley (79) and improved by Van Campen (114), Boissonas and Meyer (115) and Obogi and Broda (116) and many others, the cell is designed so that the osmotic pressure can be counterbalanced by an externally applied pressure of known magnitude. The external pressure necessary to prevent the flow of solvent into or out of the solution is taken as the osmotic pressure.

In the static method, the osmotic pressure of the solution is balanced by the liquid column due to the impulse of solvent into the solution. Static types of osmometers have been used by Schulz (117), Dobry (15), Flory (63) and others, for solutions of high polymers.

Recently Jullander (118) introduced an osmotic balance. Jullander weighed the amount of solvent passing through the membrane by suspending the osmotic cell on a balance.

As has already been mentioned, a dynamic Van Campen type of osmometer used by Robertson et al (7, 69) and McIntosh and Morrison (6) was tedious in operation. In addition, it was difficult to obtain accurate results at concentrations lower than 1 gram per 100 ml., thus leaving a long extrapolation to zero concentration.

In recent years a combined static and dynamic osmometer, designed by Flory (63) and Fuoss and Mead (119) has come into

general use. It consisted essentially of two metal plates, clamped together over the membrane by means of machine screws at the edge. The face of each disk contained a shallow well, surrounded by a carefully machined flat ring; inside this ring was a set of concentric cuts connected by a vertical cut which ran from inlet to outlet of each half-cell. When the cell was assembled, the membrane was the gasket. The membranes used were fairly soft and according to Fuoss and Mead "only moderate pressure (a little more than fingertight) was needed to prevent leakage at the edges" of the membrane. One halfcell, containing the solvent, was connected with a capillary tube, while the other, containing solution, was connected with a wide tube, within which was a capillary of bore identical with that of the first capillary. The equilibrium difference in height between the two capillaries was taken as the osmotic pressure.

The original osmometer constructed by the writer followed this type of cell. It was made of brass blocks  $4 \ge 4 \ge \frac{1}{2}$  inches. This apparatus was found unsatisfactory owing to persistent warpages.

In order to diminish warpage, another osmometer was constructed of one inch thick brass blocks, by soldering together under mechanical pressure two pieces of one-half inch thick brass plates. In order to decrease the time required to reach equilibrium, each half-cell was fitted with a capillary tube. This system was found completely inadequate. The levels in both capillaries dropped at the same time, much greater than the amount attributed to evaporation of solvent. The movement of the liquid levels in the capillaries was downwards, regardless of the relative height of the hydrostatic head of the thermostating media. This strongly suggested a diffusion of solvent from the cell into the bath. The cell was emptied of its contents, and dried, and tested with air pressure of about twenty-nine lb./sq. inch but showed no mechanical leakage under water. Bolting down the two cell blocks more firmly by the use of bolts rather than machine screws, the rate of drop decreased, but not to such an extent that serious error was eliminated. Representative data of the leakages observed are shown in Table II. Acetone was the solvent used in determining the drops.

Intensive work on several modifications of this cell proved conclusively that the membrane did not form a satisfactory gasket for sealing the cell. Carter and Record (106) reached a similar conclusion. Flory (63) admitted that his cell may have been leaking, but did not locate the leak at the sealing face. Unfortunately, after a short period of time, the cell leaked in between the soldered blocks. This cell was discarded as resoldering proved fruitless. The final osmometer will be described shortly.

Careful examination of the literature reveals further evidence of leakage through the membrane. Fuoss and Mead (119) report that when solvent is placed in both half-cells of the osmometer, using denitrated collodion membranes, a difference of one mm. or more is observed in the levels of the two capilla-

ries. This difference is ascribed to asymmetry of the membrane. Reversal of the half-cell contents does not reverse the head.

While the source of difficulty due to leakage was eliminated by Wise (104) and the writer, as will be shown shortly, and accurate osmotic pressures were being measured in this investigation. Lossing (120) reported a similar "asymmetry" to that observed by Fuoss and Mead, whose magnitude can be changed by "further tightening of the outer bolts" which seal the osmometer. Lossing at this time was studying osmometry using Fuoss and Mead osmometers under the direction of Dr. Mark at the Laboratory Clinic of the Brooklyn Polytechnic Institute. It may be further mentioned that results obtained by Fuoss and Mead using horizontal and vertical capillaries are not in good agreement (121). Foster and Hixon (122), working with a dynamic osmometer, guessed that leakage occurred apparently around the membrane and consequently applied corrections periodically with solvent in each compartment. They admitted, however, that the leakage constituted the "chief uncertainty about the measurements."

### TABLE II

Showing Typical Leakages Observed in the Osmometer

Type of Mer	nbrane Lea	kage per Hour	Remarks
6% Na(	н	0.34 cm.	3/16" machine screws made to be tightened with a small wrench.
6% Na(	ЭН	0.50 cm.	3/16" machine screws
Carter and	Record	0.33 cm.	3/16" machine screws made to be tightened with a small wrench.
Denitrated	Collodion	0.42 cm.	3/16" machine screws
Carter and	Record	0.064 cm.	$\frac{1}{4}$ " steel bolts
1.5% I	NaOH	0.067 cm.	$\frac{1}{4}$ " steel bolts

It is to be noted, however, that this conclusion is in contradiction to the majority of the recent literature (63, 118, 65, 123, 124 etc.). Therefore the experimental evidence on which the conclusion is based will be presented in some detail.

The fundamental criterion of cell behaviour lay in whether the liquid levels in the capillaries of a carefully thermostated cell remained steady over periods of several hours. Persistent dropping of the levels indicated the presence of a leak. Simple tests, such as immersing the cell in water and applying air pressures up to twenty-nine pounds per square inch, were found to be totally inadequate, although excellent in detecting mechanical flaws, such as pinholes etc. The osmotic cell, while appearing perfectly free from leaks under such a test, would still show a marked drop in the capillary levels when filled with solvent and having the membrane as the gasketing material.

#### Proof of the Diffusion Process

It was demonstrated that the difficulty was not due to improper machining of the sealing face by replacing the membrane with a sheet of 0.001 inches thick composition foil. (Supplied by the courtesy of Dominion Foil Limited, Pb - 97.5%; Sn - 0.5%; Sb - 2%). Such a system was definitely leak tight. When filled with solvent and thermostated, the levels remained constant over a period of six - eight hours. It may be mentioned again that the system leaked when replaced with a membrane about four times as thick. There was a perfect imprint of the machining marks of the sealing face on the periphery of the cellophane membrane. Several thicknesses of cellophane membranes behaved still worse. It was therefore concluded that no gross leak existed, but that it was apparent that diffusion took place directly through the membrane. The cell leaked as well in an air bath.

Numerous methods of overcoming the difficulty were examined, and some of which gave promise will be described briefly. The sealing face of one half-cell was reduced from 3/8" to 1/8". This permitted a very great pressure on the sealing face. This reduced the leak to comparatively small proportions (approx. 0.033 cm./hr.) and occasionally sealed the cell completely. The method, however, proved inconsistent, very likely due to warping of the cell. Attempts were made to seal the osmometer completely with "Sauereisen" cement and "Sealit" paint. This reduced the rate of leakage, but did not completely eliminate it. Furthermore, the method was inconsistent.

Recourse was made to gaskets of "composition" foil. These gave good sealing properties and were inert to solvents. The exact method of use will be described below.

The final osmometer was made of one inch thick cast brass plates as is shown schematically in Fig. (3).

The two brass blocks were four and one-half inches wide, five inches high and one inch thick. Into these blocks were machined alternate, concentric grooves and ridges, each 1/16"





Osmotic Cell

(Following page 58)

wide and 3/16" deep. The grooves and ridges of one half-cell exactly matched those of the other. A central vertical cut connected the circular grooves from inlet to outlet of each half-cell. The grooves thus held the liquids in use, while the ridges supported the membrane and prevented much of its motion.

Surrounding the grooves was carefully machined a flat ring 3 3/4" in outside diameter and 5/16" wide. On one halfcell this ring was level with the tops of the ridges, on the other it was 0.012" below the tops of the ridges in order to accommodate the composition foil gasket. At the outer periphery of the ring, on one-half-cell, was machined a second ring 1/8" wide and raised 0.012" above the first ring. This second ring exactly matched a groove in the sealing face of the other half-cell, 1/8" (+ 0.004" clearance) wide and 0.012" deep. In practice the membrane (F), fitted inside the matching ridge and groove, while an annulus of "composition" foil, (E), 0.014" thick, was placed over the whole sealing face and sealed at the ridge and groove. Thus the membrane was completely enclosed within the cell and protected from the thermostating media. The two half-cells were clamped together, by means of eight  $\frac{1}{4}$  inch, stainless steel bolts at the outer edge of the osmometer.

A 1/8" hole was drilled vertically into one edge of each half-cell. This hole connected with a similar one drilled with a slight downward slope from the bottom of the vertical groove.

In this fashion, the cell could be filled from the bottom, thus eliminating trapped air bubbles as much as possible. By means of a fine pipette, each compartment could be drained completely.

The top of the vertical hole was originally closed by a standard needle valve (B). This consisted of a tapered steel stem, which fitted into a cone tapered at a slightly different angle. Such a system could not be made consistently leak proof in spite of the fact that the valve appeared to sit on a sharp line. The steel stem was therefore thickly coated with hard solder (lead 50%, tin 50%) and then it was machined to approximately the same angle. This relatively soft tip could be seated with slight pressure and formed a consistently vacuum-tight seal. Such a valve would withstand repeated manipulations and required soldering about once a month.

The tops of the values were protected from contamination by the thermostating media by means of short brass tubes soldered to the brass blocks. These tubes, in use, were closed by corks and inverted test tubes, which produced air locks and prevented the entrance of oil or water. The male value stems could be removed by means of a cork borer.

Two methods were used to attach pyrex capillaries to the cell. In the first method, a stainless steel tapered joint, machined to match accurately a 10/30 ground glass female joint attached to the capillary, was soft soldered to each brass block and connected to the top of the vertical groove by means of a 1/8" drill hole. The steel joint was coated with a very thin

layer of soft solder and covered with a layer of "Denco" silvertin amalgam. The 10/30 female joint was then forced firmly over the male and allowed to harden for twelve hours. Such glass-tometal seals could often be made vacuum tight, were tedious to construct and in many cases undependable. When replacements were required, the female 10/30 joint could be removed easily by surrounding it with absorbent cotton and a small amount of liquid air poured on the surface.

A much more superior method was that used by Fuoss and Mead (119). The pyrex capillary was connected to a "Fernico" bushing, (supplied by General Electric Company, Schenectady, N.Y.), (D) through a graded seal of corning AO and uranium glass. The "Fernico" was, in turn, soldered to a brass nipple, which screwed into the top of the cell block. The joint was made leak tight by solder tipping the face of the male brass nipple. The capillaries were supported and aligned vertically by means of  $\frac{1}{4}$ " posts.

The capillary tubing used on each half-cell was cut from the same piece of tubing of calibrated uniform bore of about 0.5 mm. in diameter. The mean diameter varied by no more than  $\frac{1}{2}$  1%. Since the capillary rise was of the order of 1.5 cm. for acetone and 1.0 cm. for chloroform, the error in the readings, due to difference in capillary rise in the two tubes, was only about 0.015 cm. and 0.01 cm. respectively.

In order to eliminate errors due to evaporation of solvent from the capillaries, which was indeed appreciable for acetone

and chloroform, the ends of the capillaries were fitted with 10/30 ground glass joints and connected by a Y glass joint to a thermostated 100 c.c. reservoir half full of solvent. This reduced the rate of evaporation from 0.05 - 0.06 to 0.01 cm. per hour, which is of the order of experimental error. The reservoir was clamped on the wall of the bath.

The assembly of the cell required very great care on account of the tendency of the membrane to lose its permeability on very slight drying (106). Invariably two persons were required. The half-cell containing the composition foil gasket 0.014" thick was placed in a slightly inclined position having the filling tube in the higher level. The half-cell was fitted with two removable guide posts. As the cell was being flooded, a membrane was fitted and flooding was continued to prevent the membrane from drying until the two half-cells were firmly bolted together. More solvent was added through the filling tubes when necessary.

The cell was placed in an upright position and each halfcell was rinsed with solvent and solution, by means of a pipette which reached into the lower tip of the cell inlet. As previously mentioned, the cell could be drained almost completely.

Robertson et al (69) state that membranes treated with sodium hydroxide do not adsorb appreciable amounts of polymer from the solution. In the relatively low concentrations used in this investigation rough trials with the static osmometer

indicated that sufficient adsorption does take place to cause an error of about two - three per cent. Consequently the freshly installed membrane was accommodated by allowing it to stand for about six hours in contact with a polymer solution of approximately the concentration to be used. The cell was rinsed then three or four times with the next solution in order to ensure adequate rinsing and finally filled. The solvent was similarly replaced. Bubbles were partially removed by having a little more solution and solvent than was necessary to wet the membrane. Then the cell was oscillated from side to side for several minutes. More solvent and solution were added and the valves inserted and tightened.

Final adjustments on the liquid levels were made by adding or removing the solution and solvent through the upper ends of the vertical glass tubes connecting with the half-cells by means of a fine pipette or a small strip of Kleenex paper.

In spite of the utmost care, air bubbles frequently appeared after the cell was in use. A similar effect has been reported by Gee (123) using a Carter and Record osmometer. These bubbles manifested themselves, in extreme cases, by actual appearance of bubbles in capillaries, in milder cases, by a continuous rise in the capillary levels, or even a continuous drop - the drop however was not very severe, about 0.04 cm. per hour - without the appearance of bubbles. This phenomenon has been noted by other workers (63) but has been attributed to trapped air, which could be eliminated by

oscillating the cell. Observations made here suggest that this is not entirely correct. In some instances the osmometer appeared to be free of air bubbles, but in the majority of cases difficulties occurred. Bubbles became continually harder to eliminate as the cell was used. It has been found empirically that the bubble trouble was much more pronounced when a fresh membrane was placed in the osmometer. Once bubbles have been eliminated from a filled cell, the solution may be removed and replaced with a fresh one with comparatively little bubble formation. The difficulty due to air bubbles using benzene, was much less, perhaps due to its low wetting angle, the disadvantage being, however, that it has a low permeability through the membrane. Chloroform is more troublesome than benzene but less troublesome than acetone. Similar observations were made by Madras (125).

Carter and Record (106) eliminated bubbles by evacuating the solvent before use. This method was found of little use. Boiling the solvent just before being used was not very promising. Three other methods have been developed to overcome the difficulty. The first consisted in filling the cell and then applying suction to the ends of the capillaries until the liquid momentarily boiled. This method had two essential drawbacks. First, it introduced an unknown error into the concentration of the solution of the cell, and secondly, more bubbles were trapped as shown by the occurrence of long time lags before equilibrium was re-established. The second method consisted in placing the cell block in an oil bath at 32° C. for

several hours, with the values closed to prevent evaporation. The cell was then oscillated every twenty minutes. In this manner usually a few tiny bubbles came out of the system into the capillaries. The tubes above the valves were then rinsed with solvent and solution respectively to account for any evaporation there. With the valves open, the liquid levels were gently oscillated by blowing through the filling tubes The valves were then closed and the cell several times. placed in the thermostated bath. Unfortunately even with this treatment, bubbles made their appearance, although not in as pronounced a degree. The third method, and the preferable one, was to fill the cell slowly and oscillate after each increment of liquid. When the cell was filled, the liquid levels were gently oscillated, as before, through the filling The osmometer was placed in the 30° C. bath and ostubes. cillated periodically for the first several hours. Then. a little gentle oscillation applied on top of the capillaries removed the bubbles, which were trapped on the upper portion of the cell face adjacent to the outlet. The liquid levels were followed periodically and the same procedure applied when bubbles appeared to be present. This method was timeconsuming, but effective.

It might be mentioned that a gold plated cell of the same design as shown in Figure 3 has been used in the latter stages of this investigation. It was generally observed that the appearance of bubbles was less frequent than with the brass osmometer. With the gold plated cell, there were strong indications that the bubbles are of two types, those trapped and which could be removed during the first several hours of an experiment, and bubbles arising from the solvent which made their appearance over long periods of time. After their removal, the levels in the capillaries dropped to a height almost equivalent to that due to evaporation, relative to the original observation.

#### Constant Temperature Bath

The osmometer was thermostated at 30° C. Air, water and oil baths were tried. The air bath was found to give inadequate control over fairly long periods of time. A water bath has been used, but unfortunately the water became turbid and, for the sake of good visibility, it had to be changed weekly; the advantage being, however, that it was much cleaner to work with. With the gold-plated cell, a bath containing Shell Iris 19 oil was used. Control was achieved by means of a 150 watt bulb heater, coated with black paint to eliminate glare. Α variable resistance was wired in series with the heater. The bath was controlled by a mercury thermoregulator actuating a supersensitive relay. The thermoregulator consisted of four prongs of  $\frac{1}{2}$  inch glass and eight inches long. The prongs were connected by a common 3/4 inch glass tube of the same length; this system was made more sensitive by means of a Guoy Interrupter (126). However, a much more sensitive arrangement was obtained by installing a vibrator on the thermoregulator. This consisted of a burette clamp attached to the thermoregulator.

The clamp was attached to a long iron bar to which the stirring motors were clamped. The thermoregulator was suspended vertically by means of two wires attached on opposite walls of the bath. Control was of the order of ±0.001°C. for periods of twenty-four hours or more. The mercury thread in the Beckman thermometer, as viewed with a magnifying lens, showed little or no movement.

This osmometer could be used both as a static or a dynamic cell. In the static method, the osmometer was filled with solution and solvent and permitted to stand until the difference in levels became constant. This difference was taken as the osmotic pressure. The levels were measured with a cathetometer good to  $\pm.005$  cm. The time required to reach equilibrium depends on the specific permeability of the membrane, the diameter of the capillary, and on the rigidity with which the membrane is held in place (63). Of these the most important is the last.

If the membrane is not held rigidly enough, any differential between the two half-cells causes the membrane to bulge to one side. As the solvent passes through the membrane to eliminate the differential, the membrane moves back to its neutral position. Thus the decrease in the differential between the two capillaries is less than that represented by the amount of solvent which had passed through the membrane. When the osmotic pressure is high, its hydraulic head holds the membrane fairly rigidly in its distorted position. The
extent of "membrane flap" is thus less, and the apparent permeability greater. Consequently, the apparent permeability diminishes with decreasing osmotic pressure. When the membrane is held rigidly, the permeability of the membrane is practically constant. This is clearly shown in Table III.

The relation of permeability to osmotic pressure determines the lowest osmotic pressure which can be measured with the osmometer. When the permeability becomes so low that the osmotic pressure is not reached within a reasonable length of time, fairly satisfactory results may be arrived at by approaching the osmotic pressure from above and below and averaging the two values. This method, however, is limited by the error introduced, as the difference between the two values increases. In this investigation every effort was made to have a reasonably rigid membrane so that the two values agreed within cathetometer reading error etc.

The specific permeability is defined by Manegold and coworkers (127, 128) as

## P = D7d

where D is the ml./sq.cm/sec. under a pressure of 1 cm. of water,  $\gamma$  is the viscosity of the solvent in poises - for chloroform at 30°C.  $\gamma = 0.00522$  and d is thickness of the membrane in centimeters, about 7.5 x 10<sup>-3</sup>.

#### TABLE III

	Relation Between	Osmotic Pres	sure and Permeab	ility
Polymer	Concentration 32 gm/100 ml.	Osmotic Fressure cm. of chloroform	Permeability cm/hr/cm. of chloroform pressure	Permeability
NDR 474	0.4007 0.5030 0.6303 0.8109 0.9924	0.357 0.499 0.769 1.081 1.558	0.416 ** 0.470 ** 0.165 * 0.457 ** 0.164 *	$\begin{array}{c} 6.96 \times 10^{-12} \\ 7.88 \times 10^{-12} \\ 2.76 \times 10^{-12} \\ 7.65 \times 10^{-12} \\ 2.74 \times 10^{-12} \end{array}$
NDR 471	0.3589 0.3774 0.4508 0.5488 0.7746 0.9866	0.239 0.280 0.355 0.511 0.913 1.431	1.349 1.211 1.336 0.528 ** 1.393 0.448 **	$13.6 \times 10^{-12}$ $12.2 \times 10^{-12}$ $13.4 \times 10^{-12}$ $8.8 \times 10^{-12}$ $14.0 \times 10^{-12}$ $7.51 \times 10^{-12}$
NDR 359	0.4970 0.6093 0.8295 0.9864 alues were obtained	0.366 0.510 0.918 1.312 when the me	0.164 * 1.414 1.135 1.148 mbrane had a con	$\begin{array}{c} 2.74 \times 10^{-12} \\ 14.2 \times 10^{-12} \\ 11.4 \times 10^{-12} \\ 11.5 \times 10^{-12} \\ \end{array}$

\* The starred values were obtained when the membrane had a considerable amount of flap.

\*\* The double starred values were obtained when the membrane was held more rigidly, achieved by closer machining. The non-starred values were obtained with a similar osmometer, but having a larger working surface or cell face.

#### 6. Membranes

The preparation of suitable membranes, the most difficult and most critical step in osmotic determination, is far from being clearly understood. Robertson and Grummitt and McIntosh (69) have shown that cellophane membranes which have been treated with caustic show no appreciable adsorption of polymer and had not only increased semi-permeability but also a higher rate of solvent transference. Therefore, caustic treated membranes were used almost exclusively in this work. In the case of Gelva V 45, both caustic and swollen cellophane membranes of the types used by Carter and Record (106) and Robertson et al (69) were attempted.

The characteristics of a good membrane are as follows: (1) It must be as nearly semi-permeable as possible. With samples of polymer that are quite heterogeneous, particular care must be taken to make certain that the lower molecular weight material does not pass through the membrane. For example, the passage through the membrane of 0.1% of polymer of average molecular weight 5000 from a polymer mass of average molecular weight 100,000 would introduce an error of 4% in the osmotic pressure.

(2) It must have as high permeability for the solvent as possible. The material should be such that it can be used with a wide variety of solvents. This is not often the case. Cellophane membranes prepared in the same manner show different permeabilities with various solvents. Madras (125) found that for the same membrane chloroform has a permeability 75% that of acetone and benzene 15% that of acetone. This does not affect the equilibrium osmotic pressure.

(3) It should be as mechanically stiff as possible to eliminate membrane flap.

The starting material used for the preparation of cellophane membranes was cellophane No. 600PT (not waterproofed), contributed by Canadian Industries Limited. Cellophane has been found unsatisfactory for a few systems (129) but has been used successfully by Carter and Record (106), Hoff (107), Flory (63), and in the present investigation. Its availability, ease of preparation and uniform thickness certainly recommends its use.

The preparation of membranes from such commercial film falls into three general steps:

- (1) The removal of plasticizers
- (2) The adjustment of the permeability

(3) The accommodation of the membrane to organic solvents. The general method suggested by Carter and Record (106) was used to obtain membranes having low permeability, while the caustic treatment, suggested by Morton (131) as a method of increasing the permeability to water, gave membranes of high permeability.

Squares of cellophane were first partially freed of plasticizer by boiling for one hour in water. It was found

that the initial swelling, which takes place at this point, is not uniform in all directions. The membranes were therefore not cut to the desired size and shape until after this initial boiling. In order to allow for shrinkage, circles were cut from the squares 1/8 inch too large. Final traces of plasticizer were then removed by boiling in water a second time for one hour.

After removal of the plasticizer the membranes were soaked in 2% NaOH solution for 15 minutes at 25°C. They were then dipped for two minutes in distilled water and twice for two minutes each in 95% alcohol in a large evaporating dish. Following this the membranes were placed in ethanol prepared from 95% material which had stood over Drierite, for 15 minutes. The exact amount of water left in the ethanol in the presence of Drierite is not definitely known. The membranes were rinsed in dry chloroform and finally transferred to a desiccator containing dry chloroform over Drierite where they were stored until used. A minimum of two hours in chloroform was necessary. The amount of caustic left on the membranes after accommodation to the organic solvent varied about 25%. The minimum amount of caustic observed per membrane was 2.2 milligrams.

Although Robertson, Grummitt and McIntosh (69) have shown that the permeability of caustic treated membranes increases with the concentration of caustic used, reproducible osmotic pressures were obtained over a fairly wide range of caustic concentrations, so long as the membrane remained semi-permeable.

The preparation of less permeable membranes of the Carter and Record type was somewhat similar to the caustic membranes. After the removal of the plasticizers, etc., the membranes were dipped twice in 95% ethanol and finally stored in 95% ethanol over Drierite for at least 12 hours. The amount of water left in the alcohol was not known. Then they were finally stored in anhydrous acetone. As Robertson et al (69) have shown, Carter and Record membranes are not only less permeable, but also less semi-permeable than caustic treated membranes for the same polymer in the same solvent. It was empirically found that the Carter and Record membranes made by this method were semi-permeable when tested with a solution of 3% Gelva V 45 in acetone for two days.

Fuoss and Mead (119) claimed that membranes made from denitrated collodion were fairly soft and the osmometer could be sealed with moderate pressure to prevent leakage at the edges of the sealing face. These membranes were attempted hoping that they would seal the cell. The preparation follows the general procedure of Montonna and Jilk (129) and of Flory (63). A ring of monel metal six inches in diameter was floated on a clean mercury surface and as free from vibrations as possible. Into this was run 80 ml. of Merck's C.P. collodion, care being taken to avoid the formation of bubbles. After several hours the membrane was removed from the mercury by lifting the monel metal. The monel metal to which the membrane was firmly fastened was dipped in distilled water in order to

remove the last traces of solvent. The ridge on the periphery of the membrane was carefully cut off and the membrane denitrated. Dinitration was originally carried out in a mixture of 900 ml. of 5N ammonium hydroxide and 100 ml. of 95% ethanol, saturated with hydrogen sulphide. The observation of Fuoss and Mead (119) that this does not result in complete denitration at the centre of the membrane was substantiated in the present work. Membranes prepared in this way tended to shrink on being installed in the cell and surrounded with acetone, in spite of the fact that they had been previously kept in dry acetone for several days. An alternative denitration solution suggested by Dr. Purves (132) was adopted. This contained 125 ml. of concentrated NH40H and 325 ml. of 95% ethanol, saturated as before with hydrogen sulphide. This solution gave a better membrane. After denitration the membranes were washed in water, carbon disulphide and acetone in the order named, after which they were accommodated to solvent in the same manner as for cellophene membranes.

It may be mentioned, however, that according to Morton (131) and McBain and Kistler (133) membranes swollen in water do not decrease appreciably in swelling on treatment with alcohol, and consequently do not lose the permeability imparted to them due to the initial swelling.

#### 7. An Attempt to Determine the Osmotic Pressures of Very Dilute Solutions with Copper Ferrocyanide Membranes

The first direct measurements of osmotic pressures of aqueous sugar solutions were made by the botanist Pfeffer (134) in 1877, using inert copper ferrocyanide membranes imbedded on porous clay. Excellent agreement was found between the work of Berkeley and Hartley (79) who used a dynamic osmometer and that of Morse and Frazer (78) who used a static method for determining the molecular weight of sucrose solutions with copper ferrocyanide membranes. The work of Morse (135) has demonstrated the efficiency of this type of membrane for aqueous solutions.

With a view to eliminating and elucidating some inherent difficulties, such as membrane flap, adsorption effects, leakages through the organic membrane, and bubble formation present in most osmometers, recourse was made to the use of sintered glass impregnated with a presumably inert membrane of copper ferrocyanide. As far as the writer is aware, the use of this type of membrane with organic solvents has not appeared in the literature, although Murray (136) claims without presenting experimental evidence that copper ferrocyanide membranes are not suitable for non-aqueous solutions.

Provided that this type of static osmometer is semipermeable, which is a prerequisite for the true determination of molecular weights, leakages and membrane flap and possibly adsorption would be eliminated. The presence of bubbles could be detected visually and removed. Furthermore, the very low cost incurred in making such an osmometer, and compactness, would certainly recommend its use, especially in industry where a large number of measurements might be required.

The static osmometer used with a copper ferrocyanide membrane is shown schematically in Figure 4. The valves and glass to metal seals were made as already described in a previous section. The cell was 2.5 cm. in diameter at the base and had a capacity of 6 c.c.

Morse (135) recommended that the air in the porous portion of the osmometer should be replaced by water. The removal of air from the sintered glass was achieved by electrolysing with a solution of 0.005 N K<sub>2</sub>SO<sub>4</sub> as follows:

The cell was nearly filled with 0.005 N K<sub>2</sub>SO<sub>4</sub> solution and immersed in a 150 c.c. beaker containing the same solution to the lower limit of the glazed portion. The electrodes were of platinum and the one within the cell was made the cathode. The water within the cell was removed periodically by means of a fine pipette. The electrolysis was stopped after 60-100 c.c. of water had been removed. The cell was taken out, rinsed with distilled water and soaked in water for several hours. The arrangement for the deposition of the membrane was as follows:

The anode was made of a strip of copper and was placed in an empty 150 c.c. beaker, and within the beaker was placed the cell, carrying a platinum cathode. The circuit was closed, and as nearly simultaneously as possible the cell and the vessel outside of it were filled with  $1 \ N \ K_2(FeCN)_6$  and  $0.1 \ N \ CuSO_4$ respectively. The ferrocyanide solution was renewed periodi-



Fig. 4

## Static Sintered Glass Osmometer

Impregnated with a Copper Ferrocyanide Membrane

(Following page 76)

cally. The solutions were electrolyzed slowly for about  $\frac{1}{2}$ -hour employing 1.5 amperes for this purpose. In some cases better semi-permeability was obtained by allowing the cell to remain in contact with the solution after the circuit was broken for at least 5 to 6 hours.

After a membrane was imbedded in the sintered glass disc, the cell was thoroughly washed with ethyl alcohol and then acetone until free from water. The cell was then stored for several hours in the organic solvent to be used.

The osmometer was tested for semi-permeability with a chloroform solution of polymethyl methacrylate NDR 474, 1% concentration, for at least 10 hours. Invariably the polymer test on the solvent side on this basis was negative. Attempts were then made to determine osmotic pressures of polymethyl methacrylate NDR 359, whose molecular weight had been established with the static brass osmometer having a caustic treated cellophane membrane as has been described. Occasionally the values obtained were comparable, but after several exposures to solutions on the copper ferrocyanide membrane, the osmotic pressure drifted below that obtained with a cellophane membrane, although the osmotic pressure was constant for at least 24 hours. The permeability had increased somewhat and a very faint polymer test was found in the solvent side. Presumably, small cracks developed on the membrane, Occasionally a very small amount of air accumulated below the tapered valve seats.

The speculation is, however, the source of air is due to the fact that the solvent degasses at the higher temperature of the thermostat.

McLeod (137), moreover, in continuing this study, has been able to deposit on sintered glass discs copper ferrocyanide membranes which were semi-permeable to a 3% solution of Gelva V 45 in acetone, whose molecular weight is 10-fold less than that of polymethyl methacrylate NDR 359.

The results obtained with copper ferrocyanide membrane are summarized in Table IV. For comparative purposes a summary of the values calculated from the cellophane membranes is given.

#### TABLE IV

				or jiavo mon oco
	<u><u>π</u> <u>c</u></u>	π	Р	
	Copper	C	Specific	
Conc'n.	ferro-	Cellophane	permea-	
<u>gm/100 c.c.</u>	cyanide	membrane	<u>bility</u>	Remarks
0.6000	1.097	1.243	3.6x10 <sup>-11</sup>	differential con- stant for about 12 hours
0.8106	1.705	1.610		tt tt tt
0.988	1.955	1.925		no polymer test after 3 days
0.5981	1.100	1.240		constant differ- ential 24 hours
0.7132	1.289	1.440	1.5x10 <sup>-11</sup>	constant for 5 <sup>1</sup> / <sub>2</sub>
1.056	1.861	1.958		uays
0	0.10	0.19		

Osmotic pressure values obtained with a copper ferrocyanide membrane and caustic treated cellophane membranes for polymethyl methacrylate NDR 359 Where possible the specific permeability of the copper ferrocyanide membrane is given.

When the copper ferrocyanide membrane appeared no longer semi-permeable, it was removed with a solution of 10% sodium hydroxide containing a little "Rochelle" salt. The next membrane was precipitated as described previously.

#### RESULTS

#### 1. Viscosities of Aged Polymers

As has already been mentioned, ageing of polymethyl methacrylate studied by McIntosh et al (138) was limited to polymers dissolved in various solvents and aged at  $60^{\circ}$ C. In the present work the polymers were aged in the solid state at  $100^{\circ}$ C, since it was anticipated that the changes would be smaller.

Viscosity measurements for all aged samples were determined in benzene and in chloroform in order to obtain some idea of the interaction between solute and solvent. It was also of interest to note any changes that might occur in the characteristic constant k', as discussed in the theoretical introduction.

In Table V typical viscosity data are shown for unaged polymethyl methacrylate NDR 359 in benzene. The viscosity data of all the samples are summarized in Table VI and in Figure 5.

Typical viscosity results for unaged polymethyl methacrylate NDR 359 in chloroform are shown in Table VII. The results of all the samples are summarized in Table VIII and in Figure 6.

For the sake of clarity, only the sample aged in vacuo for the longest period of time is shown in the graphs. The others have a slightly higher intrinsic viscosity and are crowded too closely together. The calculation of C and C' has been described in a preceding section.

### TABLE V

	Unaged Polymethyl Methacrylate NDR 359 in Benzene							
Concentration gm/100 c.c.	Flow time (secs.)	CPt	<u>c: P</u> t	η	$\frac{\ln \eta}{c}$			
0.1000	279 <b>.7</b>	1.348	0.004	1.344	7.321			
0.1231	322.8	1.556	0.003	1.553	7.119			
0.1616	410.2	1.977	0.003	1.974	6.904			
0.1891	475.3	2.291	0.002	2.289	6.685			
0.2256	575.1	2.772	0.002	2.770	6.448			
0.2560	669.1	3.225	0.002	2.223	6.276			
Benzene	135.9	0.6549	0.008	0.647				
0.0					7.96			

# Typical Viscosity Measurements for

## TABLE VI

## Viscosity of Aged Polymethyl Methacrylate NDR 359 in Benzene

Lab	. No.	Tr	eatment of polymer	Concentration gm/100 c.c.	η	<u>ln <b>1</b>/10</u> C
NDR	359	Unage curv	d. Fig. 5 e No. 1	0.1000 0.1231 0.1616 0.1891 0.2256 0.2560 0.0	1.344 1.553 1.974 2.289 2.770 2.223	7.321 7.119 6.904 6.685 6.448 6.276 7.96
NDR	359 H	( in	vacuo 15 days	0.1221 0.1661 0.2030 0.2447 0.2668 0.0	1.511 1.934 2.382 2.941 3.274	6.833 6.585 6.412 6.177 6.071 7.47
NDR	359L	in (Fig.	oxygen 15 days 5 curve No.3)	0.0525 0.0855 0.0966 0.1199 0.1693 0.2302 0.2695 0.2996 0.3157 0.0	0.9211 1.144 1.213 1.404 1.816 2.481 2.911 3.381 3.624	6.988 6.736 6.612 6.507 6.156 5.865 5.619 5.552 5.491 7.26
NDR	3591	in	vacuo 90 days	0.1108 0.1399 0.1738 0.2238 0.2531 0.2881 0.0	1.392 1.662 2.000 2.611 3.087 3.614	6.971 6.785 6.530 6.263 6.195 5.992 7.52
NDR	359J	in (Fig.	oxygen 90 days 5 curve No. 4)	0.0546 0.1089 0.1453 0.1818 0.2196 0.2563 0.3011 0.0	0.9208 1.266 1.554 1.864 2.246 2.664 3.213	6.600 6.232 6.095 5.859 5.702 5.554 5.347 6.86

## TABLE VI (contd.)

## Viscosity of Aged Polymethyl Methacrylate NDR 359 in Benzene

Lab	No.	Treatment of polymer	Concentration gm/100 c.c.	ĩ	$\frac{\ln \eta}{C} \chi_0$
NDR	3590	in <b>vac</b> uo 127 days	0.0994 0.1217 0.1865 0.2222 0.2564 0.0	1.296 1.493 2.143 2.586 3.046	7.000 6.882 6.427 6.240 6.047 7.55
NDR	359P	in oxygen 127 days (Fig. 5 curve No. 5)	0.0999 0.1291 0.1648 0.2088 0.2473 0.0996 0.1920 0.2474 0.0	1.169 1.345 1.597 1.923 2.318 1.178 1.873 2.271	5.965 5.699 5.508 5.236 5.180 6.045 5.551 5.088 6.50
NDR	359M	in vacuo 195 days (Fig. 5 curve No. 2)	0.1039 0.1408 0.1759 0.2238 0.2490 0.0	1.317 1.642 2.001 2.582 2.873	6.847 6.615 6.419 6.184 5.988 7.41
NDR	359N	in oxygen 195 days (Fig. 5 curve No. 6)	s 0.0996 ) 0.1283 0.1559 0.1832 0.2210 0.2486 0.2514 0.0	1.158 1.356 1.560 1.796 2.024 2.354 2.305	5.841 5.765 5.646 5.572 5.162 5.194 5.055 6.44





Viscos	sit	y of	Polymo	ethyl Methacrylate NDR 359 in Benzene
Curve	1	NDR	359	control
11	2	NDR	359M	aged $6\frac{1}{2}$ months in vacuo
n	3	NDR	359 L	aged 2 weeks in ½ atm. oxygen
n	4	NDR	359J	aged 3 months in $\frac{1}{2}$ atm. oxygen
Ħ	5	NDR	359P	aged $4\frac{1}{4}$ months in $\frac{1}{2}$ atm. oxygen
11	6	NDR	359N	aged 6 <sup>1</sup> / <sub>2</sub> months in <sup>1</sup> / <sub>2</sub> atm. oxygen

(Following page 83)

## TABLE\_VII

Typical	Viscosity	Measurements	for	Unaged	Polymethyl	Methacrylate	NDR	359
		4	Ln Cl	hlorofor	°m –			

Concentration gm/100 c.c.	Flow time (sec.)	Cft	<u><u><u>c</u>; <i>P</i></u> t</u>	r	$\frac{\ln \eta/\eta_0}{c}$
0.1016	171.6	1.404	0.015	1.389	9.040
0.1017	171.9	1.406	0.015	1.391	9,038
0.1243	202.6	1.658	0.013	1.645	8.804
0.1413	229.6	1.878	0.011	1.867	8.590
0.1646	270.2	2.210	0.010	2.200	8.366
0.1882	313.8	2.566	0.008	2,558	8.121
0.2258	393.2	3.216	0.007	3.209	7.773
0.2503	458.5	3.751	0.006	3.745	7.632
0.2915	574.7	4.700	0.005	4.695	7.328
Solvent	72.2	0,5905	0.0356	0.5549	
0.0					10.06

## TABLE VIII

Viscosity	of	Aged	Po]	Lymethyl	Methad	crylate	NDR	359
-		-	in	Chlorof	orm	-		

Lab. No.	Treatment of polymer	Concentration gm/100 c.c.	η	<u>ln <b>1</b>/70</u> C
NDR 359	Unaged, Fig. 6 curve No. 1	$\begin{array}{c} 0.1016\\ 0.1017\\ 0.1243\\ 0.1413\\ 0.1646\\ 0.1882\\ 0.2258\\ 0.2258\\ 0.2503\\ 0.2915\\ 0.0\end{array}$	1.389 1.391 1.645 1.867 2.200 2.558 3.209 3.745 4.695	9.040 9.038 8.804 8.590 8.366 8.121 7.773 7.632 7.328 10.06
NDR <b>359K</b>	in vacuo 15 days	0.0969 0.1434 0.1813 0.2275 0.0	1.301 1.834 2.354 3.097	8.788 8.339 7.977 7.561 9.70
NDR 359L	in oxygen 15 days (Fig. 6, curve no. 3)	0.1064 0.1503 0.1835 0.2042 0.0	1.336 1.785 2.226 2.489	8.245 7.773 7.570 7.353 9.19
NDR <b>3591</b>	in vacuo 90 days	0.1104 0.1311 0.1601 0.2013 0.2357 0.0	1.452 1.691 2.048 2.667 3.266	8.553 8.366 8.048 7.711 7.447 9.59
NDR 359J	in oxygen 90 days (Fig. 6, curve no. 5)	0.1035 0.1257 0.1571 0.3010 0.2402 0.2633 0.0	1.264 1.479 1.791 2.341 2.918 3.261	7.784 7.661 7.345 7.074 6.837 6.659 8.53
NDR 359 0	in vacuo 127 days	0.1095 0.1241 0.1640 0.2114 0.2367 0.0	1.452 1.607 2.097 2.817 3.248	8.624 8.426 8.002 7.600 7.391 9.59

Lab. No.	Treatment of polymer	Concentration gm/100 c.c.	η	<u>ln η/ηο</u> C
NDR 359P	in oxygen 127 days (Fig. 6, curve no. 4)	0.0994 0.1362 0.1524 0.1862 0.2129 0.2524 0.0	1.200 1.514 1.688 2.060 2.269 2.743	7.729 7.345 7.280 7.026 6.609 6.320 8.65
NDR 359M	in vacuo 195 days (Fig. 6, curve no. 2)	0.1056 0.1231 0.1577 0.2037 0.2431 0.2761 0.0	1.395 1.579 2.010 2.675 3.386 4.025	8.563 8.352 8.052 7.635 7.369 7.114 9.48
NDR <b>359N</b>	in oxygen 195 days (Fig. 6, curve no. 6)	0.1088 0.1339 0.1731 0.2074 0.2578 0.2794 0.0	1.260 1.462 1.901 2.230 2.897 3.243	7.372 7.106 7.013 6.621 6.342 6.258 8.13

#### TABLE VIII (contd)

Viscosity of Aged Polymethyl Methacrylate NDR 359 in Chloroform

The changes in intrinsic viscosity of chloroform and benzene solutions concerning the aged polymer NDR 359 are shown graphically in Figure 7. The intrinsic viscosity is plotted versus time in months.





Viscos	Lty	of Poly	methyl Methacry	late NDR 3	59 in Chloroform
Curve	1	NDR 359	control		
Ħ	2	NDR 359	M aged 6½ mo.	in 2 vacu	10
Ĥ	3	NDR 359	L aged 2 weeks	in ½ atm.	oxygen
n	4	NDR 359	P aged $4\frac{1}{4}$ mo.	in ½ atm.	oxygen
n	5	NDR 359	J aged 3 mo.	in ½ atm.	oxygen
11	6	NDR 359	N aged 6½ mo.	in ½ atm.	oxygen
			(	06)	

(Follows page 86)

There is an appreciable amount of scattering of the  $\frac{\ln \eta_r}{2}$  values for the polymers aged in the presence of oxygen.

The dispersion appears to be more marked in benzene than in chloroform solutions. The lower molecular weight polymers such as NDR 471 and NDR 474 did not show such an obvious scattering of the viscosity values.

In order to determine whether this observed dispersion was due to insufficient time allowed to effect complete solubility, several benzene solutions of NDR 359P of approximately the same concentration were measured in the viscometer at different intervals of time. The results obtained are shown in graphical form in Figure 5, line 5, and labelled 1, 2, 3. The data are also shown in summary form in Table IX.

#### TABLE IX

Effect of Time on the Solubility of Polymethyl Methacrylate NDR 359P in Benzene

Solution No.	Conc. gm/100 c.c.	Age of sol.	$\frac{\ln \mathbf{\eta} \mathbf{r}}{C}$
1	0.1215	24 hours	5.730
2	0.1221	48 hours	5,920
3	0.1225	96 hours	5.660

On the basis of these figures the time involved in dissolving the polymer does not explain the scattering observed. It is very likely, however, since the polymer was precipitated and dried to a very porous mass, that oxygen was not accessible to some portions of the sample during the ageing process. This view is supported by viscosity measurements on the unaged samples and also on polymers aged in vacuo, where no scattering occurred beyond experimental error. On the other hand, as is evident from Figure 6, the intrinsic viscosity in chloroform of polymethyl methacrylate is approximately 25 per cent higher than that obtained with benzene. Therefore, it is reasonable to assume that the scattering is swamped to a large extent in the case of chloroform solutions. Yet the error due to scattering in chloroform solutions may still be appreciable. As demonstrated in the case of NDR 359P aged in oxygen 127 days and shown in Figure 6, curve No. 4, this sample should have a slightly lower intrinsic viscosity than NDR 359J aged in oxygen 90 days (Fig. 6, curve No. 5).

Summaries of the data for polymethyl methacrylate samples NDR 471 and NDR 474 both in benzene and in chloroform solutions are given in Tables X and XI, XII and XIII respectively. A graphical representation of the change in intrinsic viscosities of the polymers is given in Fig. 8, where the intrinsic viscosity is plotted against time.

## TABLE X

Lab. No.	Treatment of polymer	Concentration gm/100 c.c.	η	<u>ln <b>)/ ?</b>o</u> C
NDR 471	Unaged	0.0997 0.1563 0.2094 0.2555 0.3337 0.3753 0.0	0.9684 1.192 1.438 1.660 2.097 2.379	4.051 3.914 3.815 3.691 3.526 3.471 4.28
NDR <b>471K</b>	In vacuo 15 days	0.0552 0.1047 0.2083 0.3646 0.4009 0.0	0.8074 0.9763 1.425 2.232 2.497	4.185 4.021 3.836 3.423 3.393 4.29
NDR 471L	In oxygen 15 days	0.0509 0.1640 0.2215 0.2783 0.3452 0.0	0.7894 1.204 1.462 1.744 2.099	4.158 3.865 3.739 3.608 3.445 4.24
NDR 471 I	In vacuo 90 days	0.1025 0.1517 0.2019 0.2616 0.3441 0.4132 0.0	0.9812 1.183 1.400 1.737 2.176 2.647	4.132 4.024 3.859 3.768 3.547 3.427 4.36
NDR <b>471J</b>	In oxygen 90 da <b>ys</b>	0.1003 0.1368 0.1985 0.2736 0.3157 0.0	0.9442 1.079 1.308 1.619 1.821	3.841 3.796 3.583 3.378 3.301 4.09
NDR <b>471</b> O	In vacuo 127 days	0.0983 0.1420 0.2069 0.3215 0.3776 0.0	0.9660 1.128 1.401 1.992 2.319	4.084 3.918 3.736 3.500 3.390 4.28

## Viscosity of Aged Polymethyl Methacrylate NDR 471 in Benzene





Decrease in (7) with age for polymethyl methacrylate fraction NDR 359

(Following page 89)

Lab. No.	Treatment of polymer	Concentration $gm/100$ c.c.	η	<u>ln η/ηo</u> C
NDR 471P	In oxygen 127 days	0.1011 0.1466 0.2017 0.2956 0.3684 0.0	0.9259 1.080 1.276 1.631 1.981	3.571 3.516 3.383 3.137 3.046 3.82
NDR <b>471</b> M	In vacuo 195 days	0.0970 0.1510 0.2024 0.2669 0.3031 0.3704 0.0	0.9425 1.164 1.364 1.665 1.875 2.240	3.877 3.882 3.684 3.541 3.510 3.347 4.16
NDR <b>471N</b>	In oxygen 195 days	0.0971 0.2013 0.2590 0.3039 0.3623 0.0	0.9292 1.297 1.524 1.718 1.993	3.736 3.456 3.309 3.216 3.108 3.96

Viscosity of Aged Polymethyl Methacrylate NDR 471 in Benzene

TABLE X (contd)

## TABLE XI

Lab.	No.	Treatment of polymer	Concentration gm/100 c.c.	η	<u>ln 7/70</u> C
NDR	471	Unaged	0.0969 0.1264 0.1563 0.2117 0.2554 0.3048 0.0	0.9411 1.077 1.231 1.551 1.823 2.185	5.266 5.110 4.982 4.769 4.588 4.439 5.62
NDR	471K	In vacuo 15 days	0.1059 0.1678 0.2277 0.3002 0.3886 0.0	0.9618 1.270 1.601 2.095 2.763	5.194 4.935 4.656 4.426 4.131 5.59
NDR	471L	In oxygen 15 days	0.0994 0.1570 0.2126 0.3024 0.3787 0.0	0.9316 1.216 1.525 2.143 2.751	5.214 4.999 4.754 4.470 4.229 5.56
NDR	<b>471</b> I	In vacuo 90 days	0.1189 0.1553 0.2032 0.2770 0.3422 0.3919 0.0	1.044 1.225 1.494 1.979 2.491 2.911	5.168 4.980 4.785 4.528 4.337 4.184 5.58
NDR	471J	In oxygen 90 days	0.1080 0.1979 0.2934 0.3340 0.0	0.9476 1.389 1.934 2.202	4.790 4.548 4.195 4.074 5.16
NDR	<b>471</b> 0	In vacuo 127 days	0.0963 0.1479 0.2004 0.2519 0.3490 0.3951 0.0	0.9310 1.181 1.468 1.788 2.517 2.911	5.187 4.986 4.765 4.576 4.282 4.151 5.55

Viscosity of Aged Polymethyl Methacrylate NDR 471 in Chloroform

## TABLE XI (contd)

Lab	. No.	Treatment of polymer	Concentration gm/100 c.c.	η	$\frac{\ln \eta}{C}$
NDR	471P	In oxygen 127 days	0.1000 0.1525 0.2123 0.2905 0.3521 0.0	0.9040 1.127 1.397 1.830 2.187	4.703 4.528 4.266 4.047 3.846 5.04
NDR	<b>47</b> 1M	In vacuo 195 days	0.1557 0.2288 0.3036 0.3702 0.0	1.200 1.642 2.118 2.667	4.839 4.665 4.354 4.193 5.39
NDR	<b>47</b> 1N	In oxygen 195 days	0.1596 0.2492 0.3146 0.3770 0.0	1.159 1.629 2.024 2.496	4.503 4.251 4.058 3.943 4.93

## Viscosity of Aged Polymethyl Methacrylate NDR 471 in Chloroform

## TABLE XII

Lab	. No.	Treatment of polymer	Concentration gm/100 c.c.	Ŋ	$\frac{\ln \eta/\eta_0}{c}$
NDR	474	Unaged	0.0977 0.1530 0.2054 0.2815 0.3195 0.3744 0.0	0.9017 1.069 1.243 1.533 1.678 1.902	3.400 3.288 3.181 3.067 2.985 2.884 3.58
NDR	474K	In vacuo 15 days	0.1024 0.1644 0.2943 0.3583 0.4139 0.0	0.9193 1.131 1.665 1.998 2.272	3.542 3.469 3.252 3.181 3.091 3.69
NDR	474L	In oxygen 15 days	0.0500 0.1110 0.1583 0.2279 0.3133 0.3481 0.4004 0.0	0.7576 0.9183 1.049 1.285 1.582 1.722 1.930	3.361 3.243 3.116 3.056 2.887 2.842 2.755 3.43
NDR	474 I	In <b>vac</b> uo 90 days	0.1039 0.1725 0.2530 0.3148 0.3555 0.4115 0.0	0.9208 1.135 1.414 1.634 1.819 2.056	3.453 3.293 3.113 2.963 2.924 2.824 3.65
NDR	474J	In oxygen 90days	0.0954 0.1452 0.2099 0.2691 0.4005 0.0	0.8843 1.024 1.234 1.439 1.942	3.321 3.192 3.092 2.986 2.755 3.47
NDR	<b>474</b> O	In vacuo 127 days	0.1004 0.1393 0.2225 0.2476 0.3102 0.3603 0.0	0.9055 1.025 1.296 1.389 1.616 1.826	3.345 3.303 31123 3.086 2.950 2.879 3.54

Viscosity of Aged Polymethyl Methacrylate NDR 474 in Benzene

## TABLE XII (contd)

Viscosity	of	Aged	Polymethyl	Methacrylate	NDR	474
-			in Benzen	9		

Lab. No.	Treatment of polymer	Concentration gm/100 c.c.	Ŋ	<u>ln <b>η</b>/η</u> ο C
NDR 474 P	In oxygen 127 days	0.0992 0.1571 0.2086 0.2544 0.2987 0.0	0.8776 1.041 1.181 1.323 1.466	3.101 3.044 2.899 2.824 2.748 3.28
NDR <b>474</b> M	In vacuo 195 days	0.1015 0.1572 0.1986 0.2564 0.3121 0.0	0.9214 1.096 1.250 1.466 1.690	3.488 3.357 3.318 3.193 3.078 3.68
NDR <b>474 N</b>	In oxygen 195 days	0.1023 0.1517 0.2080 0.2598 0.3056 0.0	0.8896 1.017 1.185 1.357 1.497	3.118 2.984 2.914 2.854 2.148 3.27

## TABLE XIII

Lab	. No.	Treatment of polymer	Concentration gm/100 c.c.	J	<u>اn ۲/۲۰</u> ۲
NDR	474	Unaged	0.0996 0.1463 0.1711 0.2574 0.3084 0.3567 0.3758 0.0	0.8842 1.068 1.175 1.581 1.864 2.153 2.274	4.501 4.353 4.277 3.999 3.870 3.753 3.707 4.80
NDR	<b>474</b> K	In vacuo 15 days	0.1052 0.1627 0.2111 0.2913 0.36 <b>49</b> 0.0	0.8962 1.131 1.349 1.753 2.191	4.530 4.359 4.195 3.939 3.756 4.84
NDR	474L	In oxygen 15 days	0.1043 0.1547 0.2098 0.2803 0.3727 0.0	0.8788 1.063 1.292 1.619 2.124	4.374 4.180 4.015 3.809 3.594 4.66
NDR	<b>474</b> I	In vacuo 90 days	0.1105 0.1536 0.2018 0.3024 0.3567 0.4807 0.0	0.9040 1.066 1.257 1.722 2.038 2.802	4.255 4.135 3.965 3.685 3.598 3.332 4.55
NDR	474J	In oxygen 90 days	0.1229 0.1581 0.2099 0.2816 0.3629 0.0	0.9411 1.065 1.265 1.585 2.007	4.153 4.013 3.841 3.665 3.492 4.45
NDR	<b>474</b> 0	In vacuo 127 days	0.1072 0.1518 0.2022 0.2532 0.3585 0.4180 0.0	0.8965 1.062 1.276 1.519 2.080 2.447	4.309 4.159 4.031 3.906 3.637 3.508 4.55

## Viscosity of Aged Polymethyl Methacrylate NDR 474 in Chloroform

## TABLE XIII (contd)

Lab	No.	Treatment of polymer	Concentration gm/100 c.c.	મ	<u>ln]/Jo</u>
NDR	<b>474</b> P	In o <b>xyge</b> n 127 da <b>ys</b>	0.1161 0.1494 0.2109 0.2701 0.3491 0.4148 0.0	0.8910 1.011 1.220 1.465 1.826 2.187	3.928 3.895 3.652 3.530 3.360 3.264 4.17
NDR	<b>474¥</b>	In vacuo 195 days	0.0963 0.1442 0.2141 0.2578 0.3121 0.3698 0.0	0.8678 1.046 1.355 1.569 1.872 2.208	4.445 4.272 4.085 3.963 3.839 3.686 4.72
NDR	474N	In oxygen 195 days	0.0951 0.1569 0.2075 0.2537 0.3089 0.3989 0.0	0.8276 1.046 1.245 1.438 1.683 2.167	4.015 3.927 3.807 3.683 3.535 3.372 4.22

## Viscosity of Aged Polymethyl Methacrylate NDR 474 in Chloroform





Decrease in () with age for polymethyl methacrylate fractions NDR 471 and NDR 474

(Following page 96)

With reference to all the samples measured, the changes in intrinsic viscosity are greatest with NDR 359. It is interesting to note the initial marked drop in viscosity suffered by NDR 359 aged in vacuo, after which it remained practically constant with further ageing. The polymers with the longest chain length showed greatest decrease in viscosity. Polymethyl methacrylate NDR 359 will be discussed shortly under osmotic pressure determinations.

#### Effect of Concentration on Viscosity

In the case of polymethyl methacrylate NDR 359, the viscosity above 0.25 gm/100 c.c. in benzene solutions and about 0.22 in chloroform solutions does not increase proportionately to the concentration. It rises above that concentration. A similar behaviour was observed by Flory (63) in solutions of polyisobutylene in diisobutylene. As degeneration increased, the variation of ln r/C from linearity decreased, however.

According to Staudinger (17) polyvinyl derivatives are linear colloids by which the viscosity in the region gelsolution does not increase proportionately to the concentration, but it rises above that concentration. It is to be noted, however, that the viscosity in the region gel-solution deviates from Hagen-Poisseuilles' law, that is, the rate of shear is not proportional to the shearing stress.

#### Effect of different solvents on the viscosity

Many investigators (63,17,95,119,70,74, etc.) have noted that the viscosity of solutions of high polymeric substances in a good dissolving agent in which the thread-like molecules are strongly solvated is higher than in a poor dissolving agent. This effect is remarkably demonstrated with polymethyl methacrylate in benzene and in chloroform solutions. The polymer has a much higher intrinsic viscosity in the latter solvent. For comparative purposes the intrinsic viscosities and the characteristic constants k' of all the samples studied are summarized in Table XIV.

#### Hydrodynamic constant k'

In agreement with Huggins (76) and others (17, 104), the k' in this investigation appears to be very slightly dependent on the molecular weight. In spite of the marked difference in intrinsic viscosity between chloroform and benzene solutions of polymethyl methacrylate, the hydrodynamic constant k' is practically identical for the two solvents. Schulz and Blaschke (34) reported a value of 0.30 for k' in the case of fractionated and unfractionated polymethyl methacrylate in chloroform. However, other values ranging from 0.26 to 0.33 have been summarized by Schulz and co-workers (139) for the same polymer-solvent system.
## TABLE XIV

## Summary of Intrinsic Viscosities and k' Values for all samples studied in this work

			NDR	359			NDR	471			NDR	474	
		in		i	n	in		i	n	in		1	n
Tab Ma	Time aged at	Benz	ene	Chlor	oform	Benz	ene	Chlor	oform	Benz	ene	Chlor	oform
Lab. No.		<u>[7]</u>	K,	[7]	K'	<u>(7)</u>		<u>(7)</u>	k'	$(\gamma)$	K'	(7)	K'
Control	O time	7.96	0.40	10.06	0.40	4.28	0.38	5.62	0.38	3.58	0.36	4.80	0.37
К	2 wks in Vacuo	7.47	0.41	9.70	0.40	4.29	0.38	5.59	0.38	3.69	0.39	4.84	0.37
L	2 wks in $\frac{1}{2}$ atm. 02	7.26	0.39	9.19	0.39	4.24	0.37	5.56	0.38	3.43	0.36	4.66	0.37
I	3 mo.in Vacuo	7.52	0.41	9.59	0.40	4.36	0.38	5.58	0.37	3.65	0.35	4.55	0.37
J	3 mo. in 🛓 atm. 02	6.86	0.39	8.53	0.40	4.09	0.36	5.16	0.38	3.47	0.35	4.45	0.36
0	4 <sup>1</sup> / <sub>4</sub> mo. in Vacuo	7.55	0.40	9.59	0.40	4.28	0.37	5.55	0.38	3.54	0.35	4.55	0.38
Р	4¼ mo. in ½ atm. 02	6.50	0.37	8.65	0.38	3.82	0.35	5.04	0.37	3.28	0.35	4.17	0.37
М	6 <sup>1</sup> /2 mo. in Vacuo	7.41	0.40	9.48	0.40	4.16	0.38	5.39	0.39	3 <b>.6</b> 8	0.36	4.72	0.37
N	6월 mo. in 불 atm. 02	6.42	0.37	8.13	0.40	3.95	0.35	4.93	0.39	3.27	0.35	4.22	0.38
	Ave. k'		.39		0.40		0.37		0.38		0.36		0.37

#### (2) Osmotic Pressure Determinations

(a) Osmotic pressure results of polyvinyl acetate Gelva V 45
 in various solvents

Since the majority of the literature shows or assumes that the molecular weight of high polymers dissolved in various solvents is constant within experimental error, it was deemed necessary to investigate this important point with the improved osmometer. Two per cent caustic treated membranes were used. Gelva V 45 was chosen for this portion of the investigation since a considerable amount of data had been accumulated for this particular sample. The solvents employed were chloroform, benzene and acetone. The results obtained are summarized in TABLE XV and in Figure 9.

As is shown in Figure 9 two lines of different slope (curves 1 and 2) were obtained for the system chloroform - Gelva V 45, but gave identical limiting  $\frac{\Pi}{C_2}$  values. The line with the higher slope (curve 1) was obtained with an osmometer in which the membrane was held more rigidly in place; whereas, the line with the smaller slope (curve 2) was obtained with another osmometer having an appreciable amount of membrane flap. However, as closer machining was obtained and the membrane held more rigidly in place, excellent agreement resulted between the two osmotic cells. As shown in the tables, the molecular weight of Gelva V 45 in chloroform, benzene and acetone is identical. A further discussion of these results and the necessary correction terms are given in a later section.

### TABLE XV

# Osmotic Pressure Data for Gelva V 45 in Various Solvents Using 2% Caustic Treated Cellophane Membranes

System	Conc. <sup>n</sup> gm/100 c.c.	Osmotic Pressure in cm. of solvent	<b>Π</b> gm/cm <sup>2</sup>	$\frac{\pi}{c_2}$	$\frac{T}{C_2} - \frac{\mathrm{RTd}_1}{\mathrm{3M_1d_2}^3} C_2^2$
Chloroform- Gelva V 45 (Membrane flap present) (Fig. 9 Line 2)	1.186 0.7904 0.5856 0.9648 0.0	4.08 2.18 1.38 3.04	6.01 3.21 2.03 4.47	5.07 4.06 3.47 4.62 1.84	4.98 4.02 3.45 4.56 1.85
Chloroform- Gelva V 45 (Membrane flap negligible) (Fig. 9 Line 1)	1.0037 0.4053 1.0278 0.7513 0.0	3.57 0.898 3.70 2.28	5.25 1.32 5.44 3.35	5.23 3.25 5.30 4.47 <b>1.84</b>	5.17 3.24 5.23 4.44 1.87
Benzene-Gel- va V 45 (Fig. 9 Line 3	0.7880 0.9768 ) 1.177 0.0	2.81 3.77 4.93	2.44 3.27 4.28	3.09 3.35 3.64 1.83	3.05 3.30 3.56 1.84
Gelva V 45 (Fig. 9 Line 4	0.5937 ) 0.9972 0.2703 0.0	2.06 4.38 0.770	1.61 3.35 0.602	2.71 3.36 2.23 1.80	2.69 3.29 2.22 1.82



## Figure 9

Dependence of Osmotic Pressure on Concentration for Solutions of Polyvinyl Acetate, G. V 45, in Various Solvents and Various Membranes.

Curve 1 Gelva V 45 in chloroform (2% caustic membrane) Curve 2 Gelva V 45 in chloroform (2% caustic membrane) Curve 3 Gelva V 45 in benzene (2% caustic membrane) Curve 4 Gelva V 45 in acetone (2% caustic membrane) Curve 5 Gelva V 45 in acetone (Carter and Record membrane)

(Following page 101)

(b) Osmotic Pressure Results of Polyvinyl Acetate, Gelva
 V 45 in Acetone Using Carter and Record Type of
 Cellophane Membrane

As has been mentioned in a previous section, some authors, notably Carter and Record, have considered cellophane membranes satisfactory, while others have remarked that such membranes were found unsuitable (129), but have not stated the source of difficulty. Robertson (7) and McIntosh and co-workers (69) have found that membranes prepared by the Carter and Record method gave molecular weights which were not in agreement with those obtained using caustic treated cellophane membranes. They found that adsorption of polymer occurred on the cellophane membranes when the menbranes are prepared by the Carter and Record method. Furthermore, time lags in the establishment of equilibrium osmotic pressure were caused mainly by the adsorption process. Τt was decided to redetermine the molecular weight of Gelva V 45 in acetone using a Carter and Record type of membrane with the improved osmometer.

The molecular weight values were obtained with Carter and Record membranes by permitting adsorption to occur and then refilling the cell a number of times with a fresh solution of the same concentration. When the osmotic pressure of a finite concentration was obtained, the cell was rinsed until free of polymer. Consequently, the amount of adsorption could be determined for each solution. The results obtained are shown in TABLE XVI and in Figure 9, Line 5.

## TABLE XVI

## Osmotic Pressure Data for Gelva V 45 in Acetone Using a Carter and Record Membrane

Conc. gm/100 cc	Filling	Π gm/cm. <sup>2</sup>	$\frac{\pi}{c_2}$	$\frac{\Pi}{C_2} - \frac{\mathrm{RTd}_1}{\mathrm{3M_1d}_2^3} C_2^2$
0.4139	1 2 3 4	0.830 0.940 0.994 0.970	2.00 2.27 2.39 2.35	2.36
0.6284	1 2 3	1.659 1.699 1.705	2.64 2.70 2.71	2.68
1.0045	1 2 3	3.36 3.37 3.37	3.34 3.35 3.35	3.28
1.219	1 2 3	4.50 4.55 4.61	3.69 3.73 3.77	3.67
0.0			1.63	l.67

As is evident from the limiting value, the molecular weight obtained as described above does not correspond with that obtained when a caustic treated membrane is employed. The results cannot be explained by a difference in permeability of the membranes to small molecular weight material. It is to be noted that the greatest discrepancy in molecular weight determination between the improved osmometer used in this investigation and the van Campen dynamic osmotic cell, used by McIntosh and co-workers (69) lies in the use of Carter and Record type of membranes. In both osmometers the values obtained with caustic treated and Carter and Record cellophane membranes are not concordant. No satisfactory conclusion has been reached concerning the discrepancy. Presumably either the caustic treated or the Carter and Record cellophane membranes are at fault.

It is not very likely that in the case of caustic treated membranes the higher extrapolated value was due to a Donnan effect. There was never any indication of caustic on the solvent or in the solution side of the half-cells, even after being in contact with the membrane for a week. Furthermore, if caustic was free, polyvinyl acetate is easily saponified, consequently a drop in osmotic pressure should be observed as polyvinyl alcohol is insoluble in acetone or any other organic solvent used in this investigation. It may be mentioned, moreover, that possible error due to corrosion of the osmometer has been practically eliminated. A gold-plated cell of the same general design as described previously (Fig.3) was used for this particular portion of the investigation.

With caustic treated membranes, a very small amount of adsorption took place in the range of very low concentration, circa 0.5% concentration, to the extent of 2-3%. For higher concentrations the per cent adsorption was much smaller. However, it was found empirically that accommodation of the membrane and cell for about six hours with a solution of about the same concentration used in determining an osmotic pressure was sufficient to satisfy the adsorption effects. Subsequent washing with fresh solution of the same concentration did not change the equilibrium value previously observed. The amount of alkali which much be retained on the membrane is not known exactly, but relatively wide variation of the caustic content does not appear to alter the membrane behaviour appreciably.

Referring to the expression due to Huggins (101)

 $\frac{\pi}{c_2} - \frac{RTd_1}{3M_1d_2^3} \quad C_2^2 = \frac{RT}{M_2} + \frac{RTd_1}{M_1d_2^2} \quad (\frac{1}{2} - M_1) \quad C_2 = \frac{1}{2}$ 

the negative term -  $\frac{\text{RTd}_1}{3M_1 d_2 3}$  C<sub>2</sub><sup>2</sup> was calculated and sub-

tracted from the  $\frac{\pi}{C_2}$  values in all cases. The importance of this evaluation and the effect on the extrapolated value when this correction is omitted has been emphasized by

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TABLE X	VII	
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Various Characteristic Constants Obtained for Gelva V 45 in the Improved Osmometer

Solvent	Membrane	Slop <b>e</b> *	Slope	<u>π</u> *	$(\frac{\pi}{C_2}-\frac{\mathrm{RTd}_1}{\mathrm{3M_1d}_2})$	, c <sub>2</sub> 2) "*	м,	Mn* x 10 <sup>5</sup>	Mn x 10 <sup>5</sup>
				(C <sub>2</sub> = 0)	$(c_2 = 0)$				
Chloro- form	2% NaOH	3.42	3.32	1.84	1.87	0,371	0.377	1.40	1.38
Benzene	2% NaOH	1.57	1.52	1.82	1.84	0.423	0.427	1.41	1.40
Acetone	2% NaOH	1.57	1.50	1.80	1.82	0.437	0.439	1.43	1.41
Acetone	Carter and Re- cord	1.72	1.61	1.66	1 <b>.</b> 69	0.432	0.436	1,55	1.52
* Value	s obtained	when -	RTd1 3M1d2	3 c <sub>2</sub> 2	term is not i	included in t	he expi	ession	for
osmot	ic pressur	e due t	o Huggi	in <b>s (1</b> 01	).				

Huggins (76) and Weissberger (103). In the case of Gelva V 45 the omission of this correction is not very serious in the ranges of low concentrations.

For comparative purposes, data obtained for Gelva V 45 in various solvents and different membranes are summarized in TABLE XVII. Errors due to the omission of the  $-\frac{\text{RTd}_1}{3M_1\text{d}_2}$  C2<sup>2</sup>

term in Huggins' expression for osmotic pressure are indicated.

It is clear from TABLE XVII, that the molecular weight of Gelva V 45 in various solvents is identical within 1.5% when caustic treated membranes are used. In the case of Gelva V 45 when a Carter and Record membrane is used, the molecular weight observed is 8.6% greater than that obtained with<sup>8</sup> caustic membrane.

As is evident from Figure 9 and TABLE XVII, the solvent polymer-interaction is almost identical for benzene and acetone solutions of Gelva V 45. The value of  $M_1 = 0.43$  agrees well with  $M_1 = 0.43 - 45$  calculated from the results of Staudinger and Warth (17) and  $M_1 = 0.44$  from that of Wise (104) in the case of polyvinyl acetate in acetone. The value of  $M_1$  for polyvinyl acetate-chloroform from the present work is 0.377. The suggestion of Gee (123), Flory (63), Doty and Zable (73) that the slope of a plot of  $\frac{11}{C_2}$  versus C<sub>2</sub> is a rough measure of the tendency of solute to solvate is borne out in this work in the case of polyvinyl acetate in various solvents. The meaning attached to  $M_1$  by Huggins (101) and Flory (111) has been thoroughly reviewed in the theoretical discussion.

# (3) Osmotic Pressure Determinations on a Series of Polymethyl Methacrylate Fractions

Osmotic pressure measurements were taken in chloroform and 2% caustic treated cellophane membranes were used throughout this phase of the work. Owing to the high molecular of the fractions and consequently the small osmotic pressures observed in centimetres of solvent, the attainment of the utmost accuracy was particularly emphasized in this series. The osmotic pressure data obtained for polymethyl methacrylate NDR 474, NDR 471 and NDR 359 are shown in TABLE XVIII and in graphical form in Figure 10, lines 1, 2 and 4 respectively.

## (4) <u>Osmotic Pressure Determinations on Polymethyl Methacry</u>late Aged in the Presence and Absence of Oxygen

On the basis of viscosity measurements polymethyl methacrylate NDR 359 degenerated to a larger extent than NDR 474 and NDR 471 (c.f. Fig. 7 and 8). The shape of the intrinsic viscosity versus time curve was practically identical with that of NDR 474 and NDR 471. Therefore, for a more complete analysis of the ageing of polymethyl methacrylate, the osmotic pressure determinations were carried out on representative samples of aged NDR 359. The osmotic pressure data for this sample are given in TABLE XIX and represented graphically in Fig. 10, lines 3 and 4.

Although 195 days of ageing in a vacuum caused a marked decrease in viscosity, no change in molecular weight occurred according to osmotic pressure measurements, as shown in

## TABLE XVIII

## Osmotic Pressure Data for a Series of Polymethyl Methacrylate Polymers

Polymethyl Methacry- late	Conc. gm/100 cc.	Osmotic Pressure in cm. of chloroform	$\pi_{gm/cm^2}$		$\frac{\pi}{c_2} - \frac{\mathrm{RTd}_1}{\mathrm{3M}_1 \mathrm{d}_2} \mathrm{3} \mathrm{c_2}^2$
NDR 474 Unaged (Figure 10 Curve No.1)	0.9924 0.6303 0.4007 0.5030 0.8104	1.559 0.729 0.357 0.499 1.081	2.29 1.071 0.525 0.735 1.590	2.312 1.702 1.311 1.461 1.961	2.250 1.677 1.301 1.445 1.920
NDR 471 Unaged (Figure 10 Curve No.2)	0.0 0.3589 0.4508 0.7746 0.3774 0.9866 0.5488 0.0	0.239 0.355 0.913 0.280 1.437 0.511	0.3515 0.522 1.340 0.412 2.11 0.751	0.612 0.979 1.158 1.732 1.091 2.14 1.368 0.390	0.635 0.971 1.146 1.694 1.082 2.08 1.349 0.415
NDR 359 Unaged (Figure 10 Curve No.4)	1.165 0.4970 0.9864 0.6093 0.8295 0.4435 0.0	1.753 0.366 1.312 0.510 0.918 0.302	2.58 0.538 1.931 0.750 1.349 0.444	2.21 1.081 1.955 1.231 1.623 1.000 0.19	2.13 1.066 1.894 1.208 1.580 0.988 0.225

## TABLE XIX

## Osmotic Pressure Data for Aged Polymethyl Methacrylate NDR 359

Lab No.	Treatment g	Conc. m/100 cc.	Osmotic Pressure in cm. of chloro- form	$\pi_{gm/cm^2}$	$\frac{\Pi}{C_2}$	$\frac{\Pi}{C_2} - \frac{\mathrm{RTd}_1}{\mathrm{3M}_1 \mathrm{d}_2} \mathbf{c_2}^2$
NDR 359M	Aged in vacuo 195 days (Figure 10 Curve No.4)	0.5381 0.7469 0.9917 0.5880 0.0	0.414 0.780 1.296 0.473	0.609 1.148 1.905 0.696	1.132 1.534 1.920 1.183 0.19	1.114 1.499 1.858 1.161 0.225
NDR 359L	Aged in Oxygen 15 days (Figure 10 Curve No.3)	0.8048 0.5440 1.0030 0.6658 0.4731 0.0	0.951 0.458 1.404 0.682 0.357	1.400 0.674 2.065 1.001 0.525	1.738 1.238 2.050 1.505 1.111 0.290	1.697 1.219 1.990 1.477 1.097 0.335
NDR 359J	Aged in Oxygen 90 days (Figure 10 Curve No.3)	1.0117 0.5031 0.0	1.443 0.404	2.12 0.595	2.09 1.181 0.290	2.03 1.165 0.335
NDR 359N	Aged in Oxygen 195 days (Figure 10 Curve No.3)	0.5471 1.052 0.0	0.466 1.540	0.686 2.27	1.252 2.15 0.290	1.233 2.08 0.335



Fig. 10

Dependence of Osmotic Pressure on a Series of Polymethyl Methacrylate Polymers

Line	1	NDR 474
Line	2	NDR 471
Line	3	Aged NDR 359 in Oxygen
		Open circle-NDR 359L, aged for 15 days
		Upper half circle filled-NDR 359J, aged for 90 days
		Lower half circle filled-NDR 359N, aged for 195 days
Line	4	Circle filled-NDR 359, unaged
		Circle half filled on right-NDR 359M, aged for 195 days in vacuo

(Following page 110)

Fig. 10, line 4 (circle half-filled on the right). Since the osmotic pressure values for the unaged and the sample aged in vacuo were not distinguishable, they are represented by a common curve in Fig. 10, line 4.

A much greater decrease in viscosity was caused by the presence of oxygen. Two weeks of ageing in the presence of oxygen not only caused a marked lowering in the intrinsic viscosity, but also an appreciable increase in the osmotic pressure. Moreover, subsequent ageing in oxygen up to 195 days showed no change in osmotic pressure, although the intrinsic viscosity had decreased appreciably. Since the osmotic pressure values for the samples aged in the presence of oxygen are not distinguishable, they are represented by a common line in Figure 10, curve 3.

As in the case of Gelva V 45, the negative term in the osmotic pressure expression is evaluated. For comparative purposes the error incurred when this term is omitted is shown in TABLE XX.

#### (5) <u>Calculation of Characteristic Constants</u>

Reference has been made in detail to the use of the characteristic constants  $k^1$  and  $\mathcal{M}_i$ . Both factors are theoretically dependent on the interaction between solute and solvent. Since their theoretical bases are so completely different that they may be used to check each other, TABLE XXI summarizes the  $k^1$ and  $\mathcal{M}_i$  factors for a number of samples studied.

## TABLE XX

Various Characteristic Constants for Polymethyl Methacrylate in Chloroform

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Polymeth <b>yl</b> Methacrylate	Slope*	Slope	$\left(\frac{\pi}{c_2}\right)_{c_2=0}$	$\left(\frac{\pi}{c_2} - \frac{\operatorname{RTd}_1 c_2^2}{\operatorname{3M}_1 d_2^3}\right)_{c_2} =$	<b>µ</b> ₁* =0	Ml	<sup>Mn* 5</sup> x 10	$^{Mn}_{x l0}$ 5
NDR 474 (unaged)	1.71	1.620	0.612	0.635	0.423	0.427	4.20	4.05
NDR 471 (unaged)	1.76	1.680	0.39	0.415	0.422	0.424	6.59	6.19
NDR 359 (unaged)	1.76	1.67	0.190	0.225	0.422	0.424	13,52	11.42
NDR 359M (aged in vacuo 195 days)	1.76	1.67	0.190	0.225	0.422	0.424	13.52	11.42
NDR 359L (ag <b>ed</b> in oxygen 15 days)	1.77	1.67	0.290	0.335	0.421	0.424	8.87	7.68
NDR 359J (aged in oxygen 90 days)	1.77	1.67	0.290	0.335	0.421	0.424	8.87	7.68
NDR 359N (aged in oxygen 195 days)	1.77	1.67	0.290	0.335	0.421	0.424	8.87	7.68

\* Starred values, the correction is excluded.

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#### TABLE XXI

Characteristic Constants of Polymethyl Methacrylate NDR 474, NDR 471 and NDR 359 in Chloroform

Treatment of sample	Mn x 10 <sup>5</sup>	<b>~</b> 1	[7]	k <sub>1</sub>
NDR $474$ unaged	4.05	0.427	4.80	0.369
NDR 471 unaged	6.19	0.424	5.62	0.376
NDR 359 unaged	11,42	0.424	10.06	0.400
Aged 15 days in vacuo			9.70	0.400
Aged 15 days in oxygen	7.68	0 <b>.</b> 42 <b>4</b>	9.19	0.393
Aged 90 days in vacuo			9.59	0.399
Aged 90 days in oxygen	7.68	0.424	8.53	0.401
Aged 195 days in vacuo	11.42	0.424	9.48	0.402
Aged 195 days in oxygen	7.68	0.424	8.13	0.395

No change appears on  $M_1$ , the slight drift in  $k^1$  may be attributed to the slight dependence of  $k^1$  on molecular weight (76). The values of  $M_1 = 0.42$  agrees fairly well with the values of  $M_1 = 0.44 - 0.45$  calculated from the data of Staudinger and Warth (17).

#### TABLE XXII

Treatment of Sample	(7)	$Mn \times 10^5$	β
NDR 474 unaged	4.80	4.05	6.10
NDR 471 unaged	5.62	6.19	5.72
NDR 359 unaged	10.06	11.42	6.58
15 days in oxygen	9.19	7.68	7.20
90 da <b>ys i</b> n oxygen	8.53	7.68	6 <b>.87</b>
195 days in vacuo	9.48	11.42	6.34
195 d <b>ays</b> in oxygen	8.13	7.68	6.67

Evaluation of  $\beta$ <sup>2</sup> for Aged Polymethyl Methacrylate from an Arbitrary K

#### (7) Pressure Changes

In order to investigate further the nature of the change undergone by polymethyl methacrylate during ageing, a sample of NDR 359 was aged in oxygen in a bomb fitted with a small manometer. The change in pressure with time was very small and in contrast to polyvinyl acetate (104) oxygen was absorbed by the polymer. It was also observed visually that mercury from the manometer was distilling off into the flasks. The pressure change test was not very conclusive, therefore.

#### Discussion

#### 1. Osmotic Pressures

It has now been established that the use of a cellulose membrane gasket is inadequate completely to seal an osmometer. The process of leakage has been shown to be caused by the diffusion of solvent through the membrane, rather than by leaks arising from faulty construction of the sealing faces. Presumably, on the basis of this investigation, a similar leak may have been present in all osmometers, used by other workers, which depended on a cellulose membrane gasket to seal the osmometer. Consequently, it is necessary to consider critically all osmotic data determined by other workers on osmometers using cellulose membranes as the packing material against leakage in order to determine to what extent credence may be given them.

In spite of the fact that there is sufficient evidence of leakage to be found in the literature, there is also occasional evidence of a surprising degree of consistency of results. For example, Flory (63), in one case, presented determinations on a sample of polyisobutylene in cyclohexane, carried out by using membranes, both of denitrated collodion and of cellophane, which agreed within 3%. Fuoss and Mead (119) reported osmotic pressures which checked ultracentrifuge data within 2%. Finally, the results of McIntosh et al (69) on Gelva V 45, determined by means of a dynamic osmometer sealed with a caustic treated membrane gasket, are within 2% of the value obtained with the

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improved osmometer.

On the other hand, an examination of the results of Fuoss and Mead (121) showed that the osmotic pressure curve determined by using a horizontal capillary is straight, whereas, by using a vertical capillary it is curved. There is a difference of 25% in slope for two fractions of polymethyl methacrylate in chloroform calculated from the data of Staudinger and Warth (140).

Many workers (119, 122, 120 etc.) recognized the need for a zero point correction factor, although they attributed it to various causes rather than leakage through the membrane. The accuracy of the results, therefore, is dependent on the care with which this factor was determined. Such a method could conceivably yield osmotic pressures of a high degree of accuracy. By this means, McIntosh and co-workers (69) obtained results with a van Campen type of dynamic osmometer which are in excellent agreement with the improved osmometer in spite of the leakage at the cell face. In general, however, it is unavoidable that some uncertainty should be introduced by the use of zero point corrections. It is not certain that a zero point, once determined, would remain constant, because other factors must be considered.

(1) For example, if diffusion from the solution side is dependent on the viscosity of the solution, the zero point correction, determined with pure solvent on both sides, would be invalidated. Similarly, if the rate of diffusion of liquid out of the cell is dependent on the height of solvent in the

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capillaries, the error introduced by the leak would be dependent on the osmotic pressure. This is unlikely, as the rate of leak observed in this work was not affected by an opposing hydrostatic head of the thermostating media.

(2) The zero point correction might change. As Lossing (120) stated, the zero point can be altered by tightening the outer bolts on the osmometer. Such an occurrence might elucidate the discrepancy in the results of Bartovics and Mark (65) where all curves of  $\frac{\pi}{C}$  versus C with the exception of one, have the same slope. Such an exception might be due to a change in leak.

(3) The determination of a zero point correction may be rendered inadequate owing to the presence of bubbles.

In this work, the criteria for acceptable osmotic pressure measurements are:

(a) The observed osmotic pressure must remain constant over periods of several hours.

(b) The same value must be attained when equilibrium is approached from either side.

(c) At equilibrium, the individual levels must remain constant. A drop of 0.01 cm. per hour, as a result of evaporation, is permissible.

Although the improved osmometer is accurate, yet it proved tedious in operation. Most of this difficulty has been caused by the time required to remove bubbles. A gold-plated cell shown in Figure 11 has been used in the latter stages of the investigation. This cell is equipped with a flooding ridge, thus requiring only one person to assemble it. The cell face is similar to that shown in Figure 3. Attention is drawn to the imprint of the sealing faces on the composition foil annulus. It may also be seen from the ridge marks on the membrane, that it was held rigidly in place. The gold-plated cell was found to be much superior in operation because of the less frequent appearance of bubbles. For this reason, osmometers made from non-corrosive metals should be less tedious in operation. However, an improvement could be made on this type of osmometer by having vertical instead of concentric ridges and grooves. It is conceivable that trapped bubbles could be removed immediately after filling the half-cell compartments. Bubbles that arise from the solvent at the higher temperature of the thermostat, would appear in the capillaries, without remaining trapped in the various sections within the cell.

#### 2. Membranes

It has been demonstrated by McIntosh and co-workers (69) and redetermined in this investigation that adsorption of polymer is observed when membranes are made by the Carter and R<sup>o</sup>cord method. The molecular weight thus obtained is not in agreement with that obtained when caustic treated membranes are used. The reason for this discrepancy is not definitely known.

The osmotic pressure measurements obtained with the improved osmometer are considered as giving dependable molecular weights when caustic treated membranes are employed. The logic of this conclusion is based on the following factors: (1) Inappreciable amounts of adsorption take place on caustic treated membranes.

(2) Identical molecular weights were obtained for GelvaV 45 in chloroform, benzene and acetone.

(3) The ratio  $\frac{\pi}{C}$  of osmotic pressure to concentration has been found, in the case of polymethyl methacrylate, to vary linearly with concentration in agreement with recent theories advanced by Huggins (97) and Flory (71). In addition, the slopes of the lines as shown in Figure 10 and TABLE XX are the same within experimental error. This is in contrast to the lines obtained by Staudinger and Warth (140) on polymethyl methacrylate in chloroform where, in some cases, a variation of 25% in slope has been calculated.

The precise form of the  $\frac{\tau r}{C_2}$  versus  $C_2$  extrapolation to zero concentration has been subject to controversy. Thus Meyer and co-workers (84) draw a straight line for the system rubber - toluene. Gee and Treloar (108) obtained lines with upward curvature for the system rubber - benzene. Mark and coworkers (64) find the relationship to be linear for polystyrene in toluene when the polystyrene has been prepared above 100°, but curved upwards when prepared at 60° C. Flory (63) found upward curvature for the system polyisobutylene in cyclohexane. In the latter case, it appears as if a straight line could be drawn through all the points. If this were the case, the agreement in molecular weight of polyisobutylene in benzene and in cyclohexane in the case of the high molecular weight fractions would be doubtful. According to Huggins (76), Flory's (63) osmotic pressures of polyisobutylene in cyclohexane may be cited as an example of an instance in which the negative term in Huggins' expression for osmotic pressure is not negligible. Needless to say, when this correction was applied, straight lines were obtained. This may be true of other upward curved lines reported by other workers.

The writer feels that if adsorption takes place on the surface of the membranes and osmotic determinations are made in the order of increasing concentrations, a line concave upwards arises. This is true only when the adsorption effects have not been satisfied. It is conceivable, however, that if osmotic pressures are carried out in order of decreasing concentrations, a straight line would be obtained, as subsequent  $\frac{\pi}{c_2}$  values would be determined on an accommodated membrane.

#### 3. Ageing of Polymethyl Methacrylate

As predicted by McIntosh et al(138) dispersion in a solvent is not a necessary step for the degeneration of polymers. Moreover, the magnitude of the changes of solid polymers is, in many cases, of approximately the same order as for those aged in solution (2). The changes in viscosity with time are more clearly shown in Figures 7, 8 and 10 in the preceding section.

As anticipated from the work of McIntosh and co-workers (3,4,5,6) and others (22,27,28 etc.) the changes in oxygen were much greater than for polymers aged in vacuo. Morrison (3) has shown that oxygen does not act merely as a catalyst, but is used up in the ageing process. The samples aged in vacuum, such as NDR 474 and NDR 471, did not change very much in intrinsic viscosity. The drop was within the experimental error in the case of NDR 474, but slightly beyond it in NDR 471. However, the viscosity of NDR 359 dropped markedly. The inference was that the lower molecular weight fractions, according to viscosity measurements, are more stable to ageing in vacuo.

The changes in intrinsic viscosity for all the polymers aged in oxygen were marked, but greatest for NDR359 and least for NDR 474. A similar behaviour was observed by Wise (104) on aged solid polyvinyl acetate polymers under the same conditions. Naunton (27) found that rubber photogels in excess oxygen degraded to a limiting viscosity.

Osmotic pressure determinations on the aged NDR 359 polymer indicated that no change in molecular weight occurred in the case of the sample aged in vacuo for the longest period of time, although a marked decrease in intrinsic viscosity was observed. Furthermore, the same polymers aged in oxygen for two weeks increased in osmotic pressure. Hence a lower molecular weight was No further change in molecular weight was observed obtained. with subsequent ageing even up to 195 days, whereas the intrinsic viscosity continued to decrease beyond two weeks of ageing, but became almost constant beyond three months in the presence of This behaviour strongly suggests two processes taking oxygen. place, namely, change in the geometrical configuration of the polymer, without suffering variations in  $k^{\perp}$  and secondly, some

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type of bond rupture.

The first process is in agreement with Morrison's (3) hypothesis that viscosity changes can be explained as changes in their geometric form and flexibility. This, however, does not affect the number average molecular weight which involves the number of molecules in a given concentration.

The second process, which evidently takes place predominantly in the presence of oxygen, leads directly to the hypothesis that long chain polymers possess, at certain points along the chain, bonds which are weaker than normal. When enough energy is accumulated at these particular bonds (141) chain splitting takes place. This is in contrast to the assumptions of Mark and Simka (31, 142) that all bonds are of equal strength. Jellinek (30), however, arrived at a similar conclusion. The exact nature of these weak links is, as yet, undecided.

The constancy of the characteristic constants,  $k^{\perp}$  and  $\mathcal{M}_{1}$  (TABLE XXI) indicated that major changes in solute - solvent interaction do not take place. The sensitivity of these two constants is rather dubious. The hydrodynamic constant  $k^{\perp}$  is identical for benzene and chloroform solutions of polymethyl methacrylate, although the intrinsic viscosities in the two solvents are markedly different. Similarly  $\mathcal{M}_{1}$  is also insensitive since a variation of 25% in the slope of  $\frac{\Pi}{C}$  versus C causes a variation of 2.5% in the value of  $\mathcal{M}_{1}$ . In addition,  $\mathcal{M}_{1}$  may be slight-ly dependent on concentration (76) and on molecular weight (111).

These effects have not been observed in this work. Also  $k^{1}$  may be slightly dependent on molecular weight (76, 7). This is evident from TABLE XXI.

The calculation of  $\beta^2$ , however, is based on assumptions of an initially symmetrical distribution of the form expressed by the Lansing and Kraemer formula (1), discussed in a previous section. In addition, it assumes that in the case of degraded samples, the symmetry of distribution is retained. This is incompatible with the concept of an initial preferential split of one fraction of the polymer and secondly, a change in shape of the filament molecule. Therefore, owing to the irregularities in the ageing process, the  $\beta^2$  factors determined here as shown in TABLE XXII are doubtful.



Gold-plated Osmometer

#### CLAIMS TO ORIGINAL WORK AND CONTRIBUTIONS TO KNOWLEDGE

(1) A source of error was found in osmometers described in the literature which used treated cellulose sheets which acted both as a membrane and gasket to seal the osmometer. This error was found to be caused by diffusion of solvent through the periphery of the cellulose membrane in a manner independent of an opposing hydrostatic head of oil or water. A new osmometer was developed to permit the use of "composition" foil gaskets to completely seal the membrane from the thermostating media.

(2) Techniques were developed for investigating the changes in polymethyl methacrylate when aged in the presence and absence of oxygen. Bombs were constructed and utilized along with an apparatus for evacuating them or filling them with gases.

An apparatus was designed for determining the pressure changes during ageing.

(3) An osmometer was attempted employing copper ferrocyanide membranes impregnated on sintered glass for use in organic solutions of macromolecules.

(4) By viscometric and osmometric investigation of aged polymethyl methacrylate, it was found that:

- (a) Dispersion in a solvent is not required for viscosity changes in polymethyl methacrylate.
- (b) The major viscosity changes are due to changes in molecular weight of the polymer.
- (c) Oxygen is effective in splitting chains of polymethyl methacrylate.
- (d) Ageing in vacuo with heat is effective in changing the shape of polymethyl methacrylate.
- (e) Ageing in the presence of oxygen causes a scission of the chains and also a change in shape for the polymethyl methacrylate molecules.
- (f) The chains of polymethyl methacrylate split predominantly at a few weak links.
- (g) Viscometric changes in the aged samples is greater in the case of the long chain members.

(5) Adsorption on Carter and Record type of cellulose membranes was confirmed with the improved osmometer.

(6) Osmometers having a non-corrosive surface are less tedious in operation.

# REFERENCES

(1)	Kraemer E.O. and Lansing W.D., J. Am. Chem. Soc. <u>57</u> 1369 (1935)
(2)	Schulz G.V. and Dinglinger A., J. Prakt. Chemie, <u>158</u> , 136 (1941)
(3)	Morrison J.A., Thesis, McGill University (1943)
(4)	Grummitt W.E., Thesis, McGill University (1943)
(5)	Holmes J.M., Thesis, McGill University (1944)
(6)	McIntosh R. and Morrison J.A., McGill University,
(7)	Robertson R.E., Thesis, McGill University (1944)
(8)	Mark H. and Raff R., High Polymeric Reactions, Inter- science (1941)
(9)	Pauling L., The Nature of the Chemical Bond, 2nd Ed., Ithaca (1940)
(10)	Mark H., High Polymers, Vol. II, P207, Interscience (1940)
(11)	Melville H.W., Trans. Far. Soc. <u>40</u> , 217 (1944)
(12)	McBain J.W. and McBain M.E., J. Am. Chem. Soc. <u>59</u> , 342 (1937)
(13)	Staudinger H., Die Hochmolekularen Organischen Verbindungen, Julius Springer (1932)
(14)	Kraemer E.O., Ind. Eng. Chem. <u>30</u> , 1200 (1938)
(15)	Dobry A., J. Chim. Phys. <u>31</u> , 568 (1934) <u>32</u> , 50 (1935)
(16)	Gee G., Trans. Far. Soc. <u>40</u> , 261 (1944)
(17)	Staudinger H. and Warth H., J. Prakt. Chem. 155, 261 (1940)
(18)	Kemp J.D. and Pitzer K.S., J. Chem. Phys. <u>4</u> , 749 (1936)
(19)	Kistiakowsky G.B. and Nazmi F., J. Chem. Phys. <u>6</u> , 18 (1938)
(20)	Kauzmann W. and Eyring H., J. Am. Chem. Soc. 62, 3113 (1940)

(21)Powell R.E., Clark C.R. and Eyring H., J. Chem. Phys. 9, 268 (1941) (22)Blaikie K.G. and Crozier R.N., Ind. Eng. Chem. 28 1155 (1936) (23)Mead D.J. and Fuoss R.M., J. Am. Chem. Soc. 64, 277 (1942) (24)Jirginson B., J. Prakt. Chem. 160, 21 (1942) (25)Bartell F.E. and Cowling H., Ind. Eng. Chem. 34, 607 (1942) Burk R.E. and Grummitt O., The Chemistry of Large (26)Molecules, Interscience (1943); Chapt. VIII Ott E., The Chemistry of Cellulose and Cellulose Derivatives (27)Naunton W.J.S., Trans. Far. Soc. 38, 332 (1942) (28)Tobolsky A.V., Andrews R.D. and Mesrobian R.B., Princeton University, Report No. CR-227, Dec. 6, 1943 (29) Simha R., J. App. Phys. 12, 569 (1941) (30)Jellinek H.H.G., Trans. Far. Soc. 40, 266 (1944) (31)Mark H. and Simha R., Trans. Far. Soc. 36, 611 (1940) (32)Simond and Ellis, Handbook of Plastics, D. Von Nostrand (1943), P500 (33) E.I. Dupont de Nemours and Co., Ind. Eng. Chem. 28, 1160 (1936) (34)Schulz G.V. and Blaschke F., J. Prakt. Chem. 158, 130 (1941) Einstein A., Ann. Physik., (4) 19, 289 (1906) (35) ibid 34, 591 (1911) (36)Staudinger H. and Heuer W., Ber. Dtsch. Chem. Ges., 63, 222 (1930) (37) Mark H., High Polymers, Vol. II, P277 et seq., Interscience (1940)(38) Berl E., Z. ges. Schiess, u. Sprengstoffw 5, 82 (1910) Biltz W., Z. physik. Chem. 73, 481 (1910) 83, 625, 683 (1913) (39)(40)Staudinger H. and Schulz G.V., Ber. Dtsch. Chem. Ges., <u>68</u>, 2320 (1935)

(41)	Schulz G.V. and Husemann E., Z. physik Chem., <u>B36</u> , 184 (1937)
(42)	Dobry A., J. Chim. Phys. <u>32</u> , 882 (1935)
(43)	Kraemer E.O. and Van Natta F.J., J. Phys. Chem. <u>36</u> , 3175 (1932)
(44)	Meyer K.H. and van der Wyk, Helv. Chim. Acta, <u>18</u> , 1067 (1935) <u>19</u> , 218 (1936)
(45)	Jefferey G.B., Proc. Roy. Soc. Lon., <u>A102</u> , 161 (1923)
(46)	Eisenschitz R., Z. physik.Chem. <u>A158</u> , 78 (1931)
(47)	Eisenschitz R., Z. physik. Chem. <u>A163</u> , 133 (1933)
(48)	Kuhn W., Z. physik. Chem. <u>A161</u> , 1 (1932)
(49)	Boeder P., Z. physik. Chem. <u>75</u> , 258 (1932)
(50)	Huggins M.L., J. Phys. Chem. <u>42</u> , 911 (1938)
(51)	Kuhn W., Angew Chem. <u>49</u> , 858 (1936)
(52)	Huggins M.L., J. Phys. Chem. <u>43</u> , 439 (1939)
(53)	Huggins M.L., J. App. Phys. <u>10</u> , 700 (1939)
(54)	Huggins M.L., J. Am. Chem. Soc. <u>64</u> , 2716 (1942)
(55)	Huggins M.L., J. App. Phys. <u>14</u> , 246 (1943)
(56)	Haller W., Kolloid-Z, <u>56</u> , 257 (1931)
(57)	Fordyce R. and Hibbert H., J. Am. Chem. Soc. <u>61</u> , 1910 (1939)
(58)	Fordyce R., Lovell E.L. and Hibbert H., J. Am. Chem. Soc. <u>62</u> , 2140 (1940)
(59)	Flory P.J. and Stickney P.B., J. Am. Chem. Soc. <u>62</u> , 3032 (1940)
(60)	Mark H., Z. Electrochem, <u>40</u> , 449 (1934)
(61)	Mark H., Der feste Korper, S. Hirzel, Leipzig (1938) P102 et seq.
(62)	Houwink R.J., J. Prakt. Chemie <u>157</u> , 15 (1940)

(63) Flory P.J., J. Am. Chem. Soc. <u>65</u>, 372 (1943) (64)Alfrey T., Bartovics A. and Mark H., J. Am. Chem. Soc. <u>65, 2319 (1943)</u> Bartovics A. and Mark H., J. Am. Chem. Soc. 65, 1901 (1943) (65)(66)Simha R., J. Phys. Chem. 44, 25 (1940) (67) Guth E., Phys. Rev. 53, 322 (1938) (68) Staudinger H. and Heuer W., Z physik Chem. A171, 129 (1934) (69) Robertson R.E., McIntosh R. and Grummitt W.E., Can. J. Research B24, 150 (1946) (70) Alfrey T. Bartovics A. and Mark H., J. Am. Chem. Soc. 64, 1557 (1942) Flory P.J., J. Chem. Phys. 10, 51 (1942) (71)(72)Simha R., J. Chem. Phys. 13, 188 (1945) Doty P., Zable H.S., J. Polymer Sci. I, 90 (1946) (73) (74)Frith E.M., Trans. Far. Soc. 41, 17 (1945) (75) Spurlin H.M., Polymer Bull. 1, 74 (1945) (76)Huggins M.L., Ind. Eng. Chem. 35, 980 (1943) (77)Svedberg T., Chem. Rev. 14, 1 (1934) (78) Morse H.N. and Frazer J.C.W., Am. Chem. J. <u>34</u>, 1 (1905) 38, 212 (1907) (79)Earl of Berkley and Hartley E.G.J., Phil. Trans. Roy. Soc. London, <u>A206</u>, 486 (1906) (80)Butler J.A.V., The Fundamentals of Chemical Thermodynamics, MacMillan London P103 (81)Glasstone S., A Textbook of Physical Chemistry, Van Nostrand, New York (1940) P645 (82) MacDougall F.H., Thermodynamics and Chemistry, John Wiley and Sons, New York (1939) P148-149 (83) Mark H., High Polymers Vol. II, Interscience New York

(1940) P228-45

130.

- Meyer K.H. and Wertheim A., Helv. Chim. Acta <u>24</u>, 217 (1941)
  Meyer K.H., Wolff E. and Boissonnas, ibid 23, 430 (1940)
- (85) Ostwald W., Kolloid-Z 49, 60 (1929)
- (86) Schulz G.V., Z. physik. Chem. A158, 237 (1931)
- (87) Stamberger P., J. Chem. Soc. A 2318 (1928)
- (88) Huggins M.L., J. Phys. Chem. <u>46</u>, 151 (1942)
- (89) Huckel E., Zeits fur Elektrochem. 42, 753 (1936)
- (90) Guggenheim E.A., Proc. Roy. Soc. A135, 181 (1932)
- (91) Guggenheim E.A., ibid A148 304 (1935)
- (92) Fowler R.H. and Rushbrooke G.S., Trans. Far. Soc. <u>33</u> 1272 (1937)
- (93) Mark H., Physical Chemistry of High Polymeric Systems, Interscience (1940) P217
- (94) Meyer K.H., Helv. Chim. Acta 23, 1063 (1940)
- (95) Flory P.J., J. Chem. Phys. 9, 660 (1941)
- (96) Huggins M.L., J. Chem. Phys. 9, 440 (1941)
- (97) Huggins M.L., Ann. N.Y. Acad. Sci. 43, 1 (1942)
- (98) Van Laar J., Z. physik. Chem. A137, 421 (1928)
- (99) Hildebrand J.H., Chem. Rev. 18, 315 (1936)
- (100) Scatchard G., Chem. Rev. 8, 321 (1931)
- (101) Huggins M.L., Ann. N.Y. Acad. Sci. 44, 431 (1943)
- (102) Huggins M.L., Ind. Eng. Chem. 35, 216 (1943)
- (103) Weissberger A., Physical Methods of Organic Chemistry Vol. I, Interscience (1945) P254 et seq.
- (104) Wise, L.M., Thesis, McGill University (1946)
- (105) Gee G., Trans. Far. Soc. 36, 1171 (1940)
- (106) Carter S.R. and Record B.R., J. Chem. Soc. 660, 664 (1939)

- (107) Hoff E.A.W., Trans. Far. Soc. 40, 233 (1944)
- (108) Gee G. and Treloar, Trans. Far. Soc. 38, 147 (1942)
- (109) Dobry A., Koll-Z. 81, 190 (1937)
- (110) Flory P.J., J. Chem. Phys. 12, 425 (1944)
- (111) Flory P.J., J. Chem. Phys. 13, 453 (1945)
- (112) See reference 8, P56
- (113) Bingham E.C., Fluidity and Plasticity, McGraw-Hill (1922) P75
- (114) Van Campen, Rec. Trav. Chim. 50, 915 (1931)
- (115) Boissonnas C. and Meyer K.H., Helv. Chim. Acta, 20, 783 (1937)
- (116) Obogi R. and Broda E., Kolloid-Z 69, 172 (1934)
- (117) Schulz G.V., Z. physik Chem. A176, 317 (1936)
- (118) Jullander I., Archiv fur Kemi 21A, N:08 (1945)
- (119) Fuoss R.M. and Mead D.J., J. Phys. Chem. 47, 59 (1943)
- (120) Lossing F.P., "Weight and Shape of Polymer Molecules", Shawinigan Chemicals Ltd., Research Laboratories Memorandum Sept. (17-21) 1945
- (121) See reference 119, P68, Fig. 4
- (122) Foster J.F. and Hixon R.M., J. Am, Chem. Soc. 66, 557 (1944)
- (123) See ref. 105, P1162, et seq.
- (124) Sookne A.M. and Harris M., Res. N.B.S. (U.S.) 34, 459 (1945)
- (125) Madras S., McGill University, Private Communication
- (126) Sligh T.S., J. Am. Chem. Soc. <u>42</u>, 60 (1920)
- (127) Bjerrum N. and Manegold E., Kolloid-Z <u>43</u>, 5, (1927)
- (128) Manegold E. and Hoffman R., Kolloid-Z, 50 (22-39) (1930)
- (129) Montonna R.E. and Jilk L.T., J. Phys. Chem. 45, 1374 (1941)
- (130) Buchner E.H. and Samwell P.J.O., Trans. Far. Soc. <u>29</u>, 32 (1933)
- (131) Morton T.H., Trans. Far. Soc. <u>31</u>, 262 (1935)
- (132) Purves C.B., McGill University, Private Communication
- (133) McBain J.W. and Kistler S.S., Trans. Far. Soc. <u>26</u>, 157 (1930)
- (134) Pfeffer W., Osmotische Untersuchungen, Leipzig (1877)
- (135) Morse H.N., Carnegie Inst. Wash. Pub. 198, 1 (1914)
- (136) Murray N.J., J. Phys. Chem. <u>33</u>, 896 (1929)
- (137) McLeod L.A., National Research Council, Private Communication
- (138) Holmes J.M., Morrison J.A., McIntosh R.L., McGill University unpublished results.
- (139) Schulz G.V. and Gertrud Sing, J. Prakt. Chem. 161, 161 (1943)
- (140) See reference 17, P288, table 21
- (141) Hinshelwood C.N., Kinetics of Chemical Change, Oxford, 1940, P79
- (142) See reference 93, P327