STUDIES ON OSMOMETRY OF POLYMER SOLUTIONS

H. BENNINGA

STUDIES ON OSMOMETRY OF POLYMER SOLUTIONS

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WIS- EN NATUURKUNDE AAN DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFICUS Mr J. M. VAN BEMMELEN, HOOGLERAAR IN DE FACULTEIT DER RECHTSGELEERDHEID, TEGEN DE BEDENKINGEN VAN DE FACULTEIT DER WIS- EN NATUURKUNDE TE VERDEDIGEN OP WOENSDAG 24 FEBRUARI 1954, TE 16 UUR

DOOR

HARM BENNINGA

GEBOREN TE SLOCHTEREN IN 1924

UITGEVERIJ EXCELSIOR — 's-GRAVENHAGE

PROMOTOR: PROF. DR J.J. HERMANS

ERRATUM

All osmotic pressures π in fig. 6, Ch. IV, were expressed in cm toluene, except those of fractions D8 and D9, which by mistake were expressed in cm water. The points concerned must therefore be discarded. The calculations of which the results are given in table XXIV, have all been done on the assumption that π was expressed in cm toluene. Accordingly the figures referring to fractions D8 and D9 in table XXIV should be read:

Nr of fraction	Indication in text	$\lim_{c \to o} \pi/c$	A_2	$10^{-3} M_n$	$[\eta]$	$10^{-3} M_\eta$
5	D8	2.33	0.98	130	66	132
6	D9	0.91	0.80	320	114	260

Similarly the last equation in chapter IV:

$$\pi/c = 0.79 + 0.69\ c + 0.48\ c^2$$

must be replaced by:

$$\pi/c = 0.92 + 0.80\ c + 0.56\ c^2.$$

TABLE OF CONTENTS

This research was carried out as part of the program of the Foundation for Fundamental Research of Matter (FOM), supported financially by the Netherlands Organization for Pure Research (ZWO).

Chapter I

INTRODUCTION

For a chemist one of the most interesting properties of matter is that it is built up of molecules. The determination of the weight of these molecules is, therefore, important in nearly every field of chemistry. Among the various methods which permit an evaluation of molecular weights, a predominant role is played by methods in which the number of molecules in a given sample is "counted". Those properties of compounds which are mainly governed by the number of molecules present, are called colligative properties.

The domain of the colligative properties is the solution, particularly the dilute solution which has many properties that depend mainly on the number of dissolved molecules. The clearest expression of a colligative property may be found in RAOULT's law on the lowering of the vapour pressure (p) of a solution compared with the vapour pressure of the solvent (p^o),

$$(p^o - p)/p^o = x_2 ,$$

where x_2 is the mole fraction of the solute. Nowadays, solutions which obey RAOULT's law are called ideal solutions. At infinite dilution all solutions obey RAOULT's law.

The methods commonly employed for the determination of molecular weights from colligative properties in the low molecular weight region are the lowering of the freezing point and the elevation of the boiling point. The effects to be measured in these methods as well as that of the vapour pressure lowering are too small, however, for substances that have molecular weights above 1,000 – 10,000. Fortunately, the osmotic pressure is a much larger effect. The range of molecular weights which can be determined is extended by this method to molecular weights of about 1,000,000. The osmotic pressure is, therefore, a very important property of polymer solutions.

The osmotic pressure of an ideal solution is given by

$$\pi = - \Delta g_1/v_1 = -(RT/v_1).\ln(1-x_2) ,$$

where Δg_1 is the free energy of dilution and v_1 the partial molar volume of the solvent. Expanded in powers of x_2:

$$\pi = (RT/v_1)x_2 + (RT/2v_1)x_2^2 \ldots\ldots$$

For $x_2 \ll 1$ this yields VAN 'T HOFF's law:

$$\pi = (RT/v_1)x_2 = (RT/M_2)c,$$

where c is the weight concentration and M_2 the molecular weight of the solute. It is obvious that for large values of M_2 the second term of the series is very small, even at high weight concentrations. Most polymer solutions, however, show large deviations from ideal behaviour. Whereas in the low molecular weight region a single cryoscopic determination is sufficient for the calculation of the molecular weight *), this is by no means true for the osmotic pressure determination in a polymer solution. Cases in which a one percent solution has an osmotic pressure twice VAN 'T HOFF's value are by no means exceptional. It is necessary, therefore, to determine the osmotic pressures of a number of solutions of different concentrations and to extrapolate the reduced osmotic pressure (π/c) to zero concentration. The extrapolation procedure for solutions of non-electrolytes is well established, since MCMILLAN and MAYER have proved that π can be expressed in a convergent power series in c:

$$\pi = (RT/M_2)c + A_2c^2 + A_3c^3 \ldots\ldots$$

where the coefficient A_2, A_3 ..... are the so-called virial coefficients of the osmotic pressure. In the case of polymer solutions these virial coefficients are a measure of the deviation from ideal behaviour.

These deviations are primarily due to the large dimensions of the dissolved macromolecules in comparison with the dimensions of the solvent molecules. A calculation of the influence of molecular size on the thermodynamic properties of the mixture can be carried out by means of the methods of statistical mechanics.

A simple model of a liquid mixture is the quasi-lattice model. For a mixture of two kinds of molecules which have identical force fields (athermal mixtures), the entropy of mixing can be calculated from the number of distinct configurations of the molecules on the lattice. For ideal mixtures, i.e. athermal mixtures in which the two kinds of molecules are of equal size, the entropy of mixing is

$$\Delta S_{id.} = -R(n_1 \ln x_1 + n_2 \ln x_2),$$

where n_1 and n_2 are the number of solvent and solute molecules respectively.

*) The accuracy of the molecular weight determination in the low molecular weight region is usually rather small. This is, in general, not important, because the purpose of such a determination is only to confirm whether the elementary formula or a multiple of it is the correct molecular weight.

The first calculations for solutions of macromolecules have been performed by FLORY and HUGGINS who found for the entropy of mixing

$$\Delta S_{ath.} = -R(n_1 \ln\varphi_1 + n_p \ln\varphi),$$

where φ_1 and φ are the volume fractions of the solvent and the polymer, respectively, and n_p the number of polymer molecules. FLORY and HUGGINS calculated the entropy from the number of distinct configurations when arranging the solvent molecules and polymer segments of the same size on the sites of the lattices.

Although the simple quasi-lattice theory is very successful in explaining the thermodynamic properties of polymers in solution, it shows several shortcomings in the quantitative description of dilute solutions. A discussion of the quasi-lattice theory, particularly with regard to the second virial coefficient of osmotic pressure is given in chapter II. A weak point in the quasi-lattice theory is the quasi-lattice model itself. Quite another theory, which is based on the description of a solution as a continuous solvent in which distinct solute particles are dissolved, is outlined in the same chapter.

Osmotic pressure measurements are, consequently, not only interesting because they reveal the molecular weight of the dissolved polymer, but also because they give information on an important thermodynamic property of the polymer solution.

The establishment of osmotic pressures can be performed by dynamic as well as static methods. The latter methods are, in general, more reliable. If diffusion through the membrane occurs, however, neither of the two methods can give a good result. The dynamic value, obtained in such a case, depends markedly on whether it is reached from an initial pressure difference higher or lower than the equilibrium osmotic pressure. A static value, in case of diffusion, can be obtained only by extrapolating to the time of filling of the osmometer, because the pressure difference does not become constant. It has been shown by STAVERMAN, however, that this extrapolated value cannot be regarded as the osmotic pressure of the solution. An outline of STAVERMAN's theory which is based on the thermodynamics of irreversible processes is given in chapter II.

In the experimental part (chapter III) considerable attention is paid to the main limiting factor in osmotic pressure determinations: the membrane. Several methods for the characterization of membranes are considered, partly in conjunction with their behaviour in dialysis and ultrafiltration experiments. The lowest

molecular weights which can be measured with the membranes commonly employed are between 10,000 and 30,000.

For osmotic pressure determinations two types of osmometers are used: osmometers of the ZIMM-MYERSON type and of the FUOSS-MEAD type. The first type of osmometer has several advantages, of which the greater accuracy is the most important. A number of osmotic pressure determinations is reported (chapter IV), molecular weights and second virial coefficients are calculated for several polystyrene fractions, for sodium carboxy methyl cellulose, polymethacrylic acid and polyvinyl alcohol.

The fractionation of polymers for osmometry is of great importance, because of the difficulties arising when low molecular weight material is present. For polystyrene a gel-extraction method is employed, which proves to be very successful.

Chapter II

THEORY OF OSMOTIC PRESSURE

II.1. Thermodynamics

The osmotic pressure of a solution which is separated from its solvent by a semipermeable membrane, is the excess pressure which must be applied to the solution in order that the transport of solvent in the two directions through the membrane is the same [1]. In terms of thermodynamics:

The osmotic pressure of a solution which is separated from its solvent by a semipermeable membrane, is that excess pressure on the solution at which the partial molar Gibbs free energies of all permeating components are the same on the two sides of the membrane.

For two phases α and β composed of σ components and separated by a semipermeable membrane we have therefore in equilibrium:

$$g_i' = g_i''$$

where the phases α and β are denoted by one and two primes, respectively. As we are dealing with an isothermal system, this may be written:

$$g_i(p', x_s') = g_i(p'', x_s''), \qquad (1)$$

where the pressures on the two sides of the membrane are p' and p'', and x_s' and x_s'' indicate the mole fractions of all the components present. Now the partial molar volume of component i in the phase provided with a double prime is given by

$$v_i'' = (\partial g_i/\partial p)_{T, x_s},$$

where the double prime indicates that this molar volume refers to the mixture in which the concentrations are x_s''.
Eq. (1) may thus be replaced by

$$g_i(p', x_s') = g_i(p', x_s'') + \int_{p'}^{p''} v_i''\, dp\ ; \qquad v_i'' = v(p, x_s''). \qquad (2)$$

Introducing the activity coefficients f_i, the relation between the free energy and the mole fraction of component i can be written in the form

$$g_i(p, x_s) = g_i^\circ(p) + RT \ln x_i f_i,$$

where g_i° is independent of the concentrations. Hence eq. (2) gives

$$\int_{p'}^{p''} v_i'' dp = - RT \ln (x_i'' f_i'' / x_i' f_i'). \tag{3}$$

Since the compressibility of nearly all liquids is very small, the integral on the left hand side of eq. (3) can almost always be replaced by $v_i''\pi$, where $\pi = p'' - p'$, and where v_i'' is the partial molar volume of component i when the concentrations are x_s'', at any pressure between p' and p''. If, moreover, the concentrations of the non-permeating components are low, it is permissible to replace v_i'' by v_i, this being the partial molar volume at any arbitrary set of concentrations lying between x_s' and x_s'':

$$v_i \pi = - RT \ln (x_i'' f_i'' / x_i' f_i'). \tag{4}$$

We shall now apply the results obtained to specific cases.

1. Consider a solvent (phase α) in osmotic equilibrium with a solution (phase β). The solvent is permeating, the solute is not. Eq. (4) simplifies to

$$v_1 \pi = - RT \ln (x_1'' f_1'' / f_1'), \tag{5}$$

where the subscript 1 denotes the solvent. The difference between the molar free energy of component 1 in the solution and that in the pure solvent, i.e., the free energy of dilution Δg_1, is seen to be related to the osmotic pressure:

$$\Delta g_1 = g_1(p', x_2'') - g_1(p', 0) \cong - \pi v_1. \tag{6}$$

When x_2'' approaches zero, the ratio f_1''/f_1' is known to approach unity at a rate which is proportional to a power of x_2'' higher than the first (ideal solution).
Hence

$$\lim_{x_2 = 0} \pi / x_2 = RT / v_1.$$

Making use of the fact that in very dilute solutions the concentration of the solute in weight per volume is given by

$$c = x_2 M_2 / v_1,$$

we may write also (VAN 'T HOFF's law):

$$\lim_{c=0} \pi / c = RT / M_2. \tag{7}$$

The quantity π/c is called reduced osmotic pressure.

2. If Δg_1 is determined as a function of T by performing osmotic measurements at various temperatures, the heat of dilution Δh_1 can be found by means of the relation of GIBBS-HELMHOLTZ and,

hence, all other partial molar thermodynamic quantities of the solvent can be calculated as well. The corresponding quantities of the solute can be obtained by means of DUHEM – MARGULES relations.

In practice, however, the precision with which these other quantities can be calculated is much lower than the precision of the primarily determined free energy of dilution.

3. Solutions of long chain molecules have properties which are quite different from those of ideal solutions. It has been shown (see next section) that this has no influence on the limiting value of the reduced osmotic pressure. The departures from VAN 'T HOFF's law, however, usually are so large at the lowest concentrations accessible to experiment, that the evaluation of the limiting value becomes a matter of extrapolation. MCMILLAN and MAYER [3] have proved that this extrapolation in the case of solutions of non-electrolytes can be based on the relation:

$$\pi/c = RT/M + A_2c + A_3c^2 + \ldots\ldots \qquad (8)$$

The value of the coefficient A_2 can be determined by performing a series of osmotic experiments at different concentrations. When certain assumptions are made concerning the structure of the liquid and the interaction between the solvent and the solute molecules, the value of A_2 can be calculated by means of the methods of statistical thermodynamics. This will be dealt with in section II.2.

4. As nearly all polymers consist of mixtures of components varying considerably in molecular weight, it will be important to consider what kind of expressions for the osmotic pressure are obtained for solutions containing various non-permeating components. For an ideal solution of n non-permeating components, separated by a membrane from the solvent, eq. (4) gives:

$$\pi = -(RT/v_1) \ln \left[1 - \sum_{j=2}^{n} x_j\right],$$

where the non-permeating components are numbered by subscripts 2 to n. Hence, inserting

$$(x_jM_j/v_1) = c_j$$

for the weight concentration of the j-th component, we obtain for the infinitely dilute solution:

$$\pi/c = RT\left(\sum_{j=2}^{n} c_j/M_j\right)/\left(\sum_{j=2}^{n} c_j\right) = RT/M_n, \qquad (9)$$

where c is the sum of the weight concentrations of the non-permeating components and M_n their number average molecular weight.

5. If one non-permeating component is dissolved in a mixture of two liquids, both of which can permeate through the membrane, we have two expressions (4):

$$\pi = -(RT/v_1) \ln (x_1'' f_1''/x_1' f_1'),$$
$$\pi = -(RT/v_2) \ln (x_2'' f_2''/x_2' f_2').$$

Elimination of π between these equations gives the equilibrium distribution of the liquids

$$(x_1'' f_1''/x_1' f_1')^{v_1} = (x_2'' f_2''/x_2' f_2')^{v_2}. \qquad (10)$$

Hence, generally, the ratio of the two liquids in the mixtures will be different on the two sides of the membrane [3]. SCOTT [4] has shown that when eq. (10) is satisfied the limiting value of the reduced osmotic pressure is the same as in solutions in a single liquid. It remains a question whether this equilibrium distribution is attained in osmotic experiments, but it is quite possible that in practice it is sufficient if the equilibrium distribution has been established in the liquid layers adjacent to the membrane. In many experiments the limiting value of π/c is found to be independent of the composition of the solvent, although exceptions have been reported in the literature.

6. Unfractionated polymers usually contain a considerable amount of low molecular weight material, which is liable to permeate through the membrane. MÜNSTER [5] has discussed the possibility that in equilibrium the very low molecular weight material is enriched in the solvent compartment. In general, however, equilibrium in this respect will not be reached. For the very low molecular weight material one might suppose that the equilibrium distribution is attained in layers adjacent to the membrane. For the greater part of the very slowly diffusing material one might try to correct for the diffusion by extrapolating the observed π value to the time at which the osmometer was filled.

An appropriate theory for systems in which such permeation occurs can be given by the thermodynamics of irreversible processes. It will be shown in section 3 by means of this theory that neither of the above assumptions is valid.

7. A special complication arises when one or more of the non-permeating components are electrolytes (DONNAN-equilibrium). The exact evaluation of a π vs c relation is then possible only if expressions for the activity coefficients are known. At present, such expressions are not available. It has, however, been shown

experimentally as well as theoretically that for solutions of polyelectrolytes in moderately concentrated solutions of common electrolytes the limiting value for the reduced osmotic pressure is the value obtained from eq. (9) [6].

II.2. Results of statistical thermodynamics

II.2a. *The method of molecular distribution functions*

The theory of osmotic pressure of polymer solutions has been developed along two different lines. On the one hand we have the so-called "quasi-lattice" theory, developed in 1941 by FLORY [7] and HUGGINS [8], in which liquid mixtures are treated as disordered solids. On the other hand we have theories in which liquid mixtures are assumed to be composed of a continuous solvent and of separate solute particles which interact like the molecules of a real gas. These theories will be called "gas theories" *).

The basis of most "gas theories" is the theory of non-electrolyte solutions given by MCMILLAN and MAYER [2] in 1945. It has been indicated by GUGGENHEIM [9], that this theory can be used as a basis of a "quasi-lattice" theory as well. We will give a short sketch of the method and of the results of MCMILLAN and MAYER, in so far as they are of importance for an understanding of the osmotic properties of polymer solutions (See also HILDEBRAND and SCOTT [10] and MÜNSTER [11].

In the theory of MCMILLAN and MAYER the structure of a liquid is described by means of the so-called molecular distribution functions. If we use the symbol q_n as an abbreviation for all the coordinates needed to describe the positions of a set of n molecules in a system, and dq_n as an abbreviation for $dq_1 dq_2 \ldots dq_n$, we may define the general molecular distribution function $F_n(q_n)$ in such a way that

$$(1/V^n) F_n(q_n) dq_n$$

is the probability for the set of n molecules to occupy the coordinates q_n to within dq_n, where V is the total volume of the system. The molecular distribution functions are normalized by the condition:

$$\lim_{V=\infty} (1/V^n) \int \ldots\ldots \int F_n(q_n) dq_n = 1,$$

where the integration must extend over all coordinates.

By means of grand partition functions MCMILLAN and MAYER have

*) The theory of conformal solutions, recently developed by LONGUET-HIGGINS [12] will not be discussed here.

shown that the osmotic pressure π of a binary mixture can be written in the form of a convergent series expansion in powers of the weight concentration c of the solute component:

$$\pi = (RT/M_2)c + A_2c^2 + A_3c^3 + \ldots\ldots \qquad (1)$$

where M_2 is the molecular weight of the solute and the coefficients A_n are related to the molecular distribution functions for the solute molecules at the limit of infinite dilution. In analogy with the theory of real gases these coefficients A_n are called virial coefficients. The second virial coefficients is given by:

$$A_2 = -(RTN_o/2VM_2^2) \int g_2(q_2)dq_2,$$

where N_o is AVOGADRO's number and the g_2 function measures the interaction between two solute molecules in the solvent concerned:

$$g_2(q_i, q_j) = F_2(q_i, q_j) - F_1(q_i)\, F_1(q_j).$$

In other words, the g_2 function is the difference between the molecular distribution function for a pair of interacting molecules and the molecular distribution function for two non-interacting molecules. In the same manner A_3 gives an indication about the interaction in groups of three molecules.

A first consequence of the "gas theory" of solutions is the rigorous proof of VAN 'T HOFF's law: at the limit $c = o$ the relation for the osmotic pressure becomes exactly [13)14)]:

$$\pi/c = RT/M_2.$$

A second consequence is that the use of a series expansion of π in powers of c is theoretically justified. SCHULZ [11)] has proposed to apply a formula of the following type:

$$\pi = (RTc/M_2)(1 - sc)^{-1}. \qquad (1')$$

This assumes a special relation between the virial coefficients A_2, A_3 ....., for which a theoretical foundation is lacking.

For liquid systems $F_1 = 1$, and the expression for the second virial coefficient becomes

$$A_2 = -(RTN_o/2VM_2^2) \int \{F_2(q_i, q_j) - 1\} dq_i dq_j. \qquad (2)$$

MCMILLAN and MAYER [2)] have shown further that the distribution function F_2 can be related to the interaction potential ε_2 between two solute molecules averaged over all configurations of solute and solvent molecules:

$$F_2 = \exp(-\varepsilon_2/kT).$$

It is at this point that the difficulties arise: it is pro-

hibitively difficult to evaluate ε_2 in terms of the potential functions of the solvent and solute molecules. We will describe here two different approximations that have been used for the evaluation of ε_2.

(1) The solvent may be treated as a continuum in which the solute molecules behave like interacting "gas" particles. Then the problem is identical with that of a real gas except that some "mean" potential for the solvent has to be subtracted from the potential for the solute molecules. As in the theory of real gases this theory can give a clear idea of the influence of geometric interaction between the solute molecules, that is, of the volume excluded to one solute molecule by the presence of another (compare VAN DER WAALS' constant b).

(2) The structure of the solution may be treated as that of a lattice in which only short-range order exists ("quasi-lattice"). According to GUGGENHEIM, the connection between the molecular distribution theory and the lattice theory may be formulated as follows. The potential function ε_2 which in the former case had one minimum only, now has a series of minimum values for all separations between the two solute molecules in which the gap can be exactly filled by an integral number of solvent molecules. In this way the geometry of the packing of the molecules has been accounted for.

Before describing, in parts b and c of this section, some features of these theories, we will give expressions for A_2 in ideal and in regular solutions. In both cases it is easier to start from thermodynamics than from statistical mechanics [15]. For any binary system the osmotic pressure is related to the free energy of dilution Δg_1 by the following equation (see section II.1)

$$\pi = -\Delta g_1 / v_1,$$

where v_1 is the partial molar volume of the solvent. In the case of an ideal solution, both kinds of molecules having the same dimensions and force fields, this gives:

$$\pi = -(RT/v_1)\ln(1 - x_2).$$

In dilute solutions the mole fraction x_2 may be replaced by $v_1 c/M_2$; expansion of the logarithm therefore gives:

$$A_2 = RTv_1/2M_2^2.$$

For the regular solution, which has the same entropy of mixing as the ideal solution, but a heat of mixing slightly different from zero, an analogous calculation gives:

$$A_2 = (RTv_1/2M_2^2)(1 - \zeta_2),$$

in which ζ_2 represents a correction for the heat of mixing.

In general, however, the force fields and the dimensions of the solute and solvent molecules differ to a greater or lesser extent, in which case the exact calculation of the molecular distribution functions becomes very complicated, so that one has to resort to one of the approximations mentioned.

II.2b. *The continuous solvent approximation*

The first applications of the "gas theory" to solutions of macromolecules were made by ZIMM [15], who found expressions for A_2 for solutions of rigid spheres, rigid rods and flexible chain molecules. In the last mentioned case ZIMM regards the chain molecules as collections of segments which have nearly the same force fields as the solvent molecules. As a first approximation he considers only interaction between pairs of segments, and gets the result:

$$A_2 = \tfrac{1}{2}RTv_1(m/M)^2(1 - \zeta_2), \tag{3}$$

where M is the molecular weight of the chain molecule, m the number of segments per molecule, and ζ_2 the correction for the heat of mixing. This result is essentially the same as that found in the simple "lattice"-theory in which each segment occupies exactly one site on the lattice (compare eq. (15) in part c).

Another expression for the second virial coefficient in the osmotic pressure formula has been given by FLORY and KRIGBAUM [16]. The same result is obtained by GRIMLEY [17] in a more general and elegant manner. We will give a short survey of his method here.

GRIMLEY describes the configurations of the polymer chain in terms of the configurations of the so-called "equivalent chain" (KUHN [18]). If we imagine a monomer group fixed in space, the orientation of the next monomer group is largely determined by the valence angle between the two groups. After a certain number of groups, however, the orientation of the next group shows practically no correlation with the orientation of the first. This number (ν) of monomer groups forms a statistical chain-element. An equivalent chain consists of N of these statistical chain elements, which will be called chain elements for short. Thus: $N\nu = m$ is the degree of polymerization of the chain molecule. If the chain elements do not interact with each other, they are distributed around the centre of gravity of the molecule according to a Gaussian distribution:

$$W(r)dr = a.4\pi r^2\exp(-9r^2/NL^2)dr.$$

Here $W(r)$ is the probability of finding a chain element at a distance r from the centre of gravity; L is the length of a chain

element. The same result can be obtained by assuming that the chain elements are completely free from each other but placed in an external central field with potential energy

$$9r^2kT/NL^2.$$

The real chain elements, however, exert forces on each other, which implies that by the presence of one element some place is excluded to any other one (excluded volume). The interaction forces between the chain elements have a short-range character; GRIMLEY assumes that only nearest neighbour interaction need be considered and succeeds in calculating the new distribution function for the interacting elements in the same potential field. This new distribution function is a function of the excluded volume ($-\beta_1$) and provides a new basis for the evaluation of the mean molecular dimensions, now also depending on β_1.

For a calculation of the second virial coefficient from eq. (2) the molecular distribution function $F_2(q_i, q_j)$ has to be known. GRIMLEY evaluates $F_2(q_i, q_j)$ for a pair of identical chain molecules with q_i and q_j as the coordinates of the centres of gravity, on the assumption that there is interaction between pairs of chain elements only, either in one molecule or between two elements of different molecules. As the solvent is treated as a continuum it does not enter in the excluded volume ($-\beta_1$) in a well-defined manner. The resulting expression for A_2 is:

$$A_2 = -\tfrac{1}{2}\beta_1 (RTN_o/M_o^2) H, \qquad (4)$$

where M_o denotes the "molecular weight" of a chain element, and H is a rather complicated function of β_1/L^3 and N, which is always positive. In a limited interval of molecular weights this formula may be approximated to

$$A_2 = CM^{-\varepsilon}, \qquad (5)$$

where C and ε are constants depending on the molecular dimensions and the excluded volume of the representative chain element in that interval.

Let us briefly discuss the equations (4) and (5).
(1). $\beta_1 < 0$. A positive excluded volume is the more general case. As H is positive, A_2 is also positive. If at the same time N becomes very large, ε takes the limiting value ½, whereas for smaller values of N the value of ε lies between 0 and ½.
(2). $\beta_1 > 0$. If the excluded volume is negative, the second virial coefficient will be negative as well. This is at once clear from the physical interpretation of $-\beta_1$: a negative value indicates association of the solute molecules; a negative value of A_2

means that the free energy of dilution becomes less negative, hence the stability of the solution decreases. If again N is very large, A_2 becomes proportional to $\exp(N^{\frac{1}{2}})$. This causes a rather sharp transition between the length of soluble and non-soluble chain molecules.

The influence of polydispersity is estimated by GRIMLEY [17] in a qualitative manner. He concludes that A_2 from osmotic measurements on a solution of normal fractionated material will not differ significantly from its value for a solution of a perfectly monodisperse polymer with N_n chain elements per molecule (N_n is the number average of the polydisperse sample). In the same way A_2' from light scattering data equals the A_2' for a monodisperse polymer with N_w chain elements per molecule (N_w is the weight average). A_2', however, is much more sensitive to traces of high molecular weight than A_2.

From experimental data it is known that the influence of the third virial coefficient at low concentrations ($c < 1.0$ g/100 cm^3) usually can be neglected, although this depends on the particular solute-solvent system. At higher concentrations departures from linearity have been frequently reported (see also III.1f). FLORY and KRIGBAUM [16] express A_3 in terms of A_2 for the case of rigid spheres:

$$A_3 = (5/8)(M_2/RT)A_2^2, \qquad (6)$$

and use the same relationship for long chain molecules. In a more detailed analysis STOCKMAYER and CASASSA [19] replace the factor 5/8 by one whose value depends on the "softness" of the molecule and may be as low as 1/4.

II.2c. *The quasi-lattice approximation*

Let us begin with the simplest case: athermal mixtures (zero heat of mixing). RUSHBROOKE, SCOINS and WAKEFIELD [20] have carried out an exact calculation of several virial coefficients for athermal mixtures of monomers with dimers, trimers and tetramers respectively *). The results of these calculations are in reasonable agreement with those of the theories of MILLER [21] and GUGGENHEIM [22] for athermal mixtures.

In these theories the molecules of the solute are supposed to be built up of a number of segments all of which can be inter-

*) Although we have here used the quite common expression "monomer" for a molecule that occupies one lattice site, we will avoid this expression in the subsequent discussion because of the chemical difference between a monomer molecule on the one hand and the monomer group in most polymer molecules on the other hand.

changed with solvent molecules in the quasi-lattice. Thus the problem is reduced to a calculation of the number of distinct configurations g when placing the segments of the solute molecules and the solvent molecules on the lattice sites. The entropy of mixing can be obtained from the value of g by means of BOLTZMANN'S relation

$$\Delta S = k \ln g - k \ln g_1 - k \ln g_2,$$

where g_1 is the number of configurations when only solvent molecules occupy the lattice sites (hence $g_1 = 1$), and g_2 the number of configurations for the polymer molecules only. Hence:

$$\Delta S = k \ln (g/g_2). \tag{7}$$

Reviews of these calculations have been given by MILLER [23] and by VAN DER WAALS [24] and will not be repeated here. We will merely mention the result obtained for the partial molar Gibbs free energies:

$$\Delta g_1 = -T\Delta s_1 = RT[\ln(1-\varphi) - (z/2)\ln \{1-(2/z)(1-1)m/\varphi\}] \tag{8}$$

$$\Delta g_2 = -T\Delta s_2 = RT[\ln\varphi - (qz/2)\ln \{1 + 2(m-1)(1-\varphi)/(qz)\}]. \tag{9}$$

Here φ is the volume fraction of component 2 (the polymer), m the number of lattice points occupied by a single polymer molecule, and z the coordination number of the lattice, i.e., the total number of nearest neighbour sites surrounding any lattice site. The quantity qz represents the total number of nearest neighbour pairs which a polymer molecule can form with adjacent molecules; it is smaller than mz because qz does not comprise the sites occupied by segments of the polymer molecule itself but only those occupied by solvent molecules or by segments of other polymer molecules. It is clear that for unbranched chains which do not bend back on themselves:

$$mz = qz - 2m + 2. \tag{10}$$

Obviously, the difference between q and m gives expression to the fact that the segments of a polymer molecule are connected in a chain.

When $z/2$ is large, eqs. (8) and (9) may be expanded as follows:

$$\Delta g_1 = RT[\ln(1-\varphi) + (1-1/m)\varphi + (1/z)(1-1/m)^2\varphi^2]; \tag{11}$$

$$\Delta g_2 = RT[\ln\varphi - (m-1)(1-\varphi) + (1/qz)(m-1)^2(1-\varphi)^2]. \tag{12}$$

From eq. (11) we may at once derive the osmotic pressure $-\Delta g_1/v_1$. If, furthermore, we introduce the weight concentration c of the polymer according to

$$\varphi = cv_1 m/M,$$

where M is the molecular weight of the polymer, we get for small values of φ:

$$\varphi = (RT/M)c + RTv_1(m/M)^2(\tfrac{1}{2}-1/z)c^2 \qquad (13)$$

provided m is large.

So far we have exclusively considered athermal solutions. In reality few, if any, solutions will have zero heat of mixing. If the heat of mixing is small, the free energy of mixing may be obtained by simply adding the enthalpy change ΔH to the athermal free energy of mixing:

$$\Delta G = \Delta G(\text{ath}) + \Delta H.$$

Simularly the Gibbs free energy of dilution is obtained by adding the enthalpy of dilution to the athermal Gibbs free energy of dilution:

$$\Delta g_1 = \Delta g_1(\text{ath}) + \Delta h_1.$$

In doing so it is assumed that the deviation from randomness of mixing is negligible. In a great many cases a good approximation to the heat of dilution is

$$\Delta h_1 = \beta\varphi^2,$$

where β is a constant dependent on the polymer-solvent system and on the temperature. Hence, using eq. (11) we obtain, when m is large:

$$\Delta g_1 = RT[\ln(1-\varphi) + (1-1/m)\varphi + (2/z+\beta/RT)\varphi^2],$$

which, following HUGGINS [25] is usually written as

$$\Delta g_1 = RT[\ln(1-\varphi) + (1-1/m)\varphi + \mu\varphi^2]; \qquad (14)$$

and for the osmotic pressure:

$$\pi = (RT/M)c + RTv_1(m/M)^2(\tfrac{1}{2}-\mu)c^2. \qquad (15)$$

Although many attempts have been made to obtain results of a more general character, none of these attempts have led to an equation for the free energy of mixing which has proved more useful than eq. (14).

A survey of the theories of MILLER, GUGGENHEIM and HUGGINS and of various other quasi-lattice theories, as well as a discussion of their merits has been given by MÜNSTER [11]. Very recently the quasi-lattice model itself has been improved by PRIGOGINE and coworkers by taking account of the influence of neighbouring molecules on the internal degrees of freedom.

The theory of HUGGINS has been extended by SCOTT and MAGAT [26] to solutions of polymer-homologous mixtures. These authors obtain:

$$\Delta g_1 = RT[\ln(1-\varphi) + (1-1/\overline{m}_n)\varphi + \mu\varphi^2]; \tag{16}$$

$$\Delta g_j = RT[\ln\varphi_j - (m_j-1) + m_j(1-1/\overline{m}_n)\varphi + m_j\mu(1-\varphi)^2], \tag{17}$$

where the subscript j refers to the j-mer, and where $\overline{m}_n$ is the number average of m:

$$\overline{m}_n = (\sum_j n_j m_j)/(\sum_j n_j),$$

where n_j is the number of j-mer molecules.

II.2d. *Discussion*

The crucial point in all theories lies in the expression for the second virial coefficient. For convenience we will list here the expression for A_2 found by ZIMM [15] and FLORY [7] for athermal solutions:

$$A_2 = \tfrac{1}{2}RTv_1(m/M)^2; \tag{18}$$

by MILLER [21] and GUGGENHEIM [22] for athermal solutions:

$$A_2 = \tfrac{1}{2}RTv_1(m/M)^2(1-2/z); \tag{19}$$

by ZIMM [15] and HUGGINS [25] for regular solutions:

$$A_2 = \tfrac{1}{2}RTv_1(m/M)^2(1-2\mu); \tag{20}$$

by GRIMLEY [17]:

$$A_2 = \tfrac{1}{2}RT(-\beta_1 N_o/M_o^2)H \tag{21}$$

and, for comparison, the expression for an ideal dilute solution:

$$A_2 = \tfrac{1}{2}RTv_1/M^2. \tag{22}$$

In the theory of ZIMM (part b) as well as in FLORY's theory the connection between the segments in the chain molecule is only partly accounted for. In ZIMM's theory only interaction between pairs of segments is considered for the calculation of the second virial coefficient. FLORY's result is equivalent to saying instead of eq. (10) that $mz = qz$, which also means an overestimation of the number of solvent molecules surrounding the segments.

The connection between the segments is taken into account to a greater extent in the theory of MILLER and GUGGENHEIM. The only parameter that appears in the final equation for the osmotic pressure, the coordination number z, is a physically well-defined quantity. It is, therefore, interesting to see what values for z can be deduced from osmotic measurements on athermal solutions (see eq. (19)). MÜNSTER [11] has given a table of experimental z

values for seven different systems, which can be regarded as more or less athermal. Except for one system in which z was 5.5, all values of z are ranged between two and three. We must, therefore, conclude that in general the deviation from ideal behaviour (eq. (22)) is much less than is predicted by eq. (18).

In the theory of MILLER and GUGGENHEIM the influence of a bending back of the chain molecule on to itself (formation of rings) has been neglected. STAVERMAN [27] and TOMPA [28] have shown that the formation of polymer-polymer contacts between distant segments of a chain molecule also tends to decrease the deviation from ideal behaviour. This coiling-up effect, which has also been considered by ORR [29] and MÜNSTER [30] is closely related to an effect first discussed by FLORY [31]. In the highly dilute region, where osmotic measurements are most important, the concentration of the segments in the solution is not uniform, but is much larger in the neighbourhood of the centres of the macromolecules. In the theories of FLORY and KRIGBAUM [16], and of GRIMLEY [17] an attempt has been made to account for this effect. It will be obvious that for a given polymer-solvent system at a given temperature strongly coiled molecules will show less interaction with each other than weakly coiled ones, because in the latter case more segments are available for interaction with segments of a second molecule. Since bending back on itself will be the more frequent the higher the molecular weight, it is not surprising that the second virial coefficient decreases with increasing molecular weight. This, indeed, has been borne out by experiment.

Generally the heat of mixing differs from zero. For slight deviations the theory of HUGGINS [25] gives a very useful result (eq. (20)). It will be clear from the preceding discussion that the interaction parameter μ contains an enthalpy as well as an entropy term.

Although the physical significance of μ is not much better that that of z in eq. (19), HUGGINS' equations have proved their usefulness in many problems concerning the solubility of polymers (see for instance chapter III.3).

More rigorous calculations in which the heat of mixing is taken into account have been performed among others by GUGGENHEIM [22] and ORR [32]. The results of such calculations are rather complicated formulae (see the review article of MÜNSTER [11]), and sometimes contain so many independent parameters that almost any result can be explained.

As we mentioned already, the second virial coefficient often depends on the molecular weight of the polymer. According to

MÜNSTER [33] A_2 for high molecular weights is a linear function of M^{-1}:

$$A_2 = k_1/M + k_2,$$

where k_1 and k_2 are approximately constant. GRIMLEY's eq. (5): $A_2 = CM^{-\varepsilon}$ will be hardly distinguishable from MÜNSTER's result. In the table we give some ε values calculated from accurate data reported in the literature.

Dependence of A_2 on molecular weight

Polymer	Solvent	ε	reference
polymethyl methacrylate	acetone	0.21	34
polystyrene	toluene	0.15	35;36
polystyrene	toluene	0.22	37
polyisobutylene	cyclohexane	0.14	37
cellulose nitrate	acetone	0.12	38

From the calculations of BAWN and WAJID [36], however, it can be seen that the precise value of ε strongly depends on the kind of expression that is used for the π/c vs c relation. The value 0.15 is found from a quadratic equation, whereas a value of 0.33 is found when the relation of FLORY and KRIGBAUM [16] (eq. (6) in part b) is used for the third virial coefficient.

The coiling up of the macromolecules can be enhanced by the addition of a non-solvent (precipitant) to the polymer solution. It is possible, in this way, to obtain solutions which have zero A_2 values. DOBRY and OUANG CHOU HUIN [39], and GEE [40] have proposed to use such solutions for the evaluation of the first virial coefficient (RT/M) because the zero value of A_2 in the measured interval of concentrations allows a horizontal, and hence more reliable, extrapolation to zero concentration (compare section 1f in chapter III). In some cases the method has since been verified by several authors [41][42][43].

As regard the thermodynamic consequences of the use of a mixture of liquids, see section 1.

Another consequence of the method is that the liquid mixture is a poor solvent, and hence near the precipitation point. This is also evident from the consideration that when segments of one chain molecule tend to "associate", this will be the case for segments of different chain molecules as well. When performing osmotic measurements in such poor solvent systems one has to be well aware of association phenomena, because they are of more importance than usually is recognized.

II.2e. *Association phenomena*

Association phenomena are reported in several cases in which dipole-dipole interaction or hydrogen bonding is possible, for instance ethyl cellulose in aliphatic and aromatic hydrocarbons [44], amylose acetate in chloroform [45], polyvinyl chloride in dioxane [46][47] and cellulose acetate in methyl cellosolve [48].

Doty and coworkers [46][47] made an accurate study of association phenomena of polyvinyl chloride in different solvents by means of osmometry, viscometry, light-scattering and the ultracentrifuge at three different temperatures. In the poor solvent dioxane the association is most pronounced. The phenomenon is, of course, best observed in light-scattering studies. The strange fact that the association persists at the lowest concentration at which measurements were possible suggests that the association equilibrium is either very slowly established or not an equilibrium at all. The experiments of Doty confirm the first idea, as the association decreases at higher temperatures, and increases very slowly again after cooling of the solution to a lower temperature: it is only after several weeks that the solution regains its original properties. Probably the association consists in the formation of minute crystalline regions, due to the dipole-dipole interaction between polar segments of different chain molecules.

An association phenomenon in a good solvent has been reported by Trementozzi [49][50] for emulsion polymerised polystyrene in toluene. Small amounts of polar substituents, built into the chains during the polymerization may be responsible for the association. Although hydroxyl groups were not detectable by chemical analysis and infrared absorption spectroscopy, complete acetylation of the polymer suppressed all association phenomena, as was shown by light scattering measurements. It is interesting that also the addition of a small amount of a polar substance (2% dioxane or 2% dimethyl acetamide) to the toluene solution reestablished the normal behaviour.

A systematic investigation of a ternary system of two interacting polymers and one solvent has been performed by Morawetz and Gobran [57]. The two polymers used by them were methyl methacrylate copolymers with methacrylic acid and dimethylamino ethyl methacrylate, respectively. The acidic copolymer contained about 4.9 mole per cent acidic monomer groups, the basic copolymer 5.8 mole per cent basic monomer groups. Osmotic measurements on nine different mixtures of the acidic and basic polymers were done in butanone, benzene and pyridine. In all cases a pronounced association was found; for the weight ratio 1:1 the molecular weight in butanone at 30°C was five times as large as the mean molecular weight of the two unassociated copolymers. The effect was found

to be strongly temperature dependent; the same mixture in butanone at 50°C showed a degree of association of three. As in the investigations of TREMENTOZZI, there was no pronounced effect on the second virial coefficient.

From these remarks it will be clear that in case of any doubt osmotic measurements in different solvents should be compared, since association of polymers often persists at concentrations lower than those at which measurements can be carried out in the usual osmometers *).

II.3. Non equilibrium thermodynamics [52]

Nearly all previous discussions are based on the complete semipermeability of the membrane; permeable for solvent molecules, but impermeable for solute molecules. Very often, especially in the case of unfractionated polymers, the membranes are permeable for a small portion of the polymer molecules. It might be possible to account for the effect this has on the osmotic pressure by means of a model theory, but we will restrict ourselves to the general phenomenological theory described by STAVERMAN [53)54].

In the equilibrium state of an isolated system, whose energy and volume are kept constant, the entropy is at its maximum value S_o. For small deviations from this equilibrium, measured by the parameters α_1, the entropy may be developed by means of TAYLOR's theorem in terms of powers of the α_i's:

$$S = S_o + \sum_i \alpha_i \frac{\partial S_o}{\partial \alpha_i} + \tfrac{1}{2} \sum\sum_{ik} \alpha_i \alpha_k \frac{\partial^2 S_o}{\partial \alpha_i \partial \alpha_k} \cdots\cdots$$

Since $(\partial S_o / \partial \alpha_i) = 0$ is the equilibrium condition, and terms of order α^3 may be omitted when the deviations are small, we obtain

$$\Delta S = S - S_o = -\tfrac{1}{2} \sum_i \sum_k \alpha_i \alpha_k g_{ik}, \qquad (1)$$

where $\sum_i \sum_k \alpha_i \alpha_k g_{ik}$ is a positive definite expression.

In analogy to the theory of classical mechanics we may define as "forces"

$$X_i = (\partial \Delta S / \partial \alpha_i)_{\alpha_j} = -\sum_k g_{ik} \alpha_k, \qquad (2)$$

while the derivatives of the deviations with respect to time are called "fluxes"

*) The osmotic balance, developed by JULLANDER (Thesis, Uppsala, 1945) may provide a means of greater accuracy than osmometers of the conventional designs.

$$J_i = \dot{\alpha}_i. \tag{3}$$

As we are dealing with small deviations only, these fluxes will be proportional to the forces:

$$J_i = \sum_k L_{ik} X_k. \tag{4}$$

If the forces and fluxed are chosen in accordance with eq. (2) and (3), the following relations are valid [55]:

$$L_{ik} = L_{ki} \tag{5}$$

For these ONSAGER reciprocal relations to hold, the correct choice for the combinations of forces X_i and fluxes J_i must be made. One way which always leads to the correct choice is to find an expression for the time derivative of the entropy (rate of entropy production), which may be written as a sum of products of forces and fluxes:

$$\dot{\Delta S} = \sum_i J_i X_i \tag{6}$$

STAVERMAN [56] used this method in his membrane theory which will be discussed here.

For open systems, i.e. for systems which can exchange heat or matter with their surroundings, only the internal part of the entropy production may be written in the form of eq. (6) [52].

For the osmotic process (system I separated from system II by a membrane) we have the relations:

$$dm_k{}^{I} + dm_k{}^{II} = 0, \tag{7}$$

no matter being exchanged with the environment. Further,

$$dU^{I} = d_e U^{I} + d_i U^{I}$$

$$dU^{II} = d_e U^{II} + d_i U^{II}.$$

The energies of the two systems must be divided in external and internal parts; the law of conservation of energy can be applied to the internal part only:

$$d_i U^{I} + d_i U^{II} = 0 \tag{8}$$

Finally, the two systems have the same temperature:

$$T^{I} = T^{II}. \tag{9}$$

For the total contents of the systems I and II respectively, the second law of thermodynamics runs as follows:

$$\left.\begin{aligned} T^{I} dS^{I} &= dU^{I} + p^{I} dV^{I} - \sum_{k=1}^{n} g_k{}^{I}\, dm_k{}^{I}, \\ T^{II} dS^{II} &= dU^{II} + p^{II} dV^{II} - \sum_{k=1}^{n} g_k{}^{II}\, dm_k{}^{II}. \end{aligned}\right\} \tag{10}$$

Hence the change in entropy is

$$dS = dS^{I} + dS^{II} = \frac{d_e U^{I} + p^{I} dV^{I}}{T^{I}} + \frac{d_e U^{II} + p^{II} dV^{II}}{T^{II}} + \frac{d_i U^{I}}{T^{I}}$$

$$+ \frac{d_i U^{II}}{T^{II}} - \sum_{k=1}^{n} \left(\frac{g_k{}^{I}\, dm_k{}^{I}}{T^{I}} - \frac{g_k{}^{II}\, dm_k{}^{II}}{T^{II}} \right).$$

Substitution of eq. (7), (8) and (9) gives:

$$dS = \frac{d_e U^{I} + p^{I} dV^{I}}{T} + \frac{d_e U^{II} + p^{II} dV^{II}}{T} + \sum_{k=1}^{n} \frac{\Delta g_k}{T}\, dm_k{}^{I},$$

where $\Delta g_k = g_k{}^{II} - g_k{}^{I}$.
By splitting dS in an external and an internal part we obtain for $d_i S$:

$$d_i S = \sum_{k=1}^{n} \Delta(g_k/T)\, dm_k{}^{I} \tag{11}$$

and, therefore, for the rate of entropy production

$$d_i S/dt = \sum_{k=1}^{n} \Delta(g_k/T)\, \dot{m}_k, \tag{12}$$

with the "forces"

$$X_k = \Delta g_k/T \tag{13}$$

and the "fluxes"

$$J_k = dm_k/dt = \dot{m}_k. \tag{14}$$

The phenomenological equations (4) are expressions for transport of matter:

$$\dot{m}_k = \sum_{k} L_{ik}\, X_k. \tag{15}$$

The difference in thermodynamic potential Δg_k of the component k in the two parts of the osmometer is due to the difference in pressure Δp and in the concentrations

$$\Delta g_k = v_k \Delta p + \Delta g_k{}^{\circ},$$

where Δg_k° is the concentration dependent part of Δg_k, and v_k the partial molar volume of component k, which is assumed to be pressure independent for small changes in p. Hence the transport of matter can be written as due to a pressure difference and a "thermodynamic" force:

$$\dot{m}_i = \sum_{k} L_{ik}\, (v_k \Delta p + \Delta g_k{}^{\circ}) \tag{16}$$

Here STAVERMAN [53] introduces a "mechanical transport number

of component i". This is the fraction of the flow contributed by component i when all Δg_k°'s are zero:

$$\tau_i = \left[\frac{\dot{m}_i v_i}{J}\right]_{\Delta g_k^{\circ}=0} = \frac{v_i \sum_k L_{ik} v_k}{\sum_j \sum_k L_{jk} v_j v_k}, \qquad (17)$$

since

$$J_{\Delta g_k^{\circ}=0} = \sum_k \dot{m}_k v_k = \sum_j \sum_k L_{jk} v_j v_k \Delta p.$$

The experimental osmotic pressure π_{exp} is defined as the pressure at which no net flow through the membrane is observed:

$$J = \sum_i \sum_k L_{ik} v_i v_k \pi_{exp} + \sum_i \sum_k L_{ik} v_i \Delta g_k^{\circ} = 0$$

Hence, using the reciprocal relations (5):

$$\pi_{exp} = \frac{-\sum_i \sum_k L_{ik} v_i \Delta g_k^{\circ}}{\sum_i \sum_k L_{ik} v_i v_k},$$

or:

$$\pi_{exp} = -\sum_k (\tau_k / v_k) \Delta g_k^{\circ}. \qquad (18)$$

For a binary system in which solvent and solute are indicated by the subscripts 1 and 2 respectively, we have

$$-\pi_{exp} = (\tau_1/v_1)\Delta g_1^{\circ} + (\tau_2/v_2)\Delta g_2^{\circ}. \qquad (19)$$

Using the relation of DUHEM-MARGULES:

$$\Delta g_2^{\circ} = -(m_1/m_2)\Delta g_1^{\circ},$$

we obtain:

$$-\pi_{exp} = \frac{\Delta g_1^{\circ}}{v_1}\{\tau_1 - \frac{m_1 v_1}{m_2 v_2}\tau_2\}.$$

When we remember that $\tau_1+\tau_2 = 1$ and that the volume fraction of the solute is determined by

$$\varphi_2 = m_2 v_2/(m_1 v_1 + m_2 v_2)$$

we get for the experimental osmotic pressure:

$$\pi_{exp} = -(\Delta g_1^{\circ}/v_1)(1-\tau_2/\varphi_2) = \pi_{th}(1-\tau_2/\varphi_2) \qquad (20)$$

since $\pi_{th} = -\Delta g_1^{\circ}/v_1$ (section II.1) is the "theoretical" osmotic pressure, i.e. the osmotic pressure for a membrane which is completely impermeable to the solute.

Substitution of $\tau_2/\varphi_2 = 1-\sigma_2$, where σ_2 is a selection coefficient of the membrane for the solute, gives STAVERMAN's expression [56]:

$$\pi_{exp} = \sigma_2 \pi_{th}. \qquad (21)$$

The selection coefficient σ_2 describes the selectivity of the membrane for the solute molecules. When, on the one hand, we are

dealing with filtration experiments in which all solute molecules pass the membrane unhindered, σ_2 will be unity: there is no selectivity at all. In an osmotic experiment, on the other hand, no solute molecule passes the membrane, and hence $\sigma_2 = 0$. In intermediate cases we are dealing with a kind of ultrafiltration membranes, in which the permeation of the solute molecules is restricted in comparison with the unhindered filtration:

$$0 < \sigma_2 < 1. \tag{22}$$

In general, when performing osmotic measurements on solutions of heterogeneous polymers for instance, every solute component j contributes to the apparent osmotic pressure according to:

$$\pi_{exp.j} = \sigma_j \pi_{th.j}, \tag{23}$$

where σ_j is determined by eq. (17) and

$$\tau_j/\varphi_j = 1-\sigma_j.$$

For low molecular weight components in the polymer it is usually assumed that their contribution to the limiting value of the reduced osmotic pressure may be neglected, because one might expect that for these components an equilibrium distribution in layers adjacent to the membrane is rapidly set up (see also section II.1). The contribution of all solute components is inversely proportional to their molecular weight, however, so that even for very small values of σ_j a considerable contribution from the low molecular weight components may be expected when this equilibrium distribution has not yet been reached. The presence of such components can hardly be avoided, even in well-fractionated polymers. It is a frequently occuring belief that the effect of a very slow diffusion can be accounted for by extrapolating the observed osmotic pressure to zero time (time of filling the apparatus). The main merit of STAVERMAN's theory is that it shows such belief to be unjustified, because the contribution of a permeating component to the osmotic pressure never exceeds the value $\sigma_j \pi_{th.j}$ and $\sigma_j < 1$ for all permeating components.

We wish to point out, in conclusion, that the selection coefficient σ has primarily a mathematical significance. Its physical meaning is not always quite transparent. In particular, for membranes which do not strictly behave like molecular sieves, we see no reason why τ_2/φ_2 must alway be smaller than one. Toluene solutions, for instance, which contain a small percentage of water, sometimes show a negative osmotic pressure. It is a reasonable assumption that water permeates more rapidly through the membrane

than toluene, especially in the case of cellulose membranes. Then, however, τ_2/φ_2 for water is greater than one and σ_2 is negative.

It will be shown in III.2e. that the experimental determination of σ is by no means an easy matter. It is even doubtful whether it will ever be possible to measure this quantity.

References

1. E.A.Guggenheim, "Thermodynamics", Amsterdam, 1949.
2. W.G.McMillan and J.W.Mayer, J.Chem.Phys., **13**, 276 (1945).
3. F.G.Donnan and E.A.Guggenheim, Z.physik.Chem., **A162**, 346 (1932).
4. R.L.Scott, J.Chem.Phys., **17**, 268 (1949).
5. A.Münster, Z.Naturforsch., **2a**, 272 (1947).
6. D.T.F.Pals, Thesis, Groningen, 1952.
7. P.J.Flory, J.Chem.Phys., **9**, 660 (1941) and **10**, 51 (1942).
8. M.L.Huggins, J.Chem.Phys., **9**, 440 (1941).
9. E.A.Guggenheim, Disc.Faraday Soc., **15**, 66 (1953).
10. J.Hildebrand and R.L.Scott, "Solubility", 3rd ed., New York, 1950.
11. In H.A.Stuart, "Das Makromolekül in Lösungen", Berlin, 1953.
12. H.C.Longuet-Higgins, Proc.Roy.Soc.London, **A205**, 247 (1951).
13. A.Münster, Z.Elektrochem., **56**, 525 (1952) and **57**, 142 (1953).
14. R.Haase, Z.Naturforsch., **8a**, 380 (1953).
15. B.H.Zimm, J.Chem.Phys., **14**, 164 (1946).
16. P.J.Flory and W.R.Krigbaum, J.Chem.Phys., **18**, 1086 (1950).
17. T.B.Grimley, Proc.Roy.Soc.London, **A212**, 339 (1952).
18. W.Kuhn, Kolloid Z., **68**, 2 (1934).
19. W.H.Stockmayer and E.F.Casassa, J.Chem.Phys., **20**, 1560 (1952).
20. G.S.Rushbrooke, H.J.Scoins and A.J.Wakefield, Disc.Faraday Soc., **15**, 57 (1953).
21. A.R.Miller, Proc.Cambridge Phil.Soc., **38**, 109 (1942) and **39**, 54, 151 (1943).
22. E.A.Guggenheim, Proc.Roy.Soc.London, **A183**, 203 (1944).
23. A.R.Miller, "Theory of solutions of high polymers", Oxford, 1948.
24. J.H.van der Waals, Thesis, Groningen, 1950.
25. M.L.Huggins, Ann.N.Y.Acad.Sci., **44**, 431 (1943).
26. R.L.Scott and M.Magat, J.Chem.Phys., **13**, 172 (1945).
27. A.J.Staverman, Rec.trav.chim. **69**, 163 (1950).
28. B.H.Tompa, Trans.Faraday Soc., **48**, 363 (1952).
29. W.J.C.Orr, Trans.Faraday Soc., **43**, 12 (1947).
30. A.Münster, Makromol.Chem., **2**, 227 (1948).
31. P.J.Flory, J.Chem.Phys., **13**, 453 (1945).

32. W.J.C. Orr, Trans. Faraday Soc., **40**, 306 (1944).
33. A. Münster, J. chim. phys., **49**, 128 (1952).
34. J. Bischoff and V. Desreux, Bull. soc. chim. Belges, **61**, 10 (1952).
35. C.E.H. Bawn, R.E.J. Freeman and A.R. Kamaliddin, Trans. Faraday Soc., **46**, 862 (1950).
36. C.E.H. Bawn and M.A. Wajid, communicated at the Symposion on Macromolecules, Stockholm, 1953.
37. W.R. Krigbaum and P.J. Flory, J. Am. Chem. Soc., **75**, 1775 (1953).
38. H. Lang and A. Münster, Naturwissenschaften, **38**, 68 (1951).
39. A. Dobry and Ouang Chou Huin, J. chim. phys., **36**, 296 (1939).
40. G. Gee, Trans. Faraday Soc., **36**, 1171 (1940).
41. G.V. Browning and J.D. Ferry, J. Chem. Phys., **17**, 1107 (1949).
42. M.J. Schick, P. Doty and B.H. Zimm, J. Am. Chem. Soc., **72**, 530 (1950).
43. S.R. Palit, G. Colombo and H. Mark, J. Polymer Sci., **6**, 295 (1951).
44. E. Steurer, Z. physik. Chem., **A 190**, 1 (1941).
45. F.C. Cleveland and R.W. Kerr, J. Am. Chem. Soc., **71**, 16 (1949).
46. P.M. Doty and E. Mishuck, J. Am. Chem. Soc., **69**, 1631 (1947).
47. P.M. Doty, S. Singer and H. Wagner, J. Phys. & Colloid. Chem., **51**, 32 (1947).
48. A. Sookne and M. Harris, Ind. Eng. Chem., **37**, 475 (1945).
49. Q.A. Trementozzi, J. Phys. Chem., **54**, 1227 (1950).
50. Q.A. Trementozzi, R.F. Steiner and P.M. Doty, J. Am. Chem. Soc., **74**, 2070 (1952).
51. H. Morawetz and R.H. Gobran, communicated at the Symposion on Macromolecules, Stockholm, 1953.
52. S.R. de Groot, "Thermodynamics of irreversible processes", Amsterdam, 1951.
53. A.J. Staverman, Rec. trav. Chim., **70**, 344 (1951) and **71**, 623 (1952).
54. A.J. Staverman, Trans. Faraday Soc., **48**, 176 (1952).
55. L. Onsager, Phys. Rev., **37**, 405 and **38**, 2265 (1931).
56. A.J. Staverman, Chem. Weekblad, **48**, 334 (1952).

Chapter III

EXPERIMENTAL TECHNIQUES

III.1. Osmometers and the determination of osmotic pressures

This section will be divided into six parts:

a. General features of the osmometer.
b. The measuring technique.
c. The FUOSS-MEAD osmometer.
d. The ZIMM-MYERSON osmometer.
e. The accuracy of the measurements.
f. The extrapolation of the reduced osmotic pressure to zero concentration.

III.1a. *General features of the osmometer*

As we are, in the present work, interested only in the osmometry of high polymers, we will omit the older types of osmometers which were used to corroborate VAN 'T HOFF's law. These osmometers were designed for the determination of rather high osmotic pressures, for example pressures of several hundred atmospheres (FRAZER and MYRICK [1]). The absolute accuracy of these measurements was claimed to be about 0.01 at. As a consequence of this extraordinary magnitude of the osmotic pressure, the osmotic method in the study of the colligative properties of low molecular weight compounds was superseded by the methods of the lowering of the freezing point, the elevation of the boiling point and the lowering of the vapour pressure. For that very reason the osmotic method is thus far the only useful method when we are dealing with the same properties of solutions of substances with molecular weights above, say, 10,000.

A second difficulty with regard to the earlier osmometers lies in the nature of the copper ferrocyanide membrane, which was used exclusively. The preparation of these membranes is a laborious affair, they are very slow to reach equilibrium, and their usefulness is restricted to aqueous solutions. Moreover, the deposit is reported to be rather unstable; it seems to be advisable to add some $K_4Fe(CN)_6$ to the liquid in one compartment, and some $CuSO_4$ to the liquid in the other cell [2].

Among the newer osmometers we will only consider the types that have flat membranes. Although a very simple apparatus with

bag-shaped membranes has been described dy DOBRY [3], osmometers with flat membranes are more frequently used, because these membranes are more easily made and are commercially available in different degrees of permeability and suitable for organic liquids as well as for aqueous solutions. In the study of proteins, however, osmometers with bag-shaped membranes are still frequently used, because they have a great membrane area and hence show a rapid establishment of the equilibrium.

Another disadvantage of these membranes is due to the fact that they cannot be supported as well as the flat membranes.

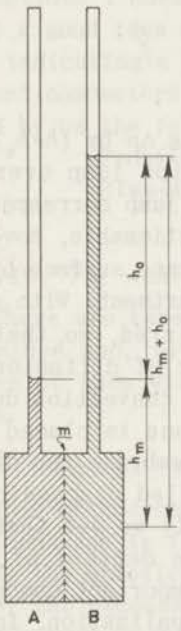

Fig. 1
Diagram of an osmometer; the dashed line indicates the position of the membrane

A diagram of an osmometer with a flat vertical membrane is shown in fig. 1. A indicates the solvent, B the solution compartment. If, for the moment, we assume that solvent and solution have the same density ρ, the equilibrium internal head h_o immediately gives the osmotic pressure:

$$\pi = h_o \rho \quad *).$$

The establishment of this internal head h_o, i.e. the difference between the heights of the menisci in the two identical capillaries is a matter of solvent flow through the membrane **), provided the latter is rigidly supported. Otherwise a displacement of the membrane may give the same result (displacement of the menisci).

The rate of flow dv/dt through the membrane is proportional to the effective area S of the membrane and to the excess pressure Δp applied:

$$dv/dt = PS\,\Delta p, \qquad (1)$$

where P is the permeability constant of the membrane for the solvent concerned. The permeation of an amount of solvent with

*) In the c.g.s. system this equation must be written as

$$\pi = h_o \rho g .$$

For convenience we will express π in cm H_2O (4^o C).

**) Diffusion of solute molecules will be considered in the section on membranes.

volume Δv through the membrane corresponds with a change in the internal head h of: $-\Delta h = \Delta v.8/\pi\, d^3$, where d is the diameter of the capillaries.

The excess pressure Δp is the hydrostatic pressure $(h-h_o)\rho$; substitution of Δv and Δp in eq. (1) gives therefore:

$$\left.\begin{aligned} dh/dt &= -\,P\,S\;8\rho(h-h_o)/\pi\,d^2 \\ \text{or}\qquad dh/dt &= -\,k\;(h-h_o)\,. \end{aligned}\right\} \qquad (2)$$

The proportionality constant k depends on the membrane properties and the osmometer dimensions:

$$k = 8\,PS\;\rho/\pi\,d^2\,. \qquad (3)$$

It has to be borne in mind that in replacing Δp by $(h-h_o)\rho$ we have tacitly assumed the correct concentration jump over the semipermeable membrane, viz. the concentration jump corresponding with the ultimate equilibrium. This may be questionable, however, due to the change in concentration at the membrane surface by the flow of solvent into or from the solution compartment. With a few exceptions [4)5)] the cell contents are not stirred, so that the equalization of the concentration is a matter of diffusion and convection. Although it has been claimed that convection due to density effects is predominant when the membrane is placed in a vertical position, whereas with a horizontal membrane the diffusion effects are more important [6)], the detailed discussion of these effects has little meaning. Qualitatively we see that the total content V of the solution cell and the depth l of this cell, perpendicular to the membrane, are the important osmometer dimensions with regard to the concentration equalization. In the next part of this section we will see that the so-called adaptation effect may entirely obscure the influence of these concentration changes in the solution.

At first sight one might suppose that l, which approximately equals the ratio V/S must be made as small as possible. This is limited, however, by two factors which influence the concentration of the solute:

1) the influx or efflux of solvent during the equilibration. This effect may be reduced by adjusting the liquid levels at once to about the expected equilibrium value when filling the osmometer.

2) Adsorption on the membrane may diminish the effective con-

centration. Such adsorption depends on the ternary system: membrane, solvent and solute.

When, nevertheless, the "driving" hydrostatic head equals the difference between the real hydrostatic head and the equilibrium osmotic head, it can be seen from eq. (2) that a greater value of k corresponds with a more rapid establishment of this equilibrium osmotic head. Hence S must be made as large as possible, whereas a very small value of d is favourable. How small this diameter may be taken is essentially a matter of the influence of surface tension effects (see III.1e). Hence, as for most osmometer constructions l does not have its minimum value, the ratio V/S will give a good idea of the rate of equilibration, a smaller value of V/S indicating a higher rate. A list of these ratios for 13 different osmometers has been given by WAGNER [7]. For the osmometers used by us the following ratios were calculated:

FUOSS-MEAD osmometer: $V/S = 0.2$ cm
ZIMM-MYERSON osmometer: $V/S = 1.0 - 1.5$ cm.

III.1b. *The measuring technique*

There are three ways in which the osmotic pressure can be determined and, although we used only two of these methods, all three of them will be described here for the sake of completeness.

The static method

This method consists in waiting until the solvent flow through the membrane is finished, the internal head of the osmometer then being the osmotic equilibrium head. For the moment we do not consider the necessary corrections (see III.1e) and assume moreover that a real equilibrium head is reached, which implies that the membrane is really semipermeable. In a later section (III.2) it will be explained that this last restriction is a very essential one.

As explained in III.1a, the ratio V/S plays an important rôle in the length of time required for a static measurement. With most types of osmometers, however, it is possible to reduce the total time for a static measurement by adjusting the initial internal head to within a few centimeters or less of the expected equilibrium head.

Besides the time needed for the equalization of the temperature in the thermostat, which is no more than 5 to 15 minutes in most cases, some time is required for the *adaptation of the membrane* to the new filling. This effect is more marked when filling with a new concentration and becomes rather large at higher con-

centrations. This adaptation effect, perhaps due to adsorption on the membrane, although deformation of the membrane during the filling procedure may be important too, will be manifest by irregular changes in the internal head, which do not obey the relation (2).

When carrying out static measurements, we always waited until the next day after filling was completed, and then controlled the difference in menisci for at least five hours. The adaptation of the membrane, however, never required more than two or three hours, so that it is of importance only in the dynamic method.

The compensation method

It has already been pointed out that the osmotic head is usually developed by the flow of solvent through the membrane. On the other hand it is also possible to exert on the solution an internal pressure of such a magnitude that this solvent flow is prevented. If the membrane is completely semipermeable (in this section we restrict ourselves to this type of membrane), the external pressure applied in the case of zero flow must equal the osmotic pressure of the solution.

BERKELEY and HARTLEY [8], who developed this method, measured the rate of movement of the meniscus in a vertical capillary at external pressures near the osmotic pressure, and interpolated to zero rate of flow. The corrections to be applied are of the same kind as discussed below (III.1e), but in addition a correction must be made for the internal head of the osmometer.

Although rapid measurements are possible by this method, the whole apparatus (including a manostat) is more complicated and does not give better results than the other methods. Only when dealing with high concentrations [9], small quantities of solution, or solutes which are liable to slow changes in composition, this method may be advantageous (for instance when dealing with solutions of proteins [7]).

The dynamic method

Although the compensation method is essentially a dynamic one, we will save this name for those methods in which no external pressure is applied. In this method the initial head h in the osmometer is adjusted to a value within a few centimeters from the expected osmotic equilibrium head. Under certain conditions, which will be clear from part (a) of this section, the difference $(h-h_o)$ is an exponential function of the time t:

$$h-h_o = H \exp(-kt) \qquad (4)$$

where H is the value of $h-h_o$ at time zero, and k is the proportionality constant indicated in eq. (2).

FUOSS and MEAD [10] approached the equilibrium head h_o from both sides, beginning with approximately the same absolute value of H. The two curves obtained were drawn on the same paper in a symmetrical manner. With a horizontal time axis the half sums of the ordinates of the two curves give the asymptote of these curves, which in its turn is the equilibrium head h_o.

In our determination of the osmotic pressures of solutions of sodium carboxy methyl cellulose (see IV.1a) in aqueous 0.3 m NaCl we compared the dynamic with the static method. It turned out that at the lowest concentrations the two methods gave nearly the same result; at the higher concentrations the static value was always somewhat higher than the dynamic one (See table I).

Table I

Osmotic pressures of NaCMC by the dynamic and the static method

Conc. (g/100 cm^3)	$\pi_{dyn.}$ (cm solvent)	$\pi_{stat.}$ (cm solvent)
0.08	0.16	0.18
	0.17	0.20
0.16	0.38	0.43
0.26	0.90	0.96
0.29	1.03	1.10
0.37	1.47	1.56

The dynamic curves are not truly symmetric, however, as can be seen from a typical example (fig. 2). It is striking that in most cases the value of the asymptote of the upper curve is nearly the same as the static value for the osmotic head. This means that equilibrium is better approached when solvent is pressed out of the solution cell.

The dynamic measurements were made about one hour after the filling of the osmometer, the static measurements after one day. When the dynamic measurements were repeated after one day, a good half sum value was found. This indicates that the reported deviation is due to the behaviour of the membrane. It seems likely that this is the same adaptation effect as mentioned before.

As the behaviour of sodium carboxy methyl cellulose may be somewhat complicated because of its polyelectrolyte character, we repeated this comparative study with solutions of polystyrene in toluene. The result was the same. Exactly the same observations have been made by MASSON and MELVILLE [11], in connection with solutions of polyvinyl xylene in benzene.

PHILIPP [12] has reported an algebraic method for the calcula-

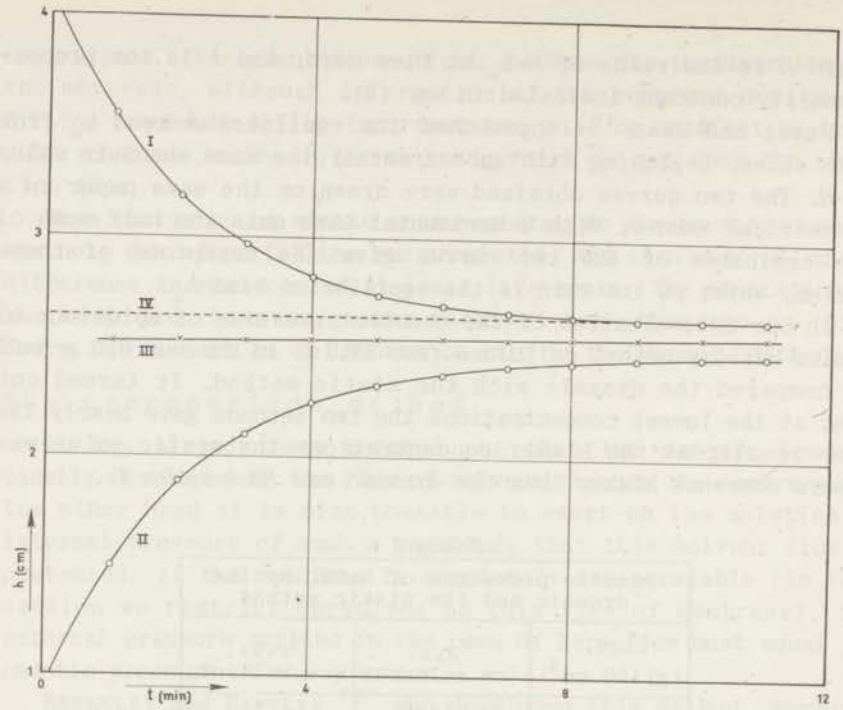

Fig. 2
Dynamic curves I and II, shifted with respect to each other in the direction of the time-axis until the best possible symmetry is attained. Solution of NaCMC 0.29 g/100 cm^3 in aqueous NaCl 0.3 m. III = half-sum values, IV = static value.

tion of the osmotic pressure from one curve only. When three consecutive measurements of h (denoted by h_1, h_2 and h_3) are done with equal time intervals, these h values are interrelated as follows:

$$(h_2-h_o)/(h_1-h_o) = (h_3-h_o)/(h_2-h_o) \qquad (5)$$

as can be derived immediately from eq. (4). Rearrangement gives for the equilibrium osmotic head:

$$h_o = (h_1h_3 - h_2^2)/(h_1 + h_2 - 2\,h_2) \qquad (6)$$

By means of this method we calculated the h_o values from the typical curves of fig. 2, and compared these values with the half-sum and the static value (Table II). The upper curve again gives the static value, whereas the lower curve yields a much lower h_o. PHILIPP finds greater values of π for the efflux curves as well, but he did not compare these values with the static ones, which were higher than the half-sum values. A slightly different method

Table II

Evaluation of the osmotic pressure by the methods of Philipp and of Fuoss and Mead (π in cm solvent)

Upper curve (Philipp)	$h_o = 2.63^5$	$\pi = 1.10^5$
Lower curve (Philipp)	$h_o = 2.49$	$\pi = 0.96$
Half sum value	$h_o = 2.56$	$\pi = 1.03$
Static value	$h_o = 2.63$	$\pi = 1.10$

for the evaluation of π from a single dynamic curve is based on eq. (2):

$$dh/dt = -k\,(h-h_o). \qquad (2)$$

To this end we plot the differences Δh_n between the successive readings of the internal head against the corresponding mean head $\bar{h}_n = \frac{1}{2}(h_{n+1} + h_n)$. The intercept of the resulting straight line with the $\bar{h}_n$-axis has the value h_o. For the two curves of fig. 2 we found nearly the same h_o values as are found by PHILIPPS's method; calculation by means of the method of least squares gives exactly the same h_o.

Concluding we may say that the validity of eq. (3) is the crucial point in the application of any of these dynamic methods. The static method will always give either the same or more accurate results, all the more as the dynamic method may obscure slow diffusion of solute molecules through the membrane. We believe that instead of performing the more laborious dynamic measurements with one osmometer, the simultaneous operation with a series of osmometers used statically gives a more reliable result in perhaps only a little more time.

III.1c. *The FUOSS-MEAD osmometer* *)

The FUOSS-MEAD osmometer [10] is a symmetrical osmometer, in our case consisting of two chromium plated brass plates with a diameter of 15 cm and a thickness of 2.5 cm. This thickness was suggested by GOLDBLUM [13], who found that with 5 mm stainless steel plates a bending of the plates could be detected when the bolts were tightened. The cells (see fig. 3) consist of a system of seven circular grooves, 3 mm wide, 2 mm deep, with a distance of 3 mm between adjacent grooves. The groove system is inter-

*) The osmometer was constructed by J.C.Heinen, instrumentmaker at the Lab. for Inorg. and Phys. Chem. in Groningen.

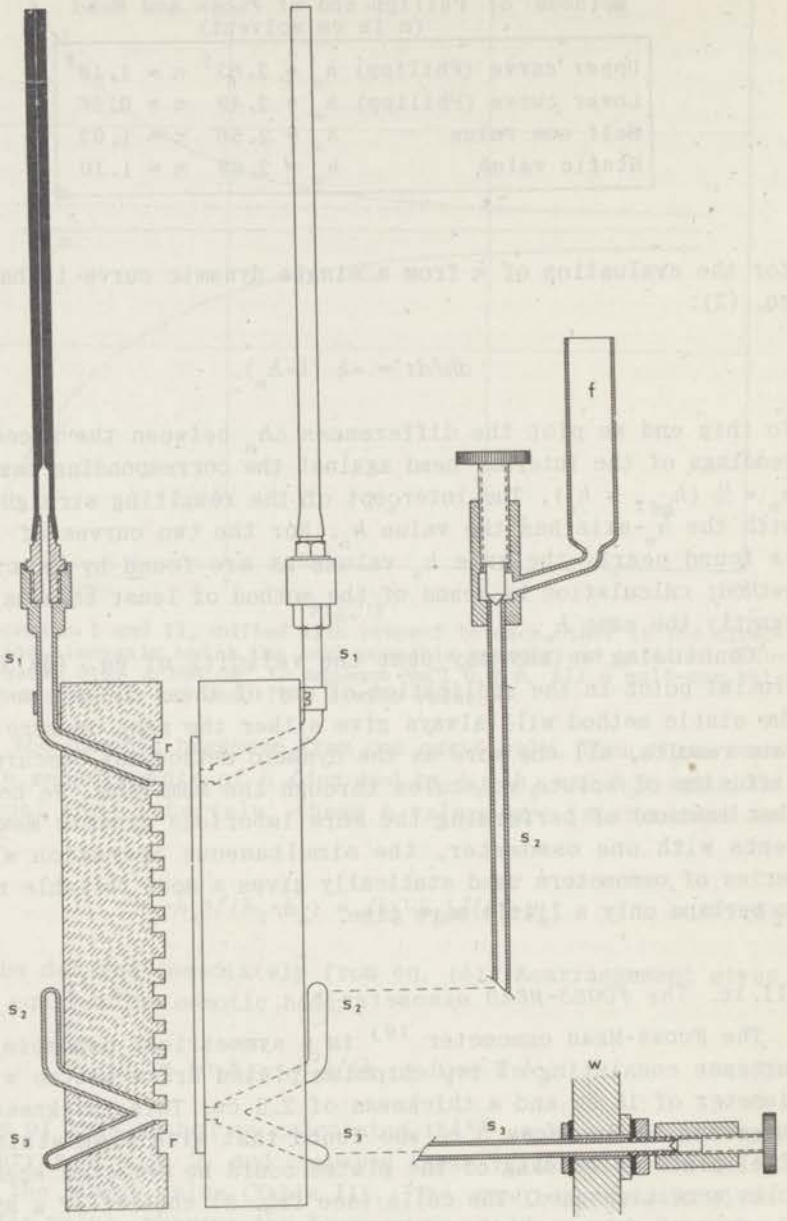

fig. 3
Our Fuoss-Mead osmometer. Insets: tube s_2 parallel to s_1 and tube s_3 perpendicular to plane of drawing; w represents the wall of the temperature bath. See text.

sected in a symmetrical manner by three radial channels (3 mm wide), one of which is vertical. The entire groove system of a cell is just opposite the groove system of the other cell, the membrane therefore supported by the ridges between the grooves. Displacement or deformation of the membrane can take place only in the narrow grooves; this was proved after the dismantling of the osmometer by the imprint of the ridges in the membrane. The outer ring (r in fig. 3) of one cell is 0.1 mm higher then corresponds with the height of the ridges. Between this ring and the opposite ridge of the other cell the membrane is still more pressed, thereby serving as a gasket.

With this design of the outer ring system, contact of the membrane with the water of the thermostat is greatly minimized. Such contact might disturb the membrane equilibrium, particularly when the membrane is swollen in a non-aqueous liquid. ("Ultracella" membranes conditioned to toluene are deteriorated by small droplets of water, which give brittle, opaque spots). Although in some instances adequate gasketing by the membrane was possible, this was rather difficult when the membranes were conditioned to organic liquids in which they shrank to a considerable extent. In such cases an extra ring of membrane material, conditioned to the same liquid, proved to be a satisfactory gasket. Some authors [14] have used an extra ring of a soft metal foil as a gasket.

In assembling the osmometer the two metal plates were clamped together by means of eight screws and wing nuts. After assembling, the empty osmometer was completely immersed in water and internally set under an excess pressure of 0.5 at. Any leakage then gave rise to a stream of air bubbles.

The standpipes s (fig. 3) which were led through the brass plates were made of a non-corrosive alloy (nickel-silver). To the upper pipes s_1 the capillary tubes were connected by screw joints and glass to metal seals *). The lower pipes s_2 were part of the filling system; by means of needle values they were cut off from the wider tubes f. The pipes s_3 were led through openings in the wall of the thermostat; once the osmometer was provided with a good membrane, the apparatus could stay in the thermostat during the filling procedure. These pipes too were closed with needle valves.

When filling the osmometer, it was necessary to eliminate air bubbles. To this end we always preheated solution and solvent to a temperature more than 10° C above the thermostat temperature. Moreover, after filling we first opened the valves in s_3 (s_2 closed) for a short moment; then the valves in s_2 were opened and

*) Soft glass to A.K.X.Steel.

the liquid in both compartments successively pressed up and down until no more bubbles appeared in the capillaries. Finally the needle valves in s_2 were raised entirely, so that any air caught in these pipes escaped.

The two capillaries mounted on s_1 may be of the same bore, as in the description of FUOSS and MEAD. In their arrangement, however, only one of the pipes s_2 was closed with a valve, the other was open. Hence the level of the meniscus in the capillary on the solution side remained constant. In our first arrengement we used at the solution side a capillary which was partly widened to a cylinder with a diameter of 2 cm and a height of 2 cm. Later on, we replaced this capillary by a glass tube with a diameter of 2 cm. In both cases it was necessary to determine the difference in the two levels when the osmometer was filled with solvent on both sides of the membrane. The capillary rise in the one remaining capillary was known, hence an asymmetry (see III.1a) of more than 1 mm was easily detected.

The reading of the menisci was done by means of a telescope with rack and pinion mounted on a revolving support. The telescope, with level and cross-hairs, was accurate to within 0.05 mm. The scale (in 0.25 mm) was placed beside the capillaries.

The temperature control must be sufficient to prevent "thermometer effects". By thermometer effects we mean the influence of a change in temperature on the volume of the liquid in the osmotic cell. Elevation of the temperature gives expansion of the liquid and therefore a rise of the menisci, and vice-versa. As the content of the osmotic cell, the diameter of the capillary and the expansion coefficient of the solvent are known, the influence of temperature fluctuations on the capillary level can be calculated, neglecting the permeation of solvent through the membrane into the open compartment. Taking into account that the accuracy in the reading of the menisci is about 0.1 mm, the temperature had to be controlled to within $0.005^{\circ}C$. In practice, however, a control to within $0.01^{\circ}C$ proved to be sufficient, because of the rather short intervals (1 min.) between the heating periods of the thermostat and of the great heat capacity of the osmometer body (2.5 kg of brass).

III.1d. *The ZIMM-MYERSON osmometer* *)

The ZIMM-MYERSON [15] osmometer is a much simpler apparatus than the FUOSS-MEAD osmometer. It consists of an all glass solu-

*) Some osmometers of this type were made by J.Wallinga and J.J.Nieboer, glassblowers at the Lab. for Inorganic and Physical Chemistry in Groningen and Leiden respectively.

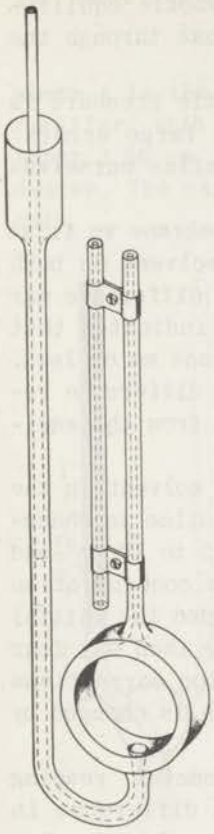

fig. 4
Modified Zimm-Myerson osmometer

tion cell with filling tube and capillary (fig. 4). In our apparatus, the glass walls of the cell were 4 to 6 mm thick, the faces were ground flat and parallel to each other to within 0.1 mm. The cell was 1.2 cm deep and had an outer diameter of 4 to 5 cm. Both open ends were covered with a semipermeable membrane which was supported by a perforated brass plate. These brass plates (4 mm thick) were clamped together with four symmetrically arranged screws. The holes through the plates had diameters of 2 mm and were 2 mm apart from each other. Leakages were detected in the same manner as described before; in many cases a second ring of membrane material was necessary for the complete gasketing.

In the design of ZIMM and MYERSON both filling tube and measuring tube are sealed to the upper side of the ring. This, however, makes filling very difficult. We therefore sealed these capillaries diametrically opposite each other onto the ring. From fig. 4 the filling and emptying procedure will be self-evident. Although ZIMM and MYERSON closed the filling tube only with a metal rod, with a diameter very close to the inner diameter of that tube, it proved to be safer to pour in addition some drops of mercury into the funnel at the top of this capillary.

Attached to the measuring capillary was a reference capillary of exactly the same bore; the lower end of this capillary dipped into the solvent to allow for an automatic correction of the capillary rise. The complete cell was fastened to a metal stand, which in turn was placed in a glass cylinder (solvent compartment). This glass vessel was closed at the upper end with a cork covered with tin foil to prevent absorption of water from the air and evaporation of the solvent. The whole assembly was placed in a thermostat with a window to allow for the reading of the meniscus. As regards the constancy of the thermostat temperature, the same conditions as with the FUOSS-MEAD osmometer had to be fulfilled. The reading of the menisci was done in exactly the same manner, but the accuracy (0.1 mm) was somewhat less, due to the disturbing influence of the two glass walls and the column of the thermostat water in the light-path.

III.1e. *The accuracy of the measurements*

Again we will restrict ourselves to a real osmotic equilibrium, assuming that no solute molecules can diffuse through the membrane.

Although the influence of temperature on osmotic pressure is small, the thermometer effect can give rise to large errors. Since this effect has been eliminated, we may confine ourselves to the inherent limitations of the apparatus.

1. When the osmometer is provided with a new membrane we first have to determine the zero pressure difference (solvent on both sides). For the first few days this zero pressure difference may be one or two cm solvent column (a higher value indicates that the membrane is useless), but soon drops to about one mm or less. Sometimes, however, a small reproducible pressure difference remains; this *asymmetry* pressure must be subtracted from the equilibrium pressure.

2. As a consequence of the influx or efflux of solvent in the solution compartment, the *concentration* of the solution is changed. As the total cell content of the osmometer is 5 to 10 cm^3 and the diameter of the capillary 0.6 to 0.8 mm, this concentration change will be of the order of 0.1% or less, provided the initial head is adjusted to a value which deviates no more than say four cm from the final (equilibrium) head. Concentration corrections are not needed, therefore, unless the concentration is changed by adsorption on the membrane.

3. *Capillary effects.* For the ZIMM-MYERSON osmometer, reading and reference capillary having the same bore, a difference in capillary rise can only be due to a difference in surface tension between solvent and solution. Generally the capillary rise for the solution of a polymer is somewhat lower than for the solvent, but in organic solvents the difference is usually negligible compared with other experimental errors. For polystyrene in toluene, for instance, the capillary rise of a 1% solution is the same as that of the solvent within 0.2%. (This has been determined for both a high and a low molecular weight product).

As we used the FUOSS-MEAD osmometer with a wide level on the solution side, the effect of a change in surface tension with concentration is ruled out. (Here we have to add algebraically the capillary rise b_o on the solvent side to the internal head measured). A much more serious correction, however, is needed here for the change in surface tension with temperature. Because the capillaries are outside the thermostat, their temperature changes with the room temperature. For pure water the temperature coefficient of the surface tension γ is:

$(d\gamma/dT) = 0.15$ dynes cm^{-1} $degree^{-1}$; 20-40°C [16], which gives for the capillary rise b:

$$b = b_o(1-0.002\ t)$$

where t is the deviation from 20°C in degrees centigrade. For a capillary with a diameter of 0.8 mm the value of b_o in water was about 3.50 cm, the temperature correction therefore 0.007 cm per degree. The capillary rise has been reduced to 20°C in all our data.

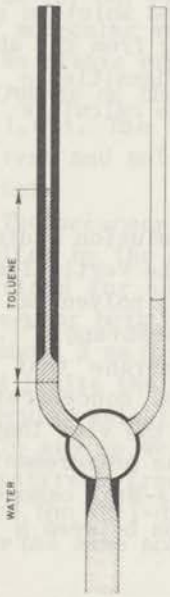

fig. 5
Capillary system used for Fuoss-Mead osmometer on solution side

The surface tension of water is still more affected by small amounts of impurities. Hence we covered the capillaries with a small glass cap, and cleaned them every day with fuming nitric acid. This, however, gave rise to many breakages of the glass to metal joints.

As the effect of impurities is much smaller in organic liquids, we tried a method by which the water in the reading capillary was covered with toluene [17]. To this end we replaced the capillary by a tube with a three way stopcock on which were sealed two vertical capillaries (fig. 5). One of these capillaries was partly filled with toluene and connected with the osmotic cell during the measurement. During the filling procedure this capillary was shut off. The water-toluene interface, however, stuck frequently, which caused false readings. We therefore rejected this method and filled the measuring capillary with a solution of wetting agent (sodium dioctyl sulfosuccinate). The surface tension of this solution is only 26 dyne/cm^{-1}, whereas that of water is 73 dyne/cm^{-1} (20°C). The surface tension of the wetting agent solution does not change much with the concentration; it is, however, necessary to control the zero pressure difference every two weeks as the wetting agent is gradually lost by diffusion. The effect of the temperature on the surface tension of the wetting agent solution is much smaller than for pure water (Table III).

4. *Density effects.* In the preceding discussions we calculated the osmotic pressure from the internal equilibrium head h_o by means of:

$$\pi = h_o\rho . \qquad \text{(see fig. 1, III.1a)}$$

However, since the osmotic pressure is the equilibrium pressure

Table III

Surface tension of wetting agent solution at different temperatures measured by J.v.Thuyl with a stalagmometer.

Conc. (g/l)	25°C	22°C	18°C	15°C
8.2	26.0	26.2	26.4	26.4
4.1	27.3	27.0	30.3	27.7

which prevents flow of solvent through the membrane, we must compare the total pressures acting on the solvent and solution side at the same height. This gives a result differing from the above formula when solvent and solution have different densities ρ_o and ρ, respectively [18)19)]. For a vertical membrane we calculate the equilibrium at the centre of the membrane:

$$\pi = (h_o + h_m)\rho_1 - h_m\rho_o \qquad (7)$$

Theoretically this is only true when in the solution sedimentation equilibrium has been established. Along the vertical membrane this is easily attained by means of flow of solvent at the upper and lower parts of the cell through the membrane [20)]. It is, therefore, only at the centre of the membrane that the osmotic equilibrium corresponds with the original concentration difference. (See, however MÜNSTER [21)], who holds the view that no sedimentation equilibrium can be set up during the measurement).

LANG [20)] has proved experimentally for a FUOSS-MEAD osmometer with capillaries of 80 cm length that the relation between h_o and h_m for the same concentration is a linear one:

$$h_o = \text{const}'. - \text{const}''. h_m, \qquad (7')$$

where const'. $= \pi/\rho_1$. The correction term in eq. (7) is $+h_m(\rho_1-\rho_o)$. In general, for low concentrations, the density difference is a linear function of the concentration:

$$\rho-\rho_o = c\ \Delta_1\rho,$$

where $\Delta_1\rho$ is the density difference between a solution with concentration $c = 1$ g/100 cm^3 and the solvent concerned. Hence:

$$\pi = h_o\rho_1 + h_m c\ \Delta_1\rho$$

and the reduced osmotic pressure becomes:

$$\pi/c = h_o\rho_1/c + h_m\Delta_1\rho \qquad (8)$$

The FUOSS-MEAD and the ZIMM-MYERSON osmometer have h_m's of 30 and 5 cm, respectively. For the polymers investigated the value of $\Delta_1\rho$ varied from 0.0018 for polystyrene in toluene to 0.0088

for polymethacrylic acid in water. From eq. (8) it can be seen that it is appropriate to apply the density correction directly to the limiting value $(\pi/c)_{c=o}$. For the FUOSS-MEAD apparatus the correction is of the order of 0.1 units in π/c (π again expressed in cm H_2O and c in g/100 cm^3). As a molecular weight of 10^5 already corresponds with a $(\pi/c)_{c=o}$ value of only 2, the density correction is always necessary (the absolute value of the correction is independent of the molecular weight).

Although the same reasoning is relevant for the ZIMM-MYERSON osmometer, the magnitude of the effect is only one sixth of the value for our FUOSS-MEAD osmometer, and need not to be considered for molecular weights less than 5.10^5.

We always replaced ρ_1 in eq. (7) by ρ_o; this has only a small influence on the slope of the π/c vs c plot (of the order of 0.1 to 1.0%). The influence of the temperature on the density of solvent and solution (in the FUOSS-MEAD apparatus) is also neglected.

The *accuracy* of an osmotic molecular weight determination is limited by the corrections discussed under 1, 3 and 4. The corrections for asymmetry and capillary effects are corrections in π; for both osmometers they give rise to a maximum deviation of about 2 mm (the accuracy of the telescope readings is 0.05 mm). This limits the use of low concentrations, especially in the high molecular weight range.

To sum up we give in fig. 6 a π/c vs c diagram for several polystyrene fractions in toluene (ZIMM-MYERSON osmometer), in which the full-drawn curves connect points that can be determined with the same accuracy (iso error lines).

III.1f. *The extrapolation of the reduced osmotic pressure to zero concentration*

From the considerations on the virial equation for the osmotic pressure (II.2) it will be clear that a linear extrapolation is only permissible for low concentrations and low molecular weights. When we remember that A_2 depends on the interaction of pairs of solute molecules, it is reasonable to expect that the influence of A_3 (interaction in clusters of three solute molecules) will become significant at lower concentrations as the value of A_2 itself increases. In general a curvature in the π/c vs c plot may be expected when A_2 has a value above 0.5 (π in cm H_2O and c in g/100 cm^3). Some reliable data in this range, however, can be represented by a linear equation as well [22)23)]. We will prefer a rectilinear equation in all cases where no definite evidence of a curvature is present.

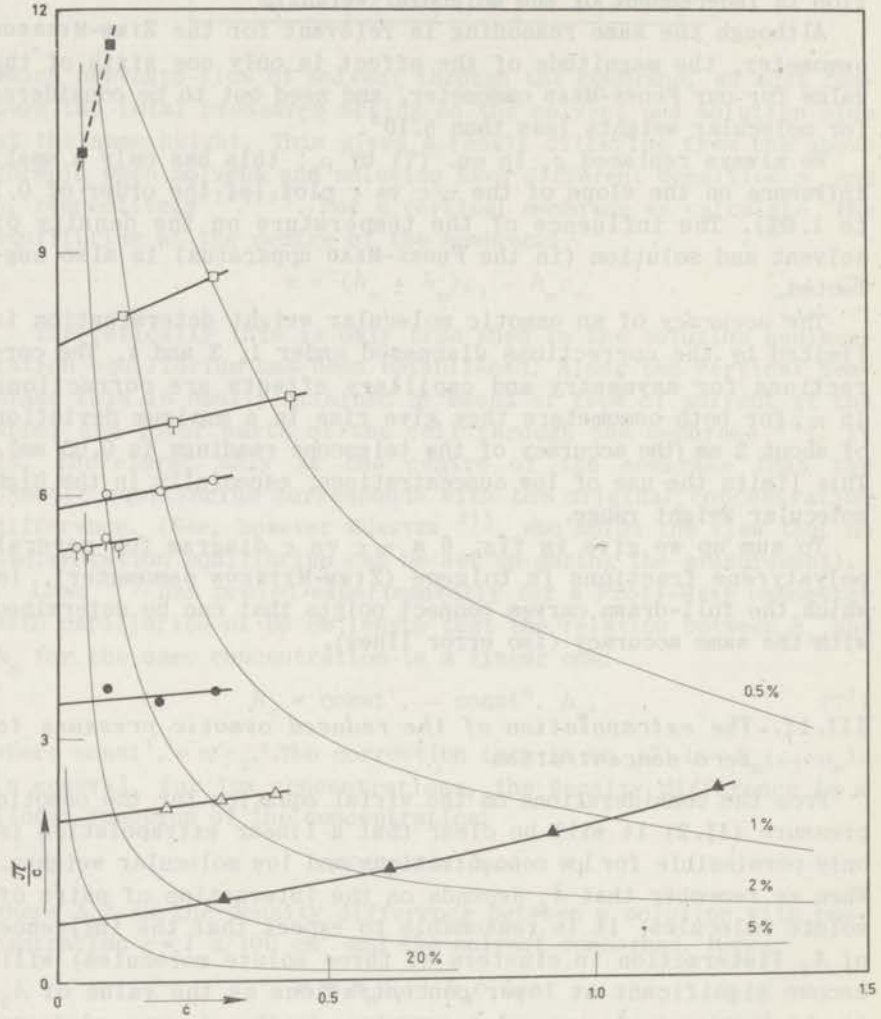

Fig. 6
Example of π/c vs c diagram with iso error lines for polystyrene fractions (D) in toluene at 25°C (see IV.4). The maximum relative error is indicated in %.

As has been shown, there does not exist a completely satisfactory theory for the relation between A_3 and A_2 as yet, all proposed theoretical [24)25)] and empirical [26)] relations being of a limited applicability [27)]. At the present time a numerical analysis is the best method for the evaluation of the values of $(\pi/c)_{c=o}$ and A_2.

DUCKER, FIELLER, HOOKWAY and TOWNSEND [22)] made a statistical analysis of their accurate measurements of osmotic pressures. By means of the *method of least squares* they investigated which of the following three equations is the best one.

$$\pi = a\,C + bC^2 \tag{9}$$

$$\pi = a\,C + bC^2 + dC^3 \tag{10}$$

$$\pi = a_1C + a_1b_1C + (5/8)a_1b_1^2C^3. \tag{11}$$

Equations (9) and (10) are the simple linear and quadratic equations for π/c, eq. (11) is FLORY's equation [24)] (see II.2). In all nine systems examined the mean square deviation of the observed values of π from the calculated ones was about the same for eqs. (9) and (10), but 10 to 20 times greater for eq. (11).

The graphical method of BAWN, FREEMAN and KAMALIDDIN [28)] is less reliable. These authors write eq. 10 in the form:

$$\pi/c = a + bc + dc^2, \tag{12}$$

and select pairs of values from their experimental *curve*, which are substracted from each other:

$$(\pi/c)_1 - (\pi/c)_2 = b(c_1-c_2) + d(c_1^2-c_2^2)$$

or

$$\frac{(\pi/c)_1 - (\pi/c)_2}{c_1 - c_2} = b + d\,(c_1 + c_2). \tag{13}$$

A plot of the left hand term against (c_1+c_2) gives a straight line with intercept b and slope d.

Quite another method for the evaluation of the molecular weight has been proposed by GUGGENHEIM and MC GLASHAN [29)]. They write eq. (II,2.15) in the form:

$$(\pi\,V_1)/(RT) = \varphi/m + \text{function}\,(\varphi,\ \beta/RT), \tag{14}$$

where φ is the volume fraction of the solute, m the ratio of the molar volume of the solute to that of the solvent and β the heat of mixing term. When comparing equal volume fractions of solutions of different fractions (1 and 2) of the same polymer, they subtract the corresponding equations (14) from each other:

$$\frac{(\pi_1 - \pi_2)\,V_1}{RT} = \left(\frac{1}{m_1} - \frac{1}{m_2}\right)\varphi. \tag{15}$$

A plot of $(\pi_1-\pi_2)v_1/RT$ against φ should give a straight line of slope $(1/m_1-1/m_2)$.

Any dependance of β (and A_2) on the molecular weight is obscured in this way; moreover, an independent determination of one m value remains necessary.

The use of physical methods to reduce the second virial coefficient to zero, and hence to obtain a horizontal linear π/c vs c plot has been discussed in chapter II.2, together with the anomalies caused by association phenomena.

III.2. Properties of membranes.

For an understanding of the phenomenon of semipermeability it is essential to have a good knowledge of membranes, permeable as well as impermeable. We will therefore treat in this section some properties of membranes which are important in this respect.

a. Introduction.
b. Characterization of membranes.
c. Determination of permeabilities.
d. Dialysis.
e. Ultrafiltration.
f. Types of membranes.
g. Some consequences for osmometry.

III.2a. *Introduction*

From the very beginning of osmotic experiments the molecular interpretation of membrane behaviour has been a much disputed question. TRAUBE held the view that membranes acted as sieves, but many later investigators have made it clear that the solubilities of solvent and solute in the membrane substance may play a predominant role, and that sorption effects cannot be neglected. A great deal of trouble seems to be due to a generalization of the properties of one type of membrane to all other types. Nearly all membranes which are used nowadays have properties characteristic for gels, or which at least can be interpreted as gel properties. We will, therefore, call them gel membranes.

According to BUNGENBERG DE JONG [30] a gel is "a colloidal system of solid character, in which the colloidal particles somehow constitute a coherent structure, the latter being interpenetrated by a (usually liquid) system consisting in kinetic units smaller than colloidal particles". In most gels the volume fraction of the solid substance may be quite small. In collodion membranes in water, for example, the volume fraction of the cellulose nitrate may be as low as 0.05. As the solid network structure in such a system must be very open, the properties of the

liquid in the gel often do not differ much from those in the pure liquid. For instance, the diffusion velocity of solute molecules in the membrane has been shown to be essentially the same as in the solvent, provided no specific interaction between solute and membrane substance occurs.

In general we may distinguish between four kinds of interaction:

a. electrokinetic interaction due to the electrolytic character of the components;
b. chemical interaction;
c. surface interaction due to positive or negative adsorption of the solute by the membrane substance;
d. geometric interference when the diffusing molecules are not small compared with the channels in the gel structure.

Although membrane behaviour governed by interactions of type (a) is of the utmost interest in aqueous systems, and has been thoroughly investigated, this type of interaction is absent in the non-electrolytic systems with which we were specially concerned. Real chemical interaction may be detected easily; there may occur a kind of chemical interaction which cannot be distinguished from adsorption, however. Sorption caused by VAN DER WAALS forces will nearly always be present; that which causes the least disturbance experimentally is a negative adsorption, by which is meant a preferential adsorption of solvent molecules by the membrane substance, resulting essentially only in an apparent increase of the geometric interference. In the following discussion we will treat the membranes to a first approximation as molecular sieves, small surface interaction being accounted for as corrections to the sieve model. This is justified only when the channels in the solid network are large compared with the dimensions of the solvent molecules. Hence, flow of liquid through the membrane must be viscous flow [31].

For any particular kind of membrane it can easily be detected whether we are dealing with viscous flow or not. For viscous flow through a circular capillary of radius r POISEUILLE's law gives the volume yield per second:

$$dv_c/dt = \pi r^4 p/8\eta l, \qquad (1)$$

where p is the pressure difference over the capillary of length l; η is the viscosity of the liquid. For a porous medium this expression takes the form:

$$dv_m/dt = KS\, p/\eta, \qquad (2)$$

where S is the area through which flow takes place (= membrane

surface), and K a constant determined by the geometry of the porous medium.

For various types of membranes eq. (2) has been checked. ERBE [32] for instance finds for collodion and cellulose membranes proportionality between dv_m/dt and p (the liquid was water; the pressure differences ranged from 5 to 30 cm Hg). The same must of course be true for all membranes to which eq. (1) in section III.1 applies:

$$dv_m/dt = PSp = KSp/\eta, \qquad (2')$$

which is the case for nearly all osmotic membranes. ERBE has pointed out that deviations from this proportionality may sometimes be due to blocking of the membrane channels by impurities in the liquid. This can be prevented by the use of ultrafiltered liquids, which therefore are recommended for this type of investigations. At higher pressures the cellulose membranes are reversibly deformed which gives a lower K (or P) value; collodion membranes are not affected in the range of pressures investigated.

A second test of relation (2) is possible by comparing different dv_m/dt and η values at the same pressure. BIGELOW [33] has measured permeability coefficients (P) for the flow of water through collodion membranes and parchment paper at temperatures between 1 and 85°C. He proved indeed that the temperature dependence of P was quantitatively in accordance with that of η:

$$P\,\eta = K = \text{constant}. \qquad (3)$$

DUCLAUX and ERERRA [34] pressed organic liquids and water through collodion, cellulose and cellulose acetate membranes which were conditioned to the same liquids. They proved also the validity of eq. (3), except for the very dense cellulose acetate membranes.

As a provisional conclusion we assert that most common osmotic membranes are gel-membranes, in which the passage of molecules is mainly governed by the geometric structure of the network, although sorption effects may be important too.

III.2b. *Characterization of membranes*

For osmometry, dialysis and ultrafiltration the most important properties of gel membranes are the permeability for the solvent and the selectivity for the solute; hence a good characterization of these properties is very desirable. It will be clear that both largely depend on the openness of the network structure of the gel, which can be expressed by the volume fraction W of the liquid in the membrane phase. Other valuable information on membrane behaviour may be obtained from the critical bubble pressure, dialysis potential and electrokinetic phenomena.

In a long series of articles MANEGOLD [35] and his coworkers

have discussed most of these properties for various idealised structures and compared the results with the empirical properties of collodion membranes. In most of these structures the membrane is treated as a homogeneous medium intersected by channels which all have the same cross-section, but are oriented at random over all directions in the membrane. It is a consequence of this model that only 1/3 of all channels is effective in transport processes through the membrane. ELFORD [36], however, who also carried out a systematic investigation on collodion membranes, assumes that the greater part of the channels crosses the membrane nearly perpendicularly and hence is completely effective in the transport processes. He further supposes that the channels are circular pores with different radii. Although MANEGOLD believes that a three-dimensional set of identical slits distributed at random over all directions in the membrane is the best mathematical model for the openness of collodion membranes, the model proposed by ELFORD can explain the membrane properties equally well. Both models are very crude approximations to the structure of a gel membrane, but they give an idea of the channel dimensions which is very useful. We will use ELFORD's model as it has some mathematical advantages.

To calculate the coefficient K of eq. (2) we divide the pore system per cm^2 of membrane into groups of n_i pores with radius r_i. Assuming that all pores have about the length l (membrane thickness), we find

$$K = (\pi/8l) \sum_i n_i r_i^4. \qquad (4)$$

If the volume fraction (W) of the liquid may be set equal to the total fraction of the membrane volume that is available for transport processes (ELFORD), the value of W is:

$$W = \sum_i n_i \pi r_i^2 \qquad (5)$$

Hence the coefficient K/W is closely related to a kind of representative pore radius (r_{av}) of the membrane:

$$K/W = (1/8l)(\sum_i n_i r_i^4 / \sum_i n_i r_i^2) = r_{av}^2/8l. \qquad (6)$$

We see from this equation that r_{av} is a statistical average which lies decidedly in the region of the highest r_i values. For the MANEGOLD model the ratio K/W is:

$$K/W = r^2/24l. \qquad (6')$$

For comparison of different membranes the expression Kl/W is the best one we can use. Apart from a numerical constant, which is different for different membrane models, this expression is a good measure of the openness of the network structure.

An essential difference between the conclusions of ELFORD and

MANEGOLD is due to their different opinions about the part of the channels which is effective. To us the idea of ELFORD [37)38)] that an orientation of the pores in a direction perpendicular to the membrane surface is favored, seems to be more reasonable than the view of MANEGOLD that all directions occur with equal frequency, although the truth may be in between. There can, however, exist no doubt that the evaporation of solvent during the gel formation (see III.2f) is to some extent at least a directing process. BARTELL and VAN LOO [39)], for instance, have followed the drying process with a microscope. They suspended coloured particles in the collodion solution and observed at first evaporation from irregularly arranged points on the surface; the solution is supplied by vortices ending in these points. After a short time the evaporation points have arranged themselves in a regular manner, which regularity may be caused by competition between the vortices. This structure which can be seen with the unaided eye as a honeycomb structure, is fixed by immersing the membrane in water. The implicit conclusion of BARTELL and VAN LOO that one vortex in the solution gives rise to one pore in the membrane, cannot be true, however, as the number of pores calculated from eq. (6) is at least of the order of 10^{10} per cm^2 [35)], which is much larger then the number of vortices. ELFORD (quoted by FERRY [38)]) indeed found no structure with the microscope, nor with the ultramicroscope. This is in accordance with the calculated average pore radius of his membranes ($r_{av} < 50$ mμ).

Some other methods which also give information about membrane geometry will now be discussed:

1. *The critical bubble pressure method* [40)41)]. The critical bubble pressure is the minimum pressure necessary to press air through a membrane imbibed with liquid. For a single capillary with radius r (in cm) the force exerted on the column of liquid is $\pi r^2 p$, where p is the excess pressure in dynes/cm^2. The counterforce which has to be overcome is due to the surface tension γ (in dyne/cm). For zero contact angle the two forces equal each other when:

$$\pi r^2 p = 2\pi r\gamma,$$

hence

$$p = 2\gamma/r \qquad (7)$$

so that air is pressed through the capillary when $p \geqq 2\gamma/r$.

In the case of a membrane we can by means of this method find the radius of the greatest pores (r_{max}). Because of the small pores in the membrane the interfacial tension air-water (73 dynes/cm) necessitates pressures which are much too high. BECHHOLD [40)] therefore replaced the system air-water by water-

isobutylalcohol, which has an interfacial tension of 1.7 dynes/cm at room temperature.

ERBE [42] refined this method for the determination of the pore radius distribution. He measured at the same time the bubble pressure and the rate of flow through the membrane, and calculated by means of equations (2), (4) and (7) the number of pores open at that pressure. At a higher pressure another group of pores is opened, the radius in this group again is given by eq. (7). The rate of flow now is determined by the sum of the transports through these pores and all wider ones. After a series of such measurements all pores are filled with the strange liquid, which manifests itself by the validity of POISEUILLE's law at a further increase in pressure [43].

ELFORD has determined the ratio $r_{max.}/r_{av}$, which for "Ultracellafilter" has a value of 3 to 6; and for "gradocol" membranes a value of about 2 (for these membranes, see part f).

The accuracy of the bubble pressure method is restricted by three factors [42].

a) Any small excess pressure opens the corresponding pores only after a long interval of time. For a determination of a pore radius distribution by ERBE's method one must, therefore, wait until the rate of flow at a new pressure becomes constant.

b) The liquids may to some extent be soluble in each other. Effects due to such mutual solubility can be avoided by the use of liquids saturated with each other.

c) The liquids will show different behaviour towards the membrane substance. In the case of isobutyl alcohol and water, for instance, the alcohol is preferentially adsorbed by collodion. For this reason the water must be pressed through the membrane after this has been conditioned to the alcohol, and not vice versa.

2. Some idea about the maximum pore radius may also be obtained from *dialysis* and *ultrafiltration* experiments. This will be discussed in parts d and e of this section.

3. The *electrochemical* and *electrokinetic* behaviour of the membrane in aqueous electrolyte solutions is closely related to its structure. Although we have not performed any experiment in this field, we will stress some important points concerning the electrochemistry of membranes [44]. A general phenomenological theory on membrane processes, including electrokinetic processes, has been developed by STAVERMAN [45] on the basis of the thermodynamics of irreversible processes. Although the results of any model theory have to be in conformity with the phenomenological laws

derived by STAVERMAN, these laws cannot afford us a kinetic picture of the membrane behaviour. For the two theories mentioned below it has been proved that they fit in with STAVERMAN's theory [44)45)].

MANEGOLD [46)] has applied the theory of the electrical double layer to electro-osmotic and related processes, although he states that such a procedure is only correct when the diameters of the pores are much larger than the thickness of the double layer. This, however, cannot be said of the usual membranes with an r_{av} of 5 to 50 mμ. MANEGOLD and SOLF [46)] have indeed found large discrepancies between theory and experiment.

A much better approach to the electrochemistry of membranes was started by MEYER and SIEVERS [47)], and TEORELL [48)] for the membrane (or dialysis) potential. These authors suppose that the membrane network carries fixed electrical charges, due to the presence of ionizable groups or formed by adsorption of ions from the imbibing solution. The number of these immobile ions per unit of volume of the liquid in the membrane will be called the membrane ion concentration A. If equilibrium at the membrane surface is established rapidly, the distribution of mobile ions in the membrane phase is governed by a DONNAN equilibrium between the membrane phase and the electrolyte solution. The two DONNAN potentials on both membrane-water interfaces may be readily expressed in A and the concentrations of the ions at either side of the membrane; the sum of these potentials plus the diffusion potential in the membrane is the membrane potential. SCHMID [44)] has used the same picture of fixed ions in the membrane network for a theory of the electrokinetic membrane-processes. He assumes that the surface of the pores is non-conducting and the counter ions are uniformly distributed in the pore liquid, although a kind of DEBYE-HUCKEL arrangement round the fixed ions would be a more representative model.

As a demonstration of this theory we will give SCHMID's [44)] treatment of the electro-osmotic pressure. Suppose we have over any arbitrary pore with length l_i a potential difference E, then the electric field strength in the pore is E/l_i. In the pore we have (for negative fixed ions) an excess of positive charge $+A$, hence the electrical force f_1 per volume element Δv is:

$$f_1 = FA\ \Delta v/l_i,$$

where F is the faraday. In the stationary state the electro-osmotic pressure π_e exerts on the volume element Δv a force f_2 of the same magnitude in the opposite direction:

$$f_2 = \Delta v\ \pi_e/l_i$$

where π_e/l_i is the pressure gradient in the pore.

Hence: $\pi_e = F\,A\,E.$

The older theory claimed an inverse proportionality between π_e and the square of the pore radius $(r_{av})^2$. MANEGOLD and SOLF [46], however, found no dependence of π_e on r_{av}.

III.2c. *Determination of permeabilities*

The permeability coefficient P of a membrane may be directly determined by measuring the rate of flow dv_m/dt through a given membrane area S when a known excess pressure p is applied:

$$dv_m/dt = PSp \qquad (2')$$

A calculation from osmotic dynamic curves is also possible by means of eq. (2) in section III.1, which for an osmometer with two identical capillaries may be written as:

$$dh/dt = -P(S/s)2g\rho(h-h_o), \qquad (8)$$

where s is the cross-section of the measuring capillary, and g is included to obtain the same c.g.s. dimensions as in eq. (2'). For an osmometer with only one narrow capillary eq. (8) is converted to [49][50][51]:

$$dh/dt = -P(S/s)g\rho(h-h_o). \qquad (8')$$

In part (a) of this section we already mentioned the influence of blocking effects and compression on the permeability of membranes. The most serious influence on the permeability may be due to a very slow interaction between the imbibing liquid and the membrane. Sometimes it has been observed that the permeability of a membrane changes considerably more when the liquid component is interchanged by another liquid than can be explained by the change in viscosity (eq. (3)). This may be due to structural changes resulting from the osmotic withdrawal of the first liquid during the conditioning process [52]. Such an effect can be avoided when the conditioning to the second liquid is done via a series of mixtures of gradually increasing concentration. In some other cases, however, the permeability in the new liquid decreases for an indefinite length of time [51]. (The opposite effect, increase in permeability, does not take such a long time, and is more exceptional). This effect, which is essentially a very slow shrinking process, is probably due to a very slow coiling up of the chains between the junction points of the network. BREITENBACH and FORSTER [51] found such an effect for "Ultracellafilter" (see III.2f) in benzene and cyclohexanone. We found for two membranes

of the same species in toluene a decrease in P of more than 5% per day for a period of two months.

For most systems equations (2') and (8') are valid, however, For a calculation of P from osmotic dynamic curves we write eq. (8') in the integrated form:

$$\ln\{(h_1-h_o)/h_2-h_o)\} = P(S/s)g\rho t = kt, \qquad (9)$$

which is eq. 4 in section III.1. There we have discussed the methods suitable for an evaluation of k; when the osmometer dimensions are known, a calculation of P is now possible. From the literature we calculated the following figures [49)50)51)]:

gel-cellophane	$P = 10\text{-}50 \cdot 10^{-8}$
denitrated collodion	$P = 100\text{-}500 \cdot 10^{-8}$
"Ultracellafilter fein"	$P = 75\text{-}250 \cdot 10^{-8}$,

where all quantities are expressed in c.g.s. units, except the time t, which is given in hours.

For the determination of permeability coefficients (in water) we used a simple apparatus of the type described among others by BJERRUM and MANEGOLD [35)]. Between two funnels of brass with the plane edges directed to each other was placed a perforated brass plate as a support for the membrane. The funnels together with two rubber packings on either side of the supported membrane were clamped onto each other by means of six symmetrically arranged screws. The apparatus was mounted with the membranes in a vertical position. The funnel at the pressure side was connected via a wide bulb (liquid reservoir) with a simple manostat (two communicating vessels filled with water or mercury) and an open manometer. The funnel at the open side was connected with a horizontal capillary in which the rate of flow was measured by the aid of a millimeter scale. The level of the liquid in the wide bulb was adjusted at the height of the capillary. For a calculation of P we have to know the diameter of the capillary and the effective surface of the membrane. A calculation of the total surface of the holes in the support gives: S=3.4 cm^2; this value was controlled by a direct determination of S:

Between a collodion membrane and the support we placed a number of filterpapers (first none, then one, two, and so on). If we assume that the inverse permeabilities which will be called resistances, are additive, we are able to calculate for every combination of membrane plus filter paper(s) the resistance of the membrane alone, provided the resistance of one filter paper is known. This was measured in a separate experiment. Calculations of the resistance for the membrane gave a constant value of 3.96

when it was supported by one or more filters; the resistance of the membrane without filterpaper support was 12.36. Hence the effective surface is 3.96/12.36 times the total area inside the rubber packing: S_{eff}=4.4 cm^2. The accuracy of this value for S, which we used in all our calculations, is not high, but sufficient in view of the other limitations of the method.

In the determination of permeabilities (see III.2f) we always measured the rates of flow at at least three different pressures, and calculated P for every pressure. The reproducibility was within 2 to 5 per cent, although the first measurements sometimes gave much higher values. In that case more measurements were made until P remained constant.

III.2d. *Dialysis*

The selectivity of the membrane to a solute can be investigated in two different manners. In the first place we may compare the diffusion of the solute under the influence of a concentrarion gradient through a membrane with the free diffusion of the same solute in the same liquid. This diffusion through a membrane will be called dialysis, although the term often is restricted to a separation process of colloids and crystalloids by means of a membrane. In the second place we can filter a solution through the membrane under the influence of a pressure and compare the concentration of the solute in the original solution with that in the filtrate. A comparison of the theoretical and experimental merits of these two methods will be given in the part on ultrafiltration.

Imagine two vessels with solutions of weight concentrations c_1 and c_2, separated from each other by a gel membrane of thickness l. It is assumed that the equilibrium between the solution and the membrane surface is established rapidly. Then, in the stationary state the concentrations in the surface layers of the membrane will be $c_{1m} = \sigma c_1$ and $c_{2m} = \sigma c_2$ respectively, where σ is the distribution coefficient for the solute between solvent and membrane phase. Hence the concentration gradient in the membrane is $(c_1 - c_2)\sigma/l$, and according to FICK's law the amount of solute (in grams) that passes through 1 cm^2 of the membrane surface per second is:

$$dn/dt = D_m(c_1-c_2)\sigma/l, \qquad (10)$$

where D_m is the diffusion coefficient in the membrane. The dialysis coefficient δ may be defined by the equation:

$$dn/dt = \delta(c_1-c_2)/l, \qquad (10')$$

hence $$\delta = D_m \sigma. \qquad (11)$$

For sieve membranes the diffusion coefficient in the membrane liquid is the same as in the outer liquid ($D_m = D$), provided the pores are large compared with the solute particles, and hence D_m can be derived from any suitable diffusion experiment. The distribution coefficient for a sieve membrane is simply the ratio of the free volume in the membrane phase to that in the solution (ELFORDS model):

$$\sigma = W. \qquad (11')$$

MANEGOLD [53] investigated the relation between σ and W to verify which of his mathematical models was most suitable. MANEGOLD again points out that the results are best fitted to the irregular slit model; ELFORDS model, however, which accounts for the results equally well, is not discussed by him.

When the membrane exhibits any kind of interaction with the solute (positive or negative adsorption), the values of σ and D_m may be entirely different from the values for sieve membranes. For instance, when positive adsorption occurs, the distribution coefficient may become greater than unity, while the diffusion coefficient is affected in an unpredictable manner, as diffusion may occur along the surface of the solid membrane substance. Negative adsorption will reduce the apparent volume available for the diffusion process, as σ is decreased. When the diameters of the channels in the membrane become comparable with the radii of the diffusing molecules, D_m will be diminished too.

COLLANDER qualitatively compared the relation between the rates of dialysis and the molecular volumes for various dialysing compounds (non-electrolytes) diffusing through cupriferrocyanide [2] and collodion membranes [54]. In general he finds smaller δ values for higher molecular volumes. The exceptions, phenol and m.nitrophenol which dialyse too rapidly through collodion membranes can be explained by the interaction between these substances and the membrane (positive adsorption).

MANEGOLD [53] compared the free diffusion coefficient for urea, sucrose and hydrochloric acid in water with their dialysis coefficient in graded collodion membranes. The minimum pore diameter which still allows for free diffusion in the membrane is about 20 Å for urea and for hydrochloric acid; the results for sucrose are not very conclusive.

A great number of dialysis experiments have been performed by BRINTZINGER [55] who improved the method to a means for determining molecular volumes of dialysing compounds. In his experiments the vessel containing the solution is rather small (volume V), where-

as the vessel containing the solvent is so large that concentration changes herein can be neglected. Eq. (10) now takes the form:

$$dc/dt = dn/VDT = -(\alpha S/Vl)c, \tag{12}$$

hence

$$c = c_o \exp\,[-\delta St/lV], \tag{13}$$

where the concentration difference over the membrane is c, the initial concentrations $c_1 = c_o$ and $c_2 = o$, and S the effective surface of the membrane *).

For the dialysis of various non-electrolytes (alcohols and sugars) in water through the same cellophane membrane BRINTZINGER found the following relation between dialysis coefficient and molecular weight:

$$\delta_k \sqrt{M_k} = \text{constant}.$$

Here M_k is the weight of the dialysing particle which in the case of hydrated particles for instance will differ from their formula molecular weight. The relation was employed in the determination of the molecular weights of many inorganic electrolytes and polyelectrolytes [35)36)]. An independent check of at least one molecular weight is, of course, necessary in this method.

JANDER and SPANDAU [47)] have demonstrated that the results obtained with BRINTZINGER's cellophane membranes were not entirely consistent with free diffusion experiments; by replacing the rather dense cellophane membrane by "Ultracellafilter" this inconsistency disappeared (see, however, BRINTZINGER [58)]). It was further shown that different rates of stirring gave different values of δ; this will be due to a reduction of the effective membrane thickness l. Osmotic and filtration effects were not important, however, when the liquid levels were adjusted at the same height. In all these experiments, and in most of BRINTZINGER's too, the dialysing particles were ions, hence a linear relationship between δ and D can only be expected when the medium is a concentrated solution of a strong electrolyte [44)]. This has been confirmed by JANDER and SPANDAU [57)].

*) When the membrane separates two identical vessels containing solutions with concentrations c_1 and c_2, it will be obvious that eqs. (12) and (13) become:

$$d\Delta c/dt = 2\, dn/Vdt = -(2\delta S/Vl).c \tag{12'}$$

and

$$\Delta c = \Delta c_o \exp\,[-2\, St/lV], \tag{13'}$$

where $\Delta c = c_1 - c_2$ and Δc_o is the initial concentration difference.

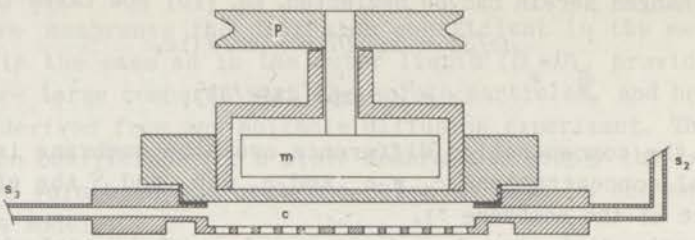

Fig. 7
Upper half of permeation apparatus; p = pulley to rotate magnet m; the cell c contains a stirring element; s_2 and s_3 are connected to valves similar to those drawn in fig. 3, while s_2 is connected in addition to a horizontal tube in which the movement of the meniscus can be measured.

By means of a so-called permeation apparatus (fig. 7) we determined the rates of dialysis for some simple organic compounds and for some polystyrene fractions. The apparatus had some resemblances with the FUOSS-MEAD osmometer (III.1c); the groove and ridge systems of both half cells were now replaced by disk-shaped compartments (0.5 cm thick, 6 cm diameter, volume 14 cm^3) to make magnetic stirring possible. The membrane was supported on both sides by perforated plates (1 mm thick, with holes of 2 mm diameter, 1 mm apart). The stirring elements were iron rods enclosed in small glass tubes. The brass blocks were clamped together in the same way as with the FUOSS-MEAD osmometer; the gasketing again was done by the membrane. Further details may be seen from the figure. In all measurements we used the apparatus with horizontal capillaries which were connected with the half cells and adjusted in the same horizontal plane. The permeation apparatus was placed in a thermostat in which the temperature was constant to within $0.01^{\circ}C$. All measurements were made at $25^{\circ}C$.

For dialysis by means of this apparatus eq. (13') is applied. Substituting $V = 14$ cm^3; $S = 8$ cm^2 and $l = 0.01$ cm (these figures being rather rough estimates) we obtain:

$$\Delta c = c_o \exp[-110\ \delta\ t] \qquad (14)$$

After measuring the concentrations in both vessels at two or more times, an approximation is possible. We always filled the lower compartment with solution (concentration c_o) and the upper one with pure solvent. After the time t both compartments were emptied, and the concentrations determined gravimetrically (evaporation of a known volume of solution). These concentrations always had to be corrected because the concentrations of the liquids in the standpipes and capillaries were not altered. Calculation as

well as direct measurement gave for the volunes in the standpipes on either side 1.5 cm^3.

Table IV

Dialysis through an "Ultracellafilter mittel" in toluene

Solute	c_o (g cm^{-3})	c (g cm^{-3})	M	t (min)	δ (cm^2 sec^{-1})
Sudan I	$5.5\ 10^{-5+}$	$3.3\ 10^{-5+}$	350	60	$1.2\ 10^{-6}$
Polystyreme (H 1)	$8.9\ 10^{-3}$	$6.93\ 10^{-3}$	4,000*	120	$1.4\ 10^{-7}$
Polystyrene (H 1)	$4.2\ 10^{-3}$	$3.28\ 10^{-3}$	4,000*	120	$1.6\ 10^{-7}$
Polystyrene (D 4)	$3.9\ 10^{-3}$	$0.97\ 10^{-3}$	18,000*	2900	$3.8\ 10^{-8}$
Polystyrene (D 5)	$5.9\ 10^{-3}$	$1.90\ 10^{-3}$	39,000*	6850	$1.1\ 10^{-8}$
Polystyrene (D 6)	$6.8\ 10^{-3}$	$3.79\ 10^{-3}$	63,000*	8590	$4.3\ 10^{-9}$

+ The concentration of the azo-dye was determined with a Zeiss-"Stufenphotometer".
* The molecular weights of the polystyrene fractions were calculated [59] from intrinsic viscosities using $[\eta] = 0.5\ 10^{-4} M^{0.80}$; see IV.4.

In table IV we give our values for an azo-dye and some polystyrene fractions in toluene. Although few experiments on the diffusion of polymers by means of what is called the cell method [60] have been reported, we have, for polystyrene in toluene, the values of ADELSTEIN and WINKLER [61]. In the cell method the diffusion through a sintered glass membrane is determined in a manner quite analogous to our dialysis experiments. From fig. 3 of ADELSTEIN and WINKLER we have taken the diffusion coefficients, which by means of our eqs. (11) and (11') are converted into dialysis coefficients (δ_{calc}) for a sieve membrane (for our "Ultracellafilter mittel" the value of W was 0.66). This gave the figures in table V.

Table V

Hindered dialysis for an "Ultracellafilter mittel"

10^{-3} M	10^7 δ_{calc} ($cm^2 sec^{-1}$)	10^7 δ_{obs} ($cm^2 sec^{-1}$)
4	70	1.5
18	55	0.38
39	63	0.11
63	45	0.04

We see from these figures that even if the difference between the values for M=4.000 is due to the different techniques, the

rapid decrease in the δ_{obs} values can only be due to strong hindrance of the free diffusion through this membrane.

The dialysis coefficient for saccharose octa acetate (mol. weight 678) in propyl alcohol through a polyvinyl alcohol membrane (see III.2f) was measured to obtain an idea about the hindrance of diffusion in this very dense type of membrane. The membrane thickness was 0.12 mm; the initial concentration in the lower half cell $c_o = 0.109$ g/100 cm^3, the concentration difference after 1240 min. $\Delta c = 0.090$ g/100 cm^3, hence:

$$\delta = 9.3 \cdot 10^{-9} \text{ cm}^2\text{sec}^{-1}.$$

Comparing this δ with the figures of Table IV we see that the polyvinyl alcohol membrane offers a much higher resistance to solute molecules of a low molecular weight than the "Ultracellafilter mittel" (δ is about 100 times smaller). The same has been found for the permeability of the solvent. Although an exact value of P (eq. (2')) cannot be given because the permeability coefficient depends on the pressure and on the time during which the pressure is acting (compression, and deviation from viscous flow), a mean value of $10\text{-}20.10^{-8}$ is found, which is about the same as for very dense cellophane membranes (see part c).

The same polyvinyl alcohol membrane after conditioning to toluene in the permeation apparatus was used for the dialysis of the polystyrene fraction (H1) of low molecular weight (4,000). While the same filling (initial concentration 0.25 g/100 cm^3) remained in the lower compartment, the liquid in the upper compartment was replaced by fresh solvent after definite time intervals t. The concentrations of these liquids were determined in duplicate by evaporation of 5 cm^3 portions is a weighed platinum crucible at 110°C. The residual weight of polymer was measured by means of a micro-balance with an accuracy of 5.10^{-3} mg. In view of the very small amounts of solute that passed the membrane, eq. (13') may be written as:

$$c'/c_o = (28S/Vl)\,t = 3.5 \cdot 10^5 . t \qquad (15)$$

where c' is the concentration in the upper compartment after a time interval t expressed in hours.

From the results (Table VI) we see that the dialysis coefficient in a polyvinyl alcohol membrane is about 500 times smaller than in an "Ultracellafilter fein", while the rate of dialysis in the course of an experiment becomes smaller and smaller. This will probably be due to the inhomogeneity of the polymer fraction: the lowest molecular weight particles dialyse more rapidly through the membrane. That we are dealing with hindered diffusion can also be seen from a comparison of the ratio δ(polystyrene H1)

Table VI

Dialysis of polystyrene (H1) in toluene through a polyvinyl alcohol membrane

$10^3\ c_o$ (g/100 cm^3)	$10^3\ C'$ (g/100 cm^3)	t (hours)	$10^{10}\ \delta$ (cm^2 sec^{-1})
250	1.7	48	4.2
248	1.5	66.5	2.6
247	0.8	74	1.3

to δ(saccharose octa acetate) for this membrane with the ratio between the molecular weights (20 and 6 respectively). In general the first ratio must be smaller than the latter.

III.2e. *Ultrafiltration*

The number of solute molecules that pass through a membrane surface of 1 cm^2 per second under the influence of any force f may be written as:

$$dn/dt = f\, c_m/w, \tag{15}$$

where c_m is the number of molecules per cm^3 in the membrane phase, and w is the resistance coefficient of one solute molecule in the membrane. When dealing with dialysis the force f is a thermodynamic "force",

$$f = -\,\partial g(x)/\partial x, \tag{16}$$

where x is the direction in the membrane perpendicular to the surface and $g(x)$ the partial thermodynamic potential of the solute at the point x. Supposing that the solution is an ideal dilute solution, and the concentration gradient over the membrane is linear, we obtain for dialysis eq. (10'):

$$dn_d/dt = -\frac{kT}{w_d}\frac{\Delta c_m}{l} = -D_m.\Delta c_m/l, \tag{10'}$$

where Δc_m is the concentration difference between the solutions on either side inside the membrane and $D_m = kT/w_d$ the diffusion coefficient according to the relation of EINSTEIN-FOKKER. For a sieve membrane eq. (10') may be written as:

$$dn_d/dt = -D\,W.\Delta c/l, \tag{17}$$

as long as no geometrical interaction occurs.

When the solution is forced through the membrane by a pressure difference p, the force per molecule is:

$$f = v_1(dp/dx), \tag{18}$$

where v_1 is the molecular volume. Assuming a linear decrease in pressure over the membrane, we get for filtration:

$$dn_f/dt = c(v_1 p/l w_f). \tag{19}$$

There is, however, no general relation between w_d and w_f. For a crude comparison of dialysis and ultrafiltration we confine ourselves to filter membranes without geometrical interaction. Hence the process of dialysis is described by eq. (17). The transport of solute molecules in filtration is now given by:

$$dn_f/dt = c\ dv_m/dt = cpW(r_{av}^2/8\,l\eta), \tag{20}$$

using equations (2) and (6). By means of STOKES' law for the free diffusion of the solute molecules with radius a:

$$w_d = 6\ \pi\eta a,$$

and the EINSTEIN-FOKKER relation $w_D = kT/D$, we find:

$$dn_f/dt = \frac{cpWD}{lkT}\ (\tfrac{3}{4}\pi r_{av}^2 a).$$

Here w_D represents the resistance factor in free diffusion and will be equal to w_d if the sieve model is taken in its strict sense.

Finally, introducing the molecular volume $v_1 = 4/3.\pi a^3$ we obtain:

$$dn_f/dt = (DWc/l)(v_1 p/kT)(3/4.\,r_{av}/a)^2 \tag{21}$$

Comparison of the rates of dialysis and ultrafiltration (eqs. (17) and (21)) is now seen to be a rather difficult matter as the two important factors $(v_1 p/kT)$ and $(3\ r_{av}/4a)^2$ may vary considerably, the first term usually being very small and the second term very large. It is only when geometrical interaction occurs ($r_{av} \cong a$) that the rate of dialysis may be much greater than the rate of ultrafiltration (at low pressures). In this case, however, some of our basic assumptions are no longer valid.

When the membrane exhibits any kind of sieve action, we return to eq. (20), which should now be replaced by:

$$-dn/dt = (1-\Phi)c\ dv_m/dt, \tag{22}$$

where Φ, the retention coefficient, is a measure of the sieve action [62], and where $n=cV$ is the number of molecules at the side where the pressure is highest. We find for the decrease in n on this side:

$$\frac{dn}{dt} = V\frac{dc}{dt} + c\frac{dV}{dt} = (1-\Phi)c\frac{dV}{dt},$$

or

$$V\,dc/dt = -\Phi\,c\,dV/dt,$$

and after rearranging and integration:

$$cV^{\Phi} = c_o V_o^{\Phi}, \qquad (23)$$

where the subscript o indicates the initial situation. Hence a number of simultaneous determinations of concentration and volume of the solution above the filter will yield the value of Φ. In this treatment we have assumed that Φ does not depend on the concentration of the solute; this has neither been confirmed nor refuted by experiment [62].

An accurate performance of such determinations is greatly restricted by stirring inefficiencies. McBain and Stuewer have shown that inefficient stirring leads to values for Φ which are much too low or even zero. This is caused by the formation of a more concentrated liquid layer at rest directly above the membrane, from which in the stationary state solution of the same composition passes into the membrane, as comes in from the bulk of the stirred solution. It seems that the only thing one can do in this respect is in all experiments to stir with the same speed.

Manegold and Hofmann [63] examined the influence of the pore size on the retention of solutions of sucrose, hydrochloric acid and chromoxyde sols; a retention of the solute was found in the same region where dialysis no longer was governed by the free diffusion coefficient of the solute. They showed further that geometrical interaction between solute molecules and membrane network may give rise to blocking effects.

Elford [36] and Ferry [38] have used "gradocol" membranes (see III.2f) for the determination of particle sizes in disperse systems (solutions of proteins, mainly). To achieve this for a particular system they filter that system through membranes with progressively finer pores until the colloidal particles are completely retained. The corresponding pore size (r_{limit}) usually is 1 to 3 times as great as the particle radius (which is known from studies with the ultracentrifuge or ultraviolet microscopy).

Our ultrafiltration experiments were done with the same permeation apparatus as we used for dialysis. An excess pressure p was applied from a simple manostat (see III.2c), which gave pressures constant to within 0.05 mm. water. This constancy was achieved by connecting the two ends of the manostat to the opposite horizontal capillaries. In this manner a closed circuit was obtained, which was insensitive to fluctuations in the air pres-

sure as well as to fluctuations in the room temperature (the manostat was not thermostatted). The lower cell of the permeation apparatus again was filled with the solution, the upper compartment with the solvent. In some experiments the solution was pressed through the membrane ("Ultracellafilter mittel"), in others the solvent. In all cases the rates of flow through the membrane were measured in both horizontal capillaries; experiments in which the differences between the readings exceeded 5% were discarded. In the tables the mean of the rates of flow in the two capillaries is given. (For the case of zero external pressure it was necessary to extrapolate the rate of flow to zero time). In all experiments we stirred with equal speeds. We assume that the rate of flow can be expressed by:

$$dv/dt = P'(p-\pi_{app}), \tag{24}$$

where π_{app} is the apparent osmotic pressure; p has a positive sign when it is applied to the solvent; a negative sign of π_{app} indicates a tendency for excess liquid flow towards the solvent compartment. P' is a permeability coefficient, closely related to the constant P of eq. (2'):

$$P' = P\,S$$

Calculation of P from the P' values of our "Ultracellafilter mittel" gave $P = 400.10^{-8}$ in the same units as used in part c of this section. Before and after a series of filtration experiments P' was determined from a permeability measurement with pure solvent in both cells.

In the first series of experiments we found $P' = (1.9 \pm 0.1).10^{-5}$, when dv/dt is expressed in $cm^3\ sec^{-1}$ and p and π in cm H_2O. In Table VII c_o is the initial concentration in the lower cell (g/100 cm^3), t the duration of the experiment in minutes, dv/dt the rate of volume flow (cm^3/sec), c_u the concentration in the upper cell at time t, and c' the concentration calculated from c_u which would have been observed after one hour if the initial concentration in the lower cell had been 0.50 g/100 cm^3. The total filtered volume was 1.0 cm^3 in each case. The polystyrene (D4) had a molecular weight of about 18,000 (see table IV) and should exhibit in a 0.50 g/100 cm^3 solution an osmotic pressure of about 8 cm H_2O.

From Table VII we see that in all cases dialysis of solute particles took place through the membrane to at least the same extent as when no external pressure was applied (pure dialysis). When pressing solution through the membrane, a considerable amount of solute molecules were dragged along. For 1.0 cm^3 solution passing unhindered, the concentration change would have been

Table VII

Ultrafiltration of polystyrene (D4) through an "Ultracellafilter mittel"

c_o	p	t	$10^4\ dv/dt$	c_u	π_{app}	c'	π_{app}/c
0.54	+ 20.2	59	+ 3.37	0.037	+ 2.5	0.033	4.6
0.53	+ 10.8	114	+ 1.65	0.036	+ 2.1	0.018	4.0
0.39	0	2902	− 0.27	0.16	+ 1.5	0.008	3.8
0.52	− 11.4	88	− 2.09	0.020	− 0.8	0.013	
0.50	− 20.7	50	− 3.92	0.006	− 0.1	0.007	

0.033 g/100 cm^3 in the upper cell. In the two first experiments a very great part of the concentration change in the solvent compartment indeed must have been due to such transport of solute molecules. The calculated apparent osmotic pressure has in both cases about the same value, which is in reasonable agreement with the zero pressure experiment (see the π_{app}/c values). The apparent osmotic pressure is only 1/4 of the theoretical osmotic pressure.

When, however, solvent was pressed through the membrane into the solution cell, no influence was found of an osmotic pressure acting in the same direction; the negative values are not very significant compared with the accuracy of the method.

To investigate whether the apparent osmotic pressure depends on the rate of flow, we measured the latter at different positive external pressures, and calculated π in the same manner as before (Table VIII). Here we used a (0.71 ± 0.01) g/100 cm^3 solution of polystyrene (D5) in toluene. The theoretical osmotic pressure of this solution is about 4 cm H_2O; the permeability coefficient P' was (1.6 ± 0.1) 10^{-5}.

Table VIII

Ultrafiltration of polystyrene (D5) through an "Ultracellafilter mittel"

P	$10^4\ dv/dt$	π_{app}
+ 4.9	0.53	1.6
+ 10.5	1.54	0.9
+ 14.9	2.21	1.0
+ 21.3	3.17	1.5
+ 17.5	2.34	2.9 *

* This measurement was made after a dialysis experiment of five days duration; the high value for π may be due to a blocking phenomenon.

Again no certain indication of a dependance of π_{app} on the rate of filtration was found.

From these experiments we get the impression that when any retention of solute molecules occurs, an apparent osmotic (counter) pressure is set up irrespective of the concentration at the other side of the membrane. Remembering that STAVERMAN's transport numbers

$$\tau_i = [\dot{n}_i v_i / J]_{\Delta g_k^\circ = o} \qquad \text{(eq. II.3.17)}$$

are defined for a situation in which no thermodynamic "forces" are active, we must conclude that a correct determination of this number is impossible. We believe that this is caused by the fact that the membrane has a finite thickness, in consequence of which a concentration gradient in the membrane originates during the filtration experiment.

III.2f. *Membranes*

In the course of our investigations we used several types of membranes. A general review on the most commonly employed osmotic membranes can be found in WAGNER [7]. We will discuss here only the membranes with which we have experience.

1. Collodion membranes

The properties of collodion membranes, which have been used almost exclusively for aqueous solutions, have been thoroughly investigated by many authors along the lines described in the preceding parts of this section. At present they can be prepared with graded permeabilities, and as it has been demonstrated that they act in water as molecular sieves, they seem to ne very suitable for osmotic and permation experiments. Moreover, their use is not restricted to aqueous solutions because it is possible to condition these membranes to other solvents [64] in such a manner that eq. (3) in part a of this section remains valid. We repeated in the first place some of the experiments of MANEGOLD and ELFORD.

Preparation of the membranes

Solutions of collodion were allowed to dry out in Petri dishes (diameter 5 and 10 cm, height of the brim 1 cm) which floated on mercury. The evaporation took place under a cover whose lower edge did not completely reach the table on which the dish was placed. The solvent vapour escaped slowly through the remaining slit of about 5 mm. No special precautions with regard to the temperature and the relative humbidity of the room were taken. After filling the dishes were first covered during half an hour with a glass plate to allow for a regular spreading of the solution over the glass surface. The amounts of solution were

different in different groups (four membranes were prepared at the same time); no definite influence of the membrane thickness on the reduced permeability coefficient was found, however. The composition of the solutions and the evaporation time (t) are the two factors which determine the permeability of the membranes. After time t the dishes were immersed in distilled water. The membranes which always adhered to the edge of the dishes, were cut loose after one night (when the membranes were detached immediately, a considerable shrinkage was observed during the first hours), and then washed with distilled water for several days.

The influence of the composition of the solution

In the first series of experiments *) (preparation of "Gradocol" membranes [36)38)65)]) we started from a stock-solution of MERCK's collodion ("für medizinische Zwecke", 4%). Four parts of this solution were diluted with one part amyl alcohol and the solution so obtained was mixed with an equal volume of a mixture of dry ethyl alcohol and diethylether (1:10). This final collodion solution will be referred to as "standard solution". Membranes prepared from this standard solution were compared with membranes from the same standard solution to which small quantities of water and acetic acid were added (prescription of ELFORD [36)]). The permeabilities were measured by means of the apparatus described in part c as the rate of movement dh/dt of the meniscus in the horizontal capillary. To obtain a more absolute figure the permeability coefficient P^{II}, calculated as $P^{II} = (dh/dt)/p$, was multiplied by the thickness l (in mμ) of the membrane [35)]. In the following discussion we will call $(P^{II}l)$ the reduced permeability coefficient. After a permeability measurement the water content W of the membrane was determined.

Table IX

The influence of the addition of small amounts of water or acetic acid to an "ELFORD" solution on the membrane permeability

group	number of membrane	addition	t (min)	W (%)	l (μ)	$P^{II}l$	r_{av} (mμ)
a	3	none	60	43	45	9.8	4.3
b	3	none	60	44	36	12.3	4.9
c	2	2% acet. acid	60	44	40	12.1	4.9
d	2	2% water	60	57	38	24	5.9

Two or three membranes were measured out of each group of

*) We acknowledge the assistance given by P. Paulusma.

four; these groups consisted of identical membranes as was proved by experiment. Two groups (a and b) prepared on different days were not exactly identical, although the difference was quite small. All measurements were done at least five days after the preparation of the membranes; washing of the membranes for a longer period as recommended by ELFORD yielded no particular effect. Finally, the average pore radii were calculated by means of eq. (6). From table IX it can be seen that there is no obvious difference between the "normal" membranes and the "acetic acid" membranes. The reduced permeability coefficients for the "water" membranes were twice as high, however. For comparison we give r_{av} values which ELFORD has found for his identically prepared "gradocol" membranes:

"Normal" membranes : 300 – 400 mμ;
"acetic acid" membranes : 5 mμ;
"water" membranes : 1000 – 1500 mμ.

We have not, therefore, been able to confirm ELFORD's results. It is possible that our collodion differed considerably from ELFORD's Necol-collodion as far as its membrane-forming properties are concerned *).

In a second series of experiments **) we used the original MERCK solution and dilutions of these with ethyl alcohol and diethyl ether. From table X we can see that by increasing the ratio alcohol:ether in the collodion solution the permeability of the membrane is greatly enhanced.

Table X

The influence of the alcohol-ether ratio on the membrane permeability

group	number of membranes	addition	t (min)	l (μ)	W (%)	$P^{II}l$	r_{av} (mμ)
a	2	none	15	68	83	227	16
b	1	1 part alc + ether (3:1)	15	82	91	1220	35
c	2		27	170	97	1380	36
d	2		45	136	96	1260	35
e	2		45	97	93	1030	32
f	1		45	165	96	1250	36
g	2	1 part alcohol	30	167	96	1920	44
h	2		30	123	96	2040	45

*) The great influence of the kind of collodion on membrane properties has been shown by SOLLNER [66]. When, in later experiments, we tried to prepare membranes from a new MERCK's collodion solution (the older one was a prewar product), we obtained very fragile membranes which could not be handled as easily as the former ones, and had quite different characteristics.

**) We acknowledge the assistance given by J. Schokkenbroek.

It is strange, however, that no definite conclusion could be drawn as to the influence of the drying time. This influence was investigated in a third series of experiments *) with membranes from another collodion solution (3.6% Brocapharm). The only variable in these experiments was t. We found, indeed, a marked dependence on t. It may be that in the former series of experiments the drying time has been too short to detect any effect.

Table XI

The influence of the drying time on the membrane permeability

time (min)	l (μ)	W (%)	$P''l$	r_{av} (mμ)
30	94	86	135	17
30	69	86	124	16
60	49	70	35	8
60	26	57	16	7
90	27	52	1.2	3.2
90	20	31	1.7	2.4

Finally we see that in spite of the great differences in the standard solutions all membranes show the same relation between water content and reduced permeability coefficient. We have plotted the value of W and r_{av} for the three tables in fig. 8. Curves of the same type have been found by BJERRUM and MANEGOLD [35].

As it is dubious whether these r_{av} figures have a real physical meaning, we determined the r_{max} value of a membrane of group d (table X) by the minimum bubble pressure method *), using isobutyl alcohol and water (see part b). The values are given in Table XII; we took for γ ERBE's value 1.73 dyne cm^{-1}; for each pressure the constant rate of flow dv_E/dt was determined, and compared with the permeability dv_m/dt calculated for a membrane of set d for the same pressure. The ratio between these rates of flow is a measure of the fraction of the total cross section of the capillaries that is effective at that pressure. Considering the accuracy of the experiments the results are in good agreement with the r_{av} value, which for this membrane was 35 mμ.

2. Denitrated collodion membranes

Preparation of the membranes

A large flat dish was placed in a desiccator and filled to a depth of about 1 cm with pure mercury. On the surface of the mer-

*) We acknowledge the assistance given by H.Bakker.
**) Assistance given by J.Schokkenbroek.

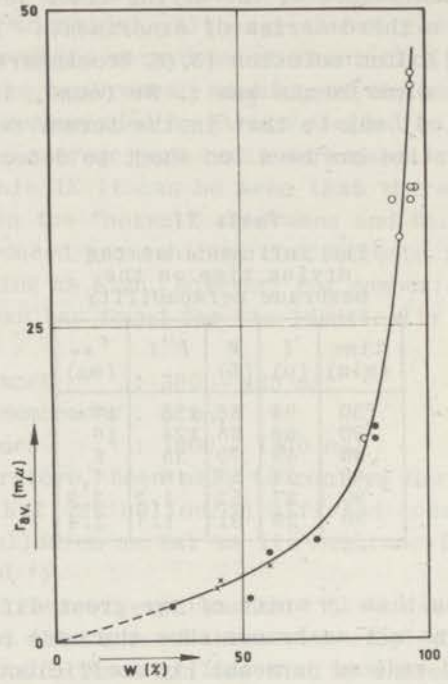

Fig. 8
Relation between r_{av} and W for collodion membranes

Table XII

Determination of pore radii
by ERBE's method

p (cm Hg)	r (mμ)	$\frac{dv_E}{dt}$	$\frac{dv_E}{dt} / \frac{dv_m}{dt}$
62.7	41 (r_{max})	117	0.21
66.7	39	135	0.23
70.8	37	164	0.25
74.9	35	195	0.29

cury was floated an iron ring, 18 cm in diameter; inside this ring, onto the mercury surface, was poured 20 cm^3 of a collodion solution (MERCK; collodion "für medizinische Zwecke", pre-war product). The desiccator which contained no desiccating agent was closed for one hour to allow for a regular spreading of the solution. Then the cover was raised to about 2 mm, and evaporation allowed for one night. The iron ring with the membrane (which was rather stretched) was then immersed in distilled water. After several hours the membrane was cut loose from the ring, and washed with fresh distilled water. When five membranes were prepared

in this manner they were denitrated together by the method of MONTONNA and JILK [67)10)]. The denitrating solution consisted of a mixture of 125 cm^3 concentrated ammonia, 325 cm^3 water and 50 cm^3 ethyl alcohol; 50 grams of hydrogen sulfide were introduced into this mixture. The membranes were kept submerged in this solution for 1.5 hours, every 15 minutes all membranes being turned over. Then the membranes were thoroughly washed with distilled water for at least five days. All membranes were conditioned to toluene by soaking for at least two hours in each of the following liquids, in sequence: 40/50 water + ethyl alcohol; ethyl alcohol (99%); 50/50 alcohol + toluene; pure toluene.

To prove (or disprove) the usefulness of these membranes, we determined the apparent osmotic pressures of 1.0 g/100 cm^3 solutions of an unfractionated polystyrene (S) with a molecular weight of about 200,000 calculated from its intrinsic viscosity in toluene $[\eta] = 0.89$ [59)]. The first series of membranes was prepared as outlined above; the second series from 30 ml collodion solution to which 5% cellosolve *) was added. In table XIII the apparent osmotic pressures for several denitrated collodion membranes are listed, together with some values obtained with "Ultracellafilter". In no case was the osmotic head constant over a period of more than one day. We therefore always extrapolated to zero time; this extrapolation was more reliable when the osmotic head was approached from a high level on the solution side. The same effect was found by dynamic osmotic measurements without diffusion (III.1b) and by ultrafiltration experiments (III.2e). Typical dynamic curves are shown in fig. 9. To make sure that our denitrated collodion membranes were comparable with those reported in the literature (see part c), we determined for the membranes 1 and 2 the permeability coefficient P by means of eq. (8'), and found 150 and 200.10^{-8} respectively (in the same units as before).

The weak point in the preparation of these membranes is the hydrolysis in a rather alkaline medium; treatment of membranes with 1 n NaOH solution leads to complete destruction. Moreover, many authors have mentioned the variability of denitrated collodion membranes, even when prepared from the best quality collodion, and since much better commercial membranes are available, the experiments with these membranes were not continued.

*) BAWN, FREEMAN and KAMALIDDIN [28)] state that cellosolve (ethylene glycol mono-ethyl ether) has a marked effect on the porosity of collodion membranes, a percentage of 5 to 10 cellosolve already yields rather impermeable membranes (i.e. impermeable to the solvent).

Table XIII

Apparent osmotic pressures of 1.0 g/100 cm^3 solutions of polystyrene (S) in toluene for denitrated collodion membranes and "Ultracellafilter".

Membrane species	Membrane number	Subsequent determinations of π (cm solvent)
Denitrated collodion series 1	1	2.35 2.37 2.36
collodion series 1	2	2.15 2.20
collodion series 1	3	1.97 2.01
collodion series 2	4	2.31 2.35
collodion series 3	5	2.03
Ultracellafilter mittel	6	1.80
Ultracellafilter fein	7	4.01 4.05
Ultracellafilter fein	8	3.15
Ultracellafilter feinst	9	4.32 4.35

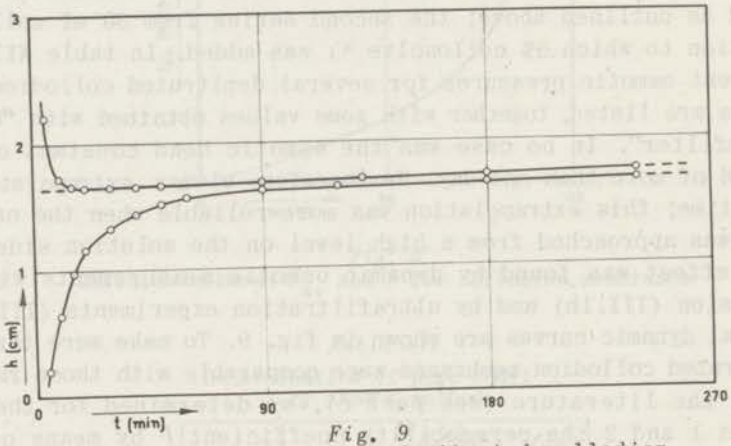

Fig. 9
Osmotic dynamic curves; denitrated collodion membrane, series 1.

3. "Ultracellafilter"

These membranes (cellulose membranes) are manufactured by the "Membranfiltergesellschaft Sartorius Werke, A.G." in Göttingen (Germany), and were at our disposal in four degrees of permeability: "mittel", "fein", "feinst" and "allerfeinst". Although a great number of our experiments were performed with these membranes, they have one disadvantage: in many organic solvents their permeability decreases for an indefinite length of time (see part c). The same has been found for denitrated collodion [64]. These membranes are, therefore, not very useful for accurate ultrafiltration and dialysis measurements. We believe that this decrease

in permeability has been the most limiting factor in our ultrafiltration experiments (part f).

In table XIII we have already given some apparent osmotic pressures obtained with these membranes. In all these cases some diffusion through the membranes was observed; this was mainly due, however, to the broad molecular weight distribution of the polystyrene (S) we used. In general, when measuring well fractionated polymers the "mittel" membranes are about as good as denitrated collodion membranes, and allow for the determination of molecular weights above 100,000 - 200,000. The densest (and slowest) "allerfeinst" membranes can be used down to about 10,000. The time required for one static measurement with these membranes in the ZIMM-MYERSON osmometer is two days.

4. Sylphrab membranes (wet-regenerated cellulose films) manufactured by the Sylvania division of the American Viscose Corporation, have about the same properties as "Ultracellafilter feinst" (the minimum molecular weight that can be determined accurately is about 30,000). They are less rigid, however.

5. Polyvinyl alcohol membranes

Recently HOOKWAY and TOWNSEND [68] have recommended the use of polyvinyl alcohol as a membrane material for the osmometry of low molecular weight polymers. The little experience we have with these membranes will be reported here.

The membranes were prepared in a manner analoguous to the preparation of the collodion membranes. In the same dishes a layer of 7 mm of a 1.5% aqueous solution of polyvinyl alcohol was allowed to dry out at 30°C in a slow air stream of 45-50% relative humidity. The parent substance, polyvinyl alcohol had a limiting viscosity number (intrinsic viscosity) in water $[\eta] = 105\ cm^3g^{-1}$, which means that the molecular weight was about 70,000 (IV.3) ; the acetate content was determined as the percentage of acetylated monomer groups: 0.8%. After three weeks *) the membranes were lifted from the bottoms of the dishes and placed for at least three more weeks in a container with a relative humidity of 75-80%. Then the membranes were soaked overnight in absolute alcohol (distilled over magnesium chips) to extract all water from the membranes. After this procedure the membranes were conditioned to toluene in the usual way.

With a modified ZIMM-MYERSON osmometer and two polyvinyl alcohol membranes (on either side) we measured the osmotic pressure

*) When the membranes are completely dried out in the dishes they adhere strongly to glass and can no longer be removed.

of polystyrene (D6; M=63,000) in toluene. The $(\pi/c)_{c=o}$ value was 5.3, which is the same value as was found with "Ultracellafilter fein" in the same osmometer (see IV.4). A polystyrene (H1) with a molecular weight of 4000, gave a rapidly decreasing pressure difference; after 48 hours the pressure difference had become zero. It was shown in part d of this section, however, that another polyvinyl alcohol membrane showed a very great resistance to the diffusion of this polystyrene.

Another complicating fact was that membranes which were kept for more than five months at a relative humidity of 75-80% had become nearly impermeable for the solvent and besides showed an asymmetry of several centimeters.

III.2g. *Some consequences for osmometry*

1. In this section we have seen again that dynamic osmotic measurements are unreliable, especially in those cases were considerable dialysis of the solute through the membrane occurs. Again, when pressing from the solution side we notice something like an apparent counter osmotic pressure; when pressing from the other side no definite influence of the concentration gradient in the membrane is seen from the rate of flow curves. Dialysis through the membrane, however, seems still to be possible against the bulk flow of liquid. An important consequence of these facts is the impossibility of separating the external pressure p and the thermodynamic "force" $(\Delta g/l)$ in filtration experiments as is necessary in the determination of STAVERMAN's selection coefficient.
2. The apparant osmotic pressures given by membranes of different species can differ to a great extent when the polymer dissolved contains much low molecular weight substance. A more or less successful extrapolation of the osmotic head to zero time gives no reliable osmotic data. When any diffusion is detected, the osmotic pressure may be considerably in error. Of the two things one can do in such a case, one (the choice of another membrane) has been discussed in this section. The next section will be devoted to the other possibility: fractionation of the polymer.

III.3. Fractionation of polymers

The separation of real polymers into fractions which are fairly homogeneous with respect to molecular weight is of the utmost importance in osmometry for several reasons, which have already been mentioned in our discussions on statistical thermodynamics of polymer solutions and on the properties of membranes.

It will be desirable, however, to pay some attention also to the fractionation methods themselves:

a. Theoretical considerations.

b. Fractionation of polystyrene.

c. Fractionation of polyvinyl alcohol.

III.3a. *Theoretical considerations*

All polymeric substances consist of components of a great number of different molecular weights, and although this heterogeneity may be of great partical importance, it offers very often great difficulties in the theoretical and experimental studies of polymer properties. We may distinguish three kinds of heterogeneity, which can occur together or separately:

1. differences in molecular weights;
2. differences in molecular shapes (branching and cross-linking);
3. differences in chemical composition *).

Nearly all theories on polymer properties are concerned with the heterogeneity due to differences in molecular weight only. This is justified in so far as we have little more than speculative information about the other two influences. This introduction will therefore be restricted to the theory of fractionation with respect to chain length.

Heterogeneity with respect to molecular weight is expressed conveniently by the so-called weight distribution function:

$$n_i = H(m_i); \quad \sum_i n_i = 1, \tag{1}$$

where n_i is the weight fraction of the component with degree of polymerization m_i.

While the form of the function $H(m_i)$ is important, we are primarily interested in methods which enable us to divide any heterogeneous polymer into more homogeneous fractions. Methods which lead only to evaluation of $H(m_i)$ have been classified by CRAGG and HAMMERSCHLAG [69] as analytical methods to distinguish these from preparative methods by which fractions are actually isolated. It will be obvious that the latter methods will in themselves permit evaluation of $H(m_i)$. Nearly all preparative methods are based on differences in solubility. Solubility, however, is not only a function of chain length, but also of chemical composition; this is the main uncertainty in such fractionations. Indeed, it will be seen (part c) that chemical differences between

*) Here, and later, we will ignore any specific influence of endgroups, whose influence is never very important when the chain length is large.

the molecules may cause great difficulties in the fractionation of polymers.

The solubility methods of fractionation fall into two classes:
1. Precipitation; the polymer is dissolved in a good solvent; to the solution is added a non-solvent (precipitant) in an amount sufficient to produce a precipitate. This precipitate (first fraction) is removed, and again some precipitant added; this gives a second fraction, and so on. In general the successive fractions have successively lower molecular weights.
2. Extraction; the polymer in the solid or gelphase in successively extracted with mixtures of increasing solvent properties. The first fractions now are the most soluble (lowest molecular weight), the order of separation of the fractions being the reverse of that in the precipitation method.

The equilibrium phase separation in both methods may be described thermodynamically. For this description we will use the quasi-lattice theory (II.2c); the molecular distribution method is not very useful here since it gives an expression for the GIBBS free energy of the solvent which cannot be converted into expressions for the solute components (of the heterogeneous polymer). We will start with SCOTT and MAGAT's [70] expression (eqs. (16) and (17) in II.2c) for the partial GIBBS free energy of the solvent:

$$\Delta g_1 = RT\,[\ln(1-\varphi)+(1-1/\bar{m}_n)\varphi + \mu\varphi^2], \qquad (2)$$

and of the solute components:

$$\Delta g_i = RT\,[\ln \varphi_i-(m_i-1)+m_i(1-1/\bar{m}_n)\varphi+\mu m_i(1-\varphi)^2]. \qquad (3)$$

Here φ_i is the volume fraction of the i-th component with degree of polymerization m_i, φ is the volume fraction of the total polymer with a number average degree of polymerization $\bar{m}_n$, and μ is HUGGINS [71] interaction constant which is supposed to be the same for all values of m_i. In these formulae we have implicitly assumed the degree of polymerization to be equal to the total number m_i of lattice sites occupied by a polymer molecule. The equilibrium conditions for phase separation are

$$\begin{aligned} \Delta g_1' &= \Delta g_1'' \,, \\ \Delta g_i' &= \Delta g_i'' \quad \text{for all polymer components,} \end{aligned} \qquad (4)$$

where a single prime refers to the dilute solution phase ("solution"), and a double prime to the swollen polymer phase ("gel"). If this is applied to equations (1) and (2), we obtain:

$$\ln(1-\varphi')+(1-1/\bar{m}_n')\varphi'+\mu(\varphi')^2 = \ln(1-\varphi'')+(1-1/\bar{m}_n'')\varphi''+\mu(\varphi'')^2 \qquad (5)$$

and $\ln \varphi_i' - (m_i - 1) + m_i(1 - 1/\bar{m}_n')\varphi' + \mu m_i(1-\varphi')^2 =$

$= \ln \varphi_i'' - (m_i - 1) + m_i(1 - 1/\bar{m}_n'')\varphi'' + \mu m_i(1-\varphi'')^2$ for all i's, (6)

where for simplicity it is assumed that μ has the same value in both phases. Transformation of eq. (6) yields for the i-th component:

$$\ln(\varphi_i''/\varphi_i') = m_i[(1-1/\bar{m}_n)\varphi' - (1-1/\bar{m}_n'')\varphi'' + \mu\{(1-\varphi'')^2 - (1-\varphi')^2\}],$$

which in conjunction with eq. (5) gives

$$\ln(\varphi_i''/\varphi_i') = m_i\left[2\mu\{\varphi' - \varphi''\} + \ln\frac{1-\varphi'}{1-\varphi''}\right].$$

Hence the partition of the components between "solution" and "gel" is given by:

$$\varphi_i''/\varphi_i' = \exp[\alpha m_i], \tag{7}$$

where

$$\alpha = 2\mu\{\varphi' - \varphi''\} + \ln\frac{1-\varphi'}{1-\varphi''}.$$

For the partition of the component i between the two phases we have also the relation

$$N_i = N_i' + N_i'', \tag{8}$$

where N_i, N_i' and N_i'' are the weights of this component in the original polymer, in the solution and in the gelphase, respectively. As $N_i' = \rho_m \varphi_i' V'$ and $N_i'' = \rho_m \varphi_i'' V''$, where V' and V'' are the volumes of the solution and the gel, and ρ_m the density of the polymer, we obtain from eqs. (7) and (8) [72]:

$$N_i' = \frac{N_i}{1+\lambda\exp(\alpha m_i)} \quad \text{and} \quad N_i'' = \frac{N_i}{1+(1/\lambda)\exp(-\alpha m_i)}, \tag{9}$$

where

$$\lambda = V''/V'.$$

Or, introducing the total weight $G = \Sigma N_i$ of the polymer, and its weight distribution function $n_i (= N_i/G) = H(m_i)$:

$$N_i'/G = \frac{H(m_i)}{1+\lambda\exp(\alpha m_i)} \quad \text{and} \quad N_i''/G = \frac{H(m_i)}{1+(1/\lambda)\exp(-\alpha m_i)} \tag{10}$$

For the sake of convenience we introduce the degree of polymerization m_r of the component which is equally distributed over the two phases: $N_r' = N_r''$, hence

$$\lambda = \exp(-\alpha m_r).$$

Then, to obtain a measure for the effectiveness of the fractionation, we consider the ratios

$$n_i'/n_r' = (n_i/n_r).2[1+\exp\ \alpha(m_i-m_r)]^{-1} \qquad (11)$$

$$n_i''/n_r'' = (n_i/n_r).2[1+\exp\ \alpha(m_r-m_i)]^{-1} \qquad (11')$$

We believe these ratios to be the best indications for the degree of success of a fractionation procedure. In fact, if for example n_i''/n_r'' is small compared with n_i/n_r when m_i is small, this proves that the ratio between the amounts of low and high molecular weight material is much smaller in the gel phase than in the original polymer.

Now, from eq. (11') it is obvious that for small values of m_i the ratio n_i''/n_r'' cannot fall below

$$2(n_i/n_r)(1+\exp\ \alpha m_r)^{-1} = 2(n_i/n_r)\lambda(1+\lambda)^{-1}.$$

If λ is of the order of 0.1, the ratio between n_i''/n_r'' and n_i/n_r for low values of m_i will at best be of the order of 0.1, showing that the "gel" phase will always contain an appreciable amount of low molecular weight material.

In the "solution" phase, however, the relative amount of high molecular weight material is considerably diminished. For, if m_i is large, the ratio n_i'/n_r' approaches zero as m_i increases (eq. (11)).

We conclude that in the precipitation method the "gel" phase contains an appreciable amount of the low molecular weight components, whereas in the extraction method the bulk of this material is already included in the first fractions, so that the higher fractions contain little or nothing of it. The extraction method is therefore more favourable when fractions without low molecular weight "tails" are to be prepared. This applies in particular to fractions which must be used for osmometry, because the contribution of any component to the osmotic pressure is inversely proportional to its molecular weight; hence low molecular weight "tails" are very undesirable. Moreover the low molecular weight components are more liable to diffuse through the membrane, which may give rise to many difficulties (see section 2 of this chapter). There is one practical objection to most extraction methods, however; the ideal equilibrium state is more closely approached by conventional precipitation methods than by extraction methods. Some years ago STAVERMAN and OVERBEEK [72] suggested a method by which equilibrium in the extraction process is as nearly attained as in precipitation method. By adding an amount of precipitant sufficient to precipitate the greater part of the polymer, a "solution" is left which can be regarded as an extract. Separating this first fraction from the gel and redissolving the latter, the procedure can be repeated in an analogous way to obtain a second extract, and so on. The establishment of

the equilibrium now proceeds in the same way as in the precipitation method, hence the advantages of both methods are combined.

III.3b. *Fractionation of polystyrene*

In all experiments described in this part we used a commercial polystyrene, Dow crystal clear. Throughout this thesis this polymer is indicated as polystyrene (D). The various fractions are distinguished by the addition of a number.

The unfractionated polymer had a broad weight distribution. In some preliminary fractionation experiments, in which the procedure was similar to that described by ALFREY, BARTOVICS and MARK [59], it was found by osmotic experiments that the first precipitates contained large amounts of dialysing material. We examined, therefore, by means of extraction methods how much low molecular weight material was present in the polymer (experiments 1 and 2). On the basis of this experience we developed a useful fractionation method which will be described in experiment 3.

All molecular weights were calculated from the limiting viscosity number in toluene at 25°C by means of the relation:

$$[\eta] = 0.5 \cdot 10^{-2} (M)^{0.80}$$

where $[\eta]$ is expressed in $cm^3 g^{-1}$. This relation has been found by ALFREY, BARTOVICS and MARK [59] for a polystyrene polymerised at 120°C and has been chosen by us because it fits our combined osmotic and viscometric results (see IV.4). Nevertheless all molecular weights must be regarded as rough approximations.

Experiment 1 *)

A solution of 50 g polystyrene (D) in 1 l butanone was slowly added to 4 l methanol at room temperature. In this and all other precipitations the tip of the buret was below the surface of the agitated precipitant, giving a much finer precipitate than could be obtained by dropwise addition of polymer solution. The colorless powder so obtained (polystyrene D1) was used in experiments 1 and 2; in an identical manner the starting product for experiment 3 was prepared.

In a round bottom flask, equipped with reflux condenser and mechanical stirrer, 7.6 grams of polystyrene (D1) in 200 cm^3 of a mixture of butanone and methanol (10:90) were boiled for four hours. After cooling, the contents of the flask were filtered, the filtrate reduced to a small volume by evaporation on a water-

*) In experiments 1 and 2 assistance was given by J.J.F. Hasselman.

bath and finally completely dried in a furnace at 110°C. The weighed extract was dissolved in toluene, and the viscosity (t) and concentration (c) of this solution determined. Viscosities were measured with an Ubbelohde viscometer with flow time t_o = 292.9 sec for the solvent. The undissolved polymer was treated in the same way with mixtures of butanone and methanol (20:80) and (30:70) respectively (see table XIV). During the third extraction the polystyrene flocculated and adhered to the walls of the flask. By extraction above 50°C with mixtures of still higher butanone content the polymer was converted completely to a gel-like floc.

Table XIV

Hot extraction of polystyrene (D1)

Number of extraction	Ratio butanone-methanol	Weight of extract	Viscosity determination	
			$10^2\ c$ (g/cm^3)	$t-t_o$ (sec)
1	10:90	0.13	0.7	1.3
2	20:80	0.41	1.1	2.3
3	30:70	0.30	0.8	3.2

The total amount of substance (0.84 g) extracted in three operations was about 11%. From the viscosity data no molecular weights can be derived, although it can be said that they all lie below 1,000.

Experiment 2

The polymer (1.860 g) was now extracted at room temperature with butanone-methanol mixtures which were progressively richer in butanone. The powder was suspended in about 400 cm^3 of such a mixture, vigorously agitated for four to five hours, filtered off and then extracted with the next mixture. The extracts were treated in the same way as in experiment 1; from the viscosities of the solutions in toluene no further conclusions could be drawn as in experiment 1. Again the total amount of extracted material was about 11% (table XV).

From experiments 1 and 2 we see that the polymer (D1) contains a large amount of very low molecular weight material. This can be extracted as well at elevated temperatures as at room temperature. Extraction of higher molecular weight fractions, however, is hindered by the gel-like properties of the polystyrene in the appropriate extracting mixtures.

The limiting viscosity number of the residual products from

Table XV

Extraction of polystyrene (D1) at room temperature

Number of extraction	Ratio butanone-methanol	Weight of extract (mg)	Appearance of the polymer
1	53:47	9	powdery
2	58:42	1	
3	63:37	17	
4	66:34	11	
5	70:30	20	
6	73:27	47	flocculant
7	77:23	43	
8	80:20	59	swollen
9	83:17	21	

both experiments showed no significant departure from the value for polystyrene (D1) itself.

Experiment 3 *)

This experiment has been done along the lines indicated in part (a) of this section. From the preceding experiment we see that the ratio butanone-methanol in the first extracting mixtures has to be about 80:20.

A solution of 50 g of polystyrene (D1) in 1 l butanone was introduced, in the manner described, into 600 cm^3 of a mixture of butanone and methanol (80:20). At the same time methanol was poured into the mixture in such amounts that a constant ratio butanone-methanol was maintained. After the solution was added, stirring was continued for about one hour. The phases then were allowed to settle for one night, the volumes of "solution" and "gel" measured, the gel dissolved in butanone and reduced by evaporation to a small volume. This small volume was introduced into a large excess of methanol in the manner described. The fraction so obtained was weighed and its limiting viscosity number in toluene determined. The other fractions were prepared in an analogous manner from the dissolved gels of the preceding fractions, except fraction 7 which is the precipitate of extraction 6. The values of φ' in table XVI are found directly from the experiment; the values of φ'' have been calculated on the assumption that for the l-th fraction:

$$N_l'' = 47.5 - \sum_{k=1}^{l} N_k',$$

where the weights of the polymer in solution and gel are indicated by N' and N'' respectively, and 47.5 is the sum of the weights

*) Assistance was given by J. Schokkenbroek.

of all fractions. The difference between this weight and the weight of the original sample will be due to the loss of very low molecular weight material. From the figures (see table XVI) we have calculated the weight distribution function in the manner described by SCHULZ and DINGLINGER [73]:

To this end eq. (1) is written as $dn = H(M)dM$, where dn is the weight of all molecules with molecular weights between M and $M+dM$. Integration gives for the total weight of all molecules with molecular weight below M :

$$I(M) = \int_1^M H(M)\ dM,$$

the function $I(M)$ has been called integral weight distribution function. SCHULZ assumes that the separate fractions have a symmetrical weight distribution so that, when we calculate $I(M)$ for the mean molecular weight of fraction 1, we have:

$$I(M) \cong \sum_{k=1}^{1-1} u_k + \tfrac{1}{2}\, u_1,$$

where u_k is the weight of fraction k divided by the total weight of original polymer. We derived by differentiation from the plot of $I(M)$ vs M a plot of $H(M)$ vs M (in fig. 10 the curves I and II respectively). Again it is striking that so much low molecular weight material is present. In addition we see that this commer-

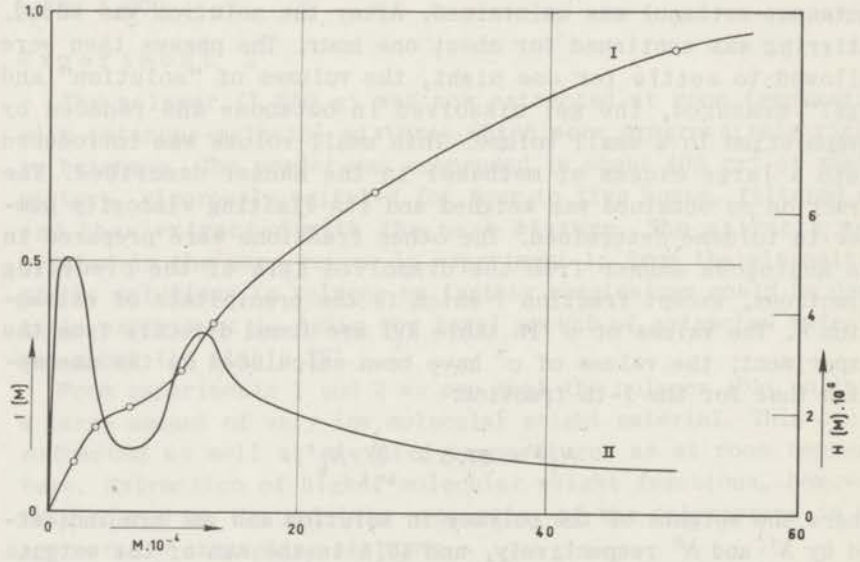

Fig. 10
Integral weight distribution $I(M)$, curve I, and (differential) weight distribution $H(M)$, curve II for polystyrene D1

cial polystyrene has two maximum values in its weight distribution function.

Finally the quantity α may be calculated in eq. (7). This can be done, however, only if μ is known. To a first approximation μ may be found by means of the relation

$$\mu_c = \tfrac{1}{2}\,[1+1/m^{\frac{1}{2}}]^2,$$

where μ_c is the μ of the mixture, in which the polymer fraction of degree of polymerization m is just precipitated. According to STOCKMAYER [74] m is a weight average, but for want of something better we derived m from the limiting viscosity number. For each fraction μ_c was calculated by using the m value of the next higher fraction; then eq. (7) yielded the value of α. In view of the assumptions made in this calculation α is remarkably constant : 0.02 (see table XVI).

Table XVI

Gel-extraction of polystyrene (D1) at room temperature

Fraction	Ratio butanone methanol	$10^2\,\lambda$	N'_{exp} (g)	N''_{calc} (g)	$10^3\varphi'_{exp}$	φ''_{calc}	$[\eta]$ (cm^3g^{-1})	$10^{-4}M$	μ_c	$10^2\alpha$
1	80:20	7.3	5.1	42.4	2.7	0.30	160	2.1	0.554	2.5
2	82:18	9.3	2.0	40.4	1.3	0.28	240	3.8	0.541	2.6
3	84:16	9.7	1.9	38.5	1.2	0.26	370	6.5	0.531	2.4
4	86:14	8.9	5.3	33.2	3.5	0.25	550	10.6	0.528	2.1
5	88:12	8.4	5.2	28.0	3.6	0.22	660	13.2	0.520	1.7
6	89:11	5.6	20.5	7.5	16.4	0.11	1140	26	0.514	1.8
7			7.5				1900	50		

Conclusion. The amount of the lowest molecular weight components ($M \cong 10{,}000$) we should have obtained in the first fraction of the precipitation method can be calculated now by means of eq. (9):

$$N''(M{=}10^4) = \frac{N(M{=}10^4)}{1+100\exp(-2)} = 0.07\,N(M{=}10^4),$$

where for λ the rather large value of one hundred has been taken. Hence a good fractionation of polystyrene (D1) by this method is very difficult. It has been found, indeed, that a threefold precipitation of the highest fraction of polystyrene (D) did not yield a good product for osmometry. The extraction method, however, gave satisfactory results (see IV.4).

III.3c. *Fractionation of polyvinyl alcohol*

As an example of a polymer which usually does not consist entirely of chemically identical monomers, we employed polyvinyl

alcohol (Elvanol, high viscosity-type B, grade 72-51, manufactured by Dupont de Nemours, to be referred to as polyvinyl alcohol (E)). The commercial polyvinyl alcohol, prepared by hydrolysis from polyvinyl acetate, nearly always has some acetate groups left. Among the interesting properties of polyvinyl alcohol we mention the membrane forming properties which already have been discussed in III.2f, its liability to degradation, and its tendency to association in solution.

It has been shown that degradation of this polymer is due to the occurrence of 1.2.glycol structures [75] and of ester bonds in the chain. The appearance of these two functions can be explained in view of the polymerization reactions of vinyl acetate [76)77)]. Degradation has been found when polyvinyl alcohol is treated with alkali, strong acids or oxydising agents such as periodates.

The association of polyvinyl alcohol in (aqueous) solution is not established with the same degree of certainty. By means of light scattering measurements DIEU [78] found association in aqueous solutions. This association decreased after prolonged heating at 75°C, and was also much less apparent when the polymer was dissolved in mixtures of water and dioxane and of water and acetone.

Experiment 1

Before performing any fractionation at all, we wanted to know whether polyvinyl alcohol (E) was liable to degradation. A solution of 5 g polyvinyl alcohol in 150 cm^3 of an aqueous HCl solution (0.02 n) was heated at 90-100°C during 24 hours. According to CLARKE and BLOUT [79] this was the only procedure by which a constant molecular weight could be obtained. After this heating period, the solution was diluted to a solution containing 2% polyvinyl alcohol; the polymer was separated from this solution by precipitation with a large excess of acetone. The powder so obtained had a limiting viscosity number $[\eta]_{25}$ = 116 cm^3g^{-1} *). For a blank experiment (an aqueous solution of polyvinyl alcohol heated for 24 hours at 90°C, and so on) we found the same value: 117 cm^3g^{-1}, whereas the value for Elvanol was: 106 cm^3g^{-1}.

Finally, for the three polymers the acetate percentage was

*) The usual extrapolation to zero concentration in the η_{sp}/c vs c plot was not admissible here, because in all experiments a definite upward curvature was found. For fraction 3 from table XVII we measured the flow times with an Ubbelohde viscometer at 25°C for eight concentrations to determine the relation between η and c. It turned out that the values obeyed exactly the relation of ARRHENIUS:

$$(1/c)\ln \eta_{rel} = [\eta]$$

We used, therefore, this relation in all calculations of $[\eta]$.

determined: 10.00 cm^3 0.02 n KOH solution plus 25 cm^3 polyvinyl alcohol solution were heated at 50 to 60°C for half an hour. After cooling the residual amount of alkali was found by titration. A solution of 25 cm^3 water plus 10.00 cm^3 0.2 n KOH solution was treated in exactly the same way. The difference between the two titrations yielded the amount of alkali that was consumed by the hydrolysis of the acetate. For polyvinyl alcohol (E) we found 0.75% acetate groups, for the acid-treated product 0.95%, while its blank contained 0.60%. The higher value of the acid-treated polymer was due to a very small percentage of chlorine.

From this experiment we draw the conclusion that degradation of this polymer during fractionation can be neglected.

Experiment 2

One of the solvent-precipitant systems for the fractionation of polyvinyl alcohol is the system water-acetone [80)81)]. We used this system for an extraction procedure as described in the preceding part of this section. From a preliminary experiment we knew that in a 50:50 mixture of water and acetone nearly all the polymer was precipitated.

A solution *) of 20 g polyvinyl alcohol in 750 cm^3 water was introduced into 1 l of a mixture of water and acetone (50:50); the composition of this mixture was maintained constant by the simultaneous addition of acetone. After one night the volumes of "solution" and "gel" were determined. From the solution the extract was prepared by evaporation to a small volume and precipitation in a large excess of acetone. The gel was redissolved in water, and treated with the next extracting mixture, and so on (Table XVII). At the third extraction no good separation was achieved, even after six days the gel had not settled. We finally obtained the greater part of the gel by centrifuging. The solution, however, remained very turbid. No exact volume could be determined here, the limiting viscosity numbers of the gel fraction and of the solution fraction were the same.

Remarks: The main fraction (3), to be referred to as polyvinyl alcohol (E 3), was less soluble in water than the unfractionated product. Moreover the solution was not quite clear, and became still more turbid after prolonged standing at room temperature. After some weeks a precipitate was formed, which could easily be redissolved by heating at 90°C. The osmotic results obtained with a solution of this fraction were rather dubious; considerable

*) At temperatures below 50°C polyvinyl alcohol does not dissolve in water. When preparing solutions of this polymer, we therefore heated it in water at 90°C until all the polymer was dissolved.

Table XVII

Gel extraction of polyvinyl alcohol (E) with water-acetone mixtures *).

Fraction	Ratio water acetone	$10^3 \lambda$	N'_{exp} (g)	N''_{calc} (g)	$10^4 \varphi'_{exp}$	φ''_{calc}	$[\eta]$ ($cm^3 g^{-1}$)	$10^{-3} M$
1	50:50	3.7	1.1	16.8	4.4	0.18	46	20
2	55:45	4.6	1.2	15.6	6.9	0.19	60	33
3	60:40		14.8	0.8			123	125
4			0.8				123	125

*) For the calculation of the molecular weights we used the relation:

$$[\eta] = 0.25\ M^{0.53}.$$

where $[\eta]$ is the limiting viscosity number in water at 25°C. It will be seen in Chapter IV,3 that this relation is not too well established.

diffusion through the membrane was demonstrated, hence a large amount of low molecular weight material was still present (see IV.3).

Experiment 3

According to CLARKE and BLOUT [79] the fractionation of polyvinyl alcohol can be performed better in ethylene diamine mixtures with benzene and dioxane. We tried, therefore, the use of ethylene diamine-benzene mixtures in the extracting procedure. The two liquids were purified: the diamine by refluxing the commercial product with 30% of its weight of solid sodium hydroxide, distilling and refluxing the clear distillate with sodium metal until no further reaction took place. Distillation yielded pure ethylene diamine, b.p.$_{76}$=116.5-117°C; n_D^{25}=1.4541 and d_4^{25}=0.9007.

The extraction of the polymer was done in the usual way: A solution [+]) of 10 g polyvinyl alcohol (E) in 200 cm^3 diamine was introduced into 200 cm^3 of a mixture of ethylene diamine and benzene (120:80); this ratio was maintained constant. After one night the "gel" was redissolved in diamine and treated as before; the "solution" was reduced to a small volume by evaporation and poured into a large excess of acetone. After decanting the liquid the powdery precipitate was washed thoroughly with acetone, filtered off, washed with ether, and dried at room temperature in a vacuum desicator over P_2O_5. The results are given in Table XVIII.

[+]) Again we noticed that the polymer was rather insoluble in the solvent at room temperature; complete dissolution took as long as four to six days. At temperature above 50°C, polyvinyl alcohol dissolved more rapidly in ethylene diamine than in water.

Table XVIII

Gel extraction of polyvinyl alcohol with ethylene diamine-benzene mixtures

Fraction	Ratio diamine benzene	N'_{exp} (g)	$[\eta]$ (cm^3g^{-1})	$10^{-3}M$
1	55:45	0.1	21	5
2	57:43	0.1	38	14
3	59:41	0.1	10	1
4	61:39	0.01		
5		9.0	99	85

Remarks: The solutions of the first fractions were turbid and unstable at room temperature. Of fraction 3 a clear solution could not be obtained at all; the greater part of the polymer separated out of the solution in less than one day. The flow times were measured at 25°C with pre-heated solutions. The main fraction (5), to be referred to as polyvinyl alcohol (E5) gave a clear aqueous solution. The stability of this solution was much higher than that of the unfractionated polymer, although after several weeks a small precipitate was formed. The osmotic results, however, were still more dubious than that of polyvinyl alcohol (E3) (see IV.3).

Conclusions: Polyvinyl alcohol (E) contains a large amount of low molecular weight material, part of which is less soluble in water than higher molecular weight components. By extraction with ethylene diamine-benzene mixtures this part of the low molecular weight components seems to be extracted readily (fraction 3). We have the impression, however, that a good fractionation of polyvinyl alcohol can be performed only at temperatures above 50°C, because at lower temperatures no thermodynamic equilibrium is attained. As regards the instability of the solution we have no opinion as to whether this is due to association phenomena or to the presence of "impurities" in the polymer.

References

1. J.C.W. Frazer and R.T. Myrick, J.Am.Chem.Soc. **38**, 1907 (1916).
2. R. Collander, Kolloidchem. Beihefte, **19**, 72 (1924).
3. A. Dobry, J.chim.phys., **32**, 46 (1935).
4. S.R. Carter and B.R. Record, J.Chem.Soc., 660, 664 (**1939**).
5. O. Albert and O. Kratky, Oesterr.Chem.Ztg., **43**, 79 (1940).
6. G.V. Schulz in H.A. Stuart, "Das Makromolekül in Lösungen", Berlin, 1953.

7. R.H.Wagner in A.Weissberger, "Physical methods of organic chemistry", Vol.I, part I, New York, 1949.
8. Earl of Berkeley and E.G.J.Hartley, Phil.Trans., **A206**, 486 (1906).
9. M.J.Schick, P.Doty and B.H.Zimm, J.Am.Chem.Soc., **72**, 530 (1950).
10. R.M.Fuoss and D.J.Mead, J.Phys.Chem., **47**, 59 (1943).
11. C.R.Masson and H.W.Melville, J.Polymer Sci., **4**, 337 (1949)
12. H.J.Philipp, J.Polymer Sci., **6**, 371 (1951).
13. K.B.Goldblum, J.Phys.& Coll.Chem., **51**, 474 (1947).
14. A.F.Sirianni, L.M.Wise and R.L.McIntosh, Can.J.Research, **25B**, 301 (1947).
15. B.H.Zimm and I.Myerson, J.Am.Chem.Soc., **68**, 911 (1946).
16. Landolt-Börnstein, "Physikalisch Chemische Tabellen", 5e Aufl.
17. J.Bourdillon, J.Biol.Chem., **127**, 617 (1939).
18. H.Lang, Kolloid Z., **122**, 165 (1951).
19. G.A.Gilbert, C.Graff-Baker and C.T.Greenwood, J.Polymer Sci., **6**, 585 (1951).
20. H.Lang, Kolloid Z., **128**, 7 (1952).
21. A.Münster, Z.Physik.Chem., **197**, 17 (1951).
22. E.Ducker, E.C.Fieller, H.T.Hookway and R.Townsend, J.Chem. Soc., 4390 (**1952**).
23. J.Bischoff and V.Desreux, Bull.soc.chim.Belges, **61**, 10 (1952).
24. P.J.Flory and W.R.Krigbaum, J.Chem.Phys., **18**, 1086 (1950).
25. W.H.Stockmayer and E.F.Casassa, J.Chem.Phys., **20**, 1560 (1952)
26. W.R.Krigbaum and P.J.Flory, J.Am.Chem.Soc., **75**, 1775 (1953).
27. L.A.McLeod and R.McIntosh, Can.J.Chem. **29**, 1104 (1951).
28. C.E.H.Bawn, R.E.J.Freeman and A.R.Kamaliddin, Trans.Faraday Soc., **46**, 862 (1950).
29. E.A.Guggenheim and M.L.McGlashan, Trans.Faraday Soc., **48**, 206 (1952).
30. In H.R.Kruyt, "Colloid Science", Vol. II, Amsterdam, 1952.
31. S.Madras, R.L.McIntosh and S.G.Mason, Can.J.Research, **27B**, 764 (1949).
32. F.Erbe, Kolloid Z., **59**, 32,195 (1932).
33. S.L.Bigelow, J.Phys.Chem., **29**, 1675 (1907).
34. J.Duclaux and J.Frerra, Kolloid Z., **38**, 54 (1926).
35. N.Bjerrum and E.Manegold, Kolloid Z., **42**, 97 and **43**, 5 (1927) E.Manegold, Kolloid Z., **61**, 140 (1932).
36. W.J.Elford, Proc.Roy.Soc.London, **112B**, 384 (1933). W.J.Elford, Trans.Faraday Soc., **33**, 1094 (1937).
37. W.J.Elford, J.Path.Bact., **34**, 505 (1931).
38. J.D.Ferry, Chem.Revs., **18**, 373 (1936).
39. F.E.Bartell and M.van Loo, J.Phys.Chem., **28**, 161 (1924).
40. H.Bechhold, Z.physik.Chem., **64**, 328 (1908).

41. H. Bechhold and R. Schuurmann, Z. Physik. Chem., **A142**, 1 (1929).
42. F. Erbe, Kolloid Z., **63**, 277 (1933).
43. M. Pisa, Kolloid Z., **63**, 139 (1933).
44. G. Schmid, Z. Elektrochem., **54**, 424 (1950) and **55**, 229 (1951). G. Schmid and H. Schwarz, Z. Elektrochem., **55**, 295, 684 (1951) and **56**, 35 (1952).
45. A. J. Staverman, Trans. Faraday Soc., **48**, 176 (1952).
46. E. Manegold and K. Solf, Kolloid Z., **55**, 273 (1931).
47. K. H. Meyer and J. F. Sievers, Helv. Chim. Acta, **19**, 649 (1936).
48. T. Teorell, Proc. Soc. Exp. Biol. Med., **33**, 282 (1935).
49. D. M. French and R. H. Ewart, Anal. Chem., **19**, 165 (1947).
50. H. J. Philipp and C. F. Bjork, J. Polymer Sci., **6**, 383 (1951).
51. J. W. Breitenbach and E. L. Forster, Makromol. Chem. **8**, 140 (1952).
52. P. H. Hermans in H. R. Kruyt, "Colloid Science", Vol. II, Amsterdam, 1952.
53. E. Manegold, Kolloid Z., **49**, 372 (1929).
54. R. Collander, Soc. Sci. Fennica Commentationes Biol. **II**, 6, 1 (1926).
55. H. Brintzinger and W. Brintzinger, Z. anorg. u. allgem. Chem., **196**, 3 (1931).
56. H. Brintzinger, Kolloid Z., **79**, 324 (1937).
57. G. Jander, and H. Spandau, Z. physik. Chem., **A185**, 325 (1939) and **A187**, 13 (1940).
58. H. Brintzinger, Z. anorg. Chem., **256**, 98 (1948).
59. T. Alfrey, A. Bartovics and H. Mark, J. Am. Chem. Soc., **65**, 2319 (1943).
60. J. H. Northrop and M. L. Anson, J. Gen. Physiol., **12**, 543 (1929).
61. P. Z. Adelstein and C. A. Winkler, Can. J. Research, **28B**, 194 (1950).
62. J. W. McBain and R. F. Stuewer, J. Phys. Chem., **40**, 1157 (1936).
63. E. Manegold and R. Hofmann, Kolloid Z. **50**, 207; **51**, 220, 308, and **52**, 19, 201 (1930).
64. W. C. Carter, R. L. Scott and M. Magat, J. Am. Chem. Soc., **68**, 1480 (1946).
65. P. Grabar and J. A. de Loureiro, Ann. inst. Pasteur, **63**, 159 (1939).
66. K. Sollner, J. Phys. Chem., **49**, 47, 171, 265 (1945).
67. R. E. Montonna and L. T. Jilk, J. Phys. Chem., **45**, 1374 (1941).
68. H. T. Hookway and R. Townsend, J. Chem. Soc., 3190 (**1952**).
69. L. H. Cragg and H. Hammerschlag, Chem. Revs., **39**, 79 (1946).
70. R. L. Scott and M. Magat, J. Chem. Phys., **13**, 172 (1945).
71. M. L. Huggins, J. Chem. Phys., **9**, 440 (1941).
72. V. Desreux and A. Oth, Chem. Weekbl., **48**, 247 (1952).
73. G. V. Schulz and A. Dinglinger, Z. physik. Chem., **B43**, 47 (1939).
74. W. H. Stockmayer, J. Chem. Phys., **17**, 588 (1949).
75. P. J. Flory and F. S. Leutner, J. Polymer Sci., **3**, 880 (1948).

76. O.L.Wheeler, S.L.Ernst and R.N.Crozier, J.Polymer Sci., **8**, 409 (1952).
77. O.L.Wheeler, E.Lavin and R.N.Crozier, J.Polymer Sci., **9**, 157 (1952).
78. H.A.Dieu, communicated at the Symposium on Macromolecules, Stockholm, 1953.
79. J.T.Clarke and E.R.Blout, J.Polymer Sci., **1**, 419 (1946).
80. A.Dobry and F.Boyer, J.chim.phys., **40**, 151 (1943).
81. K.Dialer, K.Vogler and F.Patat, Helv.Chim.Acta, **35**, 869 (1952).

Chapter IV

EXPERIMENTAL OSMOTIC PRESSURES

All measurements were performed in the manner described in chapter III.1; the temperature of the thermostat was 25° C unless stated otherwise. The dynamic method in the determination of the osmotic pressure was used only in experiment 1a. Corrections for capillary and density effects were applied, the π/c vs c relation was obtained in a graphical manner or by means of the method of least squares.

IV.1. Sodium carboxy methyl cellulose (NaCMC)

(a) In a first experiment the dynamic and static methods in the evaluation of the osmotic pressure were compared (discussion in chapter III,1b). The osmometer was the FUOSS-MEAD apparatus, the membrane "Ultrafeinfilter fein" from the "Membranfiltergesellschaft" in Gottingen. The sample NaCMC-73 was the same as used by PALS [1, 2], who found a number average molecular weight M_n = = 150,000. The polymer was dissolved in a 0,3 molar aqueous solution of sodium chloride. A table of π values found by the two methods has been given in III.1b. The density correction was applied to the reduced osmotic pressure (+ 0,14 when π is expressed in cm solvent and c in g/100 cm^3).

The relation between π/c and c in the dynamic method was found to be

$$\pi/c = 1,5 + 7c,$$

and in the static method:

$$\pi/c = 1,8 + 7c.$$

The corresponding molecular weights are 170,000 and 140,000 respectively, which is in reasonable agreement with the value of 150,000 obtained by PALS. The influence of the measuring technique on the "observed" osmotic pressure is seen to be rather large, the second virial coefficient is not much affected.

(b) Another sample of NaCMC-73 was investigated at two different temperatures. The osmometer was the FUOSS-MEAD apparatus, the membranes "Sylphrab"-membranes from the Sylvania division of the American Viscose corporation.

The fractionation procedure in the preparation of this sample was somewhat different from PALS' method (see PALS [1] p.21). The drop-wise addition of the precipitant ethyl alcohol to the aqueous solution of the polymer was stopped when the percentage alcohol in the mixtures had reached a value of 60; the polymer was then only partly precipitated. The gel was allowed to settle for one night, and the procedure was repeated with the redissolved gel. The third treatment with a large excess of ethyl alcohol was performed in the manner described by PALS, to whom we also refer for the further procedure. The yield was 20%.

The results at 25° C (Table XIX) can be represented very well by

$$\pi/c = 1.06 + 16c,$$

which gives a molecular weight of 240,000. Comparison of this value with that of experiment (a) shows that our fractionation has given a much higher molecular weight. The original polymer (a sample of the Research Laboratories of the A.K.U. Rayon Company at Arnhem) must have been rather heterogeneous with respect to chain length.

Table XIX

Osmotic pressure of solutions of NaCMC-73 in 0.10 molar aqueous solutions of NaCl

25°C			50°C		
c (g/100 cm^3)	π (cm solvent)	π/c	c (g/100 cm^3)	π (cm solvent)	π/c
0.084	0.17	2.6	0.139	0.245	1.76
0.106	0.295	2.8	0.250	0.72	2.88
0.158	0.535	3.4	0.371	1.09	2.94
0.264	1.38	5.2			

The results at 50° C can be represented by $\pi/c = 1,2 + 5c$; the accuracy is, however, much less than in the experiment at 25° C. The value obtained for the molecular weight (M_n = 210,000) is in agreement with that at 25° C; the value of the second virial coefficient is much lower.

(c) The molecular weight of the sample of NaCMC-72, used by TRAP [3] for light-scattering studies, was measured in the FUOSS-MEAD osmometer with "Sylphrab" membranes. The M_w of the sample was 86,000, whereas PALS for another sample of the same polymer obtained an osmotic molecular weight M_n = 64,000.

In the purification procedure used by TRAP the polymer was precipitated three times from an aqueous solution by a large

amount of ethyl alcohol (more than 80%). As a result of this treatment with excess ethyl alcohol he probably did not achieve a sharp fractionation.

We first determined the osmotic pressures in 0.4 molar solutions of sodium chloride. The accuracy of the measurements was rather low, which may have been due to the low molecular weight of the material, although no diffusion through the membrane was detected. Some of the solutions became turbid after several weeks, this as well as the zero value of the second virial coefficient indicate that the solution is not far from the point where it separates into two phases.

For π/c is found 7.5, which means for the molecular weight: M_n = 34,000.

Secondly we tried osmotic pressure determinations of NaCMC in mixtures of alcohol and water. After a few trials we took a mixture containing 25% ethyl alcohol, in which the NaCl concentration was 0.05 m. The scattering of the experimental points is of the same order as in the first experiment. Considering the low molecular weight, this is not surprising.

Table XX

Osmotic pressures of solutions of NaCMC-72

in 0.4 molar aqueous solutions of NaCl			in water-alcohol mixtures (75:25); NaCl concentration 0.05 m		
c (g/100 cm^3)	π (cm solvent)	π/c	c (g/100 cm^3)	π (cm solvent)	π/c
0.047	0.345	7.3	0.029	0.20	6.9
0.071	0.54	7.6	0.058	0.41	7.1
0.141	1.00	7.1	0.115	0.91	7.9
0.186	1.36	7.3			

The π/c vs c relation has the form:

$$\pi/c = 6.6 + 12c,$$

which gives a M_n = 38,000.

We may conclude from these experiments that the number average molecular weight is about 36,000 or less, because diffusion through the membrane never yields a value which is too high. The agreement with TRAP's weight average of 86,000 is very poor. The origin of this discrepancy is not clear. If diffusion of this comparatively low molecular weight material through the membrane has taken place, one should expect too high osmotic M-values rather than the reverse. According to TRAP, difficulties were experienced with bacterial growth in the purification of the

polymer. If this has resulted in partial degradation of the polymer, it is clear that a sufficient amount of high molecular weight substance was left to obtain a weight average of 86,000.

IV.2. Polymethacrylic acid (PMA)

The sample of PMA was the sample purified by Kooy [4] and used by him for viscosity determinations. We used a solution of the polymer for osmotic pressure measurements without saponification of the small percentage of ester groups which were formed during the purification procedure.

The weight average molecular weight was determined by Trap [3] from light scattering measurements in methanol solutions: M_w = = 193,000.

The osmotic pressures were measured with the Fuoss-Mead osmometer; the membrane was a Sylphrab-membrane; the solvent was 0.1 molar aqueous NaCl. To give an idea of the reproducibility of osmotic pressure determinations in general, all osmotic pressures in this experiment are listed in table XXI; in the other tables in this chapter only the average at each concentration is given. At the highest concentration the reproducibility was much less than in the other experiments. At this concentration several days were needed for the osmotic head to reach its final value, moreover these final values were much lower than might be expected from the three preceding values (lower concentrations were always measured first). In the calculation of the π/c vs c relation the values found at a concentration of 0.22 g/100 cm^3 were ignored:

$$\pi/c = 1.60 + 11c.$$

Quite exceptionally the density correction in π/c was negative: − 0.22 in our units. The molecular weight found is M_n = = 170,000 which, when compared with the weight-average derived from light-scattering, indicates that fractionation has been reasonably successful.

IV.3. Polyvinyl alcohol (PVOH)

In some preliminary experiments we tried to determine osmotic pressures of PVOH solutions in water at 25° C. This proved to be rather difficult, because the attainment of equilibrium was very slow. Even after four to six days no really static value was reached. We then changed the experimental conditions: in the first place we tried determinations of osmotic pressures of PVOH solutions in mixtures of water and ethyl alcohol (90:10) at the

Table XXI

Osmotic pressures of solutions of PMA in 0.1 molar aqueous NaCl

c (g/100 cm^3)	π cm solvent	π/c
0.0443	0.11	2.5
	0.125	2.8
	0.13	2.9
0.111	0.48	4.3
	0.48	4.3
	0.50	4.5
0.154	0.875	5.6
	0.88	5.7
	0.88	5.7
0.222	1.28	5.8
	1.34	6.0
	1.41	6.3

same temperature; in the second place we measured osmotic pressures in aqueous solutions at 50° C. The osmometer was in all cases a FUOSS-MEAD osmometer with Sylphrab-membrane. The density correction in π/c was about + 0.06. All results are collected in table XXII.

(a) Osmotic pressures of the PVOH used as membrane material in chapter III.2f were measured in water-alcohol mixtures (90:10) at 25° C. Equilibrium was reached in two or three days, the accuracy was rather low (the π values were means of values which differed 5 to 10% from each other). The π/c vs c relation proved to be

$$\pi/c = 4.0 - c,$$

which gave for M_n a value of 64,000.

(b) The polymer (E) used in the fractionation experiments of chapter III.3c, was measured at 50° C. With all solutions considerable diffusion through the membrane was observed; nevertheless, the osmotic head became constant after about three days in all experiments, except in those with the most concentrated solution (0.93 g/100 cm^3) for which no equilibrium values were obtained. From the two other values, which were triplicates, the following relation between π/c and c was calculated:

$$\pi/c = 2.5 + c,$$

which gave M_n = 100,000.

Table XXII

Osmotic pressures of solutions of four different PVOH samples (see text)

Experimental conditions	c (g/100 cm^3)	π (cm solvent)	π/c	$10^{-3} M_n$	$[\eta]$ (cm^3 g^{-1})
a) solvent: water-alcohol 90:10; temperature 25°C	0.085	0.33	3.9		
	0.17	0.62	3.7		
	0.34	1.23	3.6	64	105
b) solvent: water; temperature 50°C.	0.15	0.40	2.7		
	0.37	1.08	2.9		
	0.93	>1.3	>1.3	100	106
c) solvent: water; temperature 50°C	0.118	0.275	2.32		
	0.237	0.63	2.66		
	0.356	1.06	2.96	130	123
d) solvent: water; temparature 50°C	0.23	0.60	2.7		
	0.43	1.22	2.9		
	0.56	1.625	3.0		
	1.00	3.35	3.4	100	99

*) Regarding the determination of $[\eta]$ at 25° C see III.3c.

(c) The fraction (F3) obtained in the extraction of PVOH(E) with water-acetone mixtures (III.3c) was also measured at 50° C. Solutions of this polymer in water were always slightly turbid, even near the boiling temperature. At room temperature this turbidity was much higher, and increased visibly in the course of some weeks. Moreover, after some days a threadlike precipitate was formed. At 50° C the turbidity of the solution was not visibly changed after a period of one week, and no precipitate was found. From the values of π/c vs c at 50° C the following relation was obtained:

$$\pi/c = 2.0 + 2.8c,$$

and for the molecular weight $M_n = 130{,}000$.

The concentrations c_1 and c_2 of the liquids in the solution and solvent compartment, respectively, were determined gravimetrically after two experiments.

1) Duration of the experiment 72 hours:

$$c_1 = 0.437 \text{ g/100 cm}^3; \qquad c_2 = 0.013 \text{ g/100 cm}^3.$$

2) Duration of the experiment 48 hours:

$$c_1 = 0.361 \text{ g/100 cm}^3; \qquad c_2 = 0.006 \text{ g/100 cm}^3.$$

About 1% of the polymer had dialysed through the membrane in one day.

(d) The osmotic pressures of aqueous solutions of the fraction (F5) obtained in the extraction procedure with ethylene diamine-benzene mixtures were determined at 50° C. The solutions were remarkably clear in comparison with those of PVOH(E) and (E3). Considering the considerable diffusion through the membrane, the reproducibility of the osmotic pressures was rather good. After one or two days equilibrium was reached in all cases except at the highest concentrations. The four experimental values can be represented very well by

$$\pi/c = 2.5 + 1.0c,$$

which gives $M_n = 100{,}000$.

The concentrations c_1 and c_2 of the liquids in the two compartments were determined after two osmotic experiments:
1) Duration 48 hours: $c_1 = 0.748$; $c_2 = 0.027$ g/100 cm^3.
2) Duration 48 hours: $c_1 = 0.828$; $c_2 = 0.028$ g/100 cm^3.
Thus nearly 2% of the polymer dialysed through the membrane in one day (in experiments b, c and d the same membrane was used).

(e) The relation between $[\eta]$ and M_n for aqueous solutions of PVOH is not well established.

FLORY and LEUTNER [5] from their viscosity and osmotic pressure measurements at 25° C derived the relation $[\eta] = 0.02\ M^{0.76}$. These measurements, however, were performed on solutions of low molecular weight fractions ($M < 25{,}000$); diffusion through the membrane was found in all experiments and the rate of decrease of the osmotic head was constant only after 100 to 200 hours. The equilibrium osmotic pressures were found by extrapolating back to zero time. FLORY and LEUTNER, who were quite aware of the inaccuracy of this relation between $[\eta]$ and M, used it only for a relative comparison of molecular weights of low molecular weight PVOH's, obtained in degradation experiments.

STAUDINGER and WARTH [6] compared viscosity numbers (at 20° C) with osmotic molecular weights of PVOH fractions between 30,000 and 100,000. These authors also report some diffusion, but give no detailed information concerning their experimental technique. The molecular weights, which were calculated by means of the relation of SCHULZ (eq.(1') in chapter II.2a), have been recalculated by us from the limiting value of the reduced osmotic pressure; we obtained the limiting viscosity number from the viscosity numbers of STAUDINGER and WARTH by means of the relation of ARRHENIUS

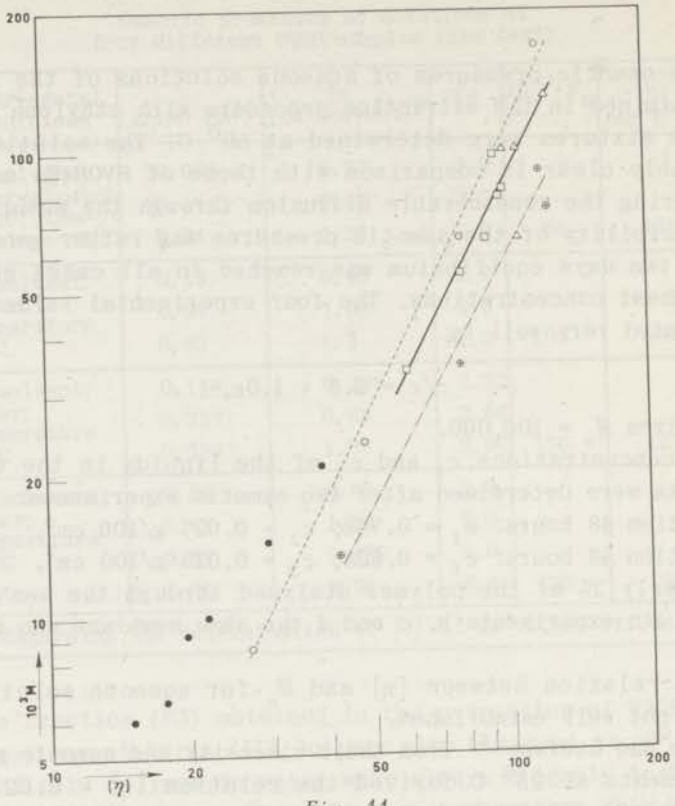

Fig. 11
Double logarithmic plot of molecular weight vs limiting viscosity number of polyvinyl alcohol in water
● FLORY and. LEUTNER, 25°
□ STAUDINGER and WARTH, 20°
○ DIALER, VOGLER and PATAT, 25°
⊕ DIEU, 25°
△ values from table XXII, 25°

$$(1/c)\ \ln \eta/\eta_o = [\eta],$$

where η and η_o are the flow times of solution and solvent, respectively.

Combination of our data Table XXII with those of STAUDINGER and WARTH gives $[\eta] = 0.25\ M^{0.53}$.

This equation is rather inaccurate although more reliable than that of FLORY and LEUTNER, for the following reason.

Limiting viscosity numbers of aqueous solutions of PVOH at 25° C have been compared with molecular weights from studies with the ultracentrifuge by DIALER, VOGLER and PATAT [7], who found $[\eta] = 0.30\ M^{0.5}$ and by DIEU [8], who found $[\eta] = 0.14\ M^{0.60}$. The

molecular weights obtained in this way lie between number average and weight average. The values obtained by these authors have been plotted in fig. 11 for comparison with the figures of STAUDINGER and WARTH [6], FLORY and LEUTNER[5] and the present investigation. The M_n values found by FLORY and LEUTNER are much higher than corresponds with the other values in the diagram; we believe this to be due to the permeability of their membranes for the fractions investigated.

We cannot exclude the possibility that our own values for M_n are still too high, because we noticed in all experiments, except in experiment (a), a slow diffusion through the membrane. Experiment (a), however, is precisely the one case in which a good agreement with the results of DIEU has been found. Our conclusion is that the relation between $[\eta]$ and M needs further study.

IV.4. Polystyrene solutions

a) Some standard samples of fractionated polystyrene were distributed some years ago under the sponsorship of the Commission on Macromolecules of the International Union of Chemistry. We investigated the sample which in the *Report* [9] of that commission is denoted by III.

Table XXIII

Osmotic pressures of sample III of the Commission on Macromolecules

c (g/100 cm^3)	0.10	0.12	0.20	0.40	0.67	1.16
π (cm solvent)	0.045	0.065	0.15	0.41	0.845	2.11
π/c	0.5	0.5	0.75	1.02	1.26	1.82

The osmometer was the FUOSS-MEAD apparatus, the membrane "Ultracellafilter fein", the solvent toluene. The density correction in π/c was + 0.06. The results are given in table XXIII; the values at the concentrations 0.10 and 0.12 g/1000 cm^3 have not been used for the calculation of the π/c vs c relation, because here the maximum deviation in π/c may be as much as 50%, whereas in all other values this is about 10% or less (see III.1f).

$$\pi/c = 0.60 + 1.10c$$

The evaluation of M_2 and A_2 will be given here as an example of such calculations.

$$M_n = RT/(\lim_{c \to o} \pi/c) = \frac{8.48 \times 10^4 \times 298}{0.60 \times 10^2 \times 0.86} = 490{,}000,$$

where R is expressed in cm water cm^3 $mole^{-1}$ $degree^{-1}$, and π/c in cm water $cm^3 g^{-1}$ (the density of toluene at 25° C is 0.86). Without density correction the limiting value for π/c is 0.54, which gives for the molecular weight M_n = 540,000. The possible error in this value does not exceed 10%. While the average value given in the Report is 630,000 for solutions in toluene and benzene, the various values reported differ considerably from one another; the lowest is 474,000 and the highest 876,000. In none of these measurements has the density correction been applied. It can be seen from our values that although this may have a relatively large influence on the value of the calculated molecular weight, it can by no means explain the great variation in results. In all probability these differences are due, as is suggested in the Report, to membrane difficulties.

Expressing π in dynes cm^{-2} and c in g cm^{-3}, the second virial coefficient *) is found in dynes $cm^4 g^{-2}$:

$$A_2 = 981 \times 0.86 \times 100^2 \times 1.10 = 0.93 \cdot 10^7 \text{ dynes cm}^4\text{g}^{-2}.$$

This value is lower than the other osmotic value for the system polystyrene III-toluene given in the report ($A_2 = 1.18 \cdot 10^7$), but higher than the values obtained for the same system from light-scattering data; in the Report $A_2 = 0.88 \cdot 10^7$, TRAP [3] gives $A_2 = 0.78 \cdot 10^7$. As has been stated in the Report the light-scattering values for A_2 seem to be more reliable, because the measurements in this method can be performed at lower concentrations, at which the influence of A_3 on the extrapolation procedure becomes less serious. BAWN, FREEMAN and KAMALIDDIN [10] and KRIGBAUM and FLORY [11], who performed osmotic measurements over a rather large concentration interval, express the concentration dependence of π/c by means of a quadratic equation in c. The values for A_2 then obtained are of about the same magnitude as the light-scattering values in the Report, and much lower than most osmotic values given there.

HUGGINS' constant μ is calculated by means of eq. (20) in chapter III.2d. Inserting for the molar volume of the solvent $v_1 = M_1/d_1$ and for the "segment molecular weight" $M/m = d_2(M_1/d_1)$ we have:

$$A_2 = \frac{RT}{M_1} \frac{d_1}{d_2^2} (\tfrac{1}{2} - \mu) = 0.93 \cdot 10^7 \text{ dynes cm}^4\text{g}^{-2}.$$

Using for the density of polystyrene the value $d_2 = 1.058$ [12], we obtain $\mu = 0.439$, whereas the average value of A_2 in the Report is $\mu = 0.429$. It is evident that any specific influence on the

*) In the Report $A_2/RT = B$ is called second virial coefficient.

solvent-solute interaction is more directly seen from a comparison of A_2 values than from HUGGINS' constant.

b) Osmotic pressures of toluene solutions of fractions obtained in the gel-extraction experiment of chapter III.3b were measured in ZIMM-MYERSON osmometers. In the sequence 1 to 7 the fractions were denoted by D_4 to D_{10}, see table XXIV. The π/c vs c values have been plotted in fig. 6 in chapter III.2e, the values of $\lim_{c\to o} \pi/c$, M_n, A_2 and $[\eta]$ at 25° C are collected in table XXIV, where also is included the molecular weight M_η calculated by means of the relation [3]

$$[\eta] = 0.5 \cdot 10^{-2} M_\eta^{0.80}.$$

The density correction in π/c was + 0.015.

A number of the most important difficulties in the osmometry of high polymers are encountered here.

Polystyrene (D4) was measured with an "old" Ultracellafilterfein membrane (see below). No diffusion could be detected; the osmotic head remained constant over a period of several days in each measurement. The two concentrations shown in the figure were measured in triplicate, and good precision was obtained. We believe, nevertheless, that the very high value of the second virial coefficient is due to a difference between the membrane permeabilities at these two concentrations; i.e., to concentration dependence of the selectivity coefficient (see II.3). Using the same A_2 as found in the other experiments we obtain for $\lim_{c\to o} \pi/c$ a value of 11, and for M_n : 27,000 (D4b). The latter value must still be regarded as a maximum value; the true number average molecular weight may be much lower.

Polystyrene (D5) was measured with the same membranes as (D4), but the first experiments (D4.a) were performed within a few days after the conditioning of the membranes, whereas the measurements (D4.b) refer to the membranes after two months use (this is the reason we called these membranes "old" in the preceding paragraph). The difference is striking; the calculated molecular weight decreases from 44,000 in the first to 38,000 in the second experiment. It is noteworthy that a slow diffusion was detected only in the second experiment (by a slow decrease in the osmotic head).

Polystyrene (D6) was first measured with the same "Ultracellafilter fein"; here no influence of the ageing of the membranes was found (D6.a). Then the fraction was measured with "Ultracellafilter allerfeinst" (D6.b). Although no diffusion in experiment (D6.a) was found, the calculated molecular weight in that experiment was higher than in experiment (D6.b): 55,000 and 49,000 respectively.

Table XXIV

Osmotic pressures of fractions of polystyrene (D)
(π in cm solvent and c in g/100 cm^3)

Number of fraction	Indication in text	$\lim_{c\to o} \pi/c$	A_2	$10^3 M_n$	$[\eta]$	$10^3 M_\eta$
1	D4.a	10	?	30	16	21
	D4.b	11		27		
2	D5.a	6.6	1.4	44	24	38
	D5.b	7.8	3.0	38		
3	D6.a	5.3	1.0	55	37	65
	D6.b	5.8	1.0	51		
4	D7	3.4		87	55	106
5	D8	2.00	0.84	147	66	132
6	D9	0.79	0.69	370	114	260
7	D10				190	500

The measurements on the polystyrene (D7) and (D8) were normal.

Solutions of polystyrene (D9) which were measured at rather high concentrations yielded a π/c vs c plot with an upward curvature. By means of the method of least squares a quadratic equation for π/c was calculated, which gave a good representation of the experimental points *):

$$\pi/c = 0.79 + 0.69c + 0.48c^2.$$

The relation between limiting viscosity number and molecular weight for polystyrene in toluene has been investigated by several authors [13)14)15)16)]. The results found by these authors differ greatly among each other. The influence of the polymerization temperature has been demonstrated by ALFREY, BARTOVICS and MARK [13)]; the influence of the fractionation of the polymer by BREITENBACH and coworkers [15)16)]. Part of the discrepancy is due to the different temperatures at which the limiting viscosity numbers were determined. The relation we used in this thesis was not exactly that found by ALFREY, BARTOVICS and MARK for a styrene polymerised at 120° C; the deviation (4%) can be neglected, however, in view of the inaccuracy of the method. The molecular weight of our fraction (D9) is much higher than corresponds with the relation $[\eta] = 0.5 \cdot 10^{-2} M_\eta^{0.80}$. We have not tried to derive any better relation from our data and those reported in the literature.

Acknowledgement. The author is much indebted to Dr R. D. Heyding for reading the manuscript and improving the English.

*) Experiment and calculations done by U. Daum.

References

1. D.T.F.Pals, thesis, Groningen 1952.
2. D.T.F.Pals and J.J.Hermans, Rec.trav.chim., **71**, 458 (1952).
3. H.J.L.Trap, thesis, Groningen, 1953.
4. J.Kooy, thesis, Groningen, 1952.
5. P.J.Flory and F.S.Leutner, J.Polymer Sci., **3**, 880 (1948).
6. H.Staudinger and H.Warth, J.prakt.Chem. [2], **155**, 26 (1940).
7. K.Dialer, K.Vogler and F.Patat, Helv.Chim.Acta, **35**, 869 (1952)
8. H.A.Dieu, communicated at the Sympsion on Macromolecules, Stockholm, 1953.
9. "Report on molecular-weight measurements of standard polystyrene samples", J.Polymer Sci., **10**, 129 (1953).
10. C.E.H.Bawn, R.F.J.Freeman and A.R.Kamaliddin, Trans.Faraday Soc., **46**, 862 (1950).
11. W.R.Krigbaum and P.J.Flory, J.Am.Chem.Soc., **75**, 1775 (1953).
12. H.Staudinger, "Die Hochmolecularen Organischen Verbindungen", Berlin, 1932.
13. T.A.Alfrey, A.Bartovics and H.Mark, J.Am.Chem.Soc., **65**, 2319 (1943).
14. A.J.Goldberg, W.P.Hohenstein and H.Mark, J.Polymer Sci., **2**, 503 (1947).
15. J.W.Breitenbach, A.J.Renner, H.P.Frank and E.Kindl, Monatsh, **81**, 455 (1950).
16. H.P.Frank and J.W.Breitenbach, Monatsh., **81**, 570 (1950).

SAMENVATTING

De osmotische druk van een oplossing is een maat voor het aantal deeltjes dat in oplossing is. Exact geldt dit slechts voor ideale oplossingen waarin de molfractie van de opgeloste stof klein t.o.v. één is (Wet van VAN 'T HOFF). Voor polymeeroplossingen (waarin de molfractie van de opgeloste stof practisch altijd erg klein is) geldt de wet van VAN 'T HOFF reeds in het gebied van de kleine gewichtsconcentraties niet meer, maar worden veel te hoge osmotische drukken gevonden. De afwijkingen, die polymeeroplossingen van ideaal thermodynamische gedrag in het algemeen vertonen, zijn ruim een decennium geleden door FLORY en HUGGINS voor het eerst op een quantitatieve manier beschreven met behulp van de quasi-rooster theorie. Speciaal voor het gedrag van verdunde polymeeroplossingen voldoet deze theorie niet bijzonder goed; mede daarom zijn sedertdien vele pogingen gedaan zowel om de quasi-rooster theorie te verbeteren, als wel om andere bruikbare theorieën voor vloeibare mengsels uit te werken. Eén van deze andere methoden geeft rechtstreeks een uitdrukking voor de gereduceerde osmotische druk als een machtreeks in de gewichtsconcentratie van de opgeloste stof; de coëfficiënten in deze machtreeks worden viriaalcoëfficiënten genoemd. De eerste term van de machtreeks, de VAN 'T HOFF term, kan dus door extrapolatie van de gereduceerde (d.i. door de concentratie gedeelte) osmotische druk naar de concentratie nul gevonden worden. De grootte van de tweede viriaalcoëfficiënt, één van de voornaamste punten in alle theorieën over de thermodynamica van polymeeroplossingen, is belangrijk voor de nauwkeurigheid van de extrapolatie. Hoewel het mogelijk is polymeeroplossingen in vloeistofmengsels te gebruiken waarin de tweede viriaalcoëfficiënt nul is, en extrapolatie bijgevolg niet meer nodig is, hebben dergelijke oplossingen een relatief grote waarde voor de vrije energie van verdunning en zijn dus thermodynamisch minder stabiel.

De bepaling van osmotische drukken van polymeeroplossingen, in principe zeer eenvoudig, is in feite een nogal gecompliceerde zaak. De meeste complicaties zijn het gevolg van de moeilijkheid om werkelijk semi-permeabele membranen te vinden, die toch permeabel genoeg zijn voor het oplosmiddel om metingen van redelijke tijdsduur mogelijk te maken. De permeabiliteit van membranen, zowel voor oplosmiddel als voor opgeloste stof, staat in nauw verband met allerlei andere membraaneigenschappen, waarvan een aantal aan een nadere beschouwing zijn onderworpen. Onafscheidelijk

van het membraanprobleem is echter het fractioneerprobleem; zo goed als alle ongefractionneerde polymeren bestaan immers uit moleculen van zeer uiteenlopend molecuulgewicht, kunnen dus fracties bevatten waarvoor het membraan permeabel is. Daar de osmotische druk een colligatieve eigenschap van de oplossing is, spelen juist dié fracties in het polymeer die het laagste molecuulgewicht hebben, relatief de grootste rol. Hierdoor wordt het fractioneerprobleem nog urgenter. Een fractioneermethode waarbij de laagste fracties goed weggezuiverd worden uit de hogere fracties, is beschreven.

Het probleem, wat de osmotische bijdrage van nog wel permeerende fracties is, blijft ondertussen bestaan. STAVERMAN heeft bewezen, dat er een verband bestaat tussen de mate waarin een bepaalde polymeerfractie door het membraan tegengehouden wordt in een permeatie-experiment, en zijn bijdrage tot de osmotische druk. Het feit, dat de theoretische osmotische druk in zo'n geval niet d.m.v. één of andere bijzondere meet- of extrapolatietechniek gevonden kan worden, is de belangrijkste oorzaak van de verschillen in de resultaten van verschillende onderzoekers. Vermoedelijk zijn zo b.v. ook de grote verschillen in de relaties tussen grensviscositeitsgetal en molecuulgewicht van vele polymeren tot membraanmoeilijkheden te herleiden.

Enkele andere problemen die bij de meettechniek naar voren komen, zoals de juiste meetmethode (dynamisch is minder goed dan statisch), het toepassen van de dichtheidscorrectie en de nauwkeurigheid van de resultaten zijn besproken en aan een aantal molecuulgewichtsbepalingen gedemonstreerd.

STELLINGEN

I

De thermodynamische redenering, die MÜNSTER tegen het toepassen van de dichtheidscorrectie op de gemeten osmotische druk geeft, leidt tot een resultaat dat in strijd is met het experiment.

A. MUNSTER, Z. physik. Chem., **198**, 17 (1951).
H. LANG, Kolloid Z., **128**, 7 (1952).

II

De hypothese van GERMANN, dat de „verbinding" van aluminiumchloride en phosgeen een zuur is met carbonyl als kation, is niet nodig om de eigenschappen van deze verbinding te verklaren.

A. F. O. GERMANN en C. R. TIMPANY, J. Phys. Chem., **29**, 1423 (1925).

III

Het door PFEIFFER en ENDERS gevonden „reactieproduct" van 2 methyleencyclohexanon en vinylacetaat is waarschijnlijk een dimeer van het 2 methyleencyclohexanon.

P. PFEIFFER en E. ENDERS, Ber., **84**, 247 (1951).
E. W. WARNHOFF en W. S. JOHNSON, J. Am. Chem. Soc., **75**, 497 (1953).

IV

De veronderstelling van CLEVERDON, LAKER en SMITH dat de osmotische druk van een oplossing afhankelijk is van de chemische samenstelling van het semipermeabele membraan is volkomen ongegrond.

D. CLEVERDON, D. LAKER en P. G. SMITH, J. polymer Sci., **11**, 225 (1953).

V

Uit „molecular orbital" berekeningen aan koolwaterstoffen met geconjugeerde systemen concluderen COULSON en JACOBS onder meer dat een vinylgroep een groter conjugerend vermogen heeft dan een phenylgroep. Deze conclusie verliest een groot deel van zijn betekenis als bij de berekeningen de afhankelijkheid van de resonantie-integraal van de atoomafstand in aanmerking wordt genomen.

C. A. COULSON en J. JACOBS, J. Chem. Soc. **1949**, 2805.
B. PULLMAN en A. PULLMAN, „Les théories électroniques de la chimie organique", Parijs 1952.

VI

Het door BAHR en BAHR gevonden nikkelcarbide is waarschijnlijk wel identiek met het door BROWNING en EMMETT onderzochte carbide.

G. MEYER en F. E. C. SCHEFFER, J. Am. Chem. Soc., **75**, 487 (1953).
H. A. BAHR en Th. BAHR, Ber. **63**, 99 (1930).
L. C. BROWNING en P. H. EMMETT, J. Am. Chem. Soc., **74**, 1680 (1952).

VII

Het is onwaarschijnlijk dat met behulp van permeabele membranen molecuulgewichtsverdelingen van polymeren te bepalen zijn volgens de door STAVERMAN voorgestelde methode.

A. J. STAVERMAN, Rec. trav. chim., **71**, 623 (1952).
Dit proefschrift.

VIII

Dat het trimethylaluminiummolecuul een pyramidale structuur heeft volgt niet zo noodzakelijk uit metingen van de dielectriciteitsconstante van deze stof in de dampphase als WISWALL en SMITH suggereren.

R. H. WISWALL en C. P. SMYTH, J. Chem. Phys., **9**, 352 (1941).
K. S. PITZER en H. S. GUTOWSKY, J. Am. Chem. Soc., **68**, 2204 (1946).

IX

Het door DEWAR voorgestelde omleggingsmechanisme van hydroxylaminen is aan gegronde twijfel onderhevig.

M. J. S. DEWAR, „Electronic theory of organic reactions", Oxford, 1949, p. 225.
H. E. HELLER, E. D. HUGHES en C. K. INGOLD, Nature, **168**, 909 (1951).

X

De invloed die de moderne techniek, inzonderheid de automatisering van steeds meer technische processen op de mens heeft, wordt door POLAK overdreven en bovendien niet op de juiste manier benaderd.

Fred. L. POLAK, Inaugurele rede, Rotterdam, 1949.
C. J. DIPPEL, Wending, **7**, 175, 453, 697 (1952).

XI

De „Wet op Woonwagens en Woonschepen" is in belangrijke mate verouderd.

„Nederlandsche Staatswetten". Editie Schuurman en Jordens No. 94, 6e druk, Zwolle, 1950.