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THERMODYNAMIC AND SOME RHEOLOGICAL PROPERTIES OF SOLUTIONS OF POLYGLYCOLS

Thesis submitted by

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PREFACE

Much of the existing thermodynamic information relating to polymer solutions and to cross-linked elastomers is limited to non-polar materials. The development of the so-called 'polypropylene glycols' which can be cross-linked to form polar elastomers, has provided an interesting class of compounds which are related to the corresponding less polar vinyl polymers by the introduction of 'ether oxygen' atoms at every second main-chain carbon atom. A range of fractions of low molecular weights from 150 to about 4000 is available and this enables studies to be made on a class of molecules intermediate in chain-length between the true 'high polymers' on the one hand and simple monomeric molecules on the other.

In the present work the thermodynamic properties of methanolic solutions of the linear short-chain polypropylene glycols have been studied with the purpose of examining the applicability of existing statistical thermodynamic theories of polymer solutions to these polar systems. Data has also been obtained which enables the Flory-Huggins polymer-solvent interaction constant (χ) to be calculated for the various systems studied and the significance of χ to be assessed for polar systems. The derivation of χ values and the assessment of their significance was undertaken in order to establish a basis for the use of χ as a parameter characterising plasticizer-polymer interaction and compatibility in the case of plasticized

cross-linked polyurethane elastomers based on the linear polyglycols studied in the present work. Complementary rheological studies have also been carried out on the pure polymers and their solutions in alcohols with the object of assessing the role of end-groups in determining the rheological properties of the polymers and investigating the dependence of intrinsic viscosity upon molecular weight in the case of short-chain polymers.

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OBJECTS OF THE WORK

The polypropylene glycols are a relatively recent development in polymer chemistry and consequently little fundamental physico-chemical work has hitherto been carried out on these materials. The present work constitutes a part of a programme of fundamental studies on the properties of plasticized polyoxypropylene elastomers.

The cross-linked elastomers may be prepared from polypropylene glycols by reaction with a bifunctional isocyanate, e.g., toluene di-isocyanate and a suitable monomeric triol in the presence of a catalyst. These elastomers have good low temperature and mechanical properties. The study of the plasticization of these rubbers is the original basis of the present work.

Before the work could be carried forward to the examination of the cross-linked materials themselves, it was considered desirable first to obtain fundamental information concerning some of the properties of the individual molecular chains comprising the cross-linked elastomers. This can best be achieved by examining the behaviour of the linear polymers in suitable compatible solvents prior to their condensation into a network.

Two approaches which lead to information on the polymer-solvent and polymer-polymer interactions have been

used in the present work as follows: (i) thermodynamic studies of the plasticizer-linear polymer interaction; (ii) dynamic studies on the rheological behaviour of the linear polymers and their solutions in suitable solvents. The work described in the present thesis and the aims of the experimental studies are summarised under the following two headings.

(a). Thermodynamic studies:- Thermodynamic studies on linear polyglycol-methanol systems have been carried out at various temperatures between -30° to $25^{\circ}C$. and over a range of concentrations and molecular weights of the polymers. The aim of these measurements has been to establish the excess thermodynamic functions for the polymer-methanol systems, the thermodynamic functions of mixing, the activities of both the components in the solutions and the characteristic polymer-solvent interaction parameters, i.e., the Flory-Huggins constant χ and the interchange energy as a function of the experimental variables. The determination of values of χ for well-defined systems (the polymer fractions in methanol) will then allow thermodynamic evaluation of the relative compatibility of other plasticizers with analogous cross-linked polymers by swelling equilibrium measurements* in methanol and other plasticizing solvents.

This aspect of the work is to be regarded as one of the

* The swelling equilibrium measurements do not constitute part of the work described in this thesis but are in progress in this department and are being carried out by another worker.

practical aims of the thermodynamic studies on the linear molecules though not necessarily the most funamental academic object of the work which is concerned rather with the studies of the structure and non-ideality of the solutions of the polar short-chain polymers in a polar solvent and also with the consideration of the significance of χ for the polar systems studied. Since the parameter χ has been suggested as a basis for evaluation of the stability of plasticizer-polymer systems, its determination as a function of composition, temperature and molecular weight of the polymer fractions has been an important aim of the present work. At the same time it has been considered necessary to examine the significance of χ for the polar systems studied in order to judge the utility of χ as a parameter characterising the plasticizer-polymer interaction in the cross-linked elastomers being studied in other work.

(b). Rheological studies:- The thermodynamic work has indicated an important dependence of the thermodynamic properties of the polyglycols upon chain-length or the related proportion of hydroxyl end-groups. Some exploratory rheological studies on the polymers of various molecular weights both in the pure form and in solutions in several hydroxylic solvents were therefore also made in order to obtain some complementary information concerning the role of end-groups in determining the properties of the polymer fractions. In this aspect of the work two approaches have been made: (i) the study of the heats of activation for flow in the pure polymers and in their solutions

and (ii) the study of the relationship between the intrinsic viscosities of the polymers in ethanol and their respective molecular weights.

The polymers studied in this work present some features of fundamental interest other than those arising simply from the plasticization problem. The low molecular weight polymers available provide an interesting group of substances for which the transition from simple to polymeric behaviour may be examined.

In addition to the two experimental approaches summarised above, the polar nature of the systems studied in the present work led us to examine the experimental data in the light of a number of theoretical relationships which have been derived by other workers from the lattice model treatment of polymer solutions. From the parameters (the polymer-solvent interaction constant χ and the interchange energy w) calculated from the theoretical equations, certain qualitative conclusions have been reached concerning the kinds of molecular interactions which may be occuring, for example orientation effects in the solvent-solvent or in the polymer-solvent interactions.

ABSTRACT

Thermodynamic and rheological studies have been carried out on a series of linear polypropylene glycols of molecular weights in the range 150 to 3350 in alcoholic solvents. The object of the studies has been to obtain fundamental thermodynamic information on the interaction of the polyglycols with a suitable compatible solvent (methanol) in relation to the study of the plasticization of cross-linked elastomers derived from the same polymers.

Measurements of the lowering of vapour pressure of the solvent and the heats of mixing in the polymer-methanol systems have been made. Vapour pressure studies have been carried out over a range of temperatures and solution compositions by means of a sensitive differential manometer. Heats of mixing have been determined by use of an isothermal phase-change calorimeter containing diphenyl-ether as the dilatometric fluid.

The experimental measurements have led to the evaluation of the partial molar free energies of each component in the solution and hence to the free energies of mixing. The experimentally determined heats of mixing have then enabled the entropies of mixing of the components (for various molecular weight fractions of the polymer) to be calculated. By comparison with the entropies and free energies of mixing calculated for the corresponding ideal solutions at the same compositions, the excess free energies and entropies of mixing have been deduced.

The Flory-Huggins equation has been applied to the results and values of the characteristic polymer-solvent interaction constant χ have been calculated as functions of composition, temperature of the solutions and molecular weights of the polymers used. The significance of χ has been discussed in terms of enthalpy and entropy contributions to the excess free energies of mixing. Previous theories of polymer solutions have been applied to the thermodynamic results obtained and interchange energies are calculated and discussed in the light of possible polymer-solvent interactions occurring in the systems examined. It is concluded that in the polar systems studied orientation effects in solvent-solvent and polymer-solvent interactions are important in determining the thermodynamic properties of the solutions.

The intrinsic viscosities of the polymers in several alcoholic solvents have been determined and the relationship of these values to the molecular weight of the polymer fractions used has been established. The heats of activation for viscous flow in the pure polymer fractions have been determined and the values related to the molecular weights of the polymers concerned. The rôle of hydroxylic end-groups has been discussed in relation to the results for the heats of activation. The free energies and entropies of activation have also been evaluated and the importance of hydrogen bonding in the various polymer fractions discussed in relation to the thermodynamic data for excess entropies of mixing in the systems.

I. INTRODUCTION

1. PRELIMINARY REMARKS

Investigations on high polymeric substances are usually carried out on two states of the materials, viz., on the pure substances or on solutions of the polymers in suitable solvents. The results of the first type of investigation contribute no information concerning the behaviour of the isolated elementary units but merely indicate their gross properties in the pure substance; such information is often of importance from the point of view of practical utility of the pure polymers. If, however, information is required on the behaviour of the individual molecules, the properties of the high polymeric substances in liquid solutions must be considered.

The relationship between physical properties and the molecular structure of polymers has been studied by a variety of techniques such as those of X-ray diffraction, infra-red absorption spectroscopy, light scattering photometry, osmometry, viscometry as well as through studies of sedimentation and diffusion rates, kinetics, thermodynamics and mechanical properties of the polymers either in their pure form or in solution. In the present work special emphasis has been placed on the study of thermodynamic and rheological properties.

In the early work, the interpretation of the experimental data was complicated owing to the difficulty of evaluating the degree of polydispersity in all synthetic polymers and most natural ones studied at the time. For the quantitative assessment of any property of a polydisperse polymer some knowledge of the molecular weight distribution is desirable. This knowledge is necessary because the various properties depend upon one or other of the two different types of molecular weight averages (i.e. "weight" and "number") which cannot be derived from one another. One way of examining the distribution of molecular weights is by fractionation or separation through sedimentation. Ultra-centrifugation is sometimes employed for the study of the molecular weight distribution of high-polymeric compounds (1,2,3,4). Strong centrifugal fields amounting to 10^4 to 10^6 times g, the acceleration due to the earth's gravitational field, can be generated. The various models by which polymer solutions may be represented involve assumptions concerning (i) the structure of the polymer and that of the polymer solution and (ii) the interaction energies between similar and dissimilar molecules in solution. The difference between the observed and calculated values of a given property usually indicates to what extent the assumptions were inappropriate and what other modifications should be made in order to construct a model on the basis of which the properties of the solution could more satisfactorily

be described. The theories of polymer solutions which have been developed (see below) involve parameters which describe the various polymer-solvent and polymer-polymer interactions. When these parameters are known for suitable systems and conditions, a more complete knowledge of the behaviour of the solution with regard, for example, to phase separation or change of properties with temperature, can be obtained. It is from this point of view that a thermodynamic study of plasticization is of value. A more detailed discussion of the theories of polymer solutions will be given in the following section.

2. THEORIES OF POLYMER SOLUTIONS

Theories of polymer solutions are based on the general theories of solutions. Accordingly it is desirable to discuss the theories for simple molecules before embarking on a discussion of polymer solutions.

A. General Theories of Solutions

The present knowledge of the liquid state is in most cases inadequate for any strictly quantitative formulation of the properties of solutions. Either of the approaches in which the liquid is regarded as (a) a quasi-crystalline lattice or (b) a dense gas-like phase have given considerable qualitative or semi-quantitative information concerning the properties of liquids and of their solutions. There is evidence that either of the above models can represent the liquid state with some

degree of accuracy depending on the conditions concerned; thus, it is reasonable to expect the dense gas model to be applicable near the critical point where, to a first approximation, molecules may move more or less independently while the quasi-crystalline lattice model would be expected to be more applicable at lower temperatures. Development of theories of solutions has been made from both of these points of view. At the temperatures for which most of the experimental data on the properties of ordinary liquid solutions are available, the lattice model is more applicable than the dense gas model.

The main purpose of these theories is to describe the properties of any solution with reference to those of the pure components or in terms of the departures of the properties of the solution from those of an 'ideal' solution.

An ideal solution is defined as one in which: (i) the activity 'a' of any component is equal to the mole fraction 'x' of that component in the solution at all concentrations, temperatures and pressures; (ii) the process of mixing brings about no change in the volume of the system upon mixing certain volumes of the components (i.e. $\Delta V = 0$) nor any change in enthalpy (i.e. $\Delta H = 0$). For any component i in the solution, the following relationships hold:

$$\Delta\mu_i = \mu_i - \mu_i^\circ = RT \ln a_i = RT \ln x_i \qquad (1)$$

or $$\overline{\Delta G}_i = \overline{G}_i - \overline{G}_i^\circ = RT \ln x_i \,, \qquad (2)$$

$$\Delta V = 0, \tag{3}$$

$$\Delta H = 0, \tag{4}$$

where μ_i and μ_i^o represent the chemical potentials* of the component i in the solution and in the pure state, respectively. $\bar{G}_i$ and $\bar{G}_i^o$ similarly represent, respectively, the partial molar free energies in the two states. The total free energy of mixing will therefore be given by

$$\Delta G = RT \sum_i n_i \ln x_i \tag{5}$$

where n_i is the number of moles of the component i. From the Gibbs-Helmholtz equation $\Delta G = \Delta H - T\Delta S$ and equation (4) we have

$$\Delta G = -T\Delta S \tag{6}$$

or

$$\Delta S = -R \sum_i n_i \ln x_i \, . \tag{7}$$

The expressions for the free energy of mixing per mole ΔG_m and the entropy of mixing per mole** ΔS_m take the following

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* The superscript o indicates that the thermodynamic functions refer to the pure components whilst the 'bar' indicates that they refer to the corresponding partial molar quantities.

** The subscript m used here and in subsequent equations indicates the value of the function calculated per mole of the component or mixture concerned.

form

$$\Delta G_m = RT \sum_i x_i \ln x_i \qquad (8)$$

and

$$\Delta S_m = -R \sum_i x_i \ln x_i \, . \qquad (9)$$

In practice, few liquids behave ideally and three types of deviations from ideal solution behaviour may be distinguished:

(i) '<u>Athermal Solutions</u>' are those for which $\Delta H = 0$, but ΔS no longer has its ideal value, i.e., the excess* entropy of mixing ΔS^E is not zero.

(ii) '<u>Regular Solutions</u>' are those for which $\Delta S^E = 0$ but ΔH is finite. Solutions for which ΔS^E is very small but not exactly zero have been described by Guggenheim as 'strictly regular solutions'.

(iii) '<u>Irregular Solutions</u>' are those for which both ΔH and ΔS deviate from their ideal values, i.e., $\Delta H \neq 0$ and $\Delta S^E \neq 0$.

Apart from deducing the thermodynamic functions for mixing by making use of the experimentally determined activities of the components in a solution, it is possible to calculate these functions theoretically with reference to suitable models of the solutions.

We may regard the solution as a quasi-crystalline lattice composed of N sites which can be occupied either by solvent or

---

* The excess entropy is defined as the entropy of the solution in excess of that of the ideal solution at the same composition, temperature and pressure.

solute molecules; it is then possible to compute the configurational entropy of a mixture of N_1 solvent and N_2 solute molecules. The number, Ω, of ways in which distinguishable arrangements of the N_1 solvent and N_2 solute molecules may be made is given by

$$\Omega = \frac{N!}{N_1!N_2!} \tag{10}$$

where $N = N_1 + N_2$. Using the Boltzmann relationship the configurational entropy of the solution is then

$$S = k\left[\ln N! - \ln N_1! - \ln N_2!\right]. \tag{11}$$

Since the configurational entropy is zero for both kinds of molecules in the pure liquid components, the above equation (11) gives the value of the change in configurational entropy ΔS upon mixing the two components. By making use of Stirling's theorem and upon introducing mole fractions, the following expression results

$$\Delta S = -R\left[n_1 \ln x_1 + n_2 \ln x_2\right]. \tag{12}$$

For ideal solutions $\Delta H = 0$ so that ΔG is given directly by the expression

$$\Delta G = RT\left[n_1 \ln x_1 + n_2 \ln x_2\right]. \tag{13}$$

In the case of non-ideal solutions, ΔH may have a finite value so that equation (13) no longer gives the free energy of mixing.

A finite heat of mixing arises when the mean of the energies of the molecular interactions in the pure substances differs from the energy of interaction between the unlike

molecules of the two components in the mixture. The theoretical evaluation of ΔH and ΔS has been the principal aim of most of the theories that have been developed both for ideal and non-ideal solutions. The various treatments are summarised below.

(a) Hildebrand and Scatchard (5,6,7,8) developed a theory of regular solutions and derived an expression

$$\Delta H = V(C_1^{1/2} - C_2^{1/2})\,\phi_1\,\phi_2 \qquad (14)$$

based on the assumption that the energy of interaction between a pair of molecules depends on the distance between them. C_1 and C_2 in equation (14) are the cohesive energy densities (C.E.D.); ϕ_1, ϕ_2 are the volume fractions* of the two components and V is the volume of the solution. The cohesive energy density is related to the energy of vaporization of the liquid and may be defined as the energy required to separate all the molecules in 1 cc. of a liquid. In this theory it has been assumed that ΔS has its ideal value. The method has been widely and successfully applied by Hildebrand (6) to liquid solutions of simple molecules. In the case of polymer solutions, the C.E.D.

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* ϕ_1 and ϕ_2 are the volume fractions given by the expression

$$\phi_i = \frac{x_i V_i}{\sum_i x_i V_i}$$

where x_i represents the mole fraction of the component i.

of the polymer is not so readily obtained. An approximate estimate can be made from knowledge of the chemical structure of the polymer but such a procedure would hardly be adequate for quantitative evaluation of the C.E.D. (9). A method of deducing it from the swelling of a non-linked polymer has been described (10) and the theory has been applied to polymer solutions.

(b) In the theory of strictly regular solutions developed by Guggenheim (11) it is assumed that the total energy of any configuration is made up of the sum of the interaction energies of the nearest neighbour pairs. He obtained the expression

$$\Delta H = z.w.\, x_1 \cdot x_2 \cdot N \qquad (15)$$

where w is a quantity called by Hildebrand and Scott (6) the interchange energy*; z is the coordination number of the lattice and N is the total number of molecules of the two components.

If ΔH can be regarded to a first approximation as being independent of temperature, then by making use of the differential form of the Gibbs-Helmholtz equation, with subsequent integration, the following expression for ΔG results:

$$\frac{\Delta G}{T} = \frac{z.w.\, x_1 \cdot x_2 \cdot N}{T} + C \qquad (16)$$

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* The interchange energy w is given by

$$w = w_{12} - 1/2(w_{11} + w_{22}) \qquad (17)$$

where w_{12}, w_{11} and w_{22} are the interaction energies of neighbouring pairs of (two liquid) molecules 1 and 2, molecules of liquid 1 and molecules of liquid 2, respectively.

where the constant C is independent of temperature. By putting $w = 0$, it is seen that C is the ideal free energy of mixing ΔG^i divided by T

$$\text{or} \quad \Delta G^E = z.w.\, x_1.x_2.N \qquad (18)$$

where ΔG^E is the excess free energy of mixing equal to $\Delta G - \Delta G^i$.

(c) Fowler and Guggenheim (12,13) developed a new method for calculation of the free energy of mixing based on statistical thermodynamics and called by them 'the quasi-chemical method'. They assumed that numbers of neighbouring pairs of molecules of different kinds denoted by x_{12}, x_{11}, x_{22} were in equilibrium in the solution, the equilibrium constant being expressed by

$$\frac{(1/2\ X_{12})^2}{X_{11}.X_{22}} = e^{-2w^*/kT} \; ; \qquad (19)$$

this result is analogous to that for a chemical equilibrium between the species 11, 22 and 12. By constructing configurational partition functions for the various pairs of molecules and by

---

* In equation (15), w was used as though it had the form of an enthalpy of interaction. In equation (19), however, it has the form of a free energy. This approximation in (15) is justified by the general assumption in the lattice theory that entropy contributions due to specific interaction between nearest neighbours are negligible compared with the configurational entropy.

algebraical manipulation, they obtained the expression*

$$\Delta H = z\, w\, K\, x_1\, x_2\, N \qquad (20)$$

for the heat of mixing and the corresponding free energy of mixing was given by

$$\frac{\Delta G}{T} = \int z.\, w\, K\, x_1\, x_2\, N\, d(1/T) \quad . \qquad (21)$$

Integration of equation (21) leads to the relation

$$\Delta G/RT = n_1 \ln x_1 + n_2 \ln x_2 + 1/2\, z\, n_1 \ln(1 - K\, x_2)/x_1 + 1/2\, z\, n_2 \ln(1 - K\, x_1)/x_2 \,. \qquad (22)$$

The last two terms on the right-hand side correspond to the excess free energy of mixing $\Delta G^E/RT$. Since we have an expression (equation 20) for the heat of mixing, the entropy and the excess entropy of mixing can hence be calculated.

There are, however, other approaches to this problem and the treatments of Kirkwood (14, 15, 16) and Longuet-Higgins (17) are of particular significance.

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* K is a new quantity defined by the equation

$$X_{12} = K\, X_{12}^{i} \qquad (20a)$$

and is related to the exchange energy w by the expression

$$1 - K = K^2 x_1\, x_2\, (e^{2w/kT} - 1) \,. \qquad (20b)$$

X_{12}^{i} is the ideal value of the number of nearest neighbour pairs of the kind X_{12}.

B. Application of the General Theories of Solutions to Polymer Solutions

In recent years it has become increasingly clear that the large deviations from ideal behaviour which are observed with solutions of polymer molecules are primarily due to the non-ideal entropy of mixing rather than to the finite heat of mixing. The rapid growth of our understanding of the thermodynamic properties of polymer solutions has been achieved mainly by the development of statistical mechanical theories for the calculation of the configurational entropy of mixing of polymers in solutions. Although Bethe (18), Chang (19, 20) and Miller (21, 22) were the first to concern themselves with the configurational problem in the case of macromolecules, the main advances were due to Flory (23), Guggenheim (24, 25) and Huggins (26). All these treatments are based on the quasi-crystalline lattice model except for the excluded volume treatment given by Hildebrand (27). It is useful to consider briefly the various independent approaches made by these workers.

(a) Flory's Expression for the Free Energy of Athermal Polymer Solutions: - The process of mixing can be visualized as the addition of the polymer molecules to the solvent "lattice" one after another; the number of ways of arranging the segments of the molecules as they come on to the lattice can be calculated. The solution is regarded as being composed of a total number of

N sites equal to $N_1 + r N_2$ sites where N_1 and N_2 are the number of solvent and polymer molecules respectively and r is the number of segments* in each polymer molecule. The reasonable assumption is made that all configurations have the same energy; it is then possible to show that the total number of configurations possible for the addition of the $(j + 1)$th molecule to the lattice is given by

$$\nu_{(j+1)} = \frac{z(z-1)^{r-2}(N - r\,j)^{r}}{N^{(r-1)}} \qquad (23)$$

where z is the coordination number** for the 'idealised' lattice. From the expression (23) the total number of configurations can be obtained by summation as

$$\Omega = \frac{1}{N_2!} \cdot \prod_{j=1}^{N} \cdot \nu_j \,. \qquad (24)$$

By substituting the values of ν_j and applying Stirling's

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* The segment referred to here is not necessarily, or usually, identical with the statistical 'segment' involved in the calculation of the average form of a polymer molecule in solution.

** It is assumed that the solute segments are of such a size as not to change radically the coordination number of the solvent lattice about the segments.

theorem for the simplification of the factorials, the following expression may be obtained

$$\ln \Omega = N_2 \ln \frac{r.N_2}{N} - N_1 \ln \frac{N_1}{N} + N_2 \left[\ln r - r + 1 + \ln z + (r-2) \ln (z-1) \right] \quad (25)$$

which, on applying the Boltzmann relationship, gives

$$S/k = -N_1 \ln \theta_1 - N_2 \ln \theta_2 + N_2 \left[\ln (rz) + (r-2) \ln (z-1) - r + 1 \right] . \quad (26)$$

In equation (26)

$$\theta_1 = N_1/(N_1 + rN_2) \text{ and } \theta_2 = rN_2/(N_1 + rN_2) . \quad (26\ a)$$

On putting $N_2 = 0$ and $N_1 = 0$ independently, equation (26) yields the following results

$$S_1^o = k \ln \Omega_1^o = 0 \quad (26\ b)$$

and

$$S_2^o = k \ln \Omega_2^o = Rn_2 \left[\ln(rz) + (r-2)\ln(z-1) - r + 1 \right] . \quad (26\ c)$$

From equations (26, 26 b and 26 c) it follows that

$$\frac{\Delta S}{R} = -n_1 \ln \theta_1 - n_2 \ln \theta_2 \quad (27)$$

and the free energy of mixing is hence given by

$$\frac{\Delta G}{RT} = n_1 \ln \theta_1 + n_2 \ln \theta_2 . \quad (28)$$

If it is assumed that the number of sites occupied by the polymer molecule is proportional to its volume, i.e., the segment is defined as that part of the polymer having a

volume equal to that of a solvent molecule, then θ_1 and θ_2 may be replaced by the corresponding volume fractions to give Flory's expression

$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 \qquad (29)$$

in which ϕ_1 and ϕ_2 are the volume fractions of the solvent and the polymer, respectively. The quantities ϕ_1 and ϕ_2 are given* by

$$\phi_1 = \frac{N_1}{N_1 + mN_2} \text{ and } \phi_2 = \frac{mN_2}{N_1 + mN_2} . \qquad (30)$$

By means of the equation (30) the relative partial molar free energies of the two components may be obtained from equation (29) as

$$\frac{\Delta\mu_1}{RT} = \ln \phi_1 + (1 - \frac{1}{m}) \phi_2 \qquad (31)$$

and

$$\frac{\Delta\mu_2}{RT} = \ln \phi_2 - (m - 1) \phi_1 . \qquad (32)$$

The expression (29) for the free energy of mixing has the same functional dependence on volume fractions as the ideal free energy of mixing has upon mole fractions. Secondly, the expression in its final form does not contain the coordination number z, and the reason for this will become evident after

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* m is defined as the ratio of the molar volume V_2 of the polymer to the molar volume V_1 of solvent so that $m = \frac{V_2}{V_1}$.

examination of Guggenheim's treatment. The treatment of Huggins (26) is analogous to that given above.

(b) Guggenheim's Treatment:- This is similar to that given by Orr (28); the lattice is regarded as having $N(= N_1 + r N_2)$ sites and the total number of nearest neighbour sites to the polymer molecule is taken as equal to a quantity q_z where q_z is given by

$$q_z = r_z - 2r + 2 . \qquad (33)$$

Another quantity α is defined as the ratio of the probability that a set of r sites be occupied simultaneously by segments of the polymer molecule to the probability that they be occupied by r solvent molecules. If we represent the solvent molecule by S and the polymer segment by P then the probability $f(S)$ that a particular site will be occupied by S and the probability $f(P)$ that it will be occupied by P may be written

$$f(S) = \theta_1 ; \quad f(P) = \theta_2 . \qquad (34)$$

We may denote the probabilities that r sites are occupied by the polymer molecule or by r solvent molecules as $f(\overline{rP})$ and $f(rS)$ respectively. Then

$$f(rS) = \theta_1 \xi_1^{r-1} \quad \text{and} \quad f(\overline{rP}) = \theta_2 K' \qquad (35)$$

where

$$\xi_1 = \frac{N_1}{N_1 + qN_2} \qquad (36\ a)$$

and the corresponding term for the component 2 is

$$\zeta_2 = \frac{qN_2}{N_1 + qN_2} \quad . \tag{36 b}$$

From equation (35) α can be obtained as

$$\alpha = \frac{f(\overline{rP})}{f(rS)} = \frac{K'\theta_2}{\theta_1 \zeta_1^{r-1}} \quad . \tag{37}$$

The value of α so obtained is related to the thermodynamic functions and can be derived rigorously by statistical mechanics. However, Guggenheim has used a more intuitive method for the same purpose. This is based on the principle of detailed balancing which requires that when a system is in equilibrium every single process must be exactly balanced by its converse. The rate of the processes of evaporation of the polymer molecule and condensation of r solvent molecules can be regarded as being proportional to $f(\overline{rP})$ and to p_1^r, respectively, where p_1 is the vapour pressure of the solvent; similarly the rates of the converse processes of condensation of the polymer molecule and evaporation of r solvent molecules may be assumed to be proportional to $f(rS)$ and to p_2, respectively, where p_2 is the vapour pressure of the polymer; α can then be shown to be given by

$$\alpha = \frac{K''p_2}{p_1^r} \quad . \tag{38}$$

By writing activities for vapour pressures if the vapours are

not ideal and introducing thermodynamic potentials instead of activities, the following equation has been obtained:

$$\mu_2 - r\mu_1 = RT \ln \alpha - RT \ln K'' \qquad (39)$$

which establishes the required connection between α and the thermodynamic quantities. Equation (39) expresses the relationship between μ_1 and μ_2, which is also given by the Gibbs-Duhem equation

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 . \qquad (40)$$

By differentiation of equation (39) at constant temperature and with subsequent elimination of $d\mu_2$ using equation (40), we can obtain

$$\frac{d\mu_1}{RT} = - \frac{\theta_2}{r} d \ln \alpha . \qquad (41)$$

By integrating this equation by parts, it follows that

$$\frac{\mu_1}{RT} = - \frac{\theta_2}{r} \ln \alpha + \frac{1}{r} \int \ln \alpha \, d\theta_2 . \qquad (42)$$

Since at $\theta_2 = 0$ equation (42) gives the value of the chemical potential of the pure component 1, we can express $\Delta\mu_1 (= \mu_1 - \mu_1^0)$ as

$$\frac{\Delta\mu_1}{RT} = - \frac{\theta_2}{r} \ln \alpha + \frac{1}{r} \int_0^{\theta_2} \ln \alpha \, d\, \theta_2 . \qquad (43)$$

Similarly, we obtain

$$\frac{\Delta\mu_2}{RT} = \theta_1 \ln \alpha - \int_0^{\theta_1} \ln \alpha . \, d\theta_1 . \qquad (44)$$

By substituting the value of α from equation (37) expressions (43) and (44) can be transformed to

$$\frac{\Delta\mu_1}{RT} = \ln \theta_1 + \frac{1}{2} z \ln \frac{\xi_1}{\theta_1} \qquad (45)$$

and

$$\frac{\Delta\mu_2}{RT} = \ln \theta_2 + \frac{1}{2} zq \cdot \ln \frac{\xi_2}{\theta_2} , \qquad (46)$$

respectively. The expression for the free energy of mixing may now be obtained since

$$\Delta G = n_1 \Delta\mu_1 + n_2 \Delta\mu_2 \quad . \qquad (47)$$

If the value of z becomes ∞ , it can be seen from equations (33) and (36) that $\theta_1 = \xi_1$ and $\theta_2 = \xi_2$, so that equation (47) reduces to Flory's expression (28). When $z = \infty$, the number of nearest neighbours to a given site becomes very large. The representative polymer segment P always has two nearest neighbour sites which are occupied by polymer segments of the same polymer chain (if the site is not at the end of a chain). These two sites may be neglected as $z \to \infty$ since there are many other neighbouring sites then available. In the deduction of Flory's expression it has been assumed that the probability of the occupation of a site in any manner is independent of how a neighbouring site is occupied. The occupation of sites by polymer segments is thus regarded to a first approximation as completely random. This would only be strictly true if z tends to infinity. We shall see later that in fact z is hardly likely to exceed six or eight.

The treatments so far considered have assumed complete uniformity of the distribution of segments in the solution

and that there was no competition for a particular site taking place between segments of different polymer molecules. In dilute polymer solutions there are necessarily regions in which relatively high segment densities occur and these are separated by regions having much lower or zero segment densities. It is also difficult to represent the solvent, the polymer and solutions of all intermediate compositions by a single lattice model. However, there is no way of avoiding this problem in the treatments developed hitherto.

(c) Free Volume Theory of the Entropy of Mixing: - It is evident that equations (28) and (29) are independent of any lattice parameters; they hence enjoy greater validity than the artificialities of the lattice model would suggest. Hildebrand (27) has in fact derived equation (29) without reference to any liquid lattice model. The assumptions involved are: (i) that the free volume* available to the molecules per unit volume of the liquid is the same for the polymer as for the solvent and (ii) that the free volume is a constant fraction ϑ_f of the total volume of the system whether it be component 1, component 2 or the mixture 1,2. For this assumption to be valid

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* The free volume is defined as the difference between the actual volume of the liquid and the minimum volume which it would occupy if the molecules were packed firmly in contact with one another.

the liquids forming the mixture should have similar chemical constitutions. The free volumes for N_1 molecules of component 1 and N_2 molecules of component 2 are then given by

$$V_{f_1} = N_1 V_1 \eta_f \tag{48}$$

and

$$V_{f_2} = N_2 V_2 \eta_f \tag{49}$$

where V_1 and V_2 are the molecular volumes of the solvent and the polymer, respectively. The free volume of the solution then follows as

$$V_{f_{12}} = (N_1 V_1 + N_2 V_2)\, \eta_f \,. \tag{50}$$

The free volume in the liquid state may be considered as the average effective volume in which the centre of gravity of a representative molecule could be considered to be able to move if all other neighbouring molecules remained momentarily fixed. By analogy with the change of entropy of a gas upon expansion, an increase in entropy of the polymer and solvent molecules occurs when they are mixed because there is an increase in free volume. The change of entropy of the solvent upon mixing is then given by

$$N_1 k \ln (V_{f_{12}}/V_{f_1}) = N_1 k \ln \frac{N_1 V_1 + N_2 V_2}{N_1 V_1} \tag{51}$$

and that of the polymer by

$$N_2 k \ln (V_{f_{12}}/V_{f_2}) = N_2 k \ln \frac{N_1 V_1 + N_2 V_2}{N_2 V_2} \,. \tag{52}$$

The reciprocals of the fractions in the logarithms are the

volume fractions of each of the two components in the solution. The total change in entropy, which is the sum of these contributions given by equations (51) and 52), is hence

$$\Delta S = - R \left[n_1 \ln \phi_1 + n_2 \ln \phi_2 \right] , \qquad (53)$$

where ϕ_1 and ϕ_2 are defined by the equations (30) and n_1 and n_2 are the numbers of moles of the two components. Equation (53) corresponds to that in Flory's treatment (equation 29). Obviously, depending on the shape and size of the polymer molecules, we may ascribe different free volume fractions ϑ_f to the two components. Zimm (29) and Huggins (30) have carried out detailed calculations for polymer molecules of different shapes and sizes, e.g., for spherical molecules of unequal size the equation for the partial molar entropy of the solvent has been shown (30) to be

$$\frac{\overline{\Delta S_1}}{R} = \frac{\phi_2}{m} + \frac{4\phi_2^2}{m} + \frac{10\,\phi_2^3}{m} + ... \qquad (54)$$

and for cylindrical rod-shaped molecules to be

$$\frac{\overline{\Delta S_1}}{R} = \frac{\phi_2}{m} + \frac{\phi_2^2}{2} + \frac{\phi_2^5}{5} + ... \qquad (55)$$

where m is the ratio of the volume of the solute to that of the solvent molecule.

(d) <u>The Flory-Huggins Equation</u>:- Flory (21, 31, 32) and Huggins (26, 33, 34, 35) have combined their expressions for the entropy of mixing in a polymer solution with that for the heat of mixing term calculated for polymer systems by Orr (28)

and Guggenheim (36, 37) in order to obtain an expression for the free energy of mixing. The equation for the heat of mixing

$$\frac{\Delta H}{RT} = \chi \phi_1 \phi_2 (n_1 + m n_2) \qquad (56)$$

is analogous to the expression of van Laar, Hildebrand and Scatchard for the heat of mixing of molecules of equal size. From the above equation, we can obtain the following relationships for the relative partial molar heat contents of the components in solution:

$$\frac{\overline{\Delta H_1}}{RT} = \chi \phi_2^2 \quad \text{and} \quad \frac{\overline{\Delta H_2}}{RT} = m \cdot \chi \phi_1^2 \, . \qquad (57)$$

By combining equations (31) and (32) with equations (57), the changes of chemical potential on mixing for the two components can be obtained as

$$\frac{\Delta \mu_1}{RT} = \ln \phi_1 + (1 - \frac{1}{m}) \phi_2 + \chi \phi_2^2 \qquad (58)$$

and

$$\frac{\Delta \mu_2}{RT} = \ln \phi_2 - (m - 1) \phi_1 + m \chi \phi_1^2 \, . \qquad (59)$$

From the relationship $\Delta G = n_1 \Delta \mu_1 + n_2 \Delta \mu_2$, the following expression for the free energy of mixing in the two-component system is obtained:

$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi \phi_1 \phi_2 (n_1 + m n_2); \qquad (60)$$

equation (60) is known as the Flory-Huggins equation and the constant χ is often referred to as the 'polymer-solvent

interaction constant'. We can rewrite equation (60) as

$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2 \qquad (61)$$

by substituting the value of m from the equations (30).

From equation (61), it appears that $-R\left[n_1 \ln \phi_1 + n_2 \ln \phi_2\right]$ represents the configurational entropy and $RT\chi n_1 \phi_2$ represents the heat of mixing. However, in accepting the configurational entropy as the entropy change in mixing, the possible entropy contributions due to specific interactions* between the neighbouring pairs are neglected. There is no justification for believing that specific interactions lead only to enthalpy changes on mixing, since orientation effects caused by molecular interactions are usually associated with significant changes in the entropy of the system, particularly if the groups concerned are polar. Consequently it is desirable to consider that χ determines not only the heat of

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* In cases where there are specific entropy contributions due to interactions between the molecules, the interchange energy w should really represent a free energy change and not simply an enthalpy change. As in the case of equation (63) the interchange energy may be expressed as

$$w = w_h + w_s \qquad (62)$$

the subscripts indicating enthalpy and entropy terms.

mixing but also any excess entropy of mixing in the system; χ may hence be written in the form

$$\chi = \chi_h + \chi_s \qquad (63)$$

where the subscripts h and s refer to enthalpy and entropy contributions, respectively.

Since

$$\Delta S = -(\partial \Delta G/\partial T)_p \qquad (64)$$

and

$$\Delta H = -T^2(\partial(\Delta G/T)/\partial T)_p , \qquad (65)$$

equation (61) leads to the values of ΔS and ΔH as

$$\Delta S = -R\left\{n_1 \ln \phi_1 + n_2 \ln \phi_2 + \left[\partial(\chi T)/\partial T\right] n_1\phi_2\right\} \qquad (66)$$

and

$$\Delta H = -R\,T^2\,(\partial\chi/\partial T)\,n_1\,\phi_2 . \qquad (67)$$

It has been observed that in some cases the value of the interaction 'constant' χ remains constant over a wide range of concentration but this is not found to be generally true.

Gee and Orr (38) have pointed out that to a large extent the deviations from ideality in the heat and entropy of mixing are mutually compensating in most systems, so that χ is apparently independent of concentration. The equations (60) and (61) therefore afford a considerably better working approximation than the individual equations for the

heat or the configurational entropy of mixing. It may be concluded that it is best to regard χ as a semi-empirical 'constant' whose application to polymer-solvent systems helps in the correlation and comparison of results of thermodynamic measurements.

(e) Flory's Theory of Dilute Solutions: - All of the treatments hitherto considered in this review are based on one important assumption that the polymer segments are uniformly distributed throughout the solution. In dilute solutions, the polymer molecules should rather be regarded as loose clusters of segments separated by regions of pure solvent. It is reasonable to expect each region of polymer segments to be approximately spherical and the segment distribution to be more or less Gaussian about the mean centre of gravity of the molecule.

Flory and Krigbaum (39, 40) have attempted, in a complex and lengthy treatment, to derive an expression for the free energy of mixing in dilute polymer solutions. The principal features of their treatment may be summarized in the following sections.

(i) The free energy of mixing of the polymer segments with solvent in a volume element δV is calculated from the Flory-Huggins expression (60) by assuming that n_2 is equal to zero.

(ii) The increase of free energy of the system in the volume δV due to overlapping of the segments of two polymer molecules is then calculated as a function of the distance of separation of the centres of the polymer molecules concerned. The change of free energy due to overlapping is integrated over all volume elements and the expression for the total change in free energy ΔG_a is then obtained (41) as

$$\Delta G_a = k\,T\,X\,e^{-3a^2/4(s^2)} \qquad (68)$$

where (s^2) denotes the average value of the square of the polar radius of gyration and X is a constant for a given polymer-solvent system and is determined by χ , (s^2) and the number of segments in the molecule.

(iii) Steps (i) and (ii) above enable the excluded volume to be evaluated. The probability that the centres of two molecules will be at a distance of separation 'a' is determined by a Boltzmann factor having the form $\exp\left[-\Delta G_a/kT\right]$. It would appear therefore that the term $\exp\left[-\Delta G_a/kT\right] . 4\pi a^2.da$ is the volume available for one of the pair of molecules if the other were fixed. From this argument, the excluded volume u may be shown to be given by the expression

$$u = \int_0^\infty (1 - e^{-\Delta G_a/kT}).\ 4\pi a^2.da \qquad (69)$$

which involves integration over all values of a from 0 to ∞ .

(iv) Having obtained the above equation for the excluded volume, the expression for the free energy of mixing is obtained from the excluded volume treament as

$$\Delta G = - n_2 k T \left[\ln V - (u/2)(n_2/V) \right] + \text{constant} \quad (70)$$

where V is the volume of the solution.

By standard thermodynamic operations the osmotic pressure may be derived as

$$\tilde{\pi} = -(\partial \Delta G / \partial V)_{T,p,n_2} \quad (71)$$

or

$$\tilde{\pi} \cong kT \left[n_2/V + (u/2)(n_2/V)^2 \right]. \quad (72)$$

Alternatively, substituting $n_2/V = c_2 N_A/M$ where c_2 is the concentration expressed in grams per unit volume and N_A is Avogadro's number, it follows that

$$\tilde{\pi}/c_2 = RT \left[1/M + (N_A u/2M^2) c_2 \right] \quad (73)$$

$$= RT \left[A_1 + A_2 c_2 + A_3 c_2^2 \ldots \right] \quad (74)$$

where

$$A_1 = 1/M \quad (75)$$

and

$$A_2 = N_A u/2M^2. \quad (76)$$

One of the important results of the theory of dilute solutions is therefore that it enables the value of the second virial coefficient in the expansion of the osmotic pressure to be calculated as a power series in concentration.

3. EXPERIMENTAL METHODS FOR THE STUDY OF POLYMER-SOLVENT INTERACTION

There are various experimental methods which may be employed in the study of polymer-solvent interaction. However, most of these approaches are complementary to one another and thus provide a range of information wider that that obtainable from any one type of study. It will be useful to discuss briefly the following important experimental methods for the examination of polymer-solvent systems.

A. Lowering of Vapour Pressure

It is well-known that the vapour pressure p_o of a solvent is lowered by the addition of a non-volatile soluble component. If the solvent vapour behaves ideally, the vapour pressure above the solution is then related to the chemical potential of the solvent through the following thermodynamic equations

$$\Delta G_1 = \Delta\mu_1 = \mu_1 - \mu_1^o = RT \ln p_1/p_o \qquad (77)$$

and

$$\Delta\mu = RT \ln a_1 \qquad (78)$$

where μ_1 is the chemical potential of the solvent and p_1 the pressure of solvent vapour over the solution. a_1 is the activity of the solvent in the solution, the standard state for the system being the pure solvent at the same temperature as that of the solution studied. By means of the Gibbs-Duhem equation (40),

the chemical potential μ_2 of the solute can be calculated. This then allows the free energy of mixing to be evaluated using the relation

$$\Delta G = n_1 \Delta\mu_1 + n_2 \Delta\mu_2 \qquad (47)$$

from which the entropy and heat of mixing may be determined with the aid of the expressions

$$\left[\frac{\partial \Delta G}{\partial T}\right]_{p,n_1,n_2} = -\Delta S \qquad (79)$$

and

$$\left[\frac{\partial (\Delta G/T)}{\partial (1/T)}\right]_{p,n_1,n_2} = \Delta H \,. \qquad (80)$$

By making use of the equations involving partial molar quantities, $\overline{\Delta H}_1$ and $\overline{\Delta S}_1$ can be obtained from equations (79) and (80) for any component. In order to obtain $\overline{\Delta H}_1$ and $\overline{\Delta S}_1$ considerable accuracy is required in the measurement of the vapour pressures since the value of ΔH obtained from equation (80) is determined by the temperature dependence of the relative lowering of vapour pressure.

There are essentially three different methods which have been employed for the study of polymer solutions by measurements of vapour pressure: (a) the absolute determination of the vapour pressure (42, 43, 44, 45) usually carried out by balancing the vapour pressure of the solvent against pressure of air or nitrogen in a manometer; (b) the differential determination of vapour pressures above the pure solvent and

the solution (46, 47, 48, 49, 50, 51) directly using a manometer and (c) the isopiestic method (46, 52, 53) in which the solution is allowed to come into equilibrium with solvent vapour at a known pressure (e.g., that above a solution of a reference substance at a known activity or above a solvent kept at a lower temperature).

A very sensitive differential manometer has been devised by Puddington (54,55) and can be applied to the measurement of relatively small differences of vapour pressure, e.g., between a dilute solution and the pure solvent or at low temperatures. It can also be used as an absolute method in cases where the vapour pressure of the solvent is relatively small. This method has been used in the present work and will be discussed in detail in the experimental section of this thesis.

B. Heat of Mixing and Dilution

As already mentioned, both the heat of mixing ΔH and the heat of dilution $\overline{\Delta H}_1$ can be obtained from the vapour pressure data by use of equation (80) and the expression

$$\left[\frac{\partial(\overline{\Delta G}_1/T)}{\partial(1/T)}\right]_{p,n_j} = \overline{\Delta H}_1 , \qquad (81)$$

respectively. However, satisfactory use of these differential equations demands a high order of accuracy in the determination of th

original vapour pressure data so that the usual small temperature dependence of ΔG or $\overline{\Delta G}_i$ can be determined with sufficient accuracy. Such determinations are made difficult in practice by adventitious non-equilibrium conditions, inadequate temperature control and unavoidable traces of impurities in the system. The heat of mixing is therefore more usually determined by direct calorimetric measurement. In the case of many high polymers, however, the extremely low rates of dissolution (if the polymers are solids) and the high viscosity of the resulting solutions present serious problems in the accurate determination of ΔH; however, the direct calorimetric measurement of ΔH is much to be preferred to its determination from vapour pressure data over a range of temperatures.

The techniques employed vary according to the system under investigation and details of the various methods are available in the literature (48, 56, 57, 58, 59, 60, 61, 62, 63, 64). In the present work, direct determination of the heats of mixing has been preferred and the calorimeter used is described in the experimental part of this thesis.

C. Viscosity of Polymer Solutions

Solutions of polymers usually have viscosities greatly exceeding that of the solvent even when the polymer is present at relatively low concentrations. Viscosity

measurements are simple to make with reasonable accuracy and this is one of the reasons why more research has been carried out on the viscosities of polymers than on any other physical property of them. The factors which determine the viscosity of a polymer solution are as follows: (i) the average linear extension of the randomly coiled, long-chain molecules; (ii) the chemical nature of the polymer and the solvent; (iii) the concentration of the polymer; (iv) the molecular weight of the polymer and (v) the temperature. From measurements of the viscosity η of the polymer solution several useful quantities listed below in Table I can be derived.

TABLE I

Nomenclature of solution viscosity

Common name of the quantities	Precise name	Symbols and the defining equations
Relative viscosity	Viscosity ratio	$\eta_r = \eta / \eta_o$ *
Specific viscosity	--	$\eta_{sp} = \eta_r - 1 = \frac{\eta - \eta_o}{\eta_o}$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = (\ln \eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp}/c)_{c \to o} = \left[(\ln \eta_r)/c\right]_{c \to o}$

* η_o is the viscosity of the pure solvent.

The intrinsic viscosity $[\eta]$ is independent of the concentration and is found to be a function of the molecular weight. It is also of value as a parameter for characterizing the polymer and the polymer-solvent interaction. In order to evaluate this quantity, measurements of η_{sp}/c made at very low concentrations are plotted against c and extrapolated to $c \longrightarrow 0$. In the range of low concentrations the reduced viscosity generally shows a linear dependence on concentration and in some cases η_{sp}/c is independent of concentration.

(a) Concentration dependence of reduced viscosity- At high concentrations the reduced viscosity is often markedly dependent upon concentration and a number of empirical relationships have been proposed which express the concentration dependence of the specific viscosity; the most common relationships are those due to Schulz and Sing (65):

$$[\eta]c = \eta_{sp}/(1 + k\,\eta_{sp}), \tag{82}$$

to Huggins (66):

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c, \tag{83}$$

and to Martin:

$$\eta_{sp}/c = [\eta]\exp(k[\eta]c). \tag{84}$$

Many authors prefer to plot $(\ln \eta_r)/c$ against c for the purpose of evaluating the intrinsic viscosity. At higher concentrations the experimental observations are better

represented by the logarithmic relationship

$$(\ln \eta_r)/c = [\eta] - k' [\eta]^2 c \qquad (85)$$

and expansion of equations (83) and (85) shows that

$$k + k' = 1/2 . \qquad (86)$$

(b) Viscosity and Molecular weight:- In 1930 Staudinger (67) suggested thst the reduced viscosity of a polymer should be proportional to its molecular weight according to the equation

$$\eta_{sp}/c = K M + A. \qquad (87)$$

This simple form of Staudinger's equation is not found to be generally applicable. In most cases the molecular weight must be related rather to the intrinsic viscosity, i.e., η_{sp}/c extrapolated to infinite dilution where interaction effects are absent. The relationship between the intrinsic viscosity and molecular weight is then found empirically to have the form

$$[\eta] = K M^a \qquad (88)$$

where a is a power usually less than unity and often near 0.5. K and a are constants for a particular system and can be determined from a double logarithmic plot of intrinsic viscosity against molecular weight. The values of some of these constants have been recorded in the literature (68) for a number of polymer-solvent systems.

(c) The Activation Theory of Viscosity: - The first attempt to develop a theory of liquid viscosity was made by Andrade (69). He depicted each molecule as vibrating about an equilibrium position at a sufficiently large frequency that many oscillations would take place during the period required for the molecule to diffuse from one equilibrium position in the liquid to another. Andrade assumed that resistance to flow arose in the process of transfer of momentum. The theory neglected the intermolecular forces between molecules. Some attempts were made to take these forces into account but there is an inherent difficulty in calculating the intermolecular forces under non-equilibrium conditions. Through an ingenious extension of the theory of absolute reaction rates, Eyring (70, 71) was successful in treating viscous flow as a process whose rate was controlled by the free energy required to overcome an energy barrier, and he based his activation theory of viscosity of the liquid state on the so-called free volume model. According to this theory each molecule in a liquid can be considered to be located in a potential energy "well". Eyring considered that irregularities in the arrangement of molecules constituted "holes" in the liquid. The process of flow was then regarded as occurring whenever there was a jump of a molecule from one potential energy well into another corresponding to a new position in a

neighbouring hole. The final expression from his theory may be written as

$$\eta = \frac{hN_A}{V} \cdot e^{\Delta G^{\neq}/RT} \qquad (89)$$

where h is Planck's constant, N_A is Avogadro's number, V the molar volume of the liquid and $\Delta G^{\neq}$ the free energy of activation. Substituting $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$ in the equation (89) the expression

$$\eta = \frac{hN_A}{V} \cdot e^{-\Delta S^{\neq}/R} \cdot e^{\Delta H^{\neq}/RT} \qquad (90)$$

may be obtained. Since the molar volume of a liquid does not vary greatly with temperature and $\Delta S^{\neq}$ being taken as approximately constant, the equation (90) can be written in the form

$$\eta = B \cdot e^{\Delta H^{\neq}_{visc.}/RT} \cdot \qquad (91)$$

It has been found that there is an empirical relationship between $\Delta G^{\neq}_{visc.}$ and the heat of vaporization expressed as

$$\frac{\Delta H_{vap.}}{\Delta G^{\neq}_{visc.}} = 2.45 \qquad (92)$$

which holds for a large number of liquids and provides a method of estimating theoretically the viscosity from the heat of vaporization of a liquid.

(d) Long-Chain Polymers: - It has been observed that activation energies for flow in long-chain polymers are very much lower than would be expected from their molecular weights.

It has therefore been suggested by Kauzmann and Eyring (72) that long-chain polymer molecules do not flow as a single unit but as segments of 20 to 40 atoms which jump together from one equilibrium position to another.

(e) Viscosity of Mixtures: - Attempts to obtain a simple expression relating the viscosity of a mixture to its composition and to the viscosities of the pure componenets in the mixture have not been successful, especially if the mixture shows an appreciable departure from ideal mixing behaviour. However, by considering the free energy of activation $\Delta G^{\neq}_{12}$ for viscosity of the mixture as an average of the free energies of activation for the pure components where $\Delta G^{\neq}_{12}$ is given by

$$\Delta G^{\neq}_{12} = x_1 \Delta G^{\neq}_1 + x_2 \Delta G^{\neq}_2 ,$$

the following empirical equation has been proposed:

$$\eta = \frac{hN_A}{V_{12}} \cdot e^{(x_1 \Delta G^{\neq}_1 + x_2 \Delta G^{\neq}_2)/RT} \qquad (93)$$

where V_{12} is the average molar volume of the components. If V_1 and V_2 are not very different, we can rewrite equation (93) in the form

$$\log \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 , \qquad (94)$$

which is the equation proposed by Kendall (73).

This equation is obeyed only by mixtures of similar liquids and the experimental data show departures from the

predictions of equation (94) in cases where the system exhibits departures from ideal mixing behaviour. A corrected form of the equation, in which allowance for the excess free energy of mixing is made, has been proposed as

$$\eta = \frac{N_A h}{V_{12}} \cdot e^{\left[(x_1 \Delta G_1^{\neq} + x_2 \Delta G_2^{\neq}) + \Delta G_m/2.45\right]/RT}. \quad (95)$$

In the case of a polymer solution, it is difficult to assess the value of V_{12} with any reasonable accuracy and the approach becomes more complicated.

4. PLASTICIZATION

Many of the natural and synthetic materials used as plastics or elastomers are of limited application without the addition of modifying agents to impart various desired properties. Such modifying agents are called plasticizers and are added to the plastic for one or more of the following reasons, the process being called plasticization:

(a) to facilitate mechanical processing by softening of the material;

(b) to modify the mechanical and elastic properties of the finished product and more generally to achieve a change in properties from those of the often hard, brittle, glass-like pure polymeric solid to those of a soft, more flexible material;

(c) to maintain desirable mechanical properties over a wider range of temperature than would be possible with the pure polymers.

It is also possible in many cases to bring about desired changes in mechanical properties by varying the chemical nature of the polymer, for example, through the introduction of large groups (74, 75) into the polymer chain. The structure is then loosened because the chains are forced apart. This results in a softening of the solid due to diminished intermolecular interactions and the process is termed 'internal plasticization'.

Since this work originated as part of a series of studies of plasticization of cross-linked polar elastomers derived from the linear polyglycols, it is considered appropriate to review briefly some of the fundamental aspects of the problem of plasticization. A polymer-plasticizer system may be regarded as a concentrated solution of the polymer in the plasticizer acting as a solvent. The study of plasticization is therefore a branch of the physical chemistry of polymer solutions. Any fundamental knowledge of the behaviour of plasticizers in polymers must be therefore gained in the first instance by studies of relatively dilute solutions of the polymer in various compatible solvents.

A. Second-Order Transition and Plasticization

Temperature has a marked influence on the properties of polymers and these properties generally show a first order or a second order transition when plotted against decreasing temperature. The first order transition is associated with the disappearance of crystalline regions in the polymer as the temperature is raised and is of importance in determining the mechanical properties on which ease of processing depends. The second phenomenon occurs at relatively lower temperatures. This temperature is called the second order transition point or glass point. It is of great importance with regard to the properties of the finished products since properties such as thermal conductivity, refractive index, dielectric loss, stiffness and viscosity change markedly at this temperature. In order to explain this change of behaviour it is necessary to assume that the macromolecules in the molten or dissolved state can execute two kinds of movements: (a) a macro-Brownian movement of the total molecule and (b) a micro-Brownian movement consisting of vibrations and rotations by the segments of the molecule.

The macro-Brownian movement is a more or less free one in the case of high polymers in the plastic state or in solution but it is much diminished by cross-linkage. The thermal micro-Brownian movement of the segments of the plastic/elastic materials

continuously decreases during cooling. Fewer and fewer segments have sufficient energy to execute vibrations or rotations and the material becomes more and more viscous. Finally the rotations are practically stopped and the polymer changes abruptly into a hard glass-like and brittle material in which local rotational motion is replaced by librational oscillation. This transition corresponds to the change of a number of important properties of the polymer, for example, the specific volume, viscosity, dielectric relaxation time and specific heat of the material. It is because of the undesirable transition of polymers to a state of brittleness at low temperature that the addition of plasticizers is desirable.

B. General Requirements for a Plasticizer

Two main requirements for a plasticizer are (a) compatibility and (b) permanence, i.e., maintenance of the plasticizer in the polymer as a single phase. The plasticizer must be miscible with the polymer. This implies a similarity in the magnitude of the intermolecular forces in the two components and explains why compatibility of plasticizers with non-polar polymers such as polyethylene is difficult to achieve. Permanence requires a low vapour pressure, low diffusion rate and chemical stability of the plasticizer within the polymer and these properties may be obtained by using high molecular

weight plasticizers. Many widely used plasticizers are high molecular weight esters such as phthalates, phosphates, adipates, sebacates etc. Other types are ketones, amides, nitriles and sulphonamides. The 'efficiency' of a plasticizer is judged by the manner in which one or more of the required properties are modified when measured with reference to the proportion of the plasticizer added; it is therefore a comparative term.

C. Mechanism of Plasticization

A more fundamental understanding of the action of plasticizers is desirable in order that the suitability of a plasticizer for a particular system may be judged and that the development of better plasticizers may be guided by less empirical considerations. Several empirical attempts have been made to treat the plasticizer-polymer interaction in terms of the secondary valence bonds dissociated (76), the solvation power of the plasticizers for the polymers (77, 78, 79, 80) and the rôle of polar or polarizable groups (81) in the components. Some authors have tried to show a connection between plasticization and viscosity (82, 83) or have tried to relate the efficiency of the plasticizer to the molecular size and shape of the interacting molecules (81, 82, 83, 84). The following general conclusions may be drawn from work of this kind:

(i) The solvating power of the plasticizer for the polymer is the primary requirement for a suitable plasticizer to have good compatibility with the polymer and this therefore suggests that polar solvents are better plasticizers for polar polymers.

(ii) Molecular size and shape of the plasticizer and the polymer play an important role in the efficiency of the plasticizer.

(iii). Addition of the plasticizer may be expected to improve the polymer material in flexibility by dilution of the polymer and by modification of the secondary interactions. The former effect is also indicated directly by the large increase of entropy of the system upon introducing the plasticizer into the polymer owing to the greater freedom of the polymeric chains.

It is generally considered that plasticization takes place through the formation of a gel which can be regarded as a solution of the liquid plasticizer in the polymer. Although polymer solutions are conventionally regarded as containing low concentrations of polymer, and plastic gels as containing high concentrations, it is not necessary to develop a separate theory for each class. In fact, much of the theory of plasticization and several of the methods of evaluation have been based on the behaviour of solutions containing low concentrations of polymer .

When large molecules mix with small ones, there is a considerable positive entropy change which in the absence of any specific interaction of the components leads to the formation of stable solutions or gels. A more quantitative treatment of plasticization follows from the study of the thermodynamic relations for polymer-solvent systems discussed in the section on theories of polymer solutions. The fundamental relationships are expressed by equations (28, 29, 31, 32, 45, 46, 58, 59, 60). The Flory-Huggins equations (written in terms of the activities of solvent and polymer)

$$\ln a_1 = \frac{\Delta\mu_1}{RT} = \ln \phi_1 + \left(1 - \frac{1}{m}\right) \phi_2 + \chi \phi_2^2 , \qquad (58)$$

$$\ln a_2 = \frac{\Delta\mu_2}{RT} = \ln \phi_2 - (m - 1) \phi_1 + \chi m \phi_1^2 , \qquad (59)$$

$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi \phi_1 \phi_2 (n_1 + m n_2) \qquad (60)$$

and

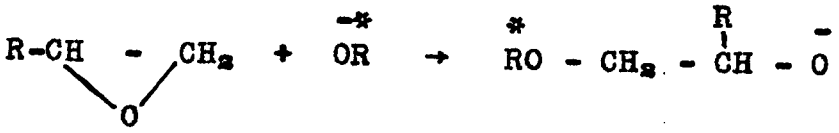
$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2 \qquad (61)$$

are particularly important in that they contain the empirical interaction constant χ which has previously been used as a parameter characterizing the stability of plasticizer-polymer systems. Instability, i.e., phase separation of the plasticizer-polymer solution is generally found if χ is much larger than 0.5.

5. THE POLYGLYCOLS

The polyglycols are formed by anionic polymerization of a low molecular weight oxide such as ethylene oxide or propylene oxide in dioxane.

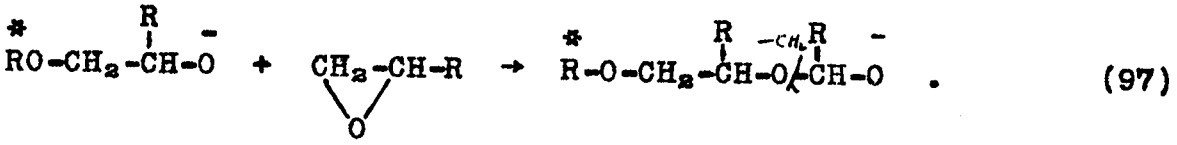
(i) Polymerization: - The initiation reaction may be formulated in general as



(96)

(Initiation)

followed by the propagation reaction



(97)

(Propagation)

Termination may be achieved by charge transfer with water or an alcohol. It is seen from the above reaction scheme that the main chain of the polyglycol is really a polyether. The polyglycols are related to the corresponding vinyl compounds through the introduction of the ether oxygen atom at every second carbon atom in the main chain. In the present work, polypropylene glycol fractions having 'number' average molecular weights varying from 150 to 3350 have been used.

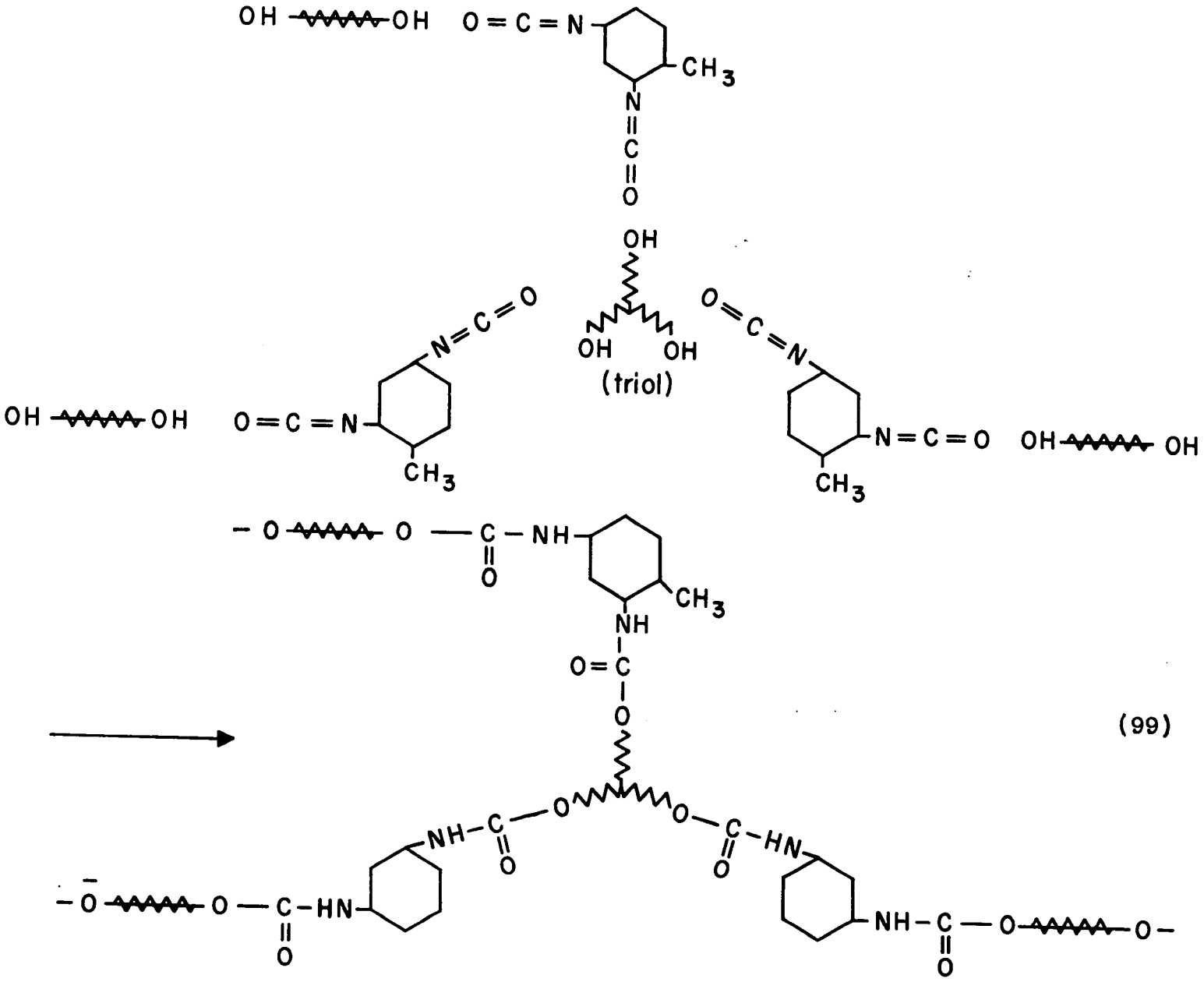
(ii) Cross-linking in polyglycols: - The polyglycols may be cross-linked in the presence of a suitable triol by means of a bifunctional isocyanate and the process, although complicated in practice by some side reactions, may be represented essentially as

$$R.N = C = O + \overset{*}{R}\ OH \rightarrow R.NH\text{---}\underset{\underset{O}{\|}}{C} - OR^{*} \qquad (98)$$

where R can contain other hydroxyl functions and the isocyanate can be bifunctional. The cross-linked elastomers are formed as shown diagramatically on the following page.

The materials obtained by cross-linkage of the polyglycols can be plasticized as in the case of other infinite network polymers and it is in connection with the problem of plasticization of these cross-linked elastomers that the present work owes its origin.

(iii) Previous thermodynamic and rheological work on linear polyglycols: - Few physico-chemical studies on the properties of linear polymers have yet been carried out. During the course of the present work, Malcolm and Rowlinson (85) have published the results of some thermodynamic studies on polyglycols in aqueous solutions and have made comparisons between the behaviour of the polyglycols and dioxane both in aqueous solutions. Comparison of the results of their work in aqueous solutions with the results obtained on solutions of the polypropylene



(99)

glycols in methanol in the present work is given in the discussion section of this thesis.

More recently Sadron and Rempp (86) have studied the rheological behaviour of the polyethylene glycols in a variety of solvents and established the dependence of intrinsic viscosities of these polymers upon the molecular weights of the fractions used.

II EXPERIMENTAL

SCOPE OF THE EXPERIMENTAL WORK

The experimental measurements made in the present work have consisted of:

(i) the determination of the relative lowering of vapour pressure of the solvent in methanolic solutions of various fractions of the polypropylene glycols and at various temperatures;

(ii) the determination of the heats of mixing of the various polymer fractions with methanol at 26.9°C. in an isothermal phase-change calorimeter, and

(iii) the determination of the viscosities of the pure polymer fractions over a range of temperatures and of the viscosities of solutions of the fractions in alcohols.

Although the investigations indicated under (i), (ii) and (iii) are widely different both in experimental techniques and in the principles involved, the results obtained from these different types of measurements are complementary for the understanding of the nature of the polymer-solvent interactions involved in the systems examined.

From the measurements listed under (i) and (ii), all the relevant thermodynamic data for the systems can be obtained, viz., the relative partial molar free energies of the components, the

activities of the components, the mixing functions, the excess mixing functions and the relative partial molar heat contents of the components.

For convenience of presentation, the experimental details and results have been described in three main sections: (1) materials used in the work, (2) thermodynamic determinations and results and (3) viscosity determinations and results.

SECTION 1

MATERIALS USED IN THE WORK

The Polymers: Five fractionated samples of the polypropylene glycols were provided through the kindness of the Union Carbide Corporation. These substances were of sufficiently high purity for the work except that they have a tendency to absorb some moisture. For the purpose of the present investigations, the samples were first dried by keeping them under vacuum at 80°C. for periods of twelve hours and then storing them in evacuated and sealed vessels until they were required for use. Before use in any experiment the samples were always evacuated again for six hours on the high vacuum line. The molecular weights of the samples had been determined by the Carbide Company but an independent check on these figures was made by determining the number of hydroxyl groups per unit weight of the sample of each polymer by the following method and then evaluating molecular weights of

the samples*.

All samples were first dried by the procedure described above. Three samples of a given polymer fraction containing between 3 and 5 mg. of hydroxyl groups were accurately weighed out into 10 ml. volumetric flasks, dissolved in dried carbon tetrachloride and then made up to the standard volume. The absorbance of each of the three solutions was determined at a wavelength of 2.9 microns in a 0.1 mm. cell using a Perkin Elmer model-21 infra-red spectrophotometer with sodium chloride optics. A calibration curve of the absorbance due to known weight fractions of hydroxyl end-groups had been determined chemically by the method of Elving and Warshowsky (87) using phthalic anhydride and pyridine. The molecular weights of other samples were then calculated from absorbance measurements on solutions containing known concentrations of the polymers. The over-all accuracy of the method is about 1% expressed in terms of the average molecular weight measured.

The five samples used were found to have molecular weights of 150, 425, 1120, 1955 and 3350. All except the last of these figures agreed with the data supplied by the Carbide Corporation for these samples to within an average of 3%. The

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* These determinations were carried out by Dr. J.L. Boivin of the Defence Research Board in collaboration with the author, since this method has been in use for some time in other work connected with the present project.

figure for the highest molecular weight sample was checked twice and deviated by 15% from that stated by the suppliers.

In the present work on the relative lowering of vapour pressure of the solvent, the concentrations of the polymer used were such as to enable deviations from ideality of the solutions to be measured. The polymer concentrations were hence too high to enable direct determinations of the molecular weights to be made from the vapour pressure data. Inspection of the extrapolations required, e.g. in Puddington's determinations of the molecular weights of "Carbowax" and sucrose myristate (88), indicates that the molecular weights of the polypropylene glycols could not have been determined with any greater accuracy by the vapour pressure method than by the analytical method described above.

Purification of Solvents: The methanol employed in the thermodynamic investigations was the 'acetone-free' reagent supplied by Brickman and Company, Canada. It contained about 1 percent of ethanol and was further purified by the following procedure.

25 g. of iodine were dissolved in 1 litre of methanol and the solution was slowly poured into 500 ml. of stirred N-NaOH solution. A small amount of a yellow precipitate of iodoform was formed. The solution was kept over-night and filtered. The methanol was refluxed over magnesium with a small amount of iodine for about 6 hours and then fractionally distilled and a fraction boiling between 64° and 67°C. was collected. This was again refluxed with a fresh quantity of magnesium in

the presence of iodine. This procedure was continued until the distilled methanol gave a vigorous reaction directly with magnesium. Methanol was finally distilled over magnesium and the fraction boiling at 64.7°C. was collected. The flask containing the methanol was sealed to the vacuum system and methanol was condensed under vacuum into the reservoir a_6 (Figure 1) after passage through a column of phosphorous pentoxide; the vessel a_6 was then sealed.

For the viscosity measurements, methanol obtained after the treatment with iodine and NaOH was refluxed and distilled several times. Ethanol and n-propanol were also distilled several times until substantial fractions with constant boiling points were obtained.

SECTION 2

THERMODYNAMIC DETERMINATIONS AND RESULTS

It was necessary to construct apparatus both for the vapour pressure measurements over a range of temperatures and for the calorimetric measurements of the heats of mixing.

A. Vapour Pressure Measurements and the Differential Manometer

The measurements of the vapour pressure of the solvent in the polymer solutions have been carried out by means of a differential manometer based on the type devised by Puddington (54); this apparatus is illustrated in Figure 1 and Plates 1,2,3

and 4. It differs from that used by Sirianni and Puddington (55) in a few minor details. The principle of operation, details of construction and the experimental procedure are discussed below.

(a) Principle of Operation: The differential manometer consists of the bulbs A_1 and A_2 connected by a U tube and partly filled with mercury. As shown in Figure 1, the bulbs A_1 and A_2 are exposed to the vapour of the solution and solvent, respectively. When there is no difference between the pressures of vapour on the mercury in the two limbs of the manometer A_1 A_2 the volume of the space above the mercury level in A_1 up to the mark h_1 is approximately equal to the volume of the bulb A_3. On closing the metal valve MV_2 and slowly opening the stopcock T_3 to the atmosphere, the mercury in A_3 could be transferred to the bulb A_1 until the mercury level just touched the mark h_1. The amount of mercury in A_3 was such that its meniscus then rested at a certain level in the lower part of the calibrated capillary C. This level was reproducible and is the 'zero-point' for the measurements. When there is a difference of vapour pressure on the mercury in the two limbs of the manometer and MV_2 is open, the levels of mercury in A_1 and A_2 are slightly different. Compared with the situation when there is equal pressure (or vacuum) on the mercury in the two limbs, this finite difference of vapour pressure has effectively caused the transfer of a small volume of mercury from A_2 to A_1, since the vapour pressure of the solvent in S_1 (Figure 1) is greater than that above the solution in S_2. When MV_2 was closed after equilibrium had been reached,

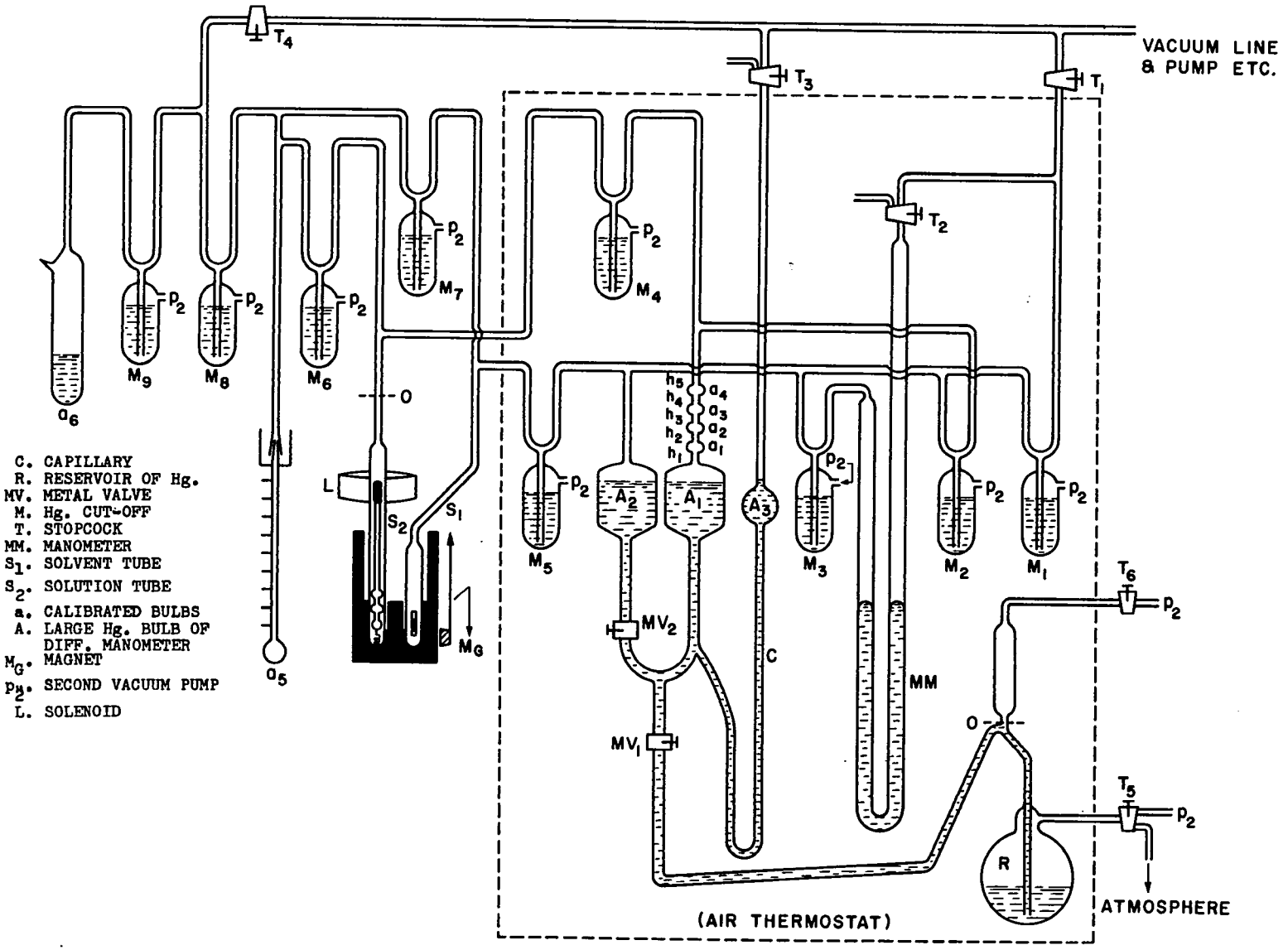

FIG. 1. DIAGRAM OF THE DIFFERENTIAL VAPOUR PRESSURE APPARATUS.

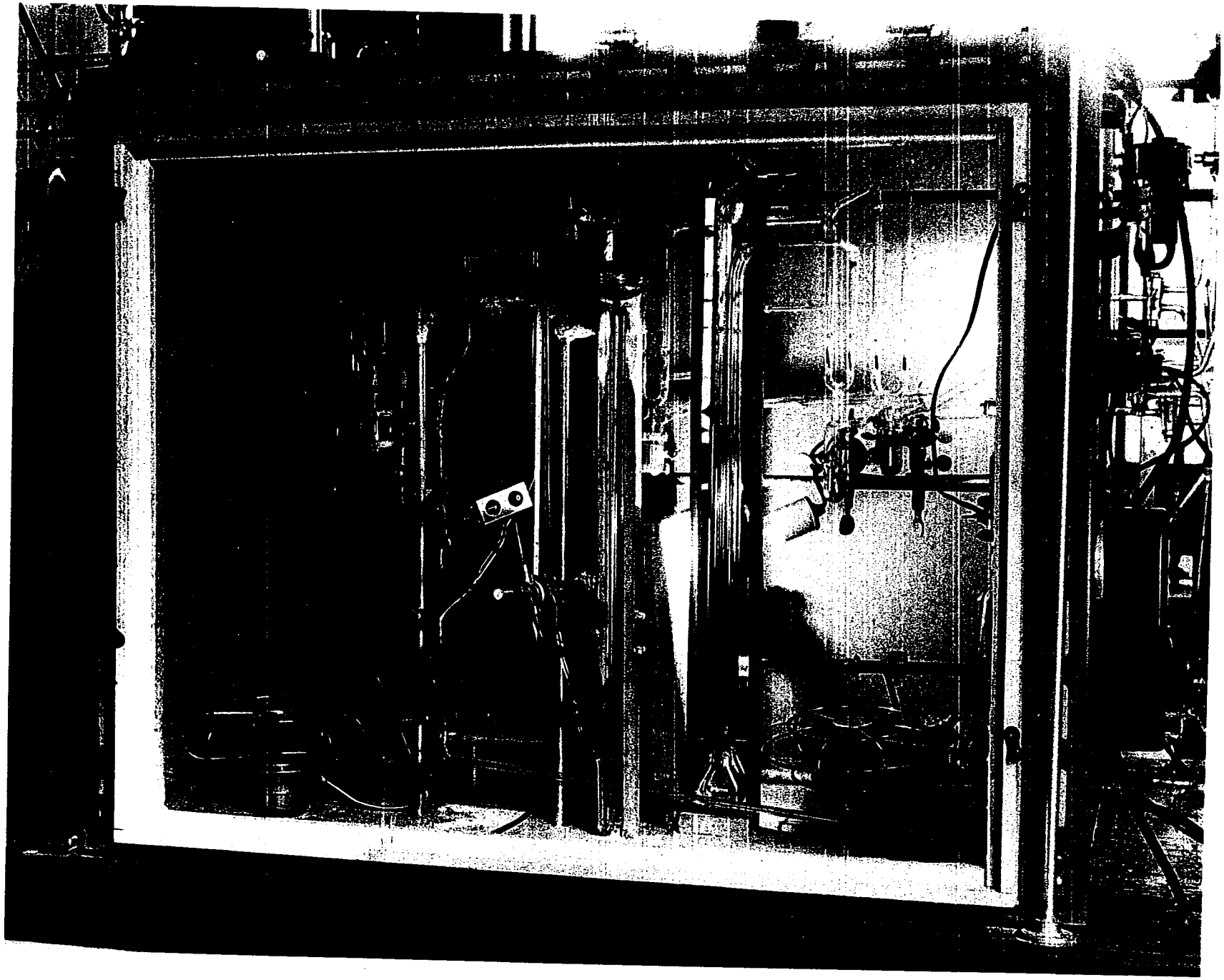

PLATE 1

PLATE 2

PLATE 3

PLATE 4

less mercury from A_3 would hence have to be admitted to A_1 for the meniscus of mercury in A_1 to reach the mark h_1. The reading on the capillary C when the meniscus in A_1 was at the mark h_1 would then be higher than that corresponding to the 'zero-point' level. The difference of levels measured in this way is proportional to the difference between the vapour pressure of the solvent and that of the solution. If the dimensions of the capillary below the bulb A_3 and the dimensions of the bulbs A_1 and A_2 are known, the difference of vapour pressure can be calculated from the difference of levels in the capillary, measured as described above. The sensitivity of the instrument depends on the cross-sectional area of the bulbs A_1 and A_2 compared with that of the capillary. Very small differences of vapour pressure can be measured accurately in the apparatus described above.

(b) Construction: The apparatus consists essentially of the differential manometer $A_1A_2A_3$, the manometer MM, the tubes S_1 and S_2 containing the solvent and the solution respectively and the various mercury cut-offs M. All parts of the apparatus were made from pyrex glass except the metal valves MV_1 and MV_2. The various components and their functions are described below.

Preparation of the bulbs A_1, A_2 and A_3: Although the principle of the Puddington method is essentially simple, its accuracy has been found (55) to depend on the reproducibility of the contact angle at the mercury-glass-vapour interface in the bulbs A_1 and

A_2. This factor is important since in the operation of the manometer it is assumed that the amount of mercury transferred from A_2 to A_1 is proportional only to the difference of pressure between the two limbs. The most convenient way of ensuring reproducibility of the contact angle is the method suggested by Puddington et al. (55) namely to etch the inner surfaces of the bulbs in the following manner. A few grams of 300 mesh carborundum, sections of flattened lead shot and a few ml. of water were put in the bulbs A_1 and A_2 before they were fixed in the apparatus. The bulbs were rotated for 24 hours at a speed just below that required to carry the pieces of lead shot around with the rotating bulbs. This treatment was then followed by thorough cleaning and steaming before the bulbs were set in the apparatus. Some traces of carborundum or residues of glass which remained on the etched surfaces of the bulbs were removed by washing with methanol.

The bulb A_3 having a volume about 75 ml. was blown from pyrex tubing and mounted together with the bulbs A_1 and A_2 on a rigid frame of aluminum rods as shown in Plate 1. The whole assembly was then set in a block of plaster of Paris. This procedure was necessary otherwise the large weight of the mercury in the bulbs might have gradually changed the relative position of these bulbs and thus led to irreproducibility of the results. An important improvement over the apparatus described by Puddington et al. (55) was the introduction of metal valves

instead of glass stopcocks between the two limbs A_1 and A_2 of the apparatus shown in Figure 1. These valves are much superior to greased stopcocks since no contamination of the mercury by grease can then occur.

Calibration and purpose of the bulbs $a_1, a_2 \ldots a_5$ It would appear from the description of the apparatus given above that it was only suitable for measurements over a limited range of differences in vapour pressure corresponding to the length of the calibrated capillary. In order to increase the range of the differential manometer, a series of small bulbs each approximately equal in volume to that of the capillary C were located in a short piece of capillary sealed to the top of the bulb A_1. The volumes of these bulbs were calibrated by weighing the mercury contained in them between etched marks. If during a measurement the end of the mercury thread was off the scale in the capillary C when the mercury in bulb A_1 had reached the first etch mark h_1 then the mercury was pushed to the next etched mark h_2 or h_3 etc. until the end of the thread of mercury appeared in the calibrated region of the capillary.

The internal diameters of the cylindrical bulbs A_1 and A_2 were determined by measuring the internal diameter of the glass tubing from which they were made. Measurements with a travelling microscope gave a mean diameter of of 7.693 cm. with an error not exceeding $\pm$ 0.001 cm. The capillary C was calibrated by measuring the length of a thread of mercury of known weight in

various parts of the capillary tube. One centimetre of the capillary tube corresponded to 0.08719 ml. ± 0.02%.

Use of the mercury cut-offs: It was considered desirable to use mercury cut-offs instead of glass stopcocks since organic vapours can be absorbed by the grease in stopcocks thus changing the concentration of the solution under investigation. This effect can introduce serious errors in the measurements of vapour pressure apart from the possibility of causing the grease to flow which may lead to leakages. For the operation of the mercury cut-offs a second vacuum pump p_2 was employed.

The sample holders for the solvent and solution: The tubes S_1 and S_2 held about 3 to 4 ml. of the solvent and the solution, respectively, and were connected to the bulbs A_2 and A_1 through the mercury cut-offs M_5 and M_4, respectively. These tubes were seated in a thick block of brass to ensure uniformity of temperature. The brass block B was maintained in an alcohol thermostat as shown in Plate 3 and was regulated by means of a large mercury thermo-regulator to a specified temperature with variations not exceeding ± 0.005°C. as determined by means of a Beckmann thermometer. It is to be expected that the temperature variation between the two sample tubes S_1 and S_2 in the brass block would not exceed ± 0.0005°C. Since the present investigations have been carried out at low temperatures, the alcohol thermostat was enclosed in another thermostat (containing a mixture of ethylene glycol and water) maintained at a controlled

temperature slightly lower than that of the alcohol thermostat by means of a powerful refrigeration unit.

Maintenance of constant temperature: As discussed above, the thermostat bath for the sample tubes was maintained at a temperature constant to $\pm$ 0.005°C. by means of a mercury relay used in conjuction with a large spiral mercury thermo-regulator. An electric heater was controlled by the relay and only a little heat was required to maintain the desired temperature. The input voltage to the heater could be adjusted by means of a variable inductance transformer. It was also necessary to maintain constancy of the temperature of the mercury in the bulbs A_1, A_2 and A_3. As indicated in Figure 1 and shown in Plates 1 and 4 most of the apparatus outside the low temperature bath was enclosed in an air-thermostat maintained at 32° $\pm$ 0.05°C. by circulation of air using two electric fans and with a heater controlled by a bimetallic regulator operating through a Sunvic relay. The fact that the large bulk of mercury in the bulbs would require considerable time to undergo a change of temperature tended to give a more constant average temperature locally at the mercury-vapour interface. That satisfactory constancy of temperature was achieved was indicated by the fact that no significant variations in the zero reading could be detected over periods of several hours and changes of the zero-reading were never more than 1 mm. during several days.

Transference of solvent under vacuum: The purified methanol was kept free from air and other impurities in the bulb a_6 and could be distilled in vacuo from the vessel a_6 into a calibrated capillary a_5 (with a bulb at its lower end as shown in Figure 1) by lowering the mercury in the cut-offs M_8 and M_9 and reducing the temperature of the capillary a_5. Several capillaries were available for transferring exact volumes (1 to 5 ml.) of methanol. After collecting known volumes of methanol in the capillary a_5 at a known temperature (generally 25°C.) mercury in the cut-offs M_8 and M_9 was raised and that in the cut-offs M_6 and M_7 lowered in order to transfer a known amount of methanol to either of the sample holders. When the required amount of methanol was condensed, the cut-offs M_6 and M_7 were closed by raising the mercury. The position of the meniscus of the condensed methanol at a given temperature could be read in the capillary to $\pm$ 0.05 cm. The total volume contained in the capillary vessel a_5 including that in the bulb was equivalent to about 50 cm. length of the calibrated part of the capillary . The volumes of the solvent used in the experiments could thus be known with an accuracy of about one part in a thousand.

Stirring of the liquids in the sample holders: In order to facilitate equilibration between the vapour and the liquids, the latter were stirred magnetically using sealed glass tubes containing pieces of soft iron. These tubes were enclosed in the sample holders S_1 and S_2 as shown in Figure 1 and caused to move by the periodic motion of a magnet outside the brass block B.

Some difficulty in stirring was experienced with the more viscous solutions of the polymers of high molecular weights but it was overcome by using a thin plunger with a soft iron core at its upper end and held in the field of a solenoid. By passing a current periodically in the solenoid the plunger could be made to move up and down in the tube S_2. This method of stirring gave satisfactory results and equilibrium could be reached in less than three to four hours as indicated by the constancy of the lowering of vapour pressure.

(c) General procedure: The whole of the apparatus was first evacuated to a pressure of 10^{-5} to 10^{-6} cm. of mercury. The required amount of carefully cleaned and distilled mercury was then introduced from the reservoir R into the bulbs A_1, A_2 and A_3 by opening the metal value MV_1 and the stopcock T_5 to the atmosphere. (The mercury in the differential manometer $A_1A_2A_3$ could be freed from any entrapped air or vapours by allowing it to fall back slowly into the reservoir R. The vacuum applied at T_6 removed any air or vapour from the mercury as it fell in a thin stream past the point $\bar{o}$ above R.) The mercury in the cut-offs M_4 and M_5 was then raised and the tube S_2 broken and a known weight of solute (i.e. the polymer) was added. The polymer had been kept under vacuum before introducing it in the tube S_2. No time was lost in resealing the tube S_2 to the apparatus lest the sample should take up any moisture. The apparatus was then evacuated again to ensure that no air or moisture remained after the tube

S_2 had been sealed to the apparatus. The required amounts of methanol were then transferred *in vacuo* to both sample holders. The solution was stirred for twelve hours to ensure complete mixing of the polymer with the solvent.

The zero reading on the capillary C was then noted. Mercury in the cut-offs M_4 and M_5 was then lowered after raising mercury in the cut-off M_2. At equilibrium the vapour pressure of the pure solvent was measured on the manometer MM and the lowering of vapour pressure was determined by the procedure discussed above. Corrections for the weight of vapour in the dead space in the apparatus were made to each concentration at every temperature. The dead space is the volume enclosed between the levels of mercury in A_1, in the manometer MM and in the cut-off M_2 and the level of liquid in the sample tube S_2. The dead space varied from 120 to 125 ml. For each system of definite composition studied, determinations of the differential vapour pressure and the vapour pressure of the solvent were made at various temperatures ranging from about -30° to $25^{\circ}C$. For each composition two or three readings were taken on the differential manometer at every temperature. The zero reading used was a mean of four measurements and was checked periodically.

The vapour pressure of the pure solvent was measured directly on the manometer MM and a mean of between six and eight readings over a period of one hour was used in the subsequent

thermodynamic calculations. Some typical data for p_o are shown in Table III for the polypropylene glycol (M.W. 1955)-methanol system. Values of p_o could be measured on the manometer MM with a mean error not exceeding 0.002 mm.

B. Calculation of the lowering of vapour pressure: The experimental measurements made on the Puddington differential manometer consisted of the determination of the zero-point level L_o of mercury in the capillary C when there was no difference of pressure on the mercury in the bulbs A_1 and A_2, and the determination of the level L when there was a finite difference of pressure. In order to calculate the lowering of vapour pressure Δp it was necessary to evaluate the magnification factor m of the instrument, i.e., the factor by which ΔL ($\Delta L = L - L_o$) must be multiplied in order to obtain one half of Δp in cm. of mercury.

If the cross-sectional area of the bulbs A_1 and A_2 is A sq. cm. and that of the capillary C is a sq. cm. then the magnification factor m is given by the relation

$$m = A/a.$$

Calibration data for the capillary and the bulbs are given in Table II from which m is seen to be 5332 for the present apparatus. The factor of one half mentioned above enters the calculation since the rise in the level of mercury in bulb A_1 due to a pressure difference Δp is only half of the change in pressure Δp.

For a given value of ΔL, Δp is hence given by

$$\Delta p = 2. \Delta l/5332.$$

TABLE II

Details of the various calibrations of the differential manometer

(i).	Volume of the calibrated capillary C per cm. of its length	=	0.008719 ml.
	Cross-sectional area of the capillary	=	0.008719 sq. cm.
(ii).	Diameter of the bulbs A_1 and A_2 as determined by a travelling microscope (based on three readings)	=	7.693 ± 0.001 cm.
(iii).	Cross-sectional area of the mercury interface in the bulbs A_1 and A_2	=	46.488 sq. cm.
(iv).	Calibration factor of the instrument, equal to 46.488/0.008719	=	5332
(v).	Volumes of the bulbs a_1, a_2, a_3, etc. in terms of the volume equivalent to the following lengths of the capillary C		
	Bulb a_1	=	50.00 cm.
	" a_2	=	51.60 "
	" a_3	=	46.96 "
	" a_4	=	45.09 "
	and " a_5	=	44.75 "

TABLE III

Typical experimental measurements of the differential vapour pressures for a polymer (M.W. 1955)-methanol system at different temperatures

Temperature °C	Weight of solvent g.	p_o mm.	ΔL mm.	Δp mm.	$100\ \Delta p/p_o$
-26.9	1.538	4.71	168	0.063	1.34
-24.4	1.538	5.58	200	0.075	1.35
-14.7	1.537	11.21	430	0.161	1.44
-10.0	1.536	15.43	581	0.218	1.41
-6.6	1.535	19.05	728	0.273	1.44
-0.2	1.533	28.74	1136	0.483	1.48
5.4	1.530	40.86	1565	0.588	1.44
5.7	1.530	41.51	1596	0.599	1.44
9.8	1.527	52.17	2162	0.811	1.56
15.8	1.523	74.19	--	1.16	1.59
16.3	1.522	76.45	--	1.21	1.56
21.2	1.516	101.25	--	1.51	1.49
21.2	1.516	101.28	--	1.58	1.56

Notes:- (i). Weight of the polymer sample taken = 0.8009 g.

(ii). Zero reading on the capillary = 137.0 $\pm$ 0.1 mm.

(Iii). Weight of the solvent given in column two decreases with increasing temperature since greater weights of solvent were present as vapour in the dead space of the instrument at higher temperatures.

(iv) Measurements of Δp for the last four temperatures were obtained on the manometer MM.

Thus if ΔL is, for example, 40.0 cm. Δp can be calculated as

$$\Delta p = 2 \times 40.0/5332 = 0.0150 \text{ cm.}$$

Very small differences of vapour pressure can thus be measured in terms of relatively large differences in the height of mercury in the capillary C. An uncertainty of 1 percent in ΔL values still enables Δp to be determined to one or two units in the fourth decimal place in the example considered above. The over-all percentage accuracy is equal to that in the determination of ΔL.

Table II also gives the calibration data for the auxiliary bulbs a_1, a_2 etc. shown in Figure 1. These were used to extend the range of differences of vapour pressure which could be measured on the apparatus. The volumes of the bulbs were about 0.5 ml. and corresponded to the volume contained in a length of the calibrated capillary C equal to about 50 cm. The exact volumes in terms of equivalent lengths of the capillary are recorded in Table II.

The maximum range of differences of vapour pressure which could be measured on the instrument using the auxiliary bulbs a_1, a_2 etc. was 1 mm. of mercury so that for the determination of values of the lowering of vapour pressure larger than 1 mm. measurements were carried out directly by means of the mercury manometer MM.

Since the differential vapour pressures for the

solutions studied were measured at about ten to fifteen different temperatures, values of 100 $\Delta p/p_o$ were interpolated at five rounded temperatures (25°, 15°, 0°, -10° and -25°C.) from the actual experimental results. A typical plot of the actual experimental values of 100 $\Delta p/p_o$ against temperature for a methanolic solution containing 0.3389 weight percent of the polypropylene glycol of molecular weight 1955 is shown in Figure 2. Each point represents the mean of at least two readings on the calibrated capillary C at a given concentration and temperature. The thermodynamic data for the range of concentrations studied and for the four molecular weight fractions examined were calculated from a number of other graphs of 100 $\Delta p/p_o$ similar to that shown in Figure 2. Typical experimental data for ΔL, p_o and 100 $\Delta p/p_o$ in one experiment are given in Table III for the polypropylene glycol (M.W. 1955)-methanol system over a range of temperatures. Data for other concentrations and polymer fractions are given in the form of fugacities in Tables V to VIII.

A test of the accuracy of the differential manometer was carried out by making differential vapour pressure measurements on a solution of biphenyl in benzene. The concentration of biphenyl was 0.6974 g. per 100 g. of solution and a mean of six values of the concentration calculated from the measurements of the lowering of vapour pressure gave a value of 0.7020 g. per 100 g. of solution with a mean deviation of ± 0.005 g./100 g. The investigations of Baxendale *et al.* (44) show that the

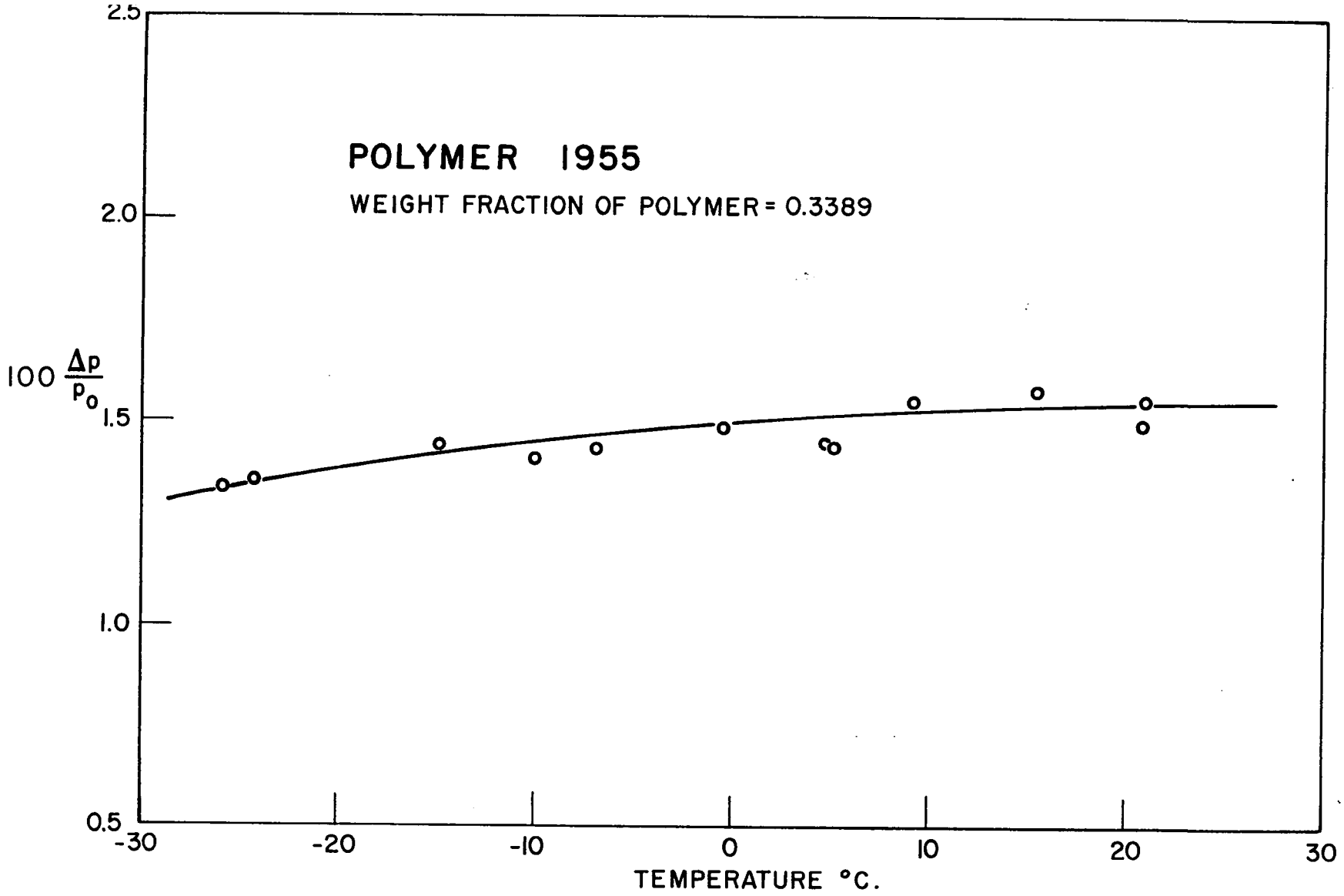

FIG. 2. PLOT OF $\Delta p/p_o$ AGAINST TEMPERATURE FOR THE SOLUTION OF 0.3389 WEIGHT FRACTION OF THE POLYMER (M.W. 1955)

biphenyl-benzene system deviates negligibly from Raoult's law particularly at such low concentrations. The agreement between the figures 0.6974 and 0.7020 is considered to be satisfactory.

C. Thermodynamic Data from the Lowering of Vapour Pressure

The activity a_1 of the solvent in a solution is given by

$$a_1 = f_1/f_o \qquad (100)$$

where f_1 and f_o are the fugacities of the vapours in equilibrium with the solution and solvent, respectively. These fugacities may be calculated from the respective vapour pressures p_1 and p_o using the general relationship

$$\ln f = \ln p + B/RT. \qquad (101)$$

The fugacity f of any vapour can be obtained in terms of the vapour pressure p and the second virial coefficient B. The values of B for methanol vapour have been expressed by Krelshmer and Wiebe (89) in the form

$$B = -100 - 2.148 \exp(1986/T) \text{ cm}^3 \text{ mole}^{-1}. \qquad (102)$$

In the present work, the pressure p_1 of vapour above a solution has not been obtained directly but has been derived from knowledge of the measured values of p_o and Δp at a given temperature, so that

$$p_1 = p_o - \Delta p. \qquad (103)$$

For the derivation of thermodynamic functions for the polymer-

methanol systems from the vapour pressure measurements it is necessary first to calculate the activities of the solvent in the solutions (referred to pure solvent at the same temperature as the standard state having unit activity). From equations (100), (101) and(103) it follows that

$$\ln a_1 = \ln \frac{f_1}{f_o} = \frac{\ln (p_o - \Delta p) + B(p_o - \Delta p)/RT}{\ln p_o + Bp_o/RT}. \qquad (104)$$

In the evaluation of $\ln a_1$ and hence of a_1 from equation (104), a difficulty arises concerning the number of decimal places to which it is legitimate to express p_1 obtained from the values of p_o and Δp. As in the case of the typical values of p_o given in Table III, p_1 (in mm.) should usually be expressed only to two decimal places; this would correspond to an accuracy of between 2 in 10,000 and 2 in 500 depending on the magnitude of p_o. However, the values of Δp(in mm.) as determined on the Puddington manometer can be specified in some cases to a maximum of four decimal places with an uncertainty of one percent in three significant figures (see Table III). Calculation of values of p_1 (using equation 103) for use in equation (104) then involves a difference of one term expressible to two decimal places and the other expressible to a larger number.

For the purpose of calculating activities of the solvent corresponding in accuracy to that of the values of Δp, it is necessary to write p_1 and p_o to the same number of decimal

places as for Δp even though p_o is not known to more than two decimal places. The relative accuracy of p_o is however between 0.02% to 0.4% as stated above. This means that in calculating values of a_1, values of p_1 should be used which differ from those of p_o by exactly Δp, irrespective of the magnitude of p_o or of the actual uncertainty in any individual values of p_o, even if this uncertainty exceeds that in Δp. The uncertainty in p_o will affect the values of f_1 and f_o to almost the same extent, so that the accuracy of the values of a_1 is almost completely determined by the accuracy of the values of Δp. This is best illustrated by the following numerical example.

If the vapour pressure p_o of the solvent in an experiment was for example 27.20 mm. and Δp for a corresponding solution at the same temperature was 0.154 mm. then the apparent pressure p_1 of the solvent vapour in equilibrium with the solution could be written as $p_1 = 27.046$. In this example it is assumed that Δp is known to one more decimal place than that to which p_o can be expressed. The fugacities of the vapour in equilibrium with solvent and solution are then given by equations (101) and (102) as

$$f_o = 27.061 \text{ mm. and } f_1 = 26.909 \text{ mm.} \qquad (105)$$

If however there was an uncertainty of unity in the second decimal place of p_o, say, for example, that p_o might be equal to 27.21 mm. instead of 27.20 mm. as written above, then

the fugacities corresponding to f_o and f_1 calculated as above, would be

$$f'_o = 27.071 \text{ mm. and } f'_1 = 26.919 \text{ mm.} \qquad (106)$$

for the same value of Δp. The activities a_1 and a'_1 corresponding to the two pairs of fugacities may be calculated from equations (105) and (106) as

$$a_1 = 0.99438(3) \text{ and } a'_1 = 0.99438(5), \qquad (107)$$

respectively. The uncertainty of 0.01 in 27.20 in p_o in this example thus affects the value of a_1 to a negligible extent (i.e., to 2 in 9×10^5). It is therefore legitimate, in the calculation of the activities of the solvent, to obtain p_1 by subtraction of Δp from p_o, even though p_1 is now expressible to more decimal places than is p_o. Similarly the fugacities f_o and f_1 may be expressed to the same number of decimal places as Δp. This does not however mean that the use of these extra decimal places in the calculation of a_1 implies a knowledge of the absolute values of these quantities to more than two decimal places.

For the various systems studied, the values of p_1 and f_1 are given in Tables V to VIII and have been expressed to a number of decimal places corresponding to those justified in expressing Δp. a_1 has been given to four decimal places, i.e., within the number justified by the accuracy of the values of Δp.

The fugacities of the pure solvent at the five temperatures stated above are recorded separately in Table IV to two,

three or four decimal places as required for expressing the corresponding values of f_1 at the same temperature (Tables V to VIII). Tables V to VIII also include the values of $\Delta\mu_1$ calculated from the values of a_1 using equation (78). The values of $\Delta\mu_1$ for the various polymer-methanol systems at one temperature (15°C.) have been plotted in Figure 3 as a function of the weight fraction of the polymers.

D. Computation of the Activity a_2 of the solute

By making use of the Gibbs-Duhem equation (40) in the form

$$x_1 \, d \ln \frac{a_1}{x_1} = - x_2 \, d \ln \frac{a_2}{x_2} , \qquad (108)$$

the activity of the solute a_2 can be determined by integrating equation (108) to give

$$\log \frac{a_2}{x_2} = - \int_{x_2=o}^{x_2=x} \frac{x_1}{x_2} \, d \log \frac{a_1}{x_1} . \qquad (109)$$

where the two limits $x_2 = x$ and $x_2 = o$ refer to the corresponding values of $\log \frac{a_1}{x_1}$. There are two methods generally employed for the evaluation of this integral from experimental values of a_1.

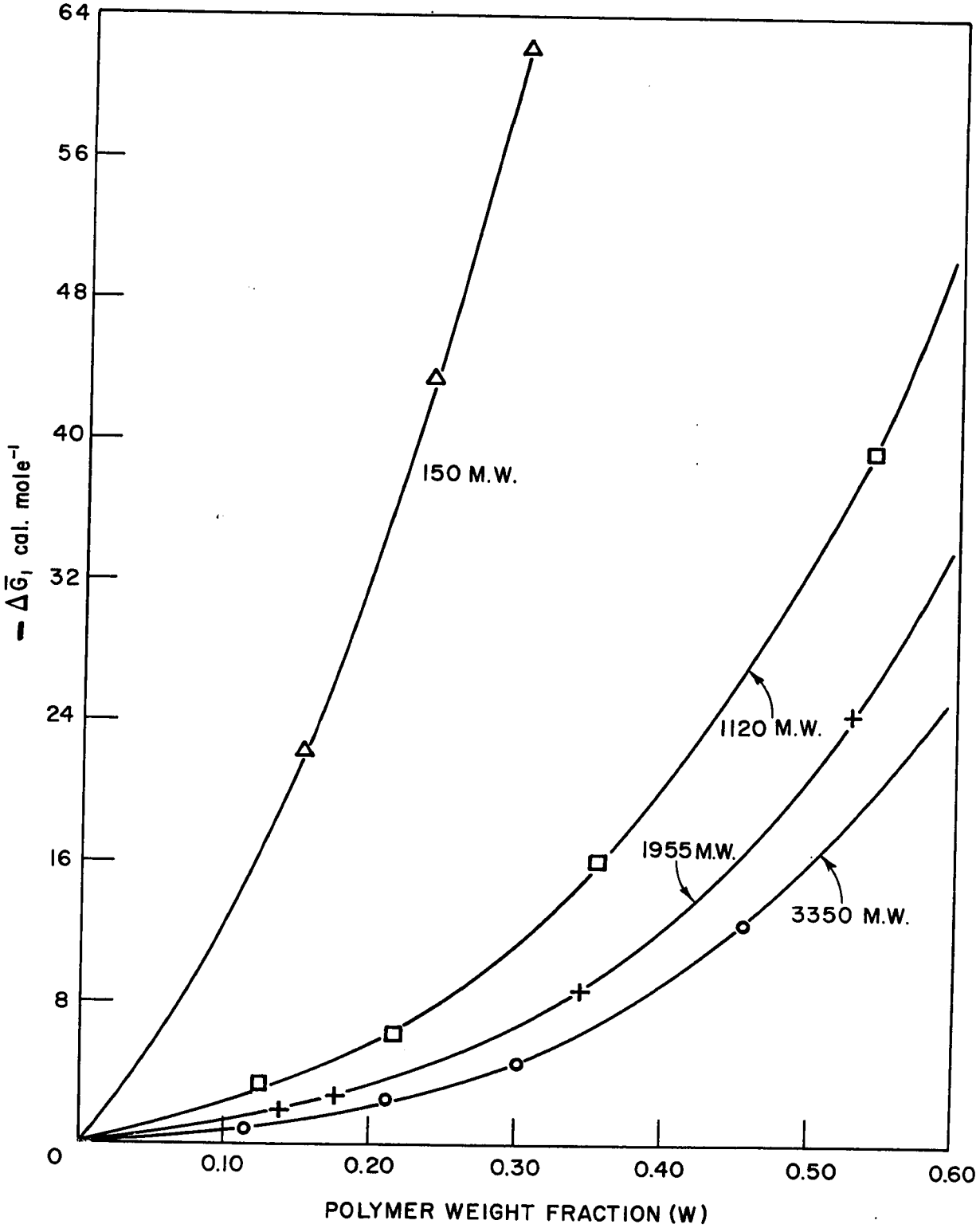

FIG. 3. PLOT OF $\overline{\Delta G}_1$ FOR THE VARIOUS POLYMER-METHANOL SYSTEMS AS A FUNCTION OF THE POLYMER WEIGHT FRACTION.

TABLE IV.

The vapour pressures and fugacities of pure methanol at different temperatures

Temperature °C.	Vapour pressure p_o mm.	Fugacities f_o mm.
25	121.30	119.94 119.936
15	69.42	68.85 68.853
0	27.23	27.09 27.092
-10	15.42	15.36 15.359
-25	5.15	5.14 5.139 5.1388

Note:- The values of fugacities at the various temperatures recorded in column 3 are given to two, three or four decimal places as required for expressing values of f_1.

TABLE V

The activities and the relative partial molar free energies of the solvent in solutions of varying concentrations of polymer (M.W. 150) in methanol

Polymer weight fraction	Temp. °C.	p_1 mm.	f_1 mm.	a_1	$\Delta\mu_1$ (Cal. mole^{-1})
0.1519	25	116.58	115.32	0.9615	-32.2
0.1511	15	66.75	66.23	0.9619	-22.2
0.1504	0	26.225	26.093	0.9631	-20.4
0.1502	-10	14.871	14.814	0.9645	-18.9
0.1500	-25	4.975	4.964	0.9681	-16.0
0.2374	25	112.51	111.42	0.9290	-43.6
0.2367	15	64.42	63.94	0.9287	-42.4
0.2362	0	25.280	25.16	0.9287	-40.1
0.2360	-10	14.317	14.265	0.9288	-38.6
0.2359	-25	4.784	4.775	0.9292	-36.2
0.3061	25	109.50	108.47	0.9044	-59.5
0.3047	15	62.68	62.22	0.9037	-57.3
0.3035	0	24.59	24.47	0.9033	-55.1
0.3032	-10	13.93	13.88	0.9036	-53.0
0.3029	-25	4.653	4.643	0.9035	-50.0
0.5024	25	96.25	95.45	0.7958	-135
0.5007	15	55.05	54.69	0.7944	-132
0.4993	0	21.58	21.49	0.7932	-126
0.4990	-10	12.25	12.21	0.7950	-120
0.4987	-25	4.120	4.113	0.8003	-110

TABLE VI

The activities and the relative partial molar free energies of the solvent in solutions of varying concentrations of polymer (M.W. 1120) in methanol

Polymer weight fraction	Temp. °C.	p_1 mm.	f_1 mm.	a_1	$\Delta\mu_1$ (Cal. mole^{-1})
0.1251	25	120.60	119.35	0.9951	-2.9
0.1244	15	69.02	68.45	0.9942	-3.4
0.1239	0	27.076	26.938	0.9943	-3.2
0.1237	-10	15.333	15.273	0.9944	-2.9
0.1236	-25	5.122	5.111	0.9945	-2.7
0.2182	25	119.95	118.72	0.9898	-5.7
0.2170	15	68.64	68.09	0.9890	-6.4
0.2160	0	26.925	26.790	0.9888	-6.1
0.2157	-10	15.247	15.187	0.9888	-5.9
0.2155	-25	5.092	5.081	0.9887	-5.6
0.3554	25	117.88	116.69	0.9729	-17.6
0.3536	15	67.48	66.94	0.9722	-16.1
0.3522	0	26.473	26.341	0.9722	-15.2
0.3518	-10	14.994	14.936	0.9725	-14.6
0.3515	-25	5.009	4.999	0.9728	-13.6
0.5434	25	113.09	111.98	0.9336	-40.7
0.5405	15	64.75	64.26	0.9333	-39.5
0.5383	0	25.42	25.30	0.9339	-37.3
0.5375	-10	14.402	14.349	0.9348	-35.5
0.5370	-25	4.814	4.804	0.9348	-32.2

TABLE VII

The activities and the relative partial molar free energies of the solvent in solutions of varying concentrations of polymer (M.W. 1955) in methanol

Polymer weight fraction	Temp. °C.	p_1 mm.	f_1 mm.	a_1	$\Delta\mu_1$ (Cal. mole^{-1})
0.1307	25	120.87	119.62	0.9973	-1.6
0.1302	15	69.18	68.61	0.9965	-2.0
0.1298	0	27.134	27.000	0.9966	-1.9
0.1296	-10	15.365	15.303	0.9963	-1.9
0.1295	-25	5.131	5.120	0.9963	-1.8
0.1790	25	120.71	119.46	0.9960	-2.4
0.1784	15	69.08	68.52	0.9952	-2.8
0.1779	0	27.099	26.960	0.9951	-2.6
0.1777	-10	15.346	15.286	0.9952	-2.5
0.1776	-25	5.126	5.114	0.9951	-2.4
0.3463	25	119.41	118.19	0.9854	-8.7
0.3445	15	68.35	67.80	0.9847	-8.8
0.3431	0	26.824	26.687	0.9850	-8.2
0.3428	-10	15.198	15.139	0.9857	-7.5
0.3424	-25	5.080	5.070	0.9866	-7.0
0.5284	25	116.13	114.96	0.9585	-25.1
0.5271	15	66.47	65.95	0.9579	-24.6
0.5259	0	26.092	25.964	0.9584	-23.1
0.5256	-10	14.796	14.739	0.9596	-21.5
0.5253	-25	4.971	4.960	0.9652	-18.6

TABLE VIII

The activities and the relative partial molar free energies of the solvent in solutions of varying concentrations of polymer (M.W. 3350) in methanol

Polymer weight fraction	Temp. °C.	p_1 mm.	f_1 mm.	a_1	$\Delta\mu_1$ (Cal. mole^{-1})
0.1167	25	121.13	119.87	0.9994	-0.3
0.1160	15	69.319	68.755	0.9986	-0.8
0.1155	0	27.187	27.049	0.9984	-0.9
0.1153	-10	15.395	15.335	0.9984	-0.8
0.1151	-25	5.1409	5.1296	0.9982	-0.9
0.2123	25	120.76	119.41	0.9956	-2.7
0.2110	15	69.11	68.55	0.9956	-2.6
0.2101	0	27.105	26.961	0.9952	-2.6
0.2098	-10	15.345	15.285	0.9952	-2.5
0.2096	-25	5.122	5.110	0.9944	-2.7
0.3035	25	120.34	119.03	0.9925	-4.4
0.3020	15	68.85	68.29	0.9919	-4.7
0.3007	0	26.998	26.858	0.9914	-4.8
0.3004	-10	15.284	15.224	0.9912	-4.6
0.3001	-25	5.103	5.091	0.9906	-4.6
0.4575	25	118.58	117.37	0.9786	-12.8
0.4553	15	67.90	67.35	0.9783	-12.6
0.4534	0	26.650	26.517	0.9788	-11.6
0.4529	-10	15.100	15.042	0.9794	-10.9
0.4525	-25	5.047	5.036	0.9799	-10.0

(i) Analytical method: If the data for the activities of one component can be expressed analytically as an empirical function of the composition of a two-component mixture it is possible in some cases to make a direct calculation of the values of the activities of the other component at various compositions. This method has been discussed by Lewis and Randall (90) in connection with the results obtained by Hildebrand and Eastman (91) which could be expressed satisfactorily by an empirical equation. This procedure depends, however, on having a range of experimental activities of one of the components, particularly at low concentrations, sufficient to enable an empirical equation to be formulated which could be relied upon to represent the experimental behaviour in limitingly dilute solutions.

(ii) Graphical method: This consists in plotting the values of x_1/x_2 against log a_1/x_1 and determining the area under the curve between the limits indicated in equation (109). However, the graphical integration presents a formidable difficulty as indicated by Lewis and Randall (90) since the curve of x_1/x_2 versus log a_1/x_1 (see Figure 4) is asymptotic to the axis of the ordinate x_1/x_2 and hence must be extrapolated to an infinite value of x_1/x_2 in order to obtain the total area under the curve. The graphical method as used hitherto (90) is only suitable when values of the activity a_2 of the solute in a solution are known and it is desired to calculate the activities a_1 of the solvent. In such a case there is no ambiguity in the integration

and satisfactory values of a_1 can be obtained from known values of a_2, as in the case of the system thallium-mercury studied by Lewis and Randall (92). A special method for carrying out the graphical integration of values of a_2 from those of a_1, by algebraically changing the function to be integrated in equation (109)has also been discussed by Lewis and Randall (90) but the graphical plot is then so sensitive that even minute defects in the experimental measurements are noticeable and render the integration uncertain. Data of a very high order of accuracy are required in order to justify the application of this method.
In view of these difficulties the author has developed an alternative method for obtaining the integral to an infinite value of x_1/x_2 as log a_1/x_1 tends to zero and the procedure used is discussed below. This method is very convenient and direct and avoids a number of the difficulties discussed by Lewis and Randall (90) which have been pointed out above.

(iii) Method of integration: As in the graphical method the values of x_1/x_2 are first plotted against log a_1/x_1 (see Figure 4). The area under the curve from the point X in Figure 4 to infinity is considered to be equal to an unknown constant C, so that the total integral up to any point on the curve is equal to C plus the area under the curve from point X to that point. If C is considered first to be equal to zero, we obtain apparent first approximation values of log a_2/x_2. The values of x_2/x_1 are now plotted against the apparent values of log a_2/x_2 as shown in Figure 5. It is found that the value of log a_2/x_2 for a value

of x_2/x_1 corresponding to the point X in Figure 4 is zero, so that the curve in Figure 5 does not pass through the origin as it should do. This indicates that if we extend the curve smoothly back to the axis of abscissae the point at which the curve meets that axis should be the actual origin. Hence all the values of the abscissae must be increased by the constant C equal to the shift of the origin along the horizontal axis. Without any further information about the course of the curve in the region covered by extrapolation there would be some uncertainty in the value of the constant C. However, in order to make a more correct extrapolation it is also possible to utilize the fact that the areaaA under the curve in Figure 5 between the true and apparent origins must be equal to log a_1/x_1 at the point X in Figure 4; this value is known directly from the experimental data. The only assumption involved in this method is that the activity coefficients of the components are smooth functions of composition, reaching unity in the case of the solvent for infinite dilution of solute. This assumption is also the basis of the analytical method. However, we make use of this assumption only in a small region of the concentration range while in the analytical method it applies to the entire range.

The above method makes it possible to compute the value

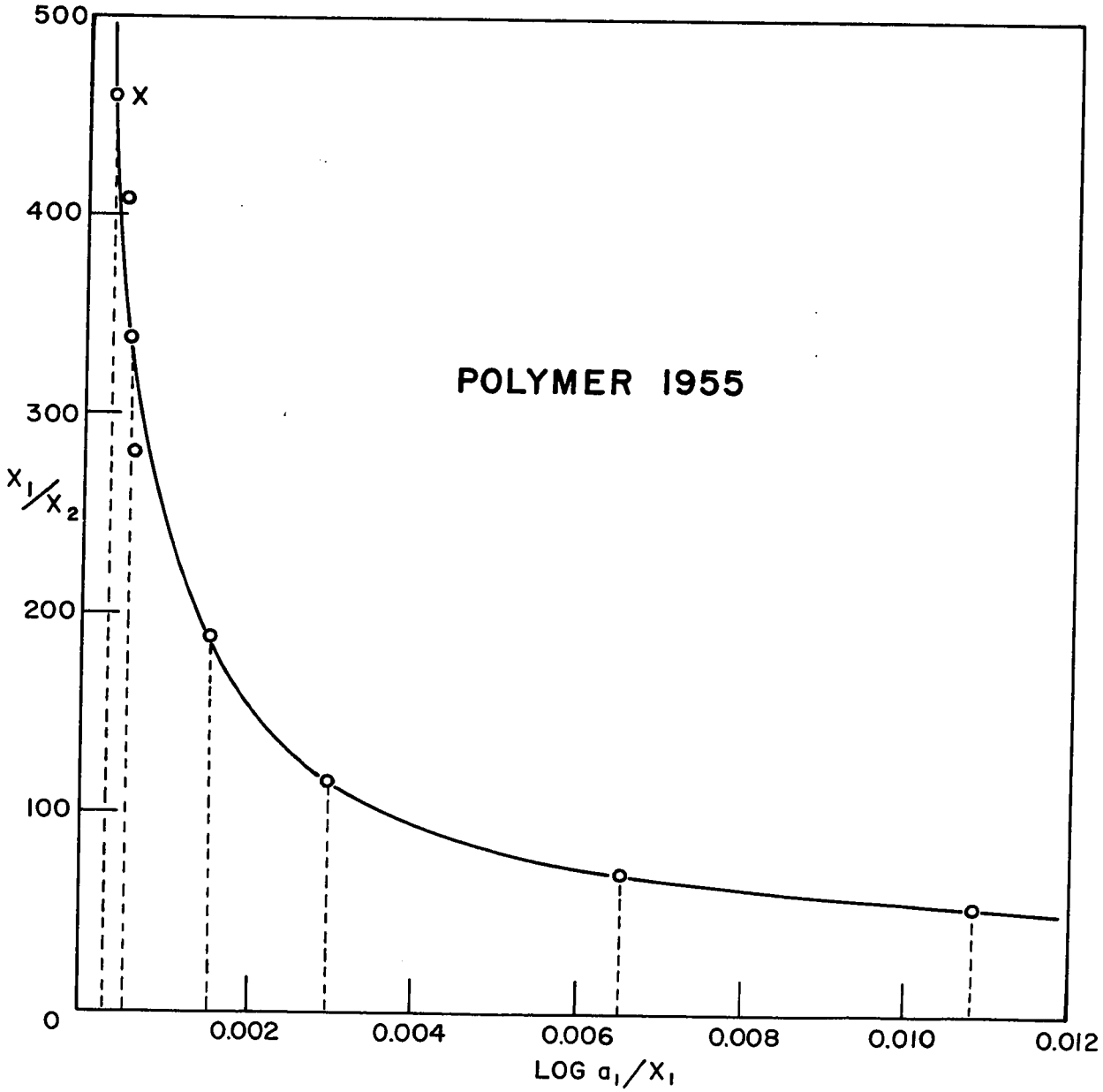

FIG. 4. PLOT OF x_1/x_2 AS A FUNCTION OF LOG a_1/x_1, FOR POLYMER (M.W. 1955)-METHANOL SYSTEM.

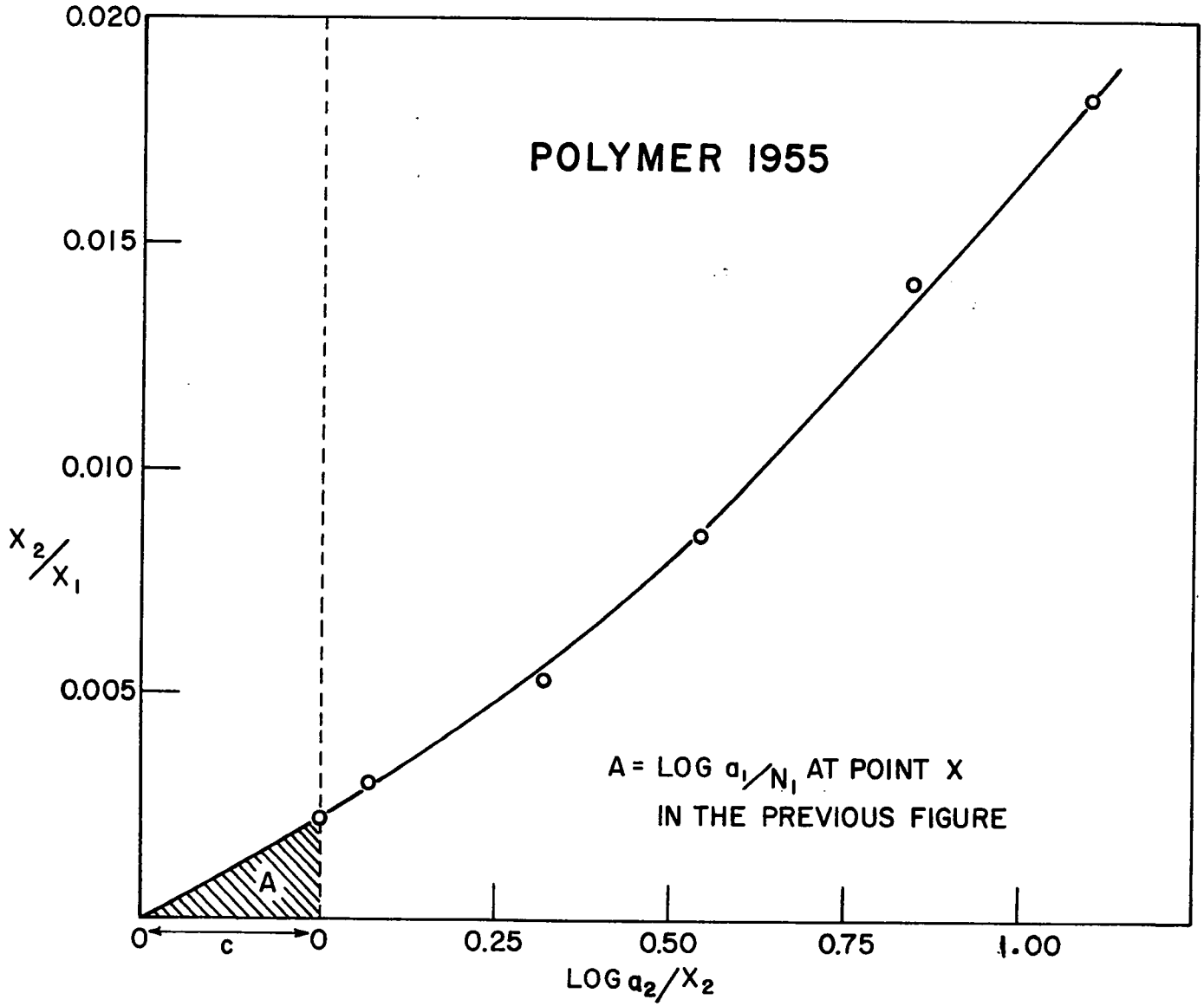

FIG. 5. PLOT OF x_2/x_1 AS A FUNCTION OF LOG a_2/x_2, FOR POLYMER (M.W. 1955)-METHANOL SYSTEM.

of C with satisfactory accuracy* and hence allows the determination of values of a_2, the activity of the solute, for various values of a_1. This method seems to have some advantages in that it is convenient and is not very sensitive to any inaccuracies in the determination of the experimental points for solutions of low concentrations.

The accuracy of this method of integration is illustrated by applying it to the data on aqueous sugar solutions discussed by Lewis and Randall (90, p. 275). From the given values of molal concentration and ln a_1, the author has calculated the values of ln a_1/N_1 (shown in column 4, Table IX). The positive value of ln a_1/N_1 for the first concentration indicates that the value of a_1 is incorrect. The last three concentrations were therefore used for the calculation of ln a_2/N_2 by the author's method and these values are given in column 5 of the table. In order to test the validity of these calculated values of ln a_2/N_2, the values of ln a_1/N_1 were back-calculated from those of ln a_2/N_2 and have been reported in column 6. Considering that only three concentrations have been used in these calculations, the agreement of the values of ln a_1/N_1 in

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* By extrapolation and using the area A beneath the curve in Figure 5 as a check on the extrapolation as described above, the value of C can be estimated with an accuracy better than + 5%. This gives values of ln a_2/N_2 with accuracies increasing from about $\pm$ 4% to 1% as the concentration of polymer is increased. The corresponding values of a_2 are accurate to better than $\pm$ 0.5%.

columns 4 and 6 of the table is very satisfactory. An estimate of the accuracy with which the values of ln a_2/N_2 can be obtained is also reported.

An attempt has also been made to assess the approximate value of ln a_1/N_1 for the first concentration. The value obtained is equal to -0.00002 to an uncertainty of $\pm$ 25%. The value of ln a_1 is therefore 0.00092 and it can be seen from Table IX that this figure is accurate to about $\pm$1 percent. Perusal of the Table IX gives an idea of the convenience and reliability of this method of integration.

The values for the activities of the polymers in the various polymer-solvent systems have been computed from the activities of the solvent and are recorded in Table X together with the corresponding values of a_1. It is now possible to calculate the free energies of mixing per mole using the relation

$$\Delta G_m = x_1 \Delta\mu_1 + x_2 \Delta\mu_2 \qquad (110)$$

where

$$\Delta\mu_1 = RT \ln a_1$$

and

$$\Delta\mu_2 = RT \ln a_2 .$$

The values of the relative partial molar free energies $\Delta\mu_1$ and $\Delta\mu_2$ of the solvent and solute respectively and the values of the free energy of mixing per mole are given in Table XI. The values of ΔG_m are plotted in Figure 6 as a function of

TABLE IX

Calculations of the activities of sugar in aqueous sugar solutions

m	N_1/N_2	ln a_1	ln a_1/N_1	ln a_2/N_2	ln a_1/N_1	ln a_1
0.050	1110	-0.00053	0.00037	-0.035±20%	-0.00002	-0.00092
0.172	322.7	-0.00324	-0.00013	-0.090 ± 5%	-0.00013	-0.00324
0.454	122.3	-0.00871	-0.00056	-0.167 ±1%	-0.00055	-0.00870
1.009	55.01	-0.02002	-0.00201	-0.274 ±1%	-0.00194	-0.01995

Notes:- (i). Values of ln a_1/N_1 and ln a_1 given in columns 6 and 7 are calculated from the values of ln a_2/N_2 (column 5) computed by the author's method.

(ii). Values of m and ln a_1 in columns 1 and 3 are the data used by Lewis and Randall (90 p. 275) where m is the molal concentration.

TABLE X

The activities of the solute and the solvent in various polymer-methanol systems at 15° C.

Polymer mol. weight	Polymer weight fraction	Activity * a_1	Activity a_2
150	0.1511	0.9619	0.040
	0.2012	0.9461	0.057
	0.2367	0.9286	0.076
	0.3047	0.9037	0.106
	0.3911	0.8636	0.160
	0.5007	0.7944	0.255
1120	0.1172	0.9948	0.006
	0.1614	0.9922	0.011
	0.2416	0.9864	0.024
	0.3536	0.9722	0.081
	0.4636	0.9535	0.235
	0.5405	0.9333	0.423
1955	0.1187	0.9972	0.004
	0.1553	0.9959	0.006
	0.2456	0.9913	0.019
	0.3445	0.9847	0.052
	0.4627	0.9714	0.179
	0.5271	0.9579	0.244
3350	0.1160	0.9986	0.002
	0.1359	0.9979	0.004
	0.2110	0.9979	0.011
	0.3020	0.9919	0.030
	0.4102	0.9855	0.087
	0.4553	0.9782	0.112

* These are the smoothened values obtained from the graphs of solvent activity against polymer concentration.

TABLE XI

Calculations of the free energies of mixing for the various polymer-methanol systems at 15° C.

Polymer weight fraction	Polymer mole fraction	$-\Delta\mu_1$ (Cal. mole^{-1})	$-\Delta\mu_2 \times 10^{-2}$ (Cal. mole^{-1})	$-\Delta G_m$ (Cal. mole^{-1})
Polymer (M.W. 150)				
0.1511	0.0368	22.2	18	89
0.2012	0.0510	31.7	16	114
0.2367	0.0660	42.9	15	137
0.3047	0.085	62.1	12.8	166
0.3911	0.120	84	10.5	200
0.5007	0.177	131	7.8	247
Polymer (M.W. 1120)				
0.1172	0.0038	2.9	29	14
0.1614	0.0055	4.4	26	19
0.2416	0.0090	7.8	21	27
0.3536	0.0154	16.1	14.3	38
0.4636	0.0241	27.2	8.3	47
0.5405	0.0322	39.5	4.9	51
Polymer (M.W. 1955)				
0.1187	0.00219	1.6	31	9
0.1553	0.00299	2.4	29	11
0.2456	0.00527	5.0	22	17
0.3445	0.0085	8.8	17	23
0.4627	0.0139	16.6	9.9	30
0.5271	0.0179	24.6	8.1	39
Polymer (M.W. 3350)				
0.1159	0.00125	0.8	36	5
0.1399	0.00150	1.2	31	6
0.2110	0.00259	2.5	25	9
0.3020	0.00418	4.7	20	13
0.4102	0.00657	8.4	13.9	17
0.4553	0.00803	12.6	12.5	22

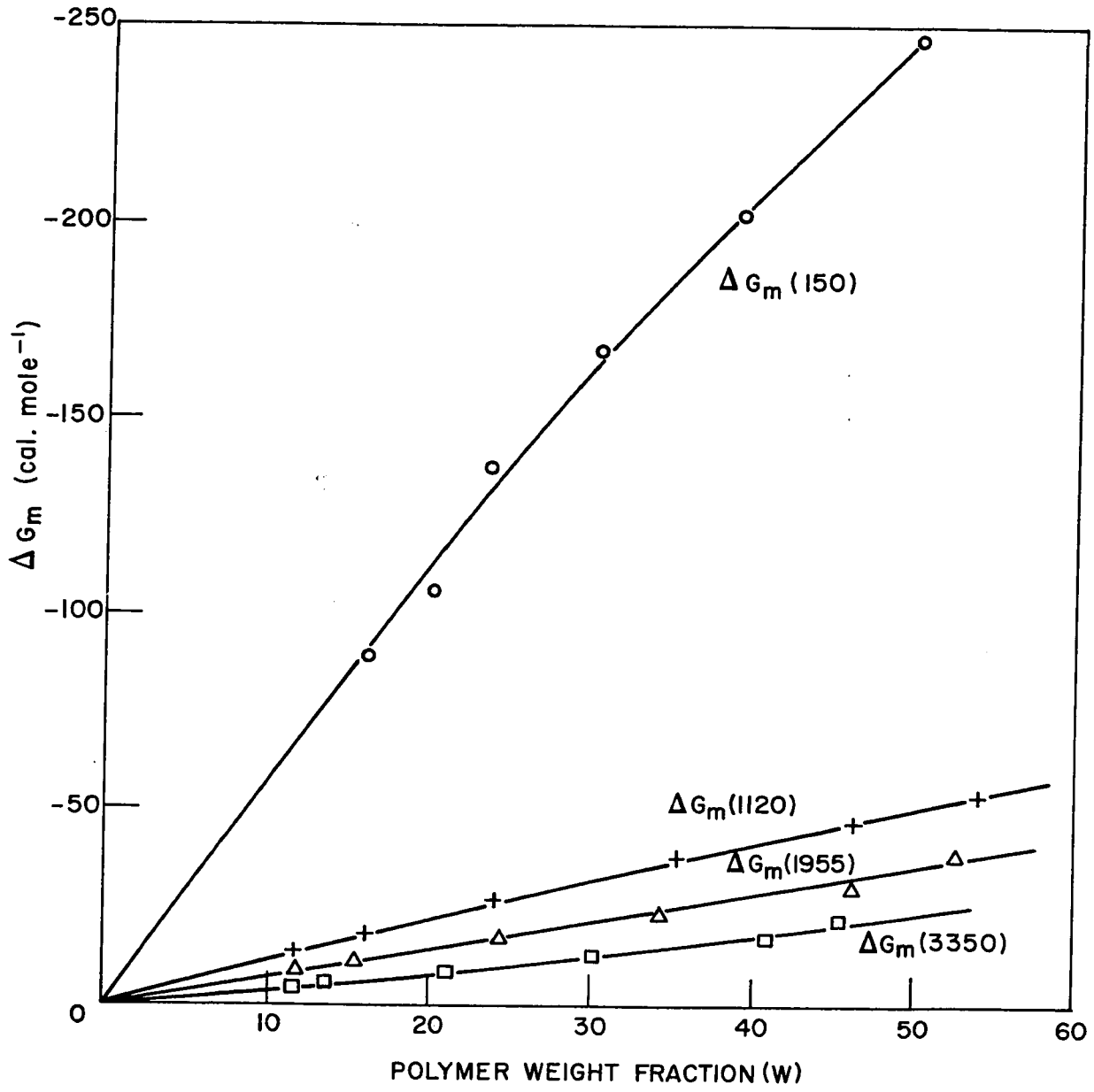

FIG. 6. PLOT OF THE FREE ENERGY OF MIXING FOR VARIOUS SYSTEMS, AS A FUNCTION OF THE POLYMER WEIGHT FRACTION.

the weight fraction of the various polymers in solution.

E. The Calorimeter and Measurements of Heats of Mixing

The determinations of the heats of mixing have been carried out in an isothermal phase-change calorimeter of the type previously described by Dainton et al. (63) employing diphenyl ether as the dilatometric fluid. The calorimeter operates at the melting point, 26.9°C., of diphenyl ether. The construction and operation of the apparatus are discussed below.

(a) Construction: The calorimeter used in the present investigations is illustrated in Figure 7 and comprises the following main features:

Mixing vessel: The central tube A shown in Figure 7 was the mixing vessel designed to accomodate glass bulbs B of 15 to 20 ml. capacity together with about 90 ml. of one of the components. A hollow evacuated stopper C made from a standard taper joint fitted into the top of the tube A. Flow of heat through the stopper between the vessel and its surroundings was diminished by having the hollow stopper evacuated. A stirrer MS passed through the stopper and carried two perforated metallic plates inside the vessel. The stirrer, which could be moved vertically, was used both for the purpose of breaking the glass bulb and for mixing the two components.

Diphenyl Ether Jacket: The tube D surrounding the mixing vessel A contained the dilatometric fluid (diphenyl ether). A

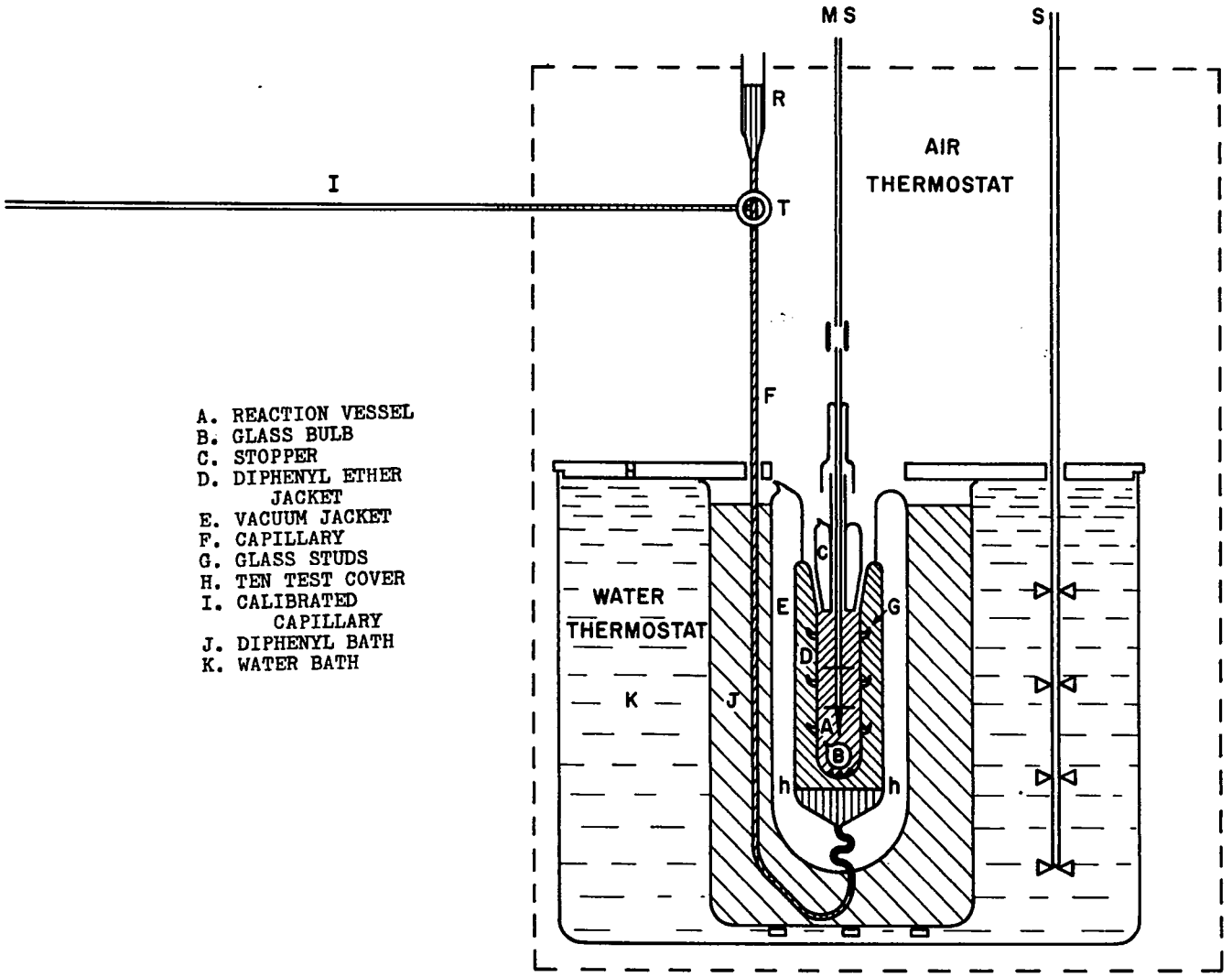

FIG. 7. THE DIAGRAM OF THE CALORIMETER USED FOR THE DETERMINATION OF HEAT OF MIXING FOR THE VARIOUS POLYMER-METHANOL SYSTEMS.

column of mercury supported the diphenyl ether above the level hh as shown in Figure 7. Diphenyl ether purified by repeated crystallization was distilled into the vessel D *in vacuo*. At its base the jacket was joined to a glass tube in the form of a spiral communicating with the capillary F which was also full of mercury. This capillary was joined to a three-way stopcock T which in one direction connected the capillary F to the reservoir of mercury R and in the other direction to the horizontal calibrated capillary I.

Vacuum Jacket: A jacket E completely enclosed the vessel D and was evacuated in order to minimise conduction of heat between the vessel D and the diphenyl ether bath J. This helped to maintain the temperature of the diphenyl ether at its melting point 26.9°C. without any significant change of state of the substance from solid to liquid or vice-versa and hence minimised drift of the position of the mercury meniscus in the calibrated capillary.

(b) Temperature Control: The calorimeter and the water thermostat K were separated by a bath of diphenyl ether at its melting point in order to maintain a steady temperature of 26.9°C. The water bath was maintained at the same temperature and fluctuations in temperature were less than $\pm$0.005°C. As an additional precaution against the transfer of heat to and from the calorimeter, the whole apparatus was enclosed in an air thermostat at 26.9° $\pm$ 0.05°C. A "ten-test" cover on the apparatus (shown in Figure 7) also

facilitated the maintenance of constant temperature.

(c) Purification of Diphenyl Ether and Filling of the Calorimeter: About 3 litres of diphenyl ether (Fisher Reagent grade) were recrystallised four times from the melt and a sample of 200 ml. was finally obtained and distilled into the inverted calorimeter in vacuo. After the required amount of liquid was distilled the diphenyl ether was sealed by mercury under vacuum. The capillary J, the stopcock T and the calibrated capillary I were then sealed to the calorimeter. The calorimeter was held inside the diphenyl ether bath J by a brass stand not shown in Figure 7.

(d) Formation of the Mantle: There was some difficulty initially in forming the diphenyl ether mantle; crystallization was initiated by lowering the temperature of the reaction vessel by touching the inside of it with dry ice; this caused nucleation and subsequent irregular crystallisation of the diphenyl ether. The temperature of the water in the thermostat was then raised by $1^{\circ}C$. in order to melt away most of the mantle. The mantle was then formed again on the remaining crystals but this time more slowly by circulating water at a temperature of $25^{\circ}C$. in the tube A.

(e) Procedure: In the determinations of the heat of mixing, approximately 80 ml. of one of the components were weighed out accurately and transferred to the reaction vessel. A weighed amount of the other component in a sealed glass bulb was then

placed in the vessel A which was carefully closed by the stopper C holding the stirrer. The sharp end of the stirrer rested on the glass bulb and the top of the stirrer outside the stopper was covered by a cotton pad. The whole apparatus was allowed to stand for about 6 hours; this was found to be sufficient time for the drift of mercury in the capillary I to become less than 0.2 mm. per minute. Such a drift rate represented constancy of the temperature in the inner vessel to better than 2×10^{-5} °C. during one minute. The bulb was then broken by pressing down the stirrer and the components were mixed by moving the stirrer up and down. Movement of the perforated discs provided efficient mixing without producing any noticeable heat of stirring, e.g., as determined in a blank experiment. The heat of mixing was indicated by the movement of the mercury meniscus in the capillary I and the position of the meniscus was read every two minutes by means of a travelling microscope. Prior to making a calorimetric determination the rate of drift was always measured for about 20 minutes. After mixing, the movement of the meniscus was followed until its rate of drift became constant. The displacement of the meniscus in the capillary arising from the heat of mixing was obtained by a graphical procedure in which allowance was made for the steady drift of mercury in the capillary occuring before and during mixing. It is seen from the typical graph of mercury displacement shown in Figure 8 that any uncertainty in the displacement due to the heat of mixing is zero or small.

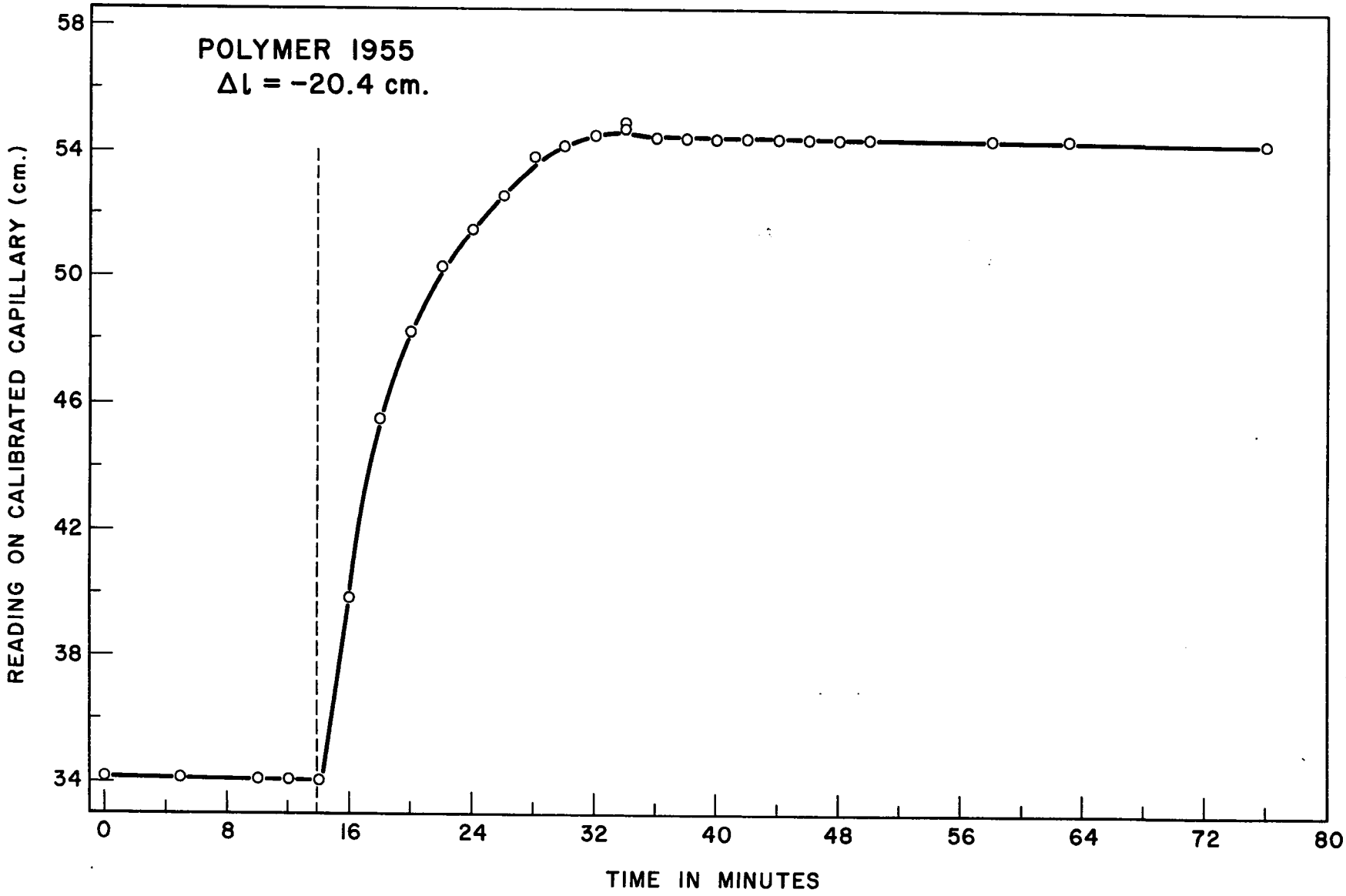

FIG. 8. PLOT OF A TYPICAL MERCURY DISPLACEMENT IN THE CALIBRATED CAPILLARY OF THE CALORIMETER FOR MIXING OF POLYMER (M.W. 1955) AND METHANOL (0.9078 WEIGHT FRACTION OF POLYMER).

(f) Calibration: The capillary I was calibrated by weighing known lengths of mercury in it and a mean of four such measurements gave a value of 0.04654 g./cm. The calibration factor is defined as the weight of mercury displaced per calorie evolved during fusion; this factor has been determined by Dainton et al. (63) and their value of 0.05295 ± 0.0001 g./cal. has been used in calibrating the movement of mercury in the capillary in terms of heat evolved or absorbed in the calorimeter. A displacement of the meniscus of mercury in the capillary by one centimetre hence corresponded to an absorption or evolution of 0.879 calories depending on the direction of movement of the meniscus.

As is evident from the dimensions of the vessel used, the maximum range of compositions (polymer in solvent and solvent in polymer) which could be examined could not be more than about 0-20% at each end of the composition range. In order to obtain the heat of mixing over the remainder of the range of compositions, a known weight of one of the pure components in the glass bulb was mixed with a measured weight of a mixture of known composition for which ΔH_m had previously been determined by direct mixing of suitable amounts of the two components. From the determination of various differential heats of mixing by this procedure, the over-all heats of mixing for intermediate compositions were calculated. Typical experimental data for the calculation of the over-all heats of mixing over a range of compositions of the

polymer (M.W. 150) in methanol are shown in Table XII. The first and the last lines in the table show the directly measured heats evolved upon mixing quantities of pure polymer and pure solvent. Other data between these lines are for successive dilutions of mixtures of the polymer and the solvent with either more polymer or more solvent in the directions shown in the table. Values of the heat change upon dilution are shown in column 4 and are written between the lines corresponding to the original and the final concentrations for each dilution step. The total number of moles of mixture at each stage of dilution is given in column 3 and the numbers of moles of solvent and polymer constituting the mixture are given in columns 1 and 2, respectively. The total heat changes accompanying the formation of mixtures of the compositions $m_1 + m_2$ (indicated in column 3) from the pure substances may then be calculated and are recorded in column 5. The heats of mixing per mole ΔH_m may be calculated from the data in columns 3 and 5 and are given in column 6. The data given in Tables XIII and XIV for the polymers of molecular weights 1120, 1955 and 3350 have been calculated similarly.

The average error of the determinations of the heats of mixing was less than 5% in the region of high concentrations of methanol, but due to the highly viscous nature of the polymers the error in the heats of mixing for the higher concentrations of polymers may be somewhat larger. It is believed that for the viscous materials more vigorous stirring may be required in order to achieve perfect mixing. This, however, could introduce a

TABLE XII

Quantities involved in the calculation of the heats of mixing ΔH_m from the experimental data for a typical polymer (M.W. 150)-methanol system

	Moles of methanol m_1	Moles of polymer m_2	Total moles $m_1 + m_2$	Heat change upon dilution (Cal.)	Total heat change (Cal.)	Heat change per mole ΔH_m (Cal. mole^{-1})
Dilution of polymer with solvent ↓	0.241	0.533	0.774	-25.4	-25.4	-33
	0.439	0.533	0.973	-15.4	-40.8	-42
	0.572	0.533	1.105	-8.8	-49.6	-45
	0.956	0.533	1.489	-15.2	-64.8	-44
Dilution of solvent with polymer ↑	2.239	0.267	2.506	-19.3	-55.6	-22
	2.239	0.153	2.392	-21.3	-36.3	-15
	2.239	0.049	2.288	-15.0	-15.0	-6.6

Note:- The accuracy of the ΔH_m values recorded in column 6 is ±5 percent in the region of low polymer concentrations but may be slightly less in the region of high polymer concentrations.

TABLE XIII

The heats of mixing of polymers (M.W. 150 and 1120) with methanol for various concentrations of polymers

Polymer (M.W. 150)			Polymer (M.W. 1120)		
Polymer weight fraction	Polymer mole fraction	ΔH_m (Cal. mole^{-1})	Polymer weight fraction	Polymer mole fraction	ΔH_m (Cal. mole^{-1})
0.912	0.689	-33	0.888	0.1846	-7.5
0.850	0.548	-42	0.793	0.0986	-14
0.808	0.472	-45	0.718	0.0679	-15
0.723	0.358	-44	0.624	0.0456	-15
0.359	0.107	-22	0.432	0.0225	-15
0.242	0.064	-15	0.347	0.0164	-13
0.094	0.022	-6.6	0.300	0.0090	-10.9
			0.143	0.0033	-5.4

Note:- The values of ΔH_m recorded in columns 3 and 6 are accurate to about ± 5 percent in the range of low polymer concentrations and slightly less than ±5 percent in the range of high polymer concentrations.

TABLE XIV

The heats of mixing of polymers (M.W. 1955 and 3350) with methanol for various concentrations of polymers

Polymer (M.W. 1955)			Polymer (M.W. 3350)		
Polymer weight fraction	Polymer mole fraction	ΔH_m (Cal. mole^{-1})	Polymer weight fraction	Polymer mole fraction	ΔH_m (Cal. mole^{-1})
0.908	0.139	65	0.867	0.0591	116
0.785	0.0564	46	0.752	0.0282	62
0.703	0.0373	33	0.666	0.0187	40
0.633	0.0274	26	0.572	0.0126	25
0.599	0.0238	10.3	0.519	0.0102	44
0.515	0.0170	5.1	0.485	0.0090	16
0.447	0.0130	0.1	0.429	0.00705	28
0.316	0.00744	-2.1	0.279	0.00368	6.2
0.224	0.00470	-2.1	0.177	0.0205	-1.8
0.113	0.00208	-1.5			

Note:- The values of ΔH_m recorded in columns 3 and 6 are accurate to about ±5 percent in the range of low polymer concentrations and slightly less than ±5 percent in the range of high polymer concentrations.

TABLE XV

The various thermodynamic functions of mixing for different polymer-methanol systems at 15°C.

Polymer Molecular weight	Polymer weight fraction	ΔG_m	ΔH_m (Cal. mole^{-1})	$T\Delta S_m$
150	0.1511	-89	-9	80
	0.2012	-114	-12	92
	0.2367	-137	-14	123
	0.3047	-166	-18	148
	0.3911	-200	-24	176
	0.5007	-247	-31	216
1120	0.1172	-14	-4	10
	0.1614	-19	-5	14
	0.2416	-27	-8	19
	0.3536	-38	-13	25
	0.4636	-47	-15	32
	0.5405	-51	-16	35
1955	0.1187	-9	-2	7
	0.1553	-11	-2	9
	0.2456	-17	-2	15
	0.3445	-23	-1	22
	0.4627	-30	0	30
	0.5271	-39	6	45
3350	0.1159	-5	-2	3
	0.1359	-6	-2	4
	0.2110	-9	1	10
	0.3020	-13	5	18
	0.4102	-17	13	30
	0.4553	-22	20	42

Note:- The values of ΔH_m given in column 4 are interpolated from the graphs of ΔH_m against composition shown in Figure 9.

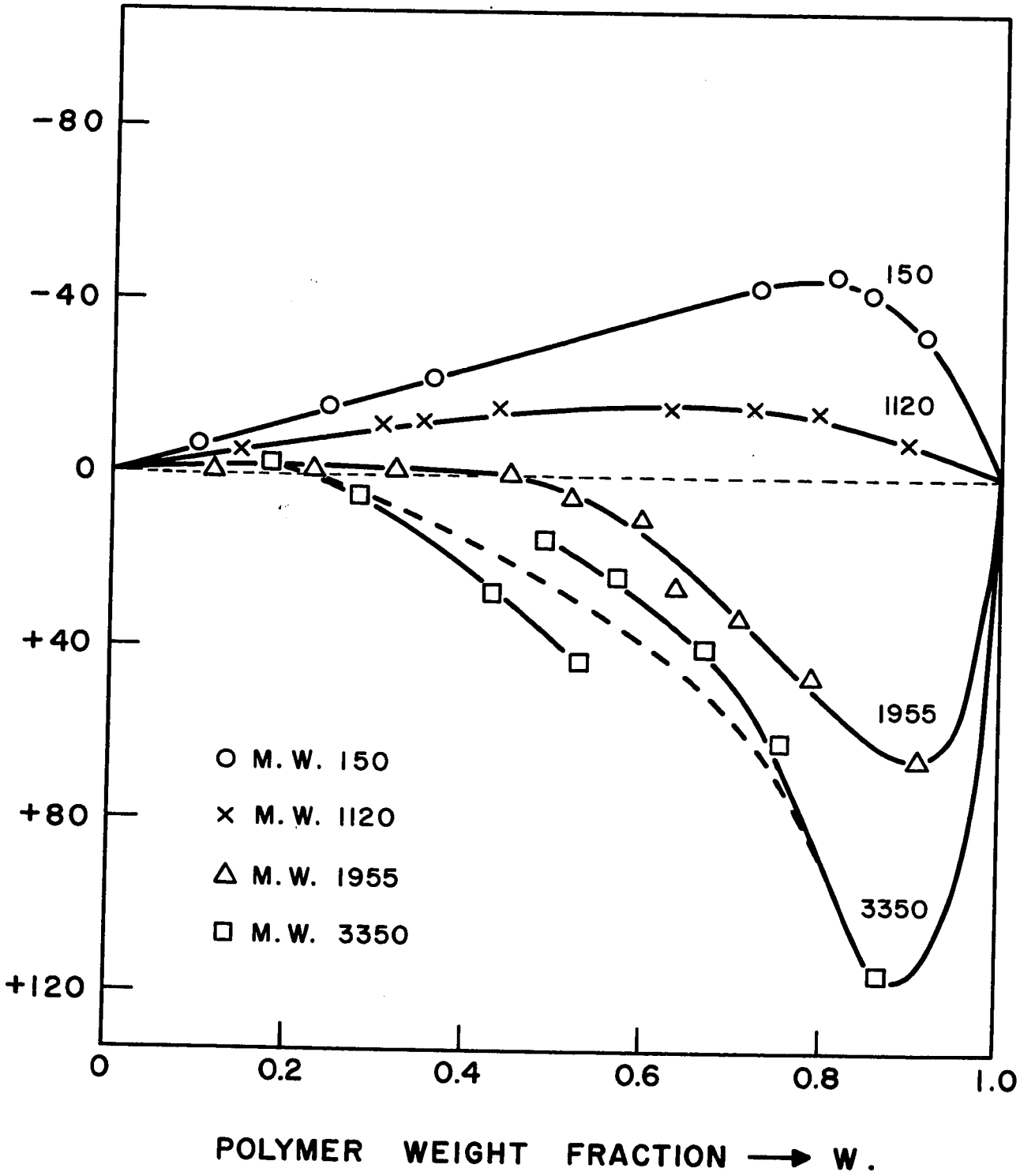

FIG. 9. PLOT OF THE HEATS OF MIXING OF VARIOUS POLYMERS AS A FUNCTION OF THEIR WEIGHT FRACTIONS IN METHANOL

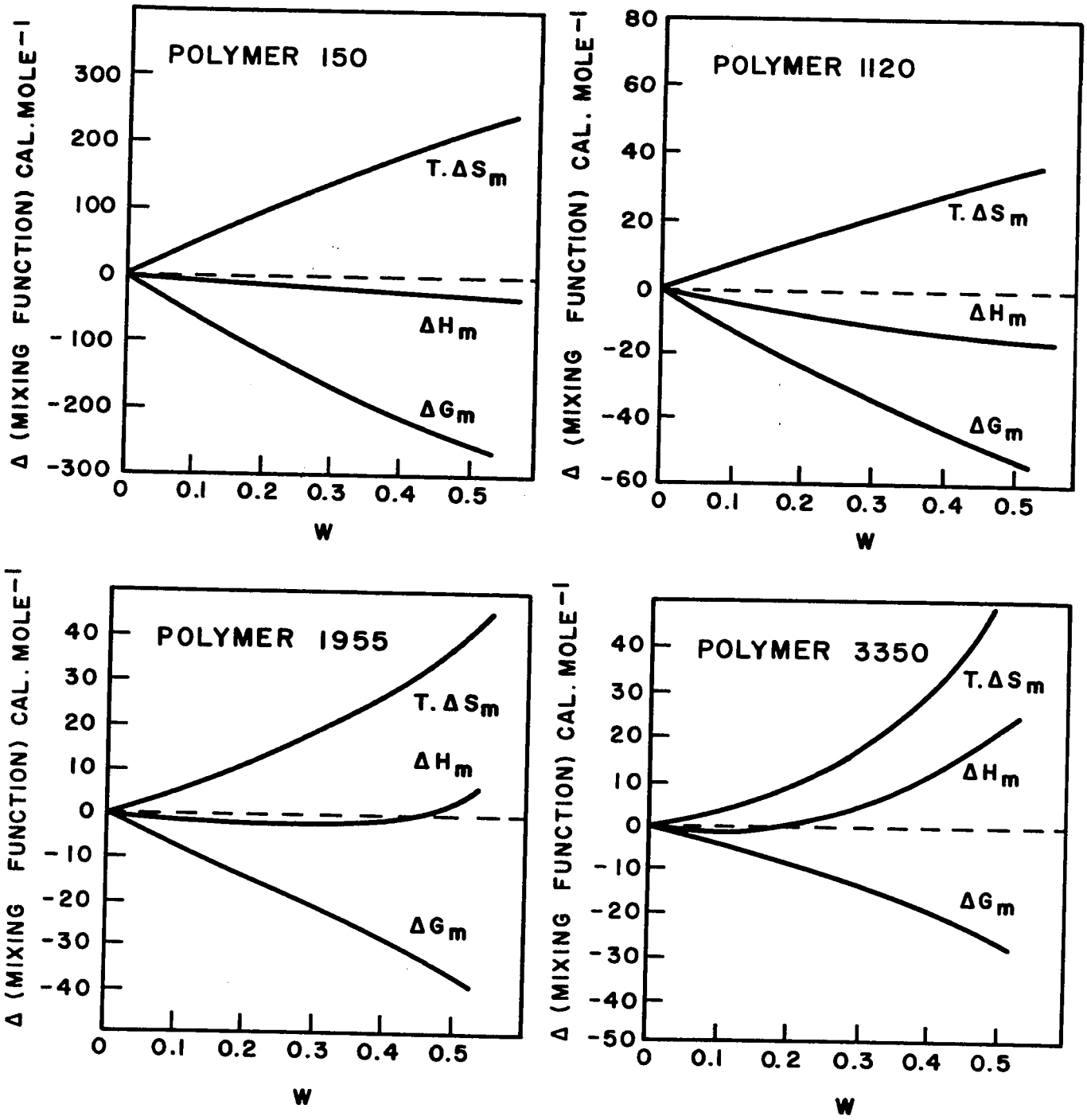

FIG. 10. PLOT OF THE DIFFERENT THERMODYNAMIC FUNCTIONS OF MIXING AS A FUNCTION OF WEIGHT FRACTION OF THE POLYMERS IN METHANOL.

significant heat of stirring, thus complicating the interpretation of the results.

The values of the heat of mixing for four polymer fractions were determined throughout the range of composition and are given in Tables XIII and XIV and plotted in Figure 9.

F. Calculation of the Entropy of Mixing

From the values of the free energy of mixing ΔG_m given in Table XI and the heats of mixing ΔH_m recorded in Tables XIII and XIV, the values of the entropy, ΔS_m, of mixing have been calculated using the familiar equation

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad . \qquad (111)$$

The values of ΔG_m, ΔH_m and $T \Delta S_m$ are given in Table XV and are plotted in Figure 10 for the four polymer fractions as a function of weight fraction of the polymer samples in solution.

SECTION 3

VISCOSITY DETERMINATIONS AND RESULTS

The work described in this section is supplementary to the principal investigations concerning the thermodynamic properties of the systems. The inference made from the thermodynamic work (see section III-1) concerning the rôle

of end-groups in determining the thermodynamic behaviour of the systems suggested that related information might be obtained from rheological studies on the polymers and their solutions. Interaction effects involving end-groups would be expected to determine (in part) the heats, free energies and entropies of activation for the flow process. In solutions, the influence of these interactions and of molecular size on the exponent a in equation (88) were also investigated. The polyglycols are for the most part too short to approach the configuration of 'random coils', being intermediate between simple monomeric molecules on the one hand and high polymers on the other. It was therefore considered to be of interest to investigate the dependence of a upon molecular weight for these short-chain molecules.

A. Viscosities of the Pure Polymers and Polymer-Solvent Systems

The viscosities of the pure polymer fractions and their solutions in methanol, ethanol and n-propanol were measured in capillary viscometers of the Ubbelohde type which are capable of giving data of satisfactory accuracy for the determination of intrinsic viscosities. The details of these measurements are given below.

(a). Viscometers: Determinations of the viscosities of the various systems were made at temperatures ranging from 50°C. to -25°C. using special Ubbelohde viscometers having capillaries of various lengths and diameters. In order to avoid evaporation

of the solvent in the work on polymer solutions the three vertical tubes on the Ubbelohde-type viscometers were connected through stopcocks at their upper ends. By manipulation of these stopcocks, the liquid could be made to flow in the viscometer without any free access of the solution to the atmosphere. This arrangement also prevented any absorption of moisture by the polymers during the determination of their viscosities. Three viscometers were used in this work having dimensions and characteristic constants given in Table XVI. The volumes of the bulbs of the viscometers were determined by weighing mercury contained in them between the etched marks, and the diameters of the capillaries were determined by weighing threads of mercury of known lengths.

TABLE XVI

Characteristic constants and dimensions of the viscometers

Quantity	Viscometers		
	A	B	C
V, the volume of the bulb between etched marks. (ml.)	5.03	4.38	5.30
h, the average head of liquid (cm.)	12.7	7.4	12.5
r, the radius of the capillary (cm.)	0.049	0.059	0.031
K, the constant in equation (112)	38	25	27
m, the coefficient in equation (113)	1.13	1.13	1.13

(b). Measurements of viscosities of pure polymers and their solutions: Solutions of the polymers in the purified alcohols were made at various compositions by weighing the polymer and then the solution in stoppered bottles. The viscosity determinations involved (i) measurements of the times of flow of the liquids in the viscometers; and (ii) densities of the solutions. Similar determinations were also made on the corresponding solvents. Five readings for the time of flow were taken at each constant temperature and concentration and the mean of these values was used in subsequent calculations. Measurements of the times of flow were reproducible to better than ± 0.5 percent. The densities of the solutions and of the solvents used were determined by means of 25 ml. pyknometers to an accuracy of ± 0.01 percent. The accuracies of the values of the viscosities calculated from these data are better than ± 1 percent. The measurements were made in a thermostat at various temperatures which were maintained constant to $\pm 0.05^{\circ}C$.

(c). Kinetic energy corrections: Owing to fairly large differences between the times of flow for the solvent and solutions except at high dilutions (see below), it was considered necessary to apply kinetic energy corrections to the data. Viscosities were therefore calculated by means of the Poiseuille equation in the corrected form

$$\frac{\eta}{\eta_o} = \frac{d\,t}{d_o\,t_o}\left[1 + K\left(\frac{1}{t_o^2} - \frac{1}{t^2}\right)\right] \qquad (112)$$

where the subscript zero refers to data for the reference fluid of known viscosity η_o . The value of K is a constant for each viscometer and is given by

$$K = m V^2/\pi^2 h g r^4 \qquad (113)$$

where V is the volume of the liquid held in the viscometer bulb between the etched marks, h is the average head of pressure of the liquid, r is the radius of the capillary and m is a coefficient having the value 1.13. Values of these quantities for the various viscometers are given in Table XVI.

The viscosities η_o of the pure solvents at five rounded temperatures have been interpolated from data given by various workers(93). Values of η_o are recorded in Table XVII for temperatures at which the viscosity data for corresponding solutions are recorded. For ease of presentation, the data on the viscosities and reduced viscosities for different compositions of various polymer-solvent systems have been given in Tables XIX to XXIII at the five rounded temperatures (50°, 30°, 10°, -10° and -25°C.). Typical experimental results for one concentration of polymer (M.W. 150) in ethanol are recorded in Table XVIII.

The viscosity data reported in Tables XIX to XXIII are accurate to better than±0.5 percent. In cases where η is substantially greater than η_o , the accuracy of the reduced viscosities is about the same as that of the viscosity data themselves. In the more dilute solution where η is comparable

TABLE XVII

Viscosities of methanol, ethanol and n-propanol at various temperatures

Temperature °C.	Viscosities of solvents in centipoises		
	Methanol	Ethanol	n-Propanol
50	0.403	0.702	1.13
30	0.510	1.003	1.72
10	0.680	1.475	2.87
-10	0.99	2.22	5.49
-25	1.29	3.25	10.09

with η_o, the accuracy of the reduced viscosities can be of the order of ±5 percent.

B. Viscosities of Dilute Solutions of the Polymers

In order to obtain intrinsic viscosities of the polymers, measurements were made in solutions as dilute as possible. Under these conditions accurate control of temperature was desirable since small differences between the times of flow for the solvent and dilute solution of the polymers in the viscometer were measured. Measurements were made by means of the viscometer C at 28.3°C. in the same thermostat bath as that used in the calorimetric measurements. The temperature of the bath could be kept constant to better than ±0.005°C. which corresponded to a constancy of viscosity of the solvent to about ±0.02 percent. The individual values of times of flow could be reproduced to ±0.2 percent and the mean deviation from the

TABLE XVIII

Typical data obtained for the determination of viscosities of a solution of polymer (M.W. 150) in ethanol at various temperatures

(Polymer weight fraction 0.4886)

Temp.	Densities		Times of flow of		Viscosities of	
°C.	solution g./ml.	reference fluid g./ml.	solution sec.	reference fluid sec.	solvent c.p.	solution c.p.
-31.4	0.9341	0.8345	740	87.2	3.79	36.1
-28.1	0.9315	0.8317	620	80.7	3.51	30.3
-17.1	0.9221	0.8220	368	65.0	2.64	16.9
-14.9	0.9205	0.8200	340	62.0	2.49	15.4
-3.2	0.9108	0.8097	200.3	48.0	1.91	9.1
14.3	0.8963	0.9992	113.8	24.6	1.16	5.13
32.2	0.8815	0.9948	68.5	17.2	0.76	3.03
49.2	0.8673	0.9884	45.6	13.9	0.555	1.89

Notes:- 1. Water was taken as the reference fluid in the determination of viscosities at the last three temperatures while at the other temperatures ethanol was taken as the reference fluid.

2. The accuracy of the figures underlined may be assessed from the percentage accuracy in the measurements of times of flow, as mentioned in the text.

TABLE XIX

The viscosities and the reduced viscosities of the solutions of the polymer (M.W. 150) in different solvents at various temperatures

V = Viscosity R = Reduced viscosity

Polymer weight fraction		Visc. and Red. visc. at various temperatures °C.				
		50	30	10	-10	-25
Solutions in methanol						
0.0531	V	0.435	0.577	0.750	1.04	1.46
	R	0.015	0.025	0.019	0.010	0.025
0.1236	V	0.547	0.67	0.94	1.18	1.79
	R	0.012	0.013	0.021	0.016	0.031
0.3522	V	0.95	1.09	1.70	2.75	4.39
	R	0.016	0.032	0.043	0.051	0.068
0.5592	V	1.44	2.36	4.07	8.4	15.3
	R	0.046	0.065	0.089	0.134	0.194
0.7086	V	1.99	4.03	8.6	25.4	68.4
	R	0.056	0.097	0.165	0.35	0.73
Solutions in ethanol						
0.0511	V	0.720	1.08	1.58	2.42	3.57
	R	0.004	0.015	0.015	0.018	0.020
0.1078	V	0.80	1.22	1.77	2.85	4.37
	R	0.012	0.020	0.019	0.026	0.032
0.2835	V	1.00	1.72	2.92	5.00	8.5
	R	0.015	0.025	0.035	0.044	0.057
0.4886	V	1.86	3.24	5.9	12.1	25.7
	R	0.037	0.046	0.061	0.091	0.142
0.6808	V	3.38	6.8	14.9	43.5	127
	R	0.056	0.085	0.133	0.273	0.56

Note:-1.The viscosities given above are in centipoises.

2.The percentage accuracy of the viscosity and the reduced viscosity data is reported in the text.

TABLE XX

The viscosities and the reduced viscosities of the solutions of the polymer (M.W. 425) in different solvents at various temperatures

V = Viscosity R = Reduced viscosity

Polymer weight fraction		Visc. and Red. visc. at various temperatures °C.				
		50	30	10	-10	-25
Solutions in methanol						
0.0470	V	0.430	0.585	0.78	1.05	1.42
	R	0.014	0.031	0.031	0.013	0.021
0.1236	V	0.540	0.660	0.93	1.31	1.84
	R	0.027	0.024	0.030	0.026	0.034
0.3522	V	0.95	1.32	2.04	3.21	5.48
	R	0.038	0.045	0.057	0.064	0.092
0.5592	V	1.78	2.86	4.73	8.32	16.6
	R	0.061	0.082	0.106	0.133	0.212
0.7475	V	3.16	6.45	12.6	38	103
	R	0.092	0.156	0.26	0.50	1.06
Solutions in ethanol						
0.0527	V	0.71	1.11	1.69	2.56	3.63
	R	0.001	0.020	0.027	0.029	0.022
0.1078	V	0.85	1.31	1.98	3.00	4.54
	R	0.019	0.028	0.032	0.033	0.037
0.3166	V	1.25	2.15	3.37	5.75	10.0
	R	0.024	0.036	0.041	0.050	0.066
0.5156	V	2.34	3.82	6.92	14.4	28.6
	R	0.045	0.054	0.072	0.107	0.151
0.7851	V	4.90	10.3	27.2	97.7	339
	R	0.076	0.119	0.22	0.55	1.31

Note:- 1. The viscosities given above are in centipoises.

2. The percentage accuracy of the viscosity and the reduced viscosity data is reported in the text.

TABLE XXI

The viscosities and the reduced viscosities of the solutions of the polymer (M.W. 1120) in methanol at various temperatures

V = Viscosity R = Reduced viscosity

Polymer weight fraction		Visc. and Red. Visc. at various temperatures °C.				
		50	30	10	-10	-25
0.0466	V	0.465	0.600	0.79	1.08	1.49
	R	0.028	0.038	0.035	0.020	0.033
0.1230	V	0.595	0.76	1.00	1.41	1.99
	R	0.039	0.040	0.038	0.035	0.044
0.3511	V	1.18	1.68	2.63	3.98	6.23
	R	0.055	0.065	0.082	0.086	0.109
0.5580	V	2.72	4.26	6.92	12.0	21.9
	R	0.103	0.13	0.16	0.20	0.29
0.7466	V	2.75	4.47	8.5	22.9	59.0
	R	0.078	0.104	0.16	0.30	0.60

Note:- 1. The viscosities given above are in centipoises.

2. The percentage accuracy of the viscosity and reduced viscosity data is reported in the text.

TABLE XXII

The viscosities and the reduced viscosities of the solutions of the polymer (M.W. 1955) in different solvents at various temperatures

V = Viscosity R = Reduced viscosity

Polymer weight fraction		Visc. and Red. Visc. at various temperatures °C.				
		50	30	10	-10	-25
Solutions in methanol						
0.0513	V	0.460	0.620	0.84	1.16	1.60
	R	0.028	0.042	0.046	0.034	0.046
0.1118	V	0.64	0.85	1.16	1.62-	2.40
	R	0.053	0.060	0.063	0.057	0.077
0.3271	V	1.42	2.18	3.13	4.94	7.9
	R	0.077	0.100	0.110	0.122	0.156
0.5687	V	4.36	7.0	11.7	22.3	43.2
	R	0.173	0.22	0.29	0.38	0.57
0.7079	V	7.7	15.2	32.1	81	--
	R	0.25	0.41	0.65	1.15	--
Solutions in ethanol						
0.0496	V	--	1.10	1.72	2.78	4.13
	R	--	0.019	0.033	0.051	0.055
0.0920	V	0.76	1.27	1.98	3.42	5.16
	R	0.008	0.029	0.037	0.059	0.064
0.3173	V	1.59	3.15	5.5	9.8	17.0
	R	0.040	0.067	0.085	0.108	0.133
0.5099	V	3.81	7.2	14.0	28.5	54
	R	0.086	0.121	0.166	0.232	0.30
0.6618	V	7.6	15.8	34.2	88	230
	R	0.147	0.22	0.33	0.58	1.05
Solutions in n-propanol						
0.0401	V	1.25	1.99	3.34	5.97	10.5
	R	0.026	0.040	0.041	0.022	0.012
0.1223	V	1.72	2.75	4.67	8.5	16.0
	R	0.042	0.049	0.051	0.045	0.049
0.2942	V	2.88	5.03	9.2	19.5	37.8
	R	0.053	0.065	0.075	0.087	0.096

Note:- 1. The viscosities given above are in centipoises.

2. The percentage accuracy of viscosity data and reduced viscosity data is reported in the text.
3. Figure 13 shows Arrhenius plots for these data.

TABLE XXIII

The viscosities and the reduced viscosities of the solutions of the polymer (M.W. 3350) in different solvents at various temperatures

V = Viscosity R = Reduced viscosity

Polymer weight fraction		Visc. and Red. Visc. at various temperatures °C. 50	30	10	-10	-25
Solutions in methanol						
0.0517	V	0.500	0.700	0.96	1.37	1.89
	R	0.046	0.072	0.080	0.075	0.089
0.2016	V	0.98	1.36	1.94	2.80	4.15
	R	0.071	0.083	0.092	0.091	0.11
0.3597	V	3.36	4.8	7.15	11.7	19.1
	R	0.205	0.23	0.266	0.30	0.38
0.5597	V	8.4	14.7	26.8	54.9	107
	R	0.35	0.70	0.69	0.98	1.46
0.7024	V	25.7	44.6	85	209	478
	R	0.89	1.23	1.77	3.00	5.3
Solutions in ethanol						
0.0576	V	0.745	1.27	2.03	3.32	4.77
	R	0.010	0.046	0.065	0.086	0.081
0.1219	V	1.05	1.82	3.03	5.05	7.55
	R	0.040	0.067	0.086	0.105	0.108
0.3052	V	2.62	4.82	8.9	16.4	25.8
	R	0.089	0.125	0.165	0.210	0.227
0.5145	V	8.7	16.8	31.8	71	140
	R	0.22	0.31	0.40	0.60	0.82
0.7071	V	25.7	54.9	126	339	900
	R	0.50	0.76	1.19	2.14	3.90
Solutions in n-propanol						
0.0432	V	2.44	3.85	6.31	11.5	19.7
	R	0.27	0.29	0.28	0.25	0.22
0.1283	V	4.07	6.6	11.0	20.0	33.9
	R	0.20	0.22	0.22	0.20	0.19
0.2895	V	5.25	8.8	15.5	32.4	63.1
	R	0.126	0.144	0.152	0.169	0.18
0.4841	V	14.7	27.9	55.7	138	331
	R	0.29	0.31	0.38	0.45	0.66
0.6902	V	37.5	78	175	543	152×10
	R	0.467	0.65	0.87	1.42	2.19

Note:- 1. The viscosities given above are in centipoises.
2. The accuracy of viscosity data and reduced visc. data is reported in the text.

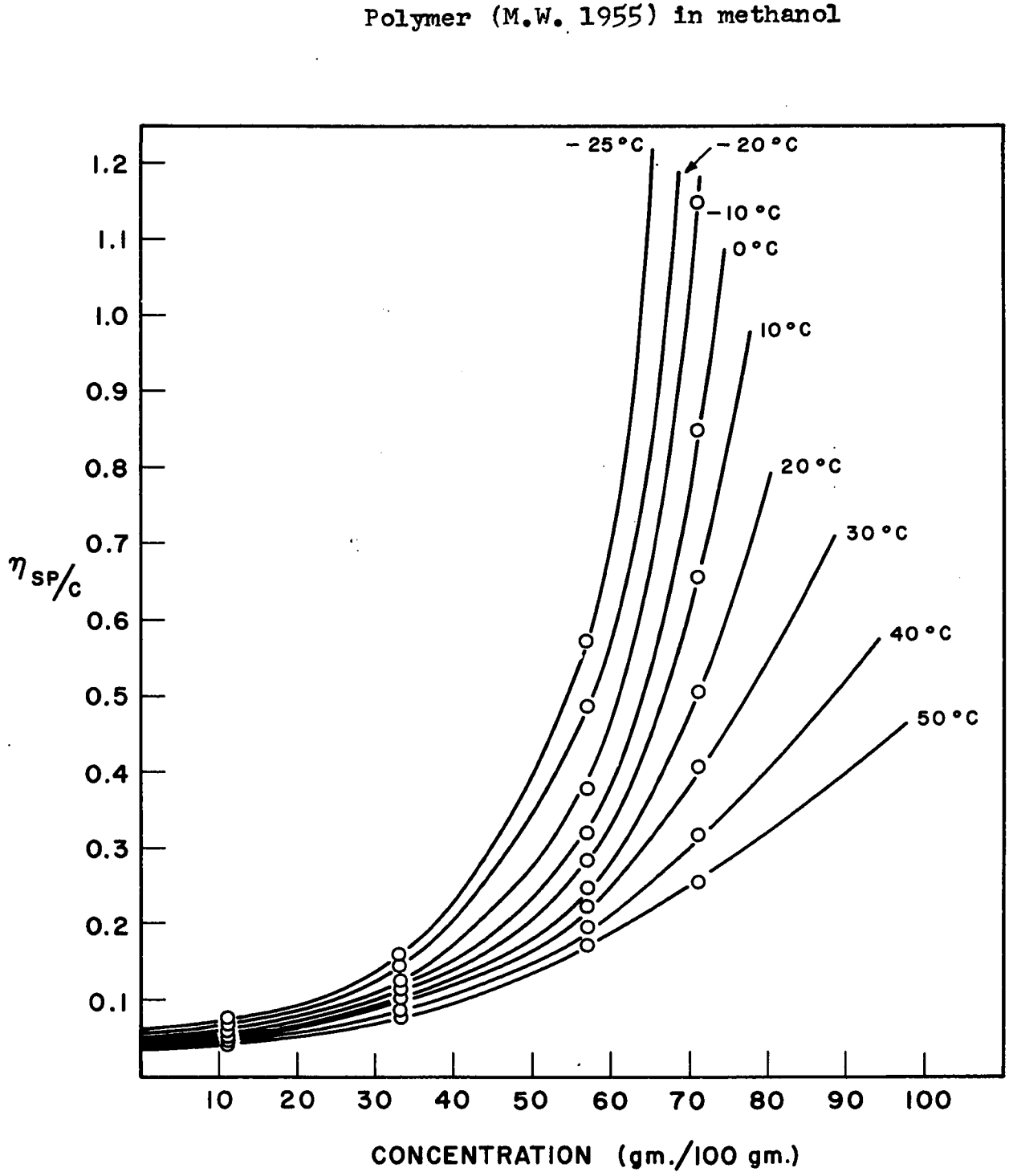

FIG. 11. PLOT OF THE REDUCED VISCOSITY AS A FUNCTION OF THE POLYMER CONCENTRATION (IN GM. PER 100 GM.).

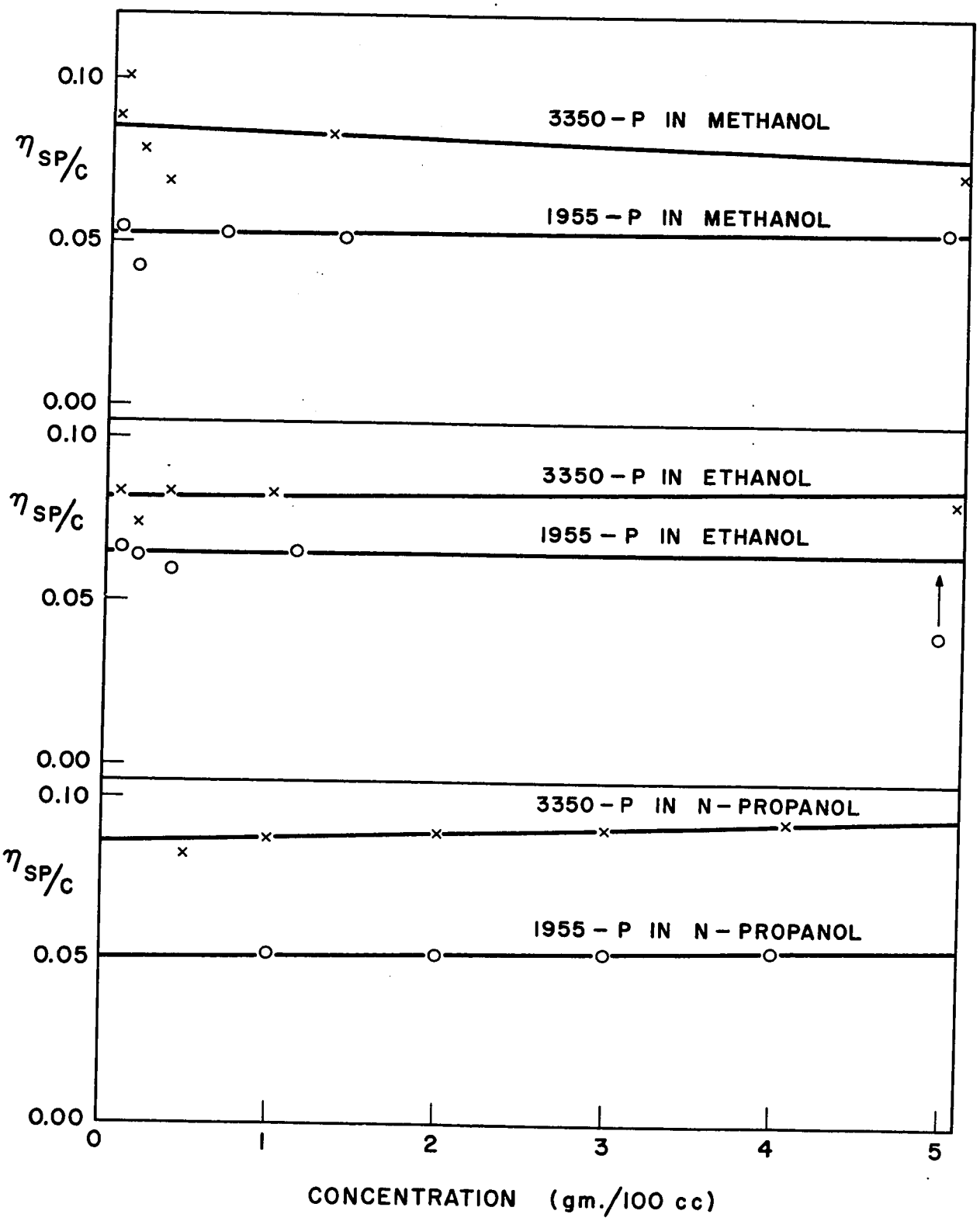

FIG. 12. PLOT OF THE REDUCED VISCOSITIES OF THE POLYMERS FOR THEIR DILUTE SOLUTIONS IN METHANOL, ETHANOL AND n-PROPANOL.

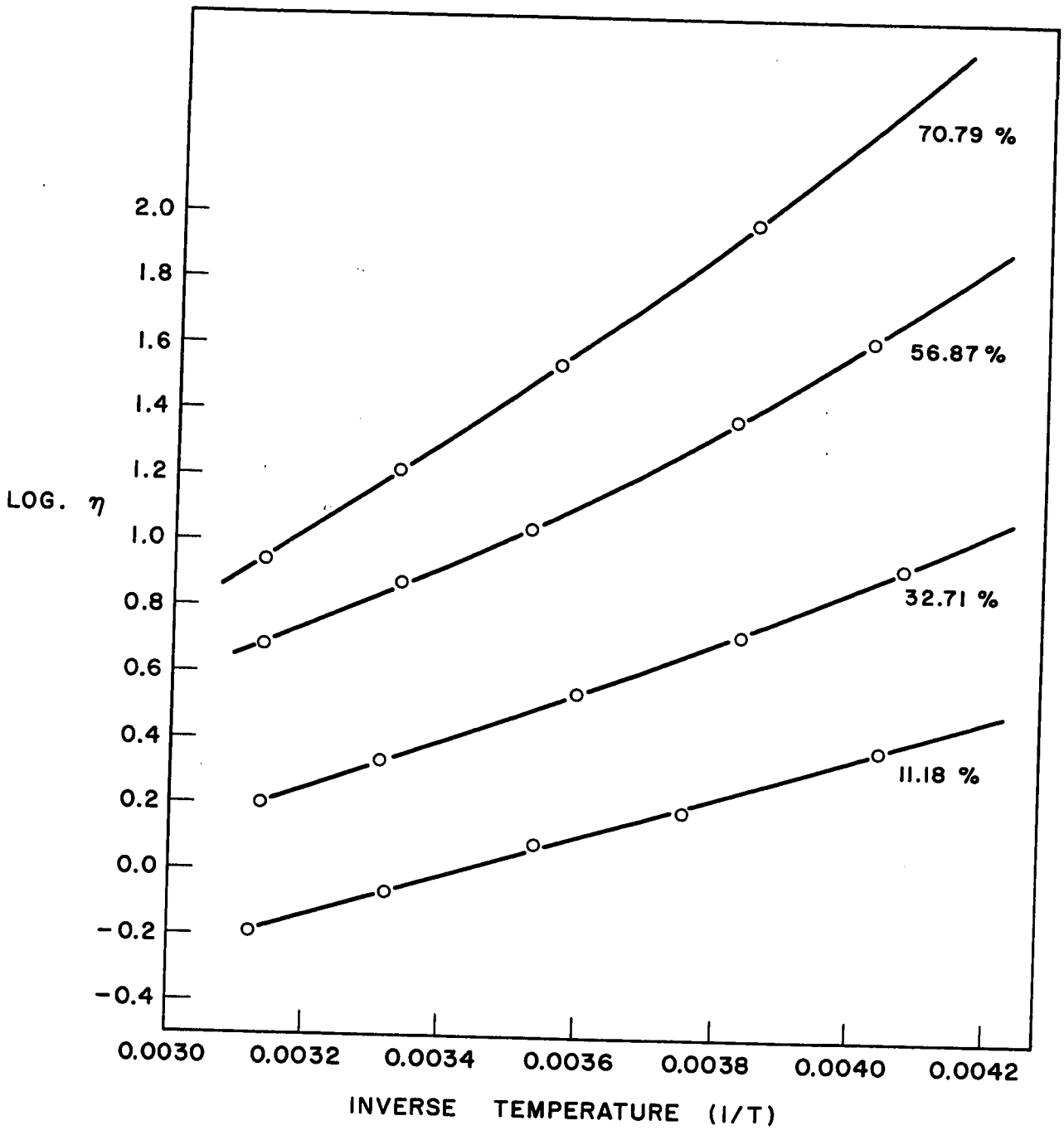

FIG. 13. PLOT OF THE LOGARITHM OF THE VISCOSITIES FOR THE POLYMER (M.W. 1955)-METHANOL SYSTEMS AS A FUNCTION OF THE RECIPROCAL OF THE TEMPERATURE.

TABLE XXIV

The reduced viscosities of the dilute solutions of polymers (M.W. 1955 and 3350) in different solvents at 28.3°C.

Polymer	Concentration (g. per 100 ml.)	Time of flow (sec.)	Solution density (g. per ml.)	Reduced viscosity
Solutions in methanol				
1955	5.000	108.42	0.79317	0.054
	1.400	92.24	0.78633	0.052
	0.700	89.46	0.78478	0.054
	0.350	88.36	0.78438	0.069
	0.175	87.04	0.78337	0.042
	0.087	86.84	0.78318	0.055
	0.000	86.46	0.78290	
3350	5.040	116.31	0.79400	0.073
	1.330	95.58	0.78598	0.083
	0.400	88.92	0.78387	0.078
	0.200	87.76	0.78334	0.078
	0.100	87.42	0.78311	0.10
	0.040	86.76	0.78295	0.09
	0.000	86.46	0.78290	
Solutions in ethanol				
1955	4.980	197.02	0.79511	0.040
	1.140	178.70	0.78548	0.065
	0.400	170.44	0.78488	0.060
	0.200	169.00	0.78306	0.064
	0.100	168.04	0.78274	0.066
	0.000	167.00	0.78242	
3350	5.020	232.37	0.79341	0.080
	0.980	181.80	0.78612	0.083
	0.400	174.32	0.78420	0.083
	0.200	171.16	0.78334	0.074
	0.100	170.20	0.78283	0.084
	0.000	168.88	0.78250	

Note:- Table continued on next page 111A.

Table XXIV (continued)

Polymer	Concentration (g. per 100 ml.)	Time of flow (sec.)	Solution density (g. per ml.)	Reduced viscosity
Solutions in n-propanol				
1955	4.016	346.4	0.80344	0.054
	3.000	330.3	0.80123	0.052
	2.000	316.2	0.79906	0.052
	1.000	302.2	0.79694	0.052
	0.500	296.8	0.79570	0.064
	0.000	288.7	0.79267	
3350	4.080	392.6	0.80380	0.093
	3.000	362.9	0.80203	0.091
	2.000	337.1	0.80000	0.089
	1.000	312.3	0.79712	0.088
	0.500	299.3	0.79613	0.082
	0.000	288.7	0.79267	

Notes:-

1. The times of flow in column 3 are averages based on five determinations. The underlined figures are included since the accuracy of the mean times is about 0.05 sec.

2. Reduced viscosities in column 5 have been calculated from the relative viscosities derived from the times of flow and the densities of the solution and the solvent.

TABLE XXV

The intrinsic viscosities of the polymers (M.W. 1955 and 3350) from viscosities of their solutions in different solvents at 28.3°C.

Polymer	Intrinsic viscosities derived from the reduced viscosities of polymer solutions in different solvents		
	Methanol	Ethanol	n-propanol
1955	0.052	0.059	0.050
3350	0.085	0.084	0.086

TABLE XXVI

The viscosities of the pure polymers at different temperatures (°C.)

Polymer		Viscosities at different temperatures (centipoises)			
150	Temp.	45.1	44.1	27.2	8.8
	Visc.	16.1	16.6	50.5	246
425	Temp.	45.2	22.7	-0.9	-15.1
	Visc.	19.7	76	502	316×10
1120	Temp.	43.4	21.4		
	Visc.	40.6	147		
1955	Temp.	49.3	22.5		
	Visc.	67	302		
3350	Temp.	63.0	35.0		
		107	432		

Note:- The accuracy of the viscosity data is reported in the text.

average of five measurements usually did not exceed ±0.05 percent. The dilute solutions were made by first weighing the polymer and then making up the solutions to known volumes with the solvent. More dilute solutions were made volumetrically by successive dilutions from original more concentrated solutions. Because of the low degree of polymerization of the polyglycols, the lowest concentrations of polymers which could be studied were about 0.05 g. per 100 ml. Adsorption errors which are difficult to avoid in the viscometry of very dilute solutions, for example, 0.001 g. per 100 ml. of high polymers, were therefore negligible in the present work. Reduced viscosity data for the polymers of molecular weight 1955 and 3350 are recorded in Table XXIV.

In the work on very dilute solutions the inaccuracies in the values of reduced viscosities range from about 2 percent to 10 percent because of the small differences between η and η_o. The inaccuracies in the corresponding intrinsic viscosities may be estimated to be about 5 to 7 percent and lead to an uncertainty in log $[\eta]$ (Figure 21) of about 0.05. The intrinsic viscosities were derived by extrapolating the plots of reduced viscosities against concentration (in g. per 100 ml.) to zero concentration (Figure 12). The values of $[\eta]$ for the polymers 1955 and 3350 derived from reduced viscosities of their solutions are reported in Table XXV. The intrinsic viscosities for polymers 150 and 425 (Table XL) were obtained from the reduced viscosity data given in Tables XIX and XX. In order to obtain the intrinsic viscosities by extrapolation of the reduced viscosities, the units of concentration in which the reduced viscosities are expressed (Tables XIX and XX) were changed to g. per 100 ml.

III. DISCUSSION

A survey of the existing literature on polymer chemistry reveals that the experimental data available on the thermodynamics of polymer solutions are by no means sufficient to verify or examine the current theories in the field. It is therefore desirable that further experimental information on a number of systems of more diverse character be obtained.

The theoretical treatment of the properties of these solutions has been largely based on the 'idealized' quasi-crystalline lattice model of liquid mixtures involving certain assumptions which have limited validity. The deviations from ideal mixing behaviour observed in the cases of non-polar polymers in non-polar solvents are fairly adequately described by the theoretical formulations already discussed in section I-2 on theories of polymer solutions. In such systems random mixing of the polymer segments with the solvent can be assumed except in very dilute solutions. In the present investigations, however, we are concerned with a rather extreme case of the mixing of polar polymer molecules with a polar solvent. Specific interactions mostly arising from hydrogen bondin between methanolic hydroxyl groups and both ether-oxygen and terminal hydroxyl groups on the polymer chains may be expected in the systems studied. It is of interest therefore to examine to what extent the theoretical formulations of the thermodynamic properties of polymer solutions can account for the behaviour of such systems.

For the thermodynamic evaluation of the polypropylene glycol-methanol systems some important quantities such as the excess thermodynamic functions for mixing, the polymer-solvent interaction constant χ and the interchange energy w have been calculated.

Some complementary information on the polymer-solvent interaction has also been obtained from studies of the rheological properties of the pure polymers and their solutions. The values of the intrinsic viscosities and the heats of activation for viscous flow in various pure polymers and polymer-solvent systems have been evaluated and are shown to be determined in part by hydrogen bonding involving the terminal hydroxyl groups on the polymer chains.

1. THERMODYNAMIC FUNCTIONS FOR MIXING

A. The Excess Thermodynamic Functions for Mixing

In any system the ideal free energy of mixing ΔG_m^i may be defined as

$$\Delta G_m^i = RT \sum_i x_i \ln x_i \, . \qquad (114\text{-a})$$

For a polymer-solvent system, athermal free energies of mixing can be calculated as discussed in section I, p.16 by making allowance for the fact that the polymer molecule is composed of segments which can be regarded as randomly mixed with the solvent. Two such athermal free energies of mixing are defined by

$$\Delta G_m^a = RT \Sigma_i x_i \ln \theta_i \qquad (114\text{-b})$$

and

$$\Delta G_m^{a'} = RT \Sigma_i x_i \ln \phi_i \qquad (114\text{-c})$$

in terms of the site fraction θ_i or the volume fraction ϕ_i of the solution occupied by the component i.

From knowledge of the free energy of mixing ΔG_m (obtained from experimental data), we may compute three excess thermodynamic functions for the free energy of mixing corresponding to the three ways of expressing the ideal and athermal free energies of mixing. Denoting excess functions by a superscript E, we may write

$$\Delta G_m^E(i) = \Delta G_m - \Delta G_m^i \quad , \qquad (115\text{-a})$$

$$\Delta G_m^E(a) = \Delta G_m - \Delta G_m^a \qquad (115\text{-b})$$

and

$$\Delta G_m^E(a') = \Delta G_m - \Delta G_m^{a'} \quad . \qquad (115\text{-c})$$

If the values of ΔH_m (which is itself directly an excess enthalpy of mixing) are known, the values of the corresponding excess entropies of mixing may be evaluated.

In the present investigations, the values of the ideal free energy and the theoretical athermal free energies of mixing have been calculated from the three equations (114) and are given

in Table XXVII. The values of the corresponding excess thermodynamic functions of mixing have been calculated from the three equations (115) and are reported in Table XXVIII; for the case of the functions $\Delta G_m^E(i)$ and $T\Delta S_m^E(i)$, the values are illustrated in Figure 14 as a function of the polymer concentration for each of the four polymer fractions studied.

From an examination of the excess thermodynamic functions it seems that there is a striking, if not surprising, agreement between the experimental values and the ideal values calculated on the basis of mole fractions. This indicates that the mixing of the polymer segments with the solvent molecules is not an entirely random process as assumed in the theoretical treatments. If this were so, the excess functions calculated in terms of site or volume fractions of the polymer should be nearer to zero than those calculated from the ideal mixing equation (115a) since the latter ignores the chain-like arrangement of polymer segments. This anomalous behaviour of the $\Delta G_m^E(i)$ function cannot be accounted for by the finite heats of mixing observed. In fact, the evaluation of the ΔS_m^E functions shows (see Table XXVIII) that a large fraction of each of the values of ΔG_m^E is accounted for by the corresponding term $-T\Delta S_m^E$ so that the finite heat of mixing determined experimentally does not account for the magnitude of the excess free energy of mixing in these systems. This therefore suggests that there may be strong interactions of the methanol molecules

TABLE XXVII

The ideal free energy of mixing and the corresponding athermal free energies of mixing for the various polymer-methanol systems at 15° C.

Polymer weight fraction	ΔG_m^i	ΔG_m^a	$\Delta G_m^{a'}$
	Cal. mole^{-1}	Cal. mole^{-1}	Cal. mole^{-1}
Polymer (M.W. 150)			
0.1511	-90	-120	-116
0.2012	-115	-131	-149
0.2367	-139	-159	-182
0.3047	-165	-212	-220
0.3911	-210	-274	-278
0.5007	-267	-370	-363
Polymer (M.W. 1120)			
0.1172	-14	-45	-61
0.1614	-19	-64	-86
0.2416	-29	-100	-135
0.3536	-45	-160	-211
0.4636	-65	-230	-301
0.5405	-81	-290	-362
Polymer (M.W. 1955)			
0.1187	-9	-43	-60
0.1553	-12	-58	-86
0.2456	-19	-97	-133
0.3445	-28	-149	-202
0.4627	-42	-225	-298
0.5271	-51	-278	-360
Polymer (M.W. 3350)			
0.1159	-5	-42	-57
0.1359	-6	-50	-68
0.2110	-10	-84	-113
0.3020	-16	-128	-172
0.4102	-23	-189	-251
0.4553	-27	-224	-293

TABLE XXVIII

The excess thermodynamic functions of mixing for the various polymer-methanol systems at 15°C.

Polymer weight fraction	$\Delta G_m^E(1)$	$\Delta G_m^E(a)$	$\Delta G_m^E(\acute{a})$	$T\Delta S_m^E(1)$	$T\Delta S_m^E(a)$	$T\Delta S_m^E(\acute{a})$
	(Cal. mole^{-1})			(Cal. mole^{-1})		
Polymer (M.W. 150)						
0.1151	1	13	27	-10	-22	-36
0.2012	1	17	35	-23	-39	-57
0.2367	2	21	45	-16	-36	-59
0.3047	-1	46	54	-17	-64	-72
0.3911	10	74	78	-34	-98	-102
0.5007	20	123	116	-51	-157	-147
Polymer (M.W. 1120)						
0.1172	0	31	47	-4	-35	-51
0.1614	0	45	67	-5	-50	-72
0.2416	2	73	108	-10	- 81	-116
0.3536	7	121	173	-20	-135	-186
0.4636	18	183	254	-33	-198	-269
0.5405	30	239	311	-46	-255	-327
Polymer (M.W. 1955)						
0.1187	0	34	51	-2	-36	-53
0.1553	1	47	69	-3	-49	-71
0.2456	2	80	116	-4	-82	-118
0.3445	5	126	176	-6	-127	-180
0.4627	12	195	268	-12	-195	-268
0.5271	12	239	321	-6	-233	-315
Polymer (M.W. 3350).						
0.1159	0	37	52	-2	-39	-54
0.1359	0	46	62	-2	-46	-64
0.2110	1	75	104	0	-74	-103
0.3020	3	115	159	2	-104	-148
0.4102	6	172	234	7	-143	-215
0.4553	5	202	271	15	-174	-233

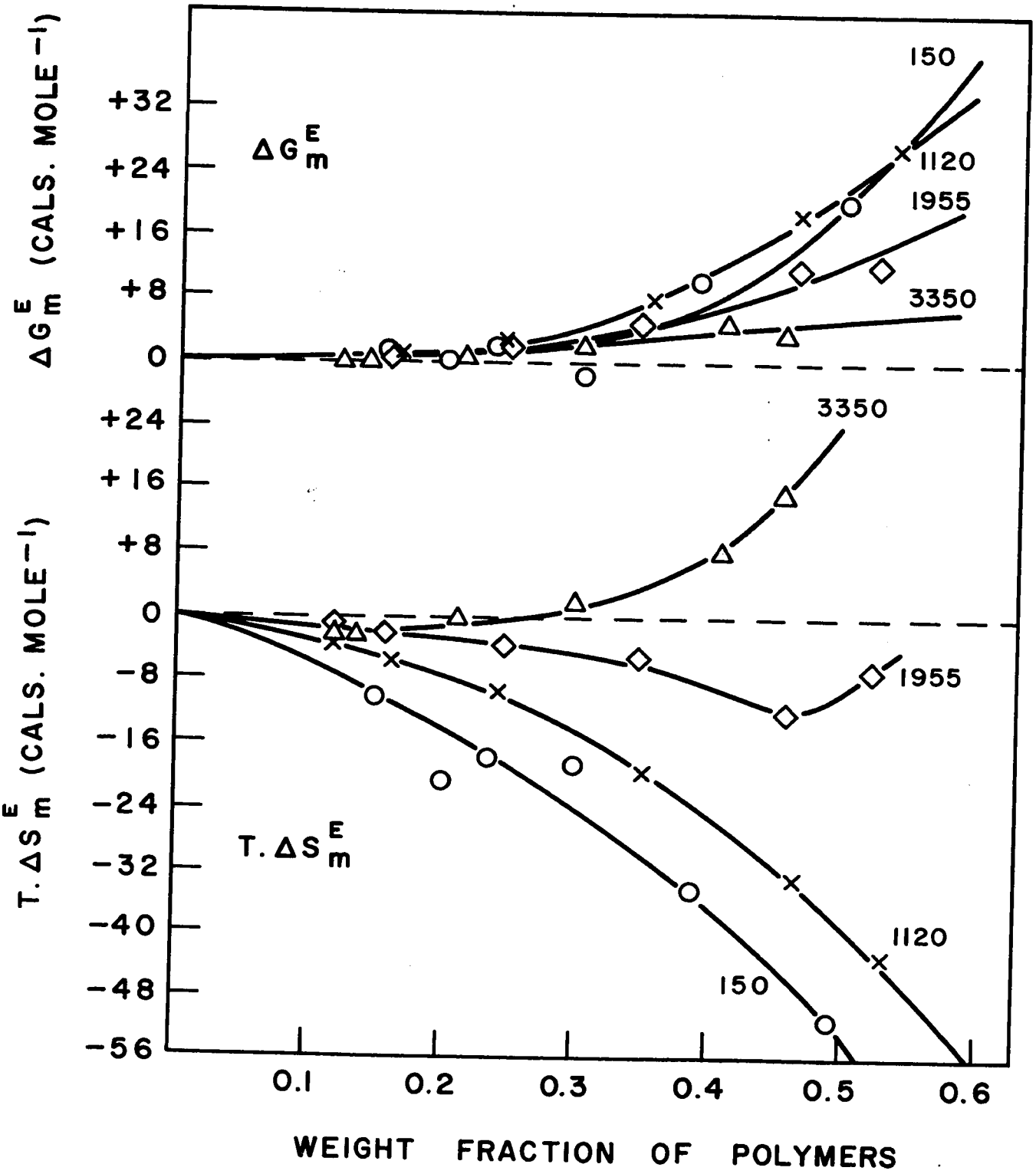

FIG. 14. PLOT OF THE EXCESS THERMODYNAMIC FUNCTIONS OF MIXING AS A FUNCTION OF THE WEIGHT FRACTION OF THE POLYMERS IN METHANOL.

with the oxygen atoms of the polymer chain, which can bring about (i) a restriction in the coiling or in the distribution of segments; and (ii) an orientation of solvent molecules near the polymer chains. The first effect may be reinforced by the presence of the $-CH_3$ groups on the polymer chain in close proximity to the oxygen atoms of the polymer chains. The decreasing excess entropy of mixing with increasing molecular weight of the polymers indicates that at least some parts of the polymer chain may experience more restriction than complete randomness would indicate. It is possible to regard the restrictions on configuration of the polymer chains as leading to a stretching of the polymer towards a somewhat more linear array of segments with the CH_3OH molecules attached to them at the ether oxygen atoms through hydrogen bonds. We may investigate the likelihood of the occurrence of this effect by calculating the change of entropy (ΔS_{st}) of the polymer chain on stretching, using the relation given by Bawn (94)

$$\Delta S_{st} = -3/2\ Nk\gamma^2 \qquad (116)$$

where

$$\gamma = (L/L_o - 1),$$

and for various assumed values of γ we obtain the following values of ΔS_{st} (Table XIX) where L is the effective length on stretching and L_o the original effective length.

TABLE XXIX

The values of the entropy change of a polymer molecule on stretching

γ	ΔS_{st} Cal. mole^{-1} degree^{-1}	$T\Delta S_{st}$ Cal. Mole^{-1}
1.00	-2.98	-858
0.50	-0.745	-214
0.33	-0.324	- 93.3
0.25	-0.186	- 53.5

If we attribute the values of the excess entropy of mixing, corresponding to the values of $T\Delta S_m^E$ given in Table XXVIII, to the stretching effect, the values of γ would have to be in the range zero to about 0.5 depending on the polymer fraction concerned.

The second effect involving changes in the entropy of the methanol molecules due to orientation would also be expected, as discussed below. Liquid methanol is regarded as having a quasi-crystalline structure (95) so that owing to the interaction between the methanol and polymer molecules through hydrogen bonds some specific orientation of the methanol molecules adjacent to the polymer molecules may be expected. This could lead on one hand to a positive 'structure breaking' entropy (96) due to disruption of hydrogen bonds between the solvent molecules themselves and on the other hand to a diminution of the freedom of motion

of the methanol molecules interacting with the polar polymer chains. Such an effect would involve a local change of entropy of the solvent molecules adjacent to the polymer chains to more negative values. Since O-H---O hydrogen bonds are involved in both cases, it is likely that these two effects may almost cancel in the systems studied in the present work.

B. Heats of Mixing

The curves of the heats of mixing ΔH_m as a function of composition of the methanolic solutions of these polymers show considerable departures from some of those obtained by Tompa (97), Newing (98) and Rowlinson et al. (85) for other systems. In the case of the polypropylene glycols of low molecular weights there is agreement between the behaviour observed in the present work and the general trend of results observed in other systems, although the curves are by no means symmetrical about the middle point of the range of values of the abscissae (see Figure 9.). However, in the case of the polymers of molecular weights 1955 and 3350, the values of ΔH_m become positive with increasing concentration of the polymers. Since methanol has a quasi-crystalline structure, it may be expected that with the orientation of the methanol molecules with OH groups directed towards the oxygen atoms in the polymer chains, there are more methanol-methanol bonds broken compared with the number of polymer-methanol bonds

made*. This would mean that the interchange energy w is no longer represented by the ordinary form of the equation (17) but the value of w may be negative depending on the number of bonds made and broken. Tompa has shown (97) that by taking into account orientation effects in the lattice theory of polymer solutions, a variety of different kinds of thermodynamic behaviour can be deduced using four empirical parameters. In particular, assymmetry of the curves of heats of mixing about the mid-point of the composition range, negative values of the heats of mixing and sigmoidal forms of the functions with respect to solution composition can be accounted for by allowing for specific interactions involving orientation of the solvent in the solvent or orientation of the solvent adjacent to the polymer molecules. The forms of the theoretical results derived are very similar to those found experimentally in the present work. Hence, although Tompa's theory cannot be used explicitly for quantitative interpretation of the present (or indeed any) experimental data owing to the number of empirical parameters involved, it is clear that the <u>form</u> of the present results appears to be explicable only in

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* This arises since the ether oxygen sites on the polymer provide bi-functional hydrogen bonding centers, whilst in the bulk of the solvent tri-functional sites (two through the 2P lone-pair orbitals on the oxygen atom and one through H in CH_3OH) exist (see also p. 155).

terms of specific orientation effects. Such a conclusion is entirely in accord with the polar nature of the hydrogen bonded systems examined in the present work.

When the heats of mixing were determined experimentally it was necessary, as explained in section II, p. 93, to make mixtures both from polymer in excess solvent and from solvent in excess polymer in order to cover the whole composition range; thus the composition containing 50 percent polymer by weight was approached from either end of the composition range. When this was done the results gave curves of the heats of mixing for the higher molecular weight fractions which were somewhat discontinuous near the middle of the composition range as shown in Figure 9, despite the fact that the solutions were apparently adequately stirred. The discontinuity may, nevertheless, be due to microscopic heterogeneity of the solutions arising, for example, from the entrapment of the solvent in aggregates of polymer molecules. Such a possibility receives some support from the recent paper of Huggins (99) in which he attempted to modify his previous equations for χ (58,59,60) by allowing for the possible entrapment of the solvent molecules among groups of the polymer molecules. His modified equation contains a correction factor which involves empirical parameters. It is apparent from the results for ΔH_m shown in Figure 9, that the entrapment of the solvent may be indicated by the non-coincidence of the curves

obtained when the heats of mixing determined by dilution of polymer with solvent-polymer mixtures and of solvent by solvent-polymer mixtures are plotted in the same diagram against composition of the resulting solutions. It is believed that in the more concentrated solutions of the higher molecular weight fractions entrapment effects can be significant since the solutions were otherwise satisfactorily stirred and only micro-heterogeneities of concentration could have existed. After normal stirring, the solutions showed no optical striations indicative of heterogeneity over any macroscopic distance, nor was there any slow evolution of heat after the stirred solutions were left to stand. Polymer aggregation and solvent entrapment effects have also been discussed by Gee (100) in relation to anomalous thermodynamic properties of polymer solutions.

For the purpose of evaluating various other thermodynamic functions, the uncertainty concerning complete molecular mixing in the calorimeter does not cause any serious difficulties since the vapour pressure data (and hence the partial molar free energies and other derived functions for the solvent) could only be obtained over the range of composition 0 to 50 percent polymer, that is mostly below the range of concentrations of polymer over which discontinuities in the curves for the heats of mixing occur. Furthermore, this effect was only apparent for the polymer of molecular weight 3350, the lower molecular weight materials having given satisfactory and unambiguous results.

2. THE POLYMER-SOLVENT INTERACTION CONSTANT χ

The Flory-Huggins expressions (equations 58 and 60) have been widely accepted as the basis for the consideration of polymer-solvent interactions. The original interpretation of χ has been modified and χ is now usually regarded as determining not only the heat of mixing through equation (57) as suggested earlier but also, in certain cases, the excess entropy of mixing term. The constant χ may therefore be written as

$$\chi = \chi_h + \chi_s \qquad (65)$$

where χ_h and χ_s are as defined as on p. 27.

From the values of the activities of the solvent in various polyglycol solutions at different temperatures given in Tables V, VI, VII and VIII, the values of χ have been calculated by making use of the expression

$$\ln a_1 = \ln \phi_1 + (1-\frac{1}{m})\phi_2 + \chi \phi_2^2 \qquad (58)$$

where m is the ratio of the partial molar volume of the solute to that of the solvent*. These values of χ computed from equation (58) are given in Tables XXX to XXXIII.

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*Since the changes in volume upon mixing of the polymer with a solvent are generally very small (as they are in the present case) it is customary to take the value of m as the ratio of the actual molar volume of the polymer to that of the solvent. The values of the molar volumes used in the present calculations are given in Table XXXIV.

TABLE XXX

The values of the polymer-solvent interaction constant for the polymer (M.W. 150) in methanol at different temperatures

Polymer weight fraction	Polymer volume fraction	Solvent volume fraction	$-\ln a_1$	Interaction constant χ	$\overline{\Delta H}_1$ (Cal. mole^{-1})
Temperature 25°C.					
0.2374	0.2009	0.7991	0.0736	0.15	4
0.3061	0.2510	0.7490	0.1005	0.13	5
0.5023	0.4338	0.5662	0.2284	0.15	16
Temperature 15°C.					
0.1511	0.1211	0.8789	0.0388	0.18	2
0.2012	0.1623	0.8377	0.0406	0.17	3
0.2367	0.2030	0.7970	0.0741	0.15	4
0.3047	0.2521	0.7479	0.1085	0.00	0
0.3911	0.3306	0.6694	0.1468	0.07	9
0.5007	0.7372	0.5628	0.2303	0.15	16
Temperature 0°C.					
0.1504	0.1216	0.8784	0.0376	0.25	2
0.2367	0.2146	0.7954	0.0754	0.15	2
0.3035	0.2541	0.7459	0.1016	0.11	4
0.4993	0.4380	0.5620	0.2317	0.14	15
Temperature -10°C.					
0.1502	0.1217	0.8783	0.0361	0.36	3
0.2360	0.2050	0.7950	0.0739	0.15	4
0.3032	0.2543	0.7459	0.1015	0.11	4
0.4989	0.4384	0.5616	0.2294	0.15	16
Temperature -25°C.					
0.1500	0.1225	0.8775	0.0324	0.58	5
0.2359	0.2062	0.7938	0.0735	0.16	4
0.3029	0.2556	0.7444	0.1014	0.11	4
0.4987	0.4410	0.5590	0.2228	0.18	21

TABLE XXXI

The values of the polymer-solvent interaction constant for the polymer (M.W. 1120) in methanol at different temperatures

Polymer weight fraction	Polymer volume fraction	Solvent volume fraction	$-\ln a_1$	Interaction constant χ	$\overline{\Delta H}_1$ Cal. mole^{-1}
Temperature 25° C.					
0.1251	0.0995	0.9005	0.0048	0.47	3
0.2182	0.1771	0.8229	0.0096	0.46	8
0.3554	0.2986	0.7014	0.0297	0.42	21
0.5433	0.4787	0.5213	0.0687	0.53	70
Temperature 15° C.					
0.1172	0.0941	0.9059	0.0052	0.33	2
0.1614	0.1308	0.8692	0.0078	0.39	4
0.2416	0.1995	0.8005	0.0137	0.43	10
0.3536	0.2998	0.7002	0.0282	0.44	22
0.4636	0.4033	0.5967	0.0690	0.44	57
Temperature 0° C.					
0.1239	0.1009	0.8991	0.0059	0.32	2
0.2160	0.1796	0.8204	0.0112	0.42	8
0.3522	0.3016	0.6984	0.0280	0.44	23
0.5382	0.4807	0.5193	0.0686	0.53	71
Temperature -10° C.					
0.1237	0.1011	0.8989	0.0056	0.33	2
0.2157	0.1797	0.8203	0.0113	0.42	8
0.3518	0.3017	0.6983	0.0279	0.44	23
0.5375	0.4805	0.5195	0.0680	0.54	71
Temperature -25° C.					
0.1236	0.1015	0.8985	0.0055	0.40	2
0.2155	0.1805	0.8195	0.0113	0.42	8
0.3515	0.3029	0.6981	0.0276	0.45	23
0.5370	0.4818	0.5182	0.0673	0.54	72

TABLE XXXII

The values of the polymer-solvent interaction constant for the polymer (M.W. 1955) in methanol at different temperatures

Polymer weight fraction	Polymer volume fraction	Solvent volume fraction	$-\ln a_1$	Interaction constant χ	$\overline{\Delta H}_1$ Cal. mole^{-1}
Temperature 25° C.					
0.1307	0.1043	0.8957	0.0027	0.56	3
0.1790	0.1439	0.8561	0.0040	0.51	6
0.3463	0.2904	0.7096	0.0147	0.52	25
0.5284	0.4641	0.5359	0.0424	0.59	73
Temperature 15° C.					
0.1187	0.0952	0.9048	0.0028	0.42	2
0.1553	0.1254	0.8746	0.0041	0.49	4
0.2456	0.2021	0.7979	0.0087	0.47	11
0.3445	0.2915	0.7085	0.0154	0.52	25
0.4627	0.4027	0.5972	0.0290	0.57	53
0.5259	0.4688	0.5312	0.0425	0.60	75
Temperature 0° C.					
0.1298	0.1063	0.8937	0.0034	0.49	3
0.1779	0.1468	0.8532	0.0049	0.47	6
0.3431	0.2936	0.7064	0.0150	0.52	16
0.5259	0.4688	0.5312	0.0425	0.60	75
Temperature -10° C.					
0.1296	0.1061	0.8939	0.0037	0.39	2
0.1777	0.1472	0.8528	0.0048	0.47	6
0.3428	0.2939	0.7061	0.0144	0.53	26
0.5256	0.4693	0.5307	0.0412	0.60	76
Temperature -25° C.					
0.1295	0.1068	0.8932	0.0040	0.40	3
0.1776	0.1478	0.8522	0.0048	0.47	6
0.3424	0.2950	0.7050	0.0144	0.53	26
0.5253	0.4683	0.5317	0.0377	0.62	77

TABLE XXXIII

The values of the polymer-solvent interaction constant for the polymer (M.W. 3350) in methanol at different temperatures

Polymer weight fraction	Polymer volume fraction	Solvent volume fraction	$-\ln a_1$	Interaction constant χ	$\overline{\Delta H}_1$ Cal. mole^{-1}
Temperature 25° C.					
0.1167	0.0932	0.9068	0.0005	0.59	3
0.2123	0.1724	0.8276	0.0045	0.49	8
0.3035	0.2514	0.7486	0.0075	0.49	19
0.4575	0.3943	0.6057	0.0216	0.58	52
Temperature 15° C.					
0.1159	0.0931	0.9069	0.0014	0.49	2
0.1359	0.1097	0.8903	0.0021	0.52	4
0.2110	0.1756	0.8244	0.0045	0.49	9
0.3020	0.2550	0.7439	0.0082	0.53	20
0.4102	0.3517	0.6483	0.0146	0.58	41
0.4553	0.3990	0.6010	0.0220	0.58	53
Temperature 0° C.					
0.1155	0.0945	0.9055	0.0016	0.54	3
0.2101	0.1744	0.8256	0.0048	0.48	8
0.3007	0.2550	0.7450	0.0089	0.52	19
0.4534	0.3977	0.6023	0.0215	0.59	52
Temperature -10° C.					
0.1153	0.0941	0.9059	0.0016	0.43	2
0.2098	0.1749	0.8251	0.0048	0.48	8
0.3004	0.2551	0.7449	0.0088	0.52	19
0.4529	0.3981	0.6019	0.0209	0.59	53
Temperature -25° C.					
0.1151	0.0947	0.9053	0.0018	0.49	2
0.2096	0.1761	0.8239	0.0058	0.52	9
0.3001	0.2566	0.7434	0.0094	0.51	19
0.4525	0.3994	0.6006	0.0203	0.60	54

TABLE XXXIV

The molar volumes of polymers and methanol at different temperatures

Temperature	The molar volumes of				
°C	Polymer M. W. 150	Polymer M. W. 1120	Polymer M. W. 1955	Polymer M. W. 3350	Methanol
25	147	1119	1955	3350	41.4
15	146	1111	1942	3330	40.6
0	145	1098	1920	3292	39.5
-10	144	1090	1906	3271	39.1
-25	142	1078	1885	3237	38.4

The values of the interaction constant obtained for the various polymer-solvent systems show some spread since the calculation is rather sensitive to small uncertainties in a_1 but nevertheless these χ values show a significant dependence upon concentration and a marked dependence on the molecular weights of the polymers. The smoothed values of χ are plotted in Figure 15 as a function of temperature at the highest concentration of each polymer in the methanolic solutions. The values of χ at 15°C. are plotted in Figure 16 as a function of the molecular weight for various constant values of ϕ_2.

Values of χ in excess of about 0.5 have usually been regarded as indicating non-compatibility of the solvent and polymer, i.e., mixtures of such components for which χ was greater than 0.5 would suffer separation into two phases because the free energy of mixing as given by equations (60) and (61) would then become positive. The values of χ for the higher molecular weight fractions studied in the present work range from 0.4 to 0.6 and must be considered unexpectedly high since the polypropylene glycols are completely miscible with methanol. This anomaly may however be understood when it is borne in mind that the χ values do not in fact determine in most cases only the ΔH_m term. It has already been shown that the polar character of both of the constituents of the systems gives rise to relatively large negative excess entropies of mixing when the latter are calculated in

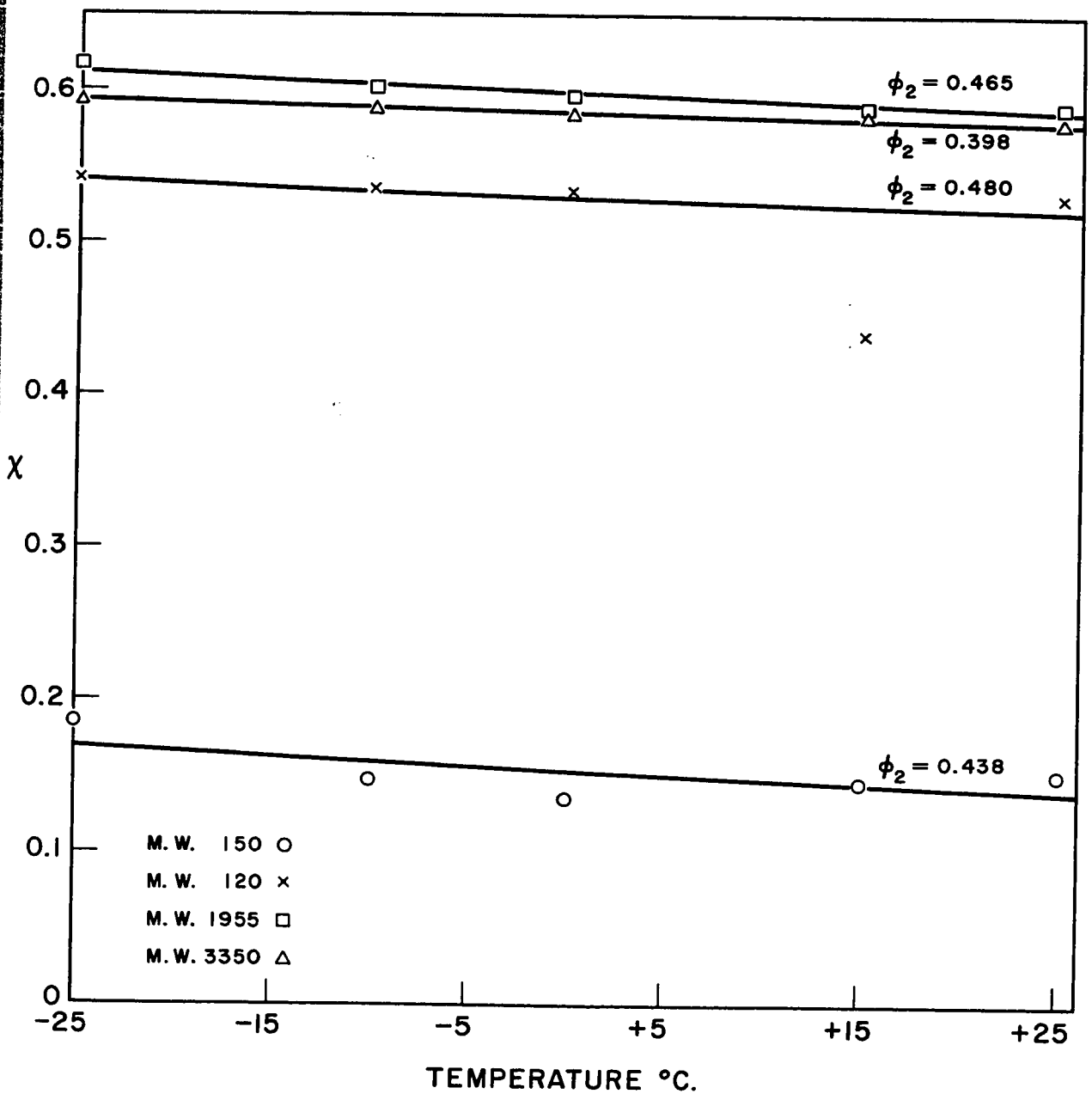

FIG. 15. χ AS A FUNCTION OF TEMPERATURE FOR CONSTANT VOLUME FRACTIONS OF THE VARIOUS POLYMERS IN METHANOL.

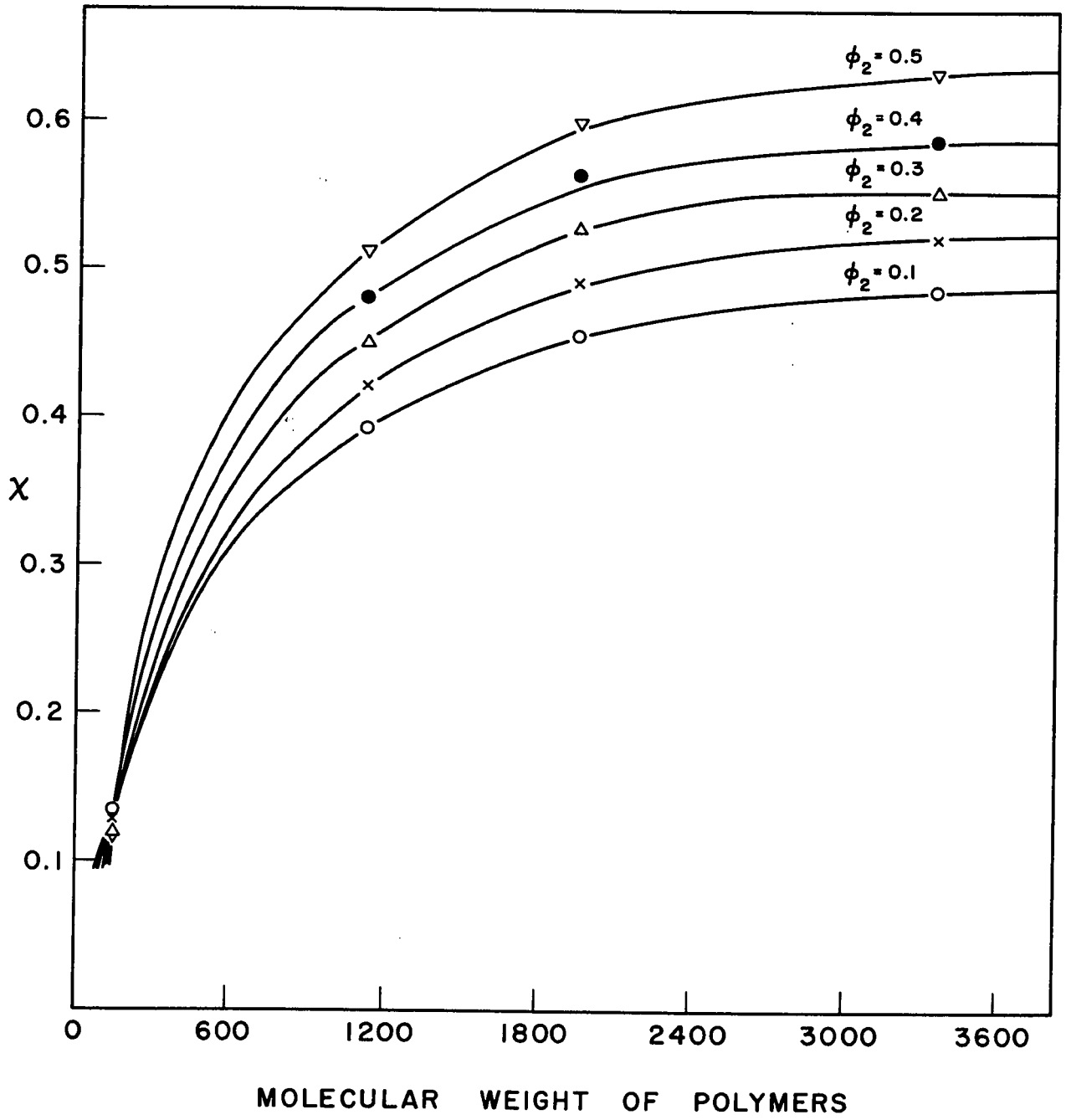

FIG. 16. χ AS A FUNCTION OF THE MOLECULAR WEIGHT OF POLYMERS AT DIFFERENT VOLUME FRACTIONS OF POLYMERS AT 15°C.

terms of volume fractions. This means that the entropies of mixing for the systems studied are in fact not given simply by the expression

$$\Delta S_m = -R \Sigma_i x_i \ln \phi_i \quad . \qquad (117)$$

Use of equation (60) for the evaluation of χ implies that the expression (117) accounts for the configurational free energy of mixing. If, as suggested above, it does not, then any deviations of the actual entropy of mixing from that given by the above term will appear in the value of χ. The constant χ will then be a parameter not only determining the enthalpy of interaction of the components in the solutions but reflecting deviations of the actual entropy of mixing from the theoretical configurational entropy of random mixing given by the equation (117) above. This may be shown more rigorously as follows:

When the contribution of the entropy of mixing to the experimentally determined free energy of mixing ΔG_m differs from the athermal values given by equation (117) we may write equation (60) in the form

$$\Delta G_m^E = RT \Sigma_i x_i \ln \phi_i - T\Delta S_m^E(a) + \Delta H_m \qquad (118)$$

but ΔH_m may be written as

$$\Delta H_m = \chi_h B \qquad (119)$$

where $B = RT\, n_1 \phi_2$.

Hence

$$\Delta G = RT \Sigma_i x_i \ln \phi_i + \chi_h B - T\Delta S_m^E(a). \qquad (120)$$

If we write the over-all values of χ determined directly from equation (60) as $\chi_h + \chi_s$, it follows that

$$\chi = \chi_h + \chi_s = \chi_h - T\Delta S_m^E(a)/B, \qquad (121)$$

so that when the excess entropy of mixing is negative there is a positive entropy contribution to χ. In the present case for the polymers of lower molecular weights, ΔH_m is negative but χ as deduced from the Flory-Huggins equation is positive. χ_h in equation (65) must hence be negative and the fact that the over-all χ is apparently positive must indicate that the entropy contribution to χ is positive and larger than $-\chi_h$ for exothermic mixing. That this is so follows from the argument given above, since the excess entropies of mixing (referred to the athermal entropies of mixing for the systems considered) are negative for the polymers of molecular weights 150 and 1120 as shown in Table XXVIII.

Also, directly from the vapour pressure data it is apparent that $\overline{\Delta H_1}$ is very small. However,

$$\overline{\Delta H_1} = RT \chi \phi_2 \qquad (57)$$

and if the values of χ deduced above are used to evaluate $\overline{\Delta H_1}$

(see Tables XXX and XXXIII) it is seen that relatively large values of this thermodynamic function are obtained. This again indicates that there is an important entropy contribution in the values of χ calculated, probably arising from the orientation effects discussed above. For other polar systems [e.g., polystyrene-methyl-ethyl-ketone and mixtures of a silicone with benzene (68)] similar conclusions have been reached.

In the case of the polymer of molecular weight 150, the heat of mixing (actually negative in this case) is significantly less than that for the higher molecular weight fractions where ΔH_m is positive, and the excess entropy of mixing calculated on the site or volume fraction basis is also smaller (more negative). These effects combine to give a lower value of χ than for the higher molecular weight fractions. At the same time it may be observed that, from general chemical considerations, χ may be expected to be lower for the fraction of molecular weight 150 than for those of higher molecular weights owing to the greater proportion of terminal hydroxyl groups per unit weight of the material. These groups will be responsible for stronger interactions with the hydroxylic groups on the solvent molecules and hence lead to greater compatibility (i.e., lower χ) of the polymer with the solvent.

3. [illegible]

From the general lattice theory of polymer solutions (41), i.e. ease Huggins' theory modified by Miller's and

considerations in Guggenheim's treatment (41, p. 83), the value of the partial molar free energy can be shown to be given by the expression

$$\frac{\Delta\mu_1}{RT} = \ln \Theta_1 + \frac{1}{2} z \ln \left(\frac{1 - K\chi_2}{\Theta_1} \right) \qquad (122)$$

where z is, as usual, the coordination number and K is given by

$$1 - K = K^2 \chi_1 \chi_2 \left(e^{2w/RT} - 1 \right) \qquad (123)$$

and other quantitites in equation (123) have been defined previously. From the inference of specific orientation discussed above and from the sizes of the molecules concerned, it is hard to believe that z could have a value greater than six. Accordingly some estimate of the probable values of w for polyglycol systems can be obtained from equations (122) and (123) using values of z of this magnitude. Since we have no <u>à priori</u> knowledge of the value of z, two sets of calculations have been made by taking z equal to the reasonable values of six and four in order to examine how w depends on the composition of the solution and the molecular weight of the polymers. Steps in a typical calculation of K in equation (122) have been illustrated in Table XXXV. The values of w then obtained from the values of K using equation (123) for z equal to six and z equal to four are given in Tables XXXVI and XXXVII, respectively. Except in a few cases the values of w are found to be positive. It is then

possible to obtain the values of the heat of mixing ΔH_m from the expression

$$\Delta H_m = z.w.\ \xi_1.\ \xi_2.\ (x_1 - q\, x_2) \qquad (124)$$

and these values are also given in Tables XXXVI and XXXVII. The values of w and ΔH_m have also been calculated on the basis of the volume fractions from the equations

$$\frac{\Delta\mu_1}{RT} = \ln \phi_1 + \frac{1}{2}\, z \ln \left(\frac{1-K\xi_2'}{\phi_1}\right) \qquad (125)$$

and

$$1 - K = K^2.\ \xi_1'\ \xi_2'\ (e^{2w/RT} - 1) \qquad (126)$$

which correspond to equations (122) and (123) written in terms of site fractions; the results are given in Tables XXXVIII and XXXIX for z = 6 and z = 4, respectively.

The values of w*, although fairly constant for each polymer system, show a small dependence on ϕ_1. The equations (122) and (125) appear to be inadequate for the description of two of the polymer-methanol systems since in the case of the polymers of M.W. 150 and 1120 the values of ΔH_m are negative while the corresponding values of w are for the most part positive. The values of ΔH_m in Tables XIII and XIV also lead to the same

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* The values of w calculated (Tables XXXVI to XXXIX) sometimes show an erratic dependence upon concentration of the polymers. This is because w depends very sensitively upon 1 - K in equations (123) and (126) and K is always very near to unity.

TABLE XXXV

Calculations of K from equation (122) in the case of solutions of polymer (M.W. 1955) in methanol at 15°C.

$\ln \theta_1$	ξ_2	$-\Delta\mu_1/RT$	$\ln(1-K\xi_2)$	$1-K\xi_2$	$K\xi_2$	K
0.0701	0.0360	0.0028	0.0364	0.9642	0.0358	0.994
0.0944	0.0485	0.0041	0.0492	0.9520	0.0480	0.990
0.1611	0.0826	0.0087	0.0849	0.9186	0.0814	0.985
0.2500	0.1276	0.0154	0.1327	0.8758	0.1242	0.973
0.3820	0.1933	0.0290	0.2055	0.8143	0.1857	0.961
0.4773	0.2365	0.0430	0.2601	0.7710	0.2290	0.968

Note:- In the case of these solutions, parameters s, r and q involved in equation (122) and in ξ_2 have been taken as 4, 33 and 17, respectively.

TABLE XXXVI

The values of the interchange energy w for the various polymer-methanol systems, calculated on the basis of site fractionswith coordination number z equal to six

χ_2	K	ΔH_m Cal. mole^{-1}	w Cal. mole^{-1}
Polymer (M.W. 150)			
0.0710	1.001	-2	-4
0.0970	0.959	62	118
0.1238	1.007	-13	-19
0.1830	0.930	124	124
0.2763	0.962	69	53
0.4068	0.952	93	57
Polymer (M.W. 1120)			
0.0470	1.000	0	0
0.0667	0.999	2	5
0.1058	0.991	16	26
0.1690	0.989	22	22
0.2430	0.974	62	40
0.3019	0.977	55	31
Polymer (M.W. 1955)			
0.0468	0.994	10	36
0.0627	0.992	13	37
0.1056	0.989	20	32
0.1610	0.980	38	41
0.2392	0.971	61	45
0.2890	0.979	48	29
Polymer (M.W. 3350)			
0.0465	0.991	14	54
0.0554	0.989	19	56
0.0920	0.991	16	30
0.1407	0.977	42	52
0.2050	0.969	63	53
0.2399	0.967	70	51

TABLE XXXVII

The values of the interchange energy w for the various polymer-methanol systems, calculated on the basis of site fractions with coordination number z equal to four

ξ_2	K	ΔH_m Cal. mole^{-1}	w Cal. mole^{-1}
Polymer (M.W. 150)			
0.0628	1.004	-5	-20
0.0860	0.929	62	205
0.1100	1.015	-19	-46
0.1406	1.197	-153	-249
0.1936	1.217	-660	-798
0.2739	1.263	-565	-505
Polymer (M.W. 1120)			
0.0365	1.000	0	0
0.0521	0.962	49	173
0.0834	0.994	7	22
0.1352	0.993	9	17
0.1980	0.981	25	33
0.2496	0.977	33	35
Polymer (M.W. 1955)			
0.0360	0.994	7	46
0.0485	0.990	11	57
0.0826	0.985	17	53
0.1276	0.973	32	65
0.1933	0.961	50	69
0.2365	0.968	42	50
Polymer (M.W. 3350)			
0.0342	1.023	-44	-313
0.0424	0.988	12	76
0.0714	0.985	17	60
0.1106	0.966	38	90
0.1639	0.952	57	93
0.1922	0.979	28	38

TABLE XXXVIII

The values of the interchange energy w for the various polymer-methanol systems, calculated on the basis of volume fractions with coordination number z equal to six

χ_2	K	ΔH_m Cal. mole^{-1}	w Cal. mole^{-1}
Polymer (M.W. 150)			
0.0947	0.995	8	16
0.1282	0.962	63	90
0.1621	0.995	9	10
0.2454	0.848	230	218
0.3432	0.790	337	261
0.4841	0.783	388	253
Polymer (M.W. 1120)			
0.0658	0.992	14	36
0.0927	0.989	19	36
0.1446	0.982	34	40
0.2252	0.962	78	60
0.3145	0.962	89	50
0.3820	0.935	162	78
Polymer (M.W. 1955)			
0.0662	0.986	23	60
0.0881	0.988	20	32
0.1458	0.975	47	55
0.2170	0.966	70	56
0.3123	0.958	109	62
0.3699	0.949	130	62
Polymer (M.W. 3350)			
0.0664	0.984	29	67
0.0763	0.988	21	46
0.1250	0.975	40	62
0.1876	0.966	66	61
0.2668	0.954	98	66
0.3081	0.951	113	65

TABLE XXXIX

The values of the interchange energy w for the various polymer-methanol systems, calculated on the basis of volume fractions with coordination number z equal to four

ξ_2	K	ΔH_m (Cal. mole^{-1})	w (Cal. mole^{-1})
Polymer (M.W. 150)			
0.0808	0.996	5	15
0.1101	0.936	62	159
0.1399	0.998	1	5
0.1771	1.021	-28	-43
0.2398	0.999	2	2
0.3316	1.024	-35	-31
Polymer (M.W. 1120)			
0.0511	0.990	11	55
0.0724	0.986	16	56
0.1144	0.976	28	64
0.1816	0.963	47	68
0.2595	0.947	74	77
0.3207	0.918	120	106
Polymer (M.W. 1955)			
0.0510	0.980	20	102
0.0682	0.982	20	74
0.1145	0.966	39	88
0.1736	0.950	61	93
0.2560	0.930	95	101
0.3079	0.924	111	100
Polymer (M.W. 3350)			
0.0475	1.017	-25	-129
0.0587	0.981	19	87
0.0976	0.964	39	104
0.1490	0.946	62	111
0.2162	0.928	92	115
0.2508	0.929	96	104

conclusion. It may therefore be appropriate to emphasise again that the lattice model as at present formulated is inadequate for a complete description of the properties of these polar systems. It appears that the lattice model is largely deficient in that it fails to determine the entropy changes which arise from the non-random mixing anticipated in polar systems. The theoretical equations formulated so far are based on the calculation of the configurational entropy changes for random mixing and it must be in the direction of evaluating non-random entropies of mixing that theoretical progress should be made, for example, as discussed by Tompa (97). The problem of solvent orientation near the polymer chain as well as that concerning restrictions on the configuration of the polymer segments requires further consideration. Quantitative treatment of such problems would be very complex since the calculations require knowledge of the structural network of the interacting units and it is not at the present time easy to set up the necessary partition functions in such a way as to obtain explicit theoretical equations free from empirical parameters (cf. 97).

4. SOME RHEOLOGICAL PROPERTIES OF POLYPROPYLENE GLYCOLS AND THEIR SOLUTIONS

A complementary approach to the study of polymer-solvent interaction is afforded by measurements of the viscosity of polymer solutions. The polymer-solvent interaction enters into the determination of the viscosity in three ways as

discussed below.

(i) The intrinsic viscosity is related to the molecular weight of the polymer according to expression (88) where the exponent 'a' depends on the molecular volume expansion factor α. The equation (88) may be written as

$$[\eta] = K' M^{1/2} \alpha^3 . \qquad (127)$$

The factor α is, in general, dependent on molecular weight and for a given polymer fraction depends upon the balance of intramolecular and polymer-solvent interactions. Its deviation from unity reflects non-idealities in the polymer solvent interaction.

(ii) The dependence of reduced viscosity upon concentration in the term k in the relationship (83) is related to the polymer-solvent interaction, and

(iii) The temperature dependence of viscosity of a given system is determined by the heat of activation $\Delta H^{\neq}$ for viscous flow in the solution or in the pure polymer. The quantity $\Delta H^{\neq}$ is determined by a fraction of the energy necessary to separate the molecules in a liquid to form a hole and then to move a neighbouring molecule into the hole. In a pure substance $\Delta H^{\neq}$ is related to the heat of vaporization and in a solution to the energy of interaction of the components.

A. Intrinsic Viscosities

In different solvents $[\eta]$ will in general vary because of the degree of expansion of the molecular random coil as determined by the constant α. In the case of the short chain polyglycols it is hardly likely that the random coil model will be applicable except for the higher molecular weight fractions and it is of interest to examine the value of the exponent in equation (127) for the short chain molecules. The relation between $[\eta]$ and M when the material is somewhat polydisperse takes the same form as that of equation (88) except that the weight average molecular weight should preferably be used in deriving a. The molecular weights determined by the analytical method described in Section II-1 are number average quantities and cannot be directly related to the corresponding weight average. The short chain materials used in the present work had already been fractionated into samples of various molecular weights. Further sub-fractionation in order to establish the molecular weight distribution is very difficult to achieve with the low molecular weight polyglycols. As in several other studies (86) on the behaviour of the polyglycols, the number average molecular weights have been used in relating $[\eta]$ to M, assuming* that the number average and weight average

* No serious error is involved in this assumption. Thus if the sample of molecular weight 150 was composed, for example, of 60% trimer and 40% dimer the number average molecular weight would differ by only 3.5% from the weight average molecular weight. Similar considerations apply to the fractions of higher molecular weight where the relative range of degrees of polymerization in a sample is likely to be much less than in the unfavourable case considered above.

molecular weights are not seriously different.

The reduced viscosity plots in Figure 12 lead to intrinsic viscosities which are not, within experimental error, recognizably dependent upon the solvent in the series methanol, ethanol and n-propanol*. This is not unexpected since most of the physical properties of these hydroxylic solvents are similar. In order to examine the dependence of $[\eta]$ for the polypropylene glycols upon molecular weight, the values of log $[\eta]$ (see Table XL) for each average molecular weight have been plotted against the logarithm of the molecular weight as shown in Figure 21. The estimated uncertainty in the values of log $[\eta]$ is indicated by the height of the vertical bars.

TABLE XL

Intrinsic viscosities of the polymers in ethanol

Polymer Mol. Wt.	$[\eta]$	Log$[\eta]$	Log M	a
150	0.019	-1.72	2.17	0.37
425	0.025	-1.60	2.62	0.41
1955	0.059	-1.23	3.29	0.56
3350	0.084	-1.07	3.53	0.62

By taking tangents to the curve in Figure 21 at the appropriate values of log M the exponent a has been evaluated.

* It should be noted that on account of the unusually low molecular weights of the polymers studied in the present work, it is impossible to obtain the same degree of accuracy in measurements of relative viscosities at high dilutions as is possible with polymers in the more usual range of molecular weights (>50,000).

Values of a obtained by this procedure are listed in Table XL and it is seen that a varies from about 0.37 for the lowest fraction to the more usual value of 0.5 to 0.6 for the higher fractions. Notwithstanding the small uncertainties in the values of log $[\eta]$, the change of a with increasing molecular weight (see Figure 21) appears to be significant. A similar variation of a with increasing chain length in the case of polyethylene glycols in benzene has also been reported recently by Sadron and Rempp (86) who have suggested that an empirical equation of the form

$$[\eta] = A + K M^a$$

would represent their results better than the more usual equation

$$[\eta] = K M^a .$$

Two possible reasons for this change in values of a may now be considered.

(i) The chemical nature of the polymers is effectively changing with increasing molecular weight since the end-group units comprise a 'fraction' of the molecule which is relatively large but which decreases in inverse proportion to the molecular weight of the polymer.

(ii) The fact that a decreases with decreasing molecular weight of the polymer implies that the values of $[\eta]$ for the low molecular weight fractions are larger than they would be if a were 0.5 - 0.6 for all the fractions. It appears that this trend of values of $[\eta]$ arises because the distribution of segments in

the 'random' coil can no longer be reasonably assumed to be Gaussian when the molecule is only a few segments long. A value of a equal to 0.5 arises only if it can be assumed that the random coil may be represented by an hydrodynamically equivalent sphere (68) having a radius proportional to the square root of the molecular weight of the polymer chain. As the chain becomes very short and the segment distribution less Gaussian, the particle will be represented more correctly by an equivalent ellipsoid than by an equivalent sphere. For a given volume of the particle, the equivalent ellipsoid has a larger hydrodynamic frictional coefficient than that of the sphere (101), so that $[\eta]$ would tend to become relatively larger than if the spherical random coil model was applicable down to very short chain lengths. Such a direction of change of $[\eta]$ is indicated by the experimental results as shown in Figure 21.

B. Activation Energy for the Flow Process

Information on molecular interaction in the pure polymers can best be obtained from viscosity determinations by measurements of the temperature dependence of viscosity, which then enables the heat, free energy and entropy of activation for the flow process to be derived. These quantities are determined by the manner in which the molecule or its segments interact with other similar molecules or segments.

The heats of activation for viscous flow in the pure polymers have been deduced from the temperature dependence of the

viscosities of the various fractions. $\Delta H^{\neq}$ as a function of molecular weight is shown in Figure 20. It is apparent that substantially higher values of $\Delta H^{\neq}$ are to be observed with the low molecular weight fractions than with the higher molecular weight materials (see Table XLI). This is the converse of what is generally found (102), namely that $\Delta H^{\neq}$ is either approximately constant or increases with increasing molecular weight, e.g., in the series of polyesters studied by Flory (103). The results shown in Figure 20 suggest that the hydroxylic end-groups play an important role in determining the viscous properties of these polymer fractions, probably owing to association effects through the formation of hydrogen bonds. Thus it appears that more hydrogen bonds have to be broken for the flow of molecules of low molecular weight than for those of higher molecular weight. The site fraction of terminal OH groups in the lower molecular weight fractions is clearly much larger than that in the higher fractions, where sections of the molecule can evidently move with less dissociation of hydrogen bonds. It is of interest to calculate the free energy and entropy of activation for viscous flow in the pure polymers. The mobile segment in polyesters contains about 30 chain atoms, i.e.,has a molecular weight of about 400. In the polypropylene glycols (where the molecular weight of the monomer unit equals 58) it is hence likely that at least for the fractions of molecular weight 150 and 425, the whole molecule is the flow unit. We can then calculate $\Delta G^{\neq}$ for

TABLE XLI

The heat of activation for viscous flow in the pure polypropylene glycol polymers and in the pure solvents (methanol, ethanol and n-propanol) at 15° C.

Molecular Wt.	$\Delta H^{\neq}_{visc.}$ Kcal. mole^{-1}.
150	13.24
425	12.74
1120	11.12
1955	10.64
3350	10.13
Methanol*	2.65
Ethanol*	3.20
n-Propanol*	4.56

* The values of $\Delta H^{\neq}_{visc.}$ for these solvents have been calculated from viscosity data given by various workers at different temperatures and summarised in the Handbook of Chemistry and Physics, 39th Edition.

the activation process from the rate equation (89), assuming that the volume of the flow segment is equal to the molar volume. It is also of interest to calculate $\Delta G^{\neq}$ for the fractions 1120 and 1955 using the data given in Table XXVI for the viscosities of these fractions. With the values of $\Delta H^{\neq}$ given in Figure 20, $\Delta S^{\neq}$ can be estimated. The values of the various thermodynamic functions for activation in the flow process are given below in Table XLII.

TABLE XLII

Apparent thermodynamic quantities for the activation process in viscous flow of the pure polypropylene glycols

Mol. Wt.	$\Delta G^{\neq}$ (T °C.) (Kcal. mole^{-1})	$\Delta H^{\neq}$ (Kcal. mole^{-1})	$\Delta S^{\neq}$ (T °C.) (Kcal. mole^{-1})
150	5.5 (45.1)	13.2	24 (45.1) 24 (8.8)
425	6.7 (45.2)	12.7	19 (45.2)
1120	7.3 (43.4)	11.1	12.1 (43.4)
1955	8.1 (49.3)	10.6	7.8 (49.3)
3350	9.2 (63.0)	10.1	2.9 (63.0)

Note:- The values of $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are accurate to about ± 2 percent.

$\Delta S^{\neq}$ decreases with increasing molecular weight in the case of the fractions of molecular weight 150 and 425. The further apparent decrease with increasing molecular weight up to 3350 is more ambiguous since we can perhaps no longer assume that the

whole molecule is the flow segment in these higher fractions. However, if the flow unit in the 1955 fraction was as small as the polymer molecule of molecular weight 425, $\Delta S^{\neq}$ would still be only 11 e.u., i.e., substantially less than that actually found for the 425 fraction assuming (more justifiably) that for this fraction almost the whole molecule is the flow unit. There thus appears to be a real decrease of $\Delta S^{\neq}$ with increasing molecular weight. This could be understood if there were a greater degree of structure in the more hydrogen bonded fractions of lower molecular weight. The activation process would then require a relatively larger increase in entropy than in cases where the initial state was already less ordered. In this respect the behaviour of these polymers resembles that of the alcohols, and H_2O and D_2O, where positive entropies of activation are found for molecular relaxation, greater values of $\Delta S^{\neq}$ being found with the "more ordered" liquids, e.g., in the cases of the pairs D_2O and H_2O, and H_2O and CH_3OH (104).

It is of interest to examine these results for the entropy of activation in relation to the excess entropies of mixing given in Table XXVIII. If the lower molecular weight polymers have a larger degree of hydrogen bonded structure than that in the higher fractions, we may anticipate that on mixing of the polymer with the solvent, some of the 'structural' negative entropy (due to hydrogen - bond 'cross-linking') will be lost. The excess entropy of mixing would then be larger on a

TABLE XLIII

The values of heat of activation ($\Delta H^{\neq}$) for viscous flow of polymer solutions at 15°C.

Molecular weight of polymer		Values of $\Delta H^{\neq}$ at different concentrations of the polymers in alcohols (Kcal. mole^{-1})				
Solutions in methanol						
150	Conc.	12.36	35.22	59.92	70.86	
	$\Delta H^{\neq}$	2.8	3.4	4.9	6.8	
425	Conc.	12.30	35.11	55.80	74.66	
	$\Delta H^{\neq}$	2.4	3.4	4.2	7.0	
1120	Conc.	12.30	35.11	55.80	74.66	
	$\Delta H^{\neq}$	3.4	3.3	4.4	6.2	
1955	Conc.	11.18	32.71	56.87	70.79	
	$\Delta H^{\neq}$	2.8	3.4	4.5	6.4	
3350	Conc.	20.16	33.78	55.97		
	$\Delta H^{\neq}$	3.0	3.5	5.5		
Solutions in ethanol						
150	Conc.	5.11	10.78	28.25	48.86	68.08
	$\Delta H^{\neq}$	3.4	3.6	4.3	5.2	7.0
425	Conc.	5.27	10.78	31.66	51.56	78.51
	$\Delta H^{\neq}$	3.4	3.5	4.3	5.1	8.4
1955	Conc.	4.96	9.20	31.73	50.99	66.18
	$\Delta H^{\neq}$	3.7	4.0	4.8	5.7	6.8
3350	Conc.	5.76	12.19	30.52	51.45	70.71
	$\Delta H^{\neq}$	4.0	4.1	4.5	5.9	7.2
Solutions in n-propanol						
1955	Conc.	4.32	12.83	28.95	48.41	69.02
	$\Delta H^{\neq}$	4.5	4.5	5.0	6.1	7.2
3350	Conc.	4.01	12.23	29.41	50.70	69.51
	$\Delta H^{\neq}$	4.4	4.5	5.3	5.8	7.3

Notes:- 1. The concentrations given above are expressed in g. per 100 g. of the solutions.

2. The values of $\Delta H^{\neq}$ given above are obtained from the Arrhenius plots similar to that shown in Figure 13.

volume (or weight) fraction basis for the more hydrogen bonded, lower molecular weight polymers, than for the higher molecular weight fractions. The thermodynamic results for $T\Delta S_m^E$ in Table XXVIII, calculated on the basis of site or volume fractions, lend support to this view, since the value of $T\Delta S_m^E$ for the fraction of molecular weight 150 is significantly less negative than the corresponding values for the higher fractions.

Since the above results for the pure polymers appeared to be related to the molecular structure or fraction of polar end-groups in the polymers, it was considered that similar studies on solutions of the polymers in alcoholic solvents might be of interest. The free energy of activation for flow in ideal mixtures is related to the corresponding values for flow in the pure components by equation (93); if the mixture is non-ideal the relationship corresponding to equation (93) is equation (95) which may be written in terms of the corresponding heats and entropies of activation and the heat of mixing. The activation energies for the flow process in solutions of the polymers of various molecular weights in the alcoholic solvents are shown as a function of composition in Figures 17, 18 and 19, and recorded in Table XLIII. It is clear from the behaviour observed (Figures 17, 18 and 19) and from the data on the heats of mixing (Tables XIII and XIV) that even for the solutions of the low molecular weight fractions equation (95) does not represent the

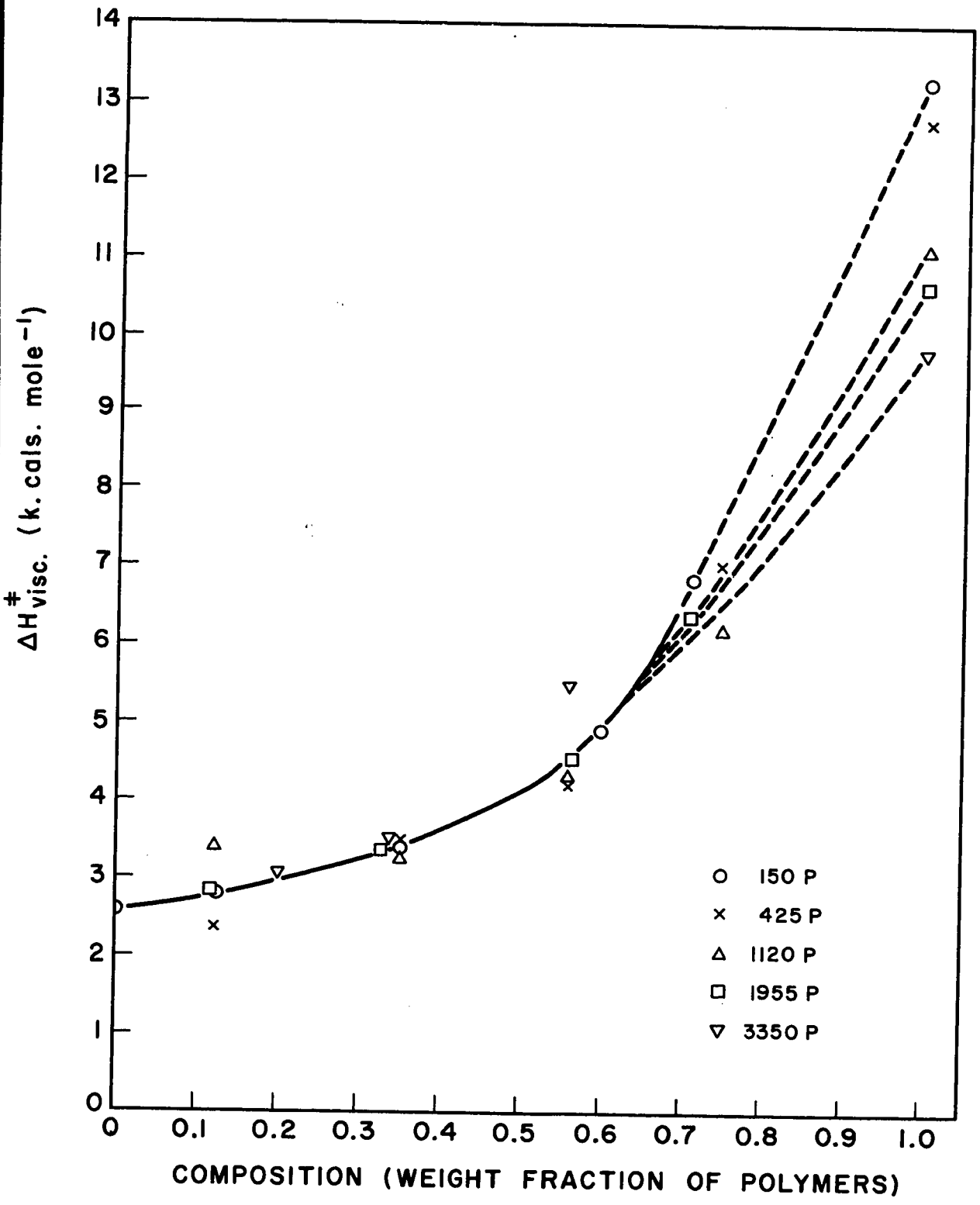

FIG. 17. HEAT OF ACTIVATION FOR VISCOSITY AS A FUNCTION OF COMPOSITION, FOR THE POLYMER-METHANOL SYSTEMS.

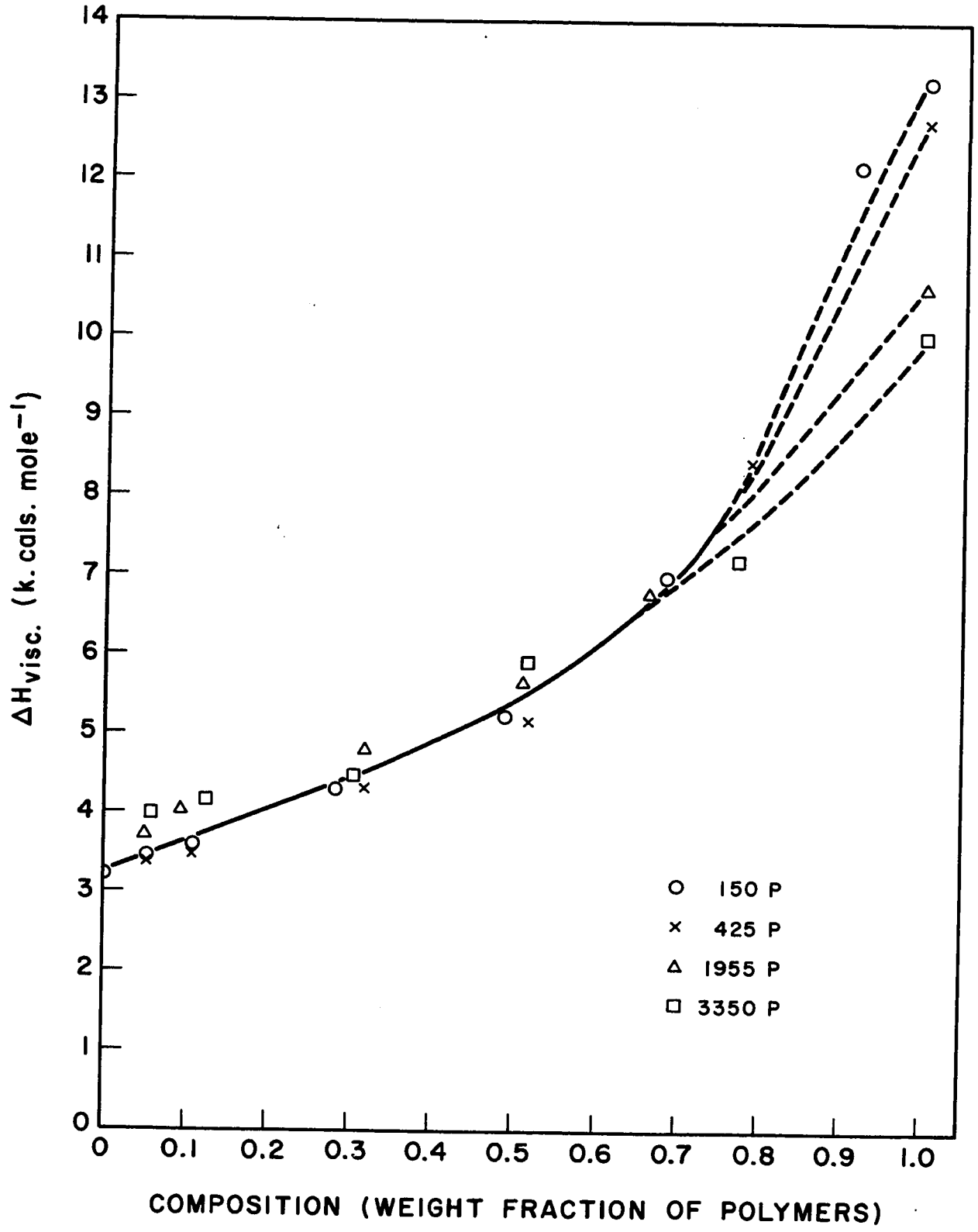

FIG. 18. HEAT OF ACTIVATION FOR VISCOSITY AS A FUNCTION OF COMPOSITION, FOR THE POLYMER-ETHANOL SYSTEMS.

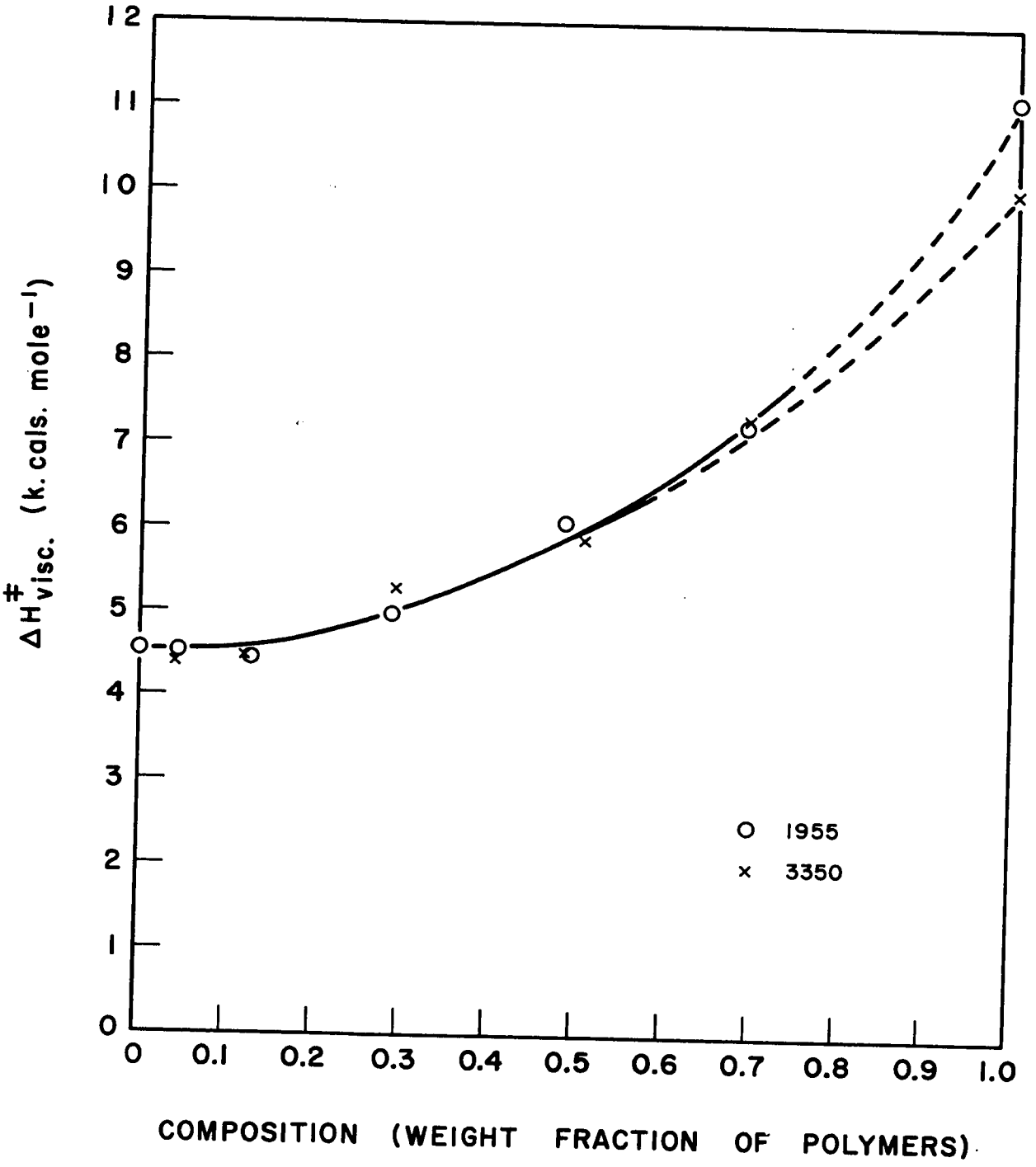

FIG. 19. HEAT OF ACTIVATION FOR VISCOSITY AS A FUNCTION OF COMPOSITION, FOR THE POLYMER-n-PROPANOL SYSTEMS.

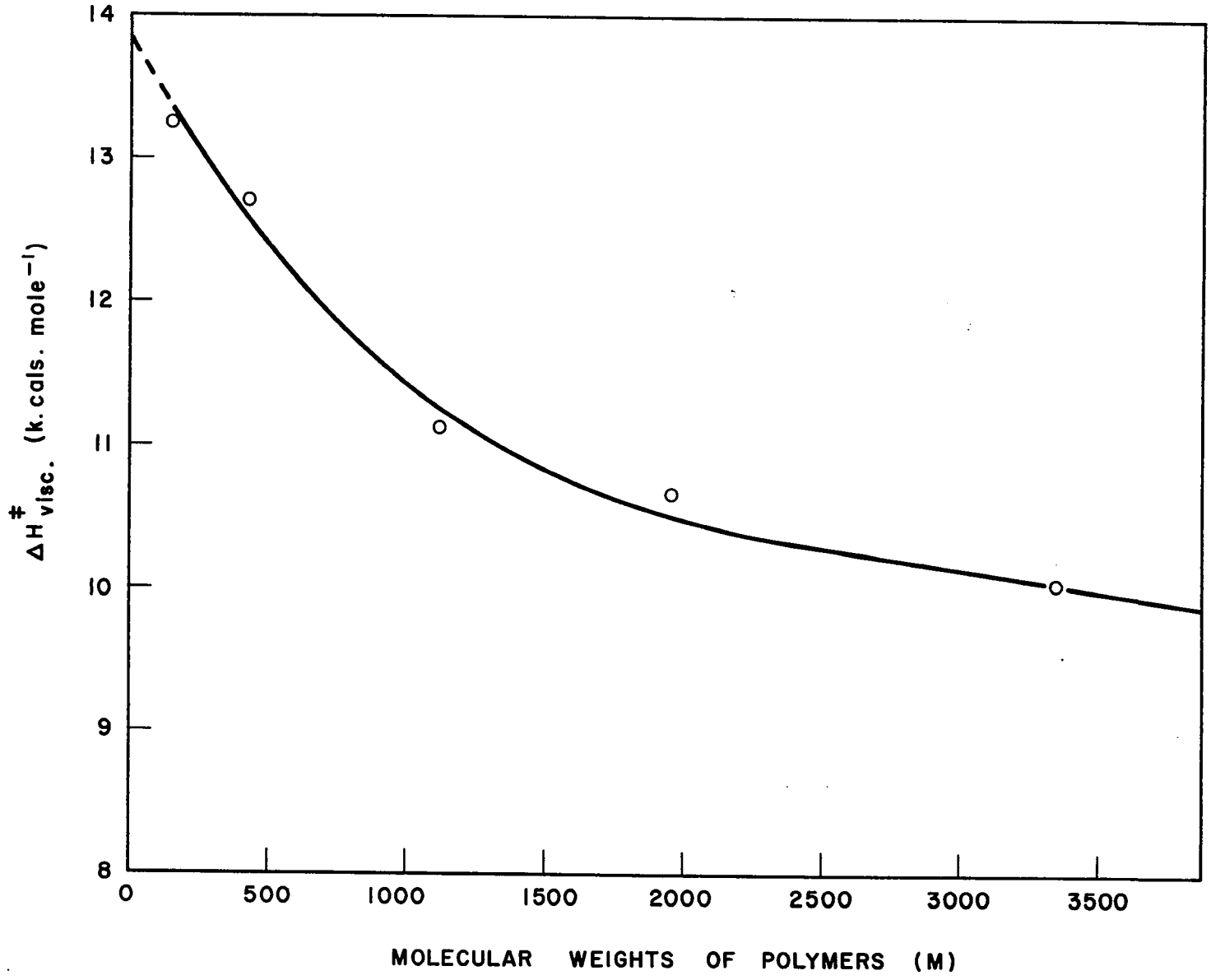

FIG. 20. HEAT OF ACTIVATION FOR VISCOSITY OF PURE POLYMERS AS A FUNCTION OF THEIR MOLECULAR WEIGHT.

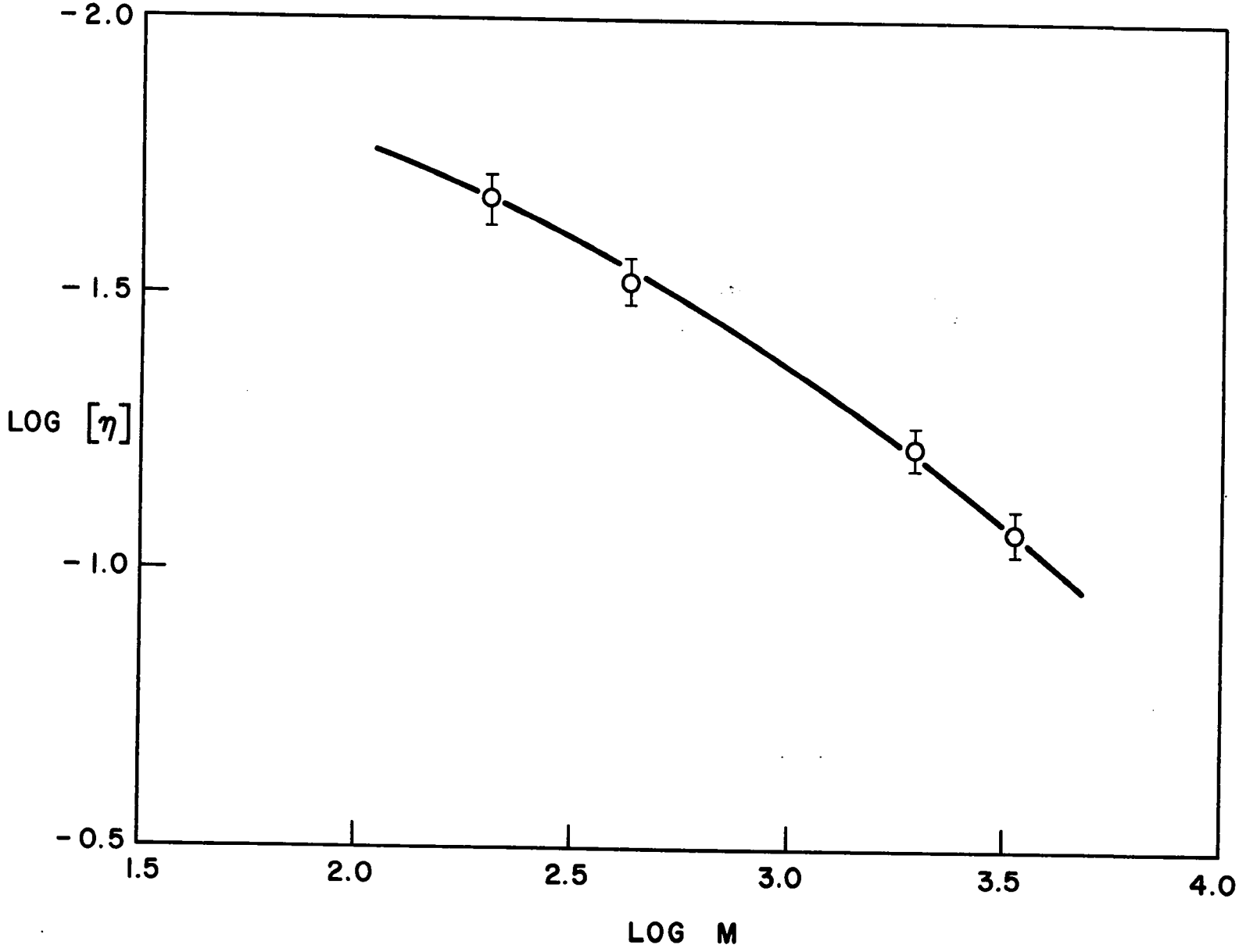

FIG. 21. PLOT OF THE LOGARITHM OF THE INTRINSIC VISCOSITIES OF THE POLYMERS AGAINST LOGARITHM OF MOLECULAR WEIGHTS OF THE POLYMERS.

results very satisfactorily, since deviations from proportional additivity in the heats of activation are much larger than the heat of mixing. It appears that the inter-polymer hydrogen bonding, which leads to a dependence of $\Delta H^{\neq}$ upon molecular weight in the case of the pure polymers, is swamped in dilute alcoholic solutions by interactions with the more plentiful hydroxyl groups on the solvent molecules.

Some conclusions concerning the interpretation of the values of the heats of mixing may also be made in relation to the values of $\Delta H^{\neq}$. In general for relatively low concentrations of polymer, the heat of mixing is negative for the low molecular weight fractions but increasingly positive for the higher fractions particularly at higher polymer concentrations. For the pure low molecular weight polymers, the values of $\Delta H^{\neq}$ have indicated more hydrogen bonding than in the higher fractions. The restrictions imposed on the interaction between the hydroxylic end-groups because of the length of polymer chain separating them could lead to a smaller chance of hydrogen bonding per OH group on the polymers than is possible between OH groups on the smaller methanolic solvent molecules. However, when such low molecular weight polymers are dissolved in methanol, the end-groups can now be "solvated" with less restriction by the excess of smaller solvent molecules so that more hydrogen bonds could on the average be formed. This could account for the higher exothermic heat of

mixing of the lower than the higher polymers with methanol. For the higher molecular weight fractions, the rôle of terminal OH groups in determining $\Delta H^{\neq}$ and also probably the heat of mixing, is less for a given weight fraction of the polymer. However, a bigger rôle will now be played by the chain atoms (particularly ether oxygens) in making new bonds between the solvent molecules and the polymer backbone at the expense of solvent-solvent hydrogen bonds. It has been indicated previously (p.122) that this could lead to a net decrease in the number of hydrogen bonds in the system and hence to more endothermic mixing as tends to occur with increasing molecular weight of the polymers (see Figure 9).

IV. CLAIMS TO ORIGINAL RESEARCH

1. The differential manometer devised by Puddington has been improved in various ways.
2. Differential vapour pressure measurements for the polypropylene glycol-methanol systems have been made.
3. Measurements of the vapour pressures of these systems have been made over a range of temperatures including relatively low temperatures.
4. Heats of mixing for these systems have been determined.
5. Activities of both the solvent and the polymers have been evaluated.
6. A semi-empirical method of calculating the solute activities using the Gibbs-Duhem equation has been developed.
7. The free energies and the entropies of mixing have been calculated for these systems.
8. The molecular weight dependence of all thermodynamic functions have been evaluated in all these systems.
9. The excess thermodynamic functions for the systems have been determined and an interpretation of the results suggested.
10. Orientation effects in the solutions are indicated from theoretical considerations in relation to the experimental results obtained.

11. The polymer-solvent interaction constant χ has been evaluated as a function of temperature, molecular weight of the polymer fractions and the composition of the solutions.

12. The significance of the interaction constant χ in the terms of enthalpy and entropy contributions to the free energy of mixing has been discussed.

13. The parameters for the interchange energy are derived from previous theories of polymer solutions.

14. Intrinsic viscosities of the polypropylene glycols in several solvents have been evaluated and it has been shown that the exponent in the relationship between the intrinsic viscosity and molecular weight of the polymers decreases significantly with decreasing molecular weight.

15. The heats of activation for viscosity of the pure polymers and their solutions have been evaluated.

16. The hydroxyl end-groups in the polypropylene glycols have been found to be important in determining the thermodynamic and rheological properties of the polymers.

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