

HEATS OF MIXING

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CONTENTS

	<u>Page</u>
1. <u>THEORETICAL INTRODUCTION</u>	
1.1 Statistical Thermodynamics of Mixtures ..	1
1.2 The Quasi-Crystalline Model	1
1.3 Separation of Degrees of Freedom	2
1.4 The Configurational Partition Function ..	4
1.5 Evaluation of the Partition Function.. ..	8
1.6 Determination of the Heat of Mixing of Non-Athermal Mixtures	12
1.7 The Nature of the Parameter w	14
1.8 Values for Comparison with Experiment ..	15
1.9 Correction to Constant Volume	18
1.10 Theory Allowing for Orientation.. ..	22
1.11 Conformal Solution Theory	22
1.12 Application of "Cell" Method	23
2. <u>PREVIOUS DETERMINATIONS OF HEATS OF MIXING..</u>	24
3. <u>DESIGN AND OPERATION OF APPARATUS</u>	
3.1 The Calorimeter	28
3.2 The Thermopile	28
3.3 The Galvanometer.. .. .	29
3.4 The Heater	29
3.5 The Potentiometer	29
3.6 The Thermostat	29
3.7 The Vacuum System	30
3.8 The Electrical Circuit	30
3.9 Experimental Procedure	30
3.10 Typical Runs	33
3.11 Purification and Storage of Materials ..	35
3.12 Experimental Accuracy.. .. .	37

4.	<u>RESULTS</u>								
4.1	Carbon tetrachloride:Chloroform..	40
4.2	Benzene:Diphenyl..	40
4.3	Carbon tetrachloride:Cyclohexane	41
4.4	n-Hexane:n-Decane	41
5.	<u>ANALYSIS OF RESULTS</u>								
5.1	Carbon tetrachloride:Chloroform..	42
5.2	Benzene:Diphenyl..	43
5.3	Carbon tetrachloride:Cyclohexane	45
5.4	n-Hexane:n-Decane	47
6.	<u>SUMMARY</u>	50
	<u>REFERENCES</u>	51

1. THEORETICAL INTRODUCTION.

The object of this investigation was to test some recent theories of the equilibrium behaviour of liquid mixtures. Much theoretical work has been done on this subject, but very few experimental measurements have been made on mixtures simple enough to be satisfactorily described by the models proposed. This work was undertaken to provide data for simple mixtures that could be expected to be reasonably well described by the theoretical models.

1.1. Statistical Thermodynamics of Mixtures.

It can be shown that for a system of prescribed temperature, volume and content the observed or equilibrium value \bar{p} of a property whose value is p_r when the system is in state r of energy E_r is given by

$$\bar{p} = \frac{\sum_r p_r e^{-E_r/kT}}{\sum_r e^{-E_r/kT}} \quad (1.1.1)$$

The quantity $\sum_r e^{-E_r/kT}$ is called the partition function of the system, and will be denoted by Q .

$$\text{i.e. } Q = \sum_r e^{-E_r/kT} \quad (1.1.2)$$

If a quantity F is defined by

$$F = -kT \ln Q \quad (1.1.3)$$

it can be shown that F has all the properties of the Helmholtz free energy. If the partition function Q can be evaluated, then F and all the other thermodynamic properties of the system may be found by appropriate differentiation.

We shall now proceed to describe a model which will allow us to make an approximate evaluation of the partition function, and hence the thermodynamic properties, of liquid mixtures.

1.2. The Quasi-Crystalline Model.

The model to be discussed, and the theoretical and mathematical treatment of the model, are due mainly to

Guggenheim.¹

In determining the thermodynamic properties of liquid mixtures we will only be concerned with the differences between the thermodynamic properties of the mixture and its pure components, so any property of the pure components that may be assumed to be unchanged on mixing will have no effect on these differences. X-ray analysis has shown that liquids have pronounced short range order in their structure, so are much more like a solid than like a gas, and remembering that properties that are unchanged on mixing will not be discussed, a reasonable model of the liquid state applicable to mixtures will be as follows.

In a crystal each lattice site is surrounded by a definite invariable number of nearest neighbours, so in a liquid mixture it will be assumed that each "lattice site" is surrounded by a definite average number, not necessarily integral, of nearest neighbours. There will be fluctuations about this average number, but these fluctuations will be assumed to be small enough to affect only a negligible fraction of lattice sites. However, these small fluctuations in the environment of nearest neighbours throughout the lattice will be sufficient to destroy all long range order.

A crystalline lattice can only be occupied by units sufficiently similar in size and shape so as to be interchangeable on the lattice without distorting it. These units may either be single molecules, in which case we shall refer to them as monomers, or in the case of mixtures of molecules of widely differing shapes and sizes they may be segments of a molecule such that the whole molecule occupies an integral number of sites. In this case we shall refer to the segment of a molecule occupying one site as an "element" of that molecule, and to the whole molecule occupying r sites (having r elements) as an r -mer.

1.3. Separation of Degrees of Freedom.

To evaluate the partition function the approximation

will be made that the energy of the system may be expressed as the sum of the energies of the different degrees of freedom of the system, assumed independent. The partition function Q can then be expressed as a product of factors relating to the separated degrees of freedom.

For a crystalline solid, the degrees of freedom relating to the positions and motions of the centers of mass of the elements occupying the lattice sites will be assumed to be separable from other degrees of freedom. It will also be assumed that the energies of such degrees of freedom as rotation are assumed independent of the environment, which seems likely to be a reasonable approximation. Then Q , the partition function, is given by

$$Q = Q_{\text{int.}} Q_{\text{tr.}} \quad (1.3.1)$$

where the internal partition function $Q_{\text{int.}}$ refers to all degrees of freedom other than those relating to the positions and motions of the centers of mass of the elements occupying the lattice sites. The free energy of mixing is then determined only by the translational partition function $Q_{\text{tr.}}$ as on comparing a mixture with its pure components all contributions to the free energy of mixing from $Q_{\text{int.}}$ will cancel.

It will now be assumed that for a crystal the translational partition function may be expressed as the product of the partition function of the positions of the elements, assumed fixed on their lattice sites, and the partition function of the vibrations of the elements about their lattice sites. Then

$$Q_{\text{tr.}} = Q_{\text{ac.}} \Omega \quad (1.3.2)$$

where $Q_{\text{ac.}}$ is the partition function for the acoustic modes of vibration and Ω is the configurational partition function relating to the arrangement of the elements, assumed to be at rest, on their lattice sites.

The approximation is now made that $Q_{\text{ac.}}$ is determined only by the number of elements of each type present, and is independent of the environment of the elements, or in other words $Q_{\text{ac.}}$ is unaffected by mixing. Then the free energy of

mixing is determined only by the change in Ω , the configurational partition function, on mixing. Later sections of this work will show how Ω may be determined using various approximations.

To the above approximations, for a quasi-crystalline liquid mixture, the free energy of mixing ΔF of N_A moles of species A and N_B moles of species B is given from equation (1.1.3) by

$$-\Delta F/kT = (N_A + N_B) \ln \Omega_m - N_A \ln \Omega_A^0 - N_B \ln \Omega_B^0 \quad (1.3.3)$$

where Ω_m denotes the configurational partition function of one mole of the mixture and Ω_A^0 , Ω_B^0 denote the configurational partition functions of one mole of pure A and pure B respectively.

1.4. The Configurational Partition Function.

The configurational partition function Ω may be written, from equation (1.1.2) as

$$\Omega = \sum_c e^{-E_c/kT} \quad (1.4.1)$$

where the summation extends over all possible configurations of the system, and E_c is the configurational energy of the system when it has the configuration specified by c .

We will now consider mixtures of straight chain or branched chain molecules occupying sites on a lattice which has a co-ordination number z . A number q_A is defined such that $z q_A$ is the number of pairs of neighbouring sites to a molecule of species A, of which one site is occupied by one of the r_A elements of species A, and the other is not. Then for straight chain and branched chain molecules, q_A is related to r_A by

$$\frac{1}{2} z (r_A - q_A) = r_A - 1 \quad (1.4.2)$$

We will consider in this work molecules which may contain two types of elements not energetically alike. We will denote these elements by "a" and "b". The treatment may be extended to molecules containing more than two types of elements (such as branched chain hydrocarbons, which contain CH_3 -, CH_2 = and

OH \equiv elements) but this work is confined to mixtures containing only two types of element. Each kind of molecule (species A or B) may or may not contain both kinds of elements. Numbers s_A and t_A are defined such that of the $z q_A$ contacts of each A molecule $z q_A s_A$ come from "a" elements and $z q_A t_A$ come from "b" elements. Then

$$s_A + t_A = 1 \quad (1.4.3)$$

The approximation will be made that the configurational energy may be regarded as the sum of the mutual energies of all pairs of nearest neighbours in the system. This approximation does not mean that all interactions between next-nearest and more distant neighbours are ignored, but merely that it is assumed that such distant interactions are regarded as making a contribution to the configurational energy which is independent of the composition of the mixture.

Guggenheim and McGlashan² have shown that for regular mixtures the effect of considering next-nearest neighbours is negligible, and the effect will be assumed to be negligible for the more general cases studied in this work.

We will denote by $2 w_{aa}/z$ the contribution of each aa contact to the energy of the configuration, and by $2 w_{bb}/z$ the contribution of each bb contact. A quantity w is defined such that $(w_{aa} + w_{bb} + w)/z$ is the contribution to the configurational energy of each ab contact. For a binary mixture of N_A molecules of species A and N_B molecules of species B, we will use the following abbreviations.

$$Q = \frac{1}{2} z (N_A q_A + N_B q_B) \quad (1.4.4)$$

$$s = \frac{N_A q_A s_A + N_B q_B s_B}{N_A q_A + N_B q_B} \quad (1.4.5)$$

$$t = \frac{N_A q_A t_A + N_B q_B t_B}{N_A q_A + N_B q_B} \quad (1.4.6)$$

We will denote the number of ab contacts in a given configuration by $2z(N_A q_A + N_B q_B)y$; this is a definition of y . We may now construct Table 1.1 by direct counting of contacts.

Table 1.1.

Kind of Contact	Energy per Contact	Number of Contacts	Energy of all such Contacts
aa	$2 w_{aa}/z$	$Q (s - y)$	$2Qw_{aa}(s-y)/z$
ab	$(w_{aa}+w_{bb}+w)/z$	$2Qy$	$2Qy(w_{aa}+w_{bb}+w)/z$
bb	$2 w_{bb}/z$	$Q (t - y)$	$2Qw_{bb}(t-y)/z$
All		Q	$2Q(sw_{aa}+tw_{bb}+yw)/z$

Then from equation (1.4.1) we may write the configurational partition function Ω as

$$\Omega = \sum_y g(N_A, N_B, Q_y) e^{-2Q(sw_{aa}+tw_{bb}+yw)/zkT} \quad (1.4.7)$$

where the summation extends over all possible values of y (i.e., over all possible configurations) and $g(N_A, N_B, Q_y)$ is the number of configurations having the same number of ab contacts and hence the same energy for a particular value of y .

Equation (1.4.7) is exact if we regard as negligible the effect of non-nearest neighbours interactions. The equation has only been solved exactly for the artificial case of a linear array (i.e., $z = 2$) of A and B molecules each occupying one site. We will now discuss the approximations that have been made to solve the equation for various types of mixtures. The terminology of Guggenheim¹ will be used.

If w is put equal to zero in equation (1.4.7) the exponential term is independent of y and may be removed from the summation. The remaining summation can now be carried out exactly only for the case when the A and B molecules each occupy one site ($r_A = r_B = 1$) as the arrangement is then completely random. This leads to formulae for ideal mixtures. If either of the molecules A or B occupy more than one site (r_A or $r_B \neq 1$) the summation cannot be carried out exactly, even though the arrangement of molecules is random. An approximate solution leads to formulae for mixtures of molecules of different sizes having zero energy of mixing, hereinafter referred to as athermal mixtures.

If w is not equal to zero approximations to both terms in the summation must be made for a solution to be obtained. The simplest approximation is made by assuming the arrangement of molecules is still completely random even though w is not equal to zero. For mixtures of monomers, formulae for regular mixtures are obtained, and for mixtures containing an r -mer, formulae for mixtures of molecules of different sizes having a finite energy of mixing, hereinafter referred to as non-athermal mixtures, are obtained. The above approximation is referred to as the zeroth approximation. More exact approximations are obtained by determining the number of ab pairs ($2Q_y$) by various approximate combinatory formulae, which allow for preferred configurations caused by w , the energy of interaction, being finite. These approximations are referred to as the first, or quasi-chemical, and higher approximations. All the above cases have been considered by Guggenheim.¹

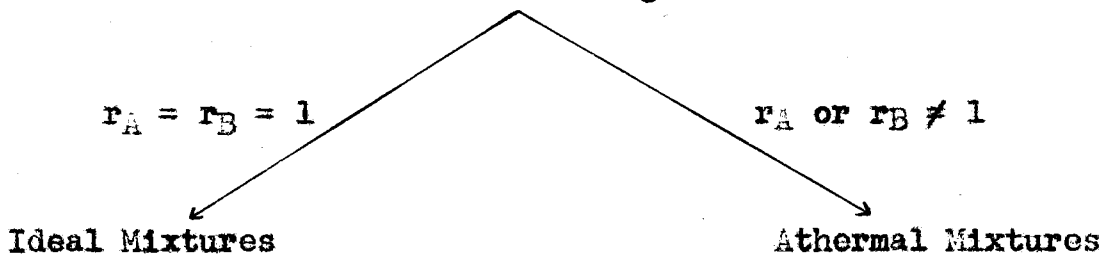
The above approximations, and the types of mixtures to which they apply, are shown in Table 1.2.

Table 1.2.

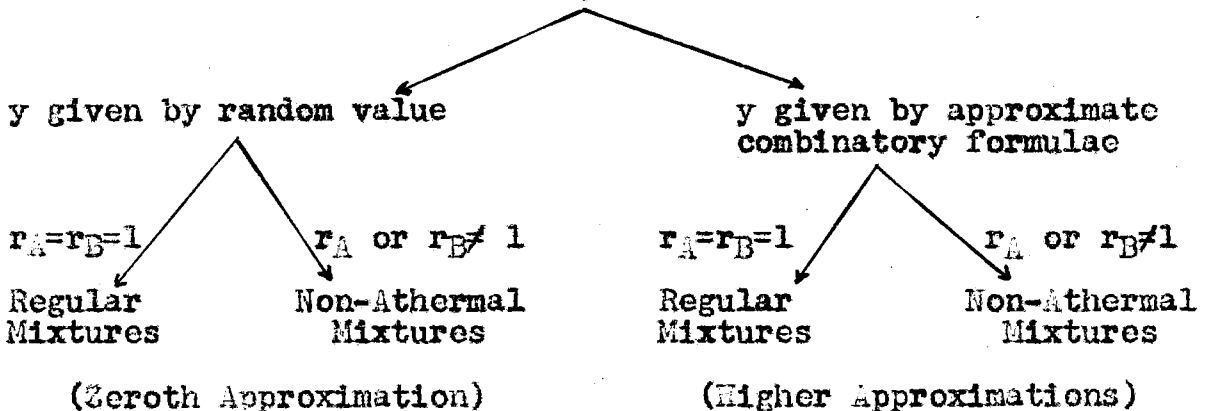
$$\Omega = \sum_y g(N_A, N_B, Q_y) e^{-2Q(sw_{aa} + tw_{bb} + yw)/zkt}$$

$$w = 0$$

Random Mixing



$$w \neq 0$$



In this work, formulae will be derived for the general case of a mixture of r_A -mers and r_B -mers. The zeroth approximation will be used (i.e., the arrangement of molecules will be regarded as random) in spite of a finite value of w . From the formulae we will derive, by putting $r_A = r_B = 1$ and $w = 0$, formulae for ideal mixtures may be obtained, and by putting $r_A = r_B = 1$ formulae for regular mixtures may be obtained. We will now proceed to find the partition function for the above general case.

1.5. Evaluation of the Partition Function.

We will now find an approximate formula for Ω for athermal mixtures. From this expression we will derive a formula for $\Delta_m S$, the molar entropy of mixing for an athermal mixture. We will then find $\Delta_m U$, the molar energy of mixing of a non-athermal mixture, assuming the arrangement of molecules to be random. By combination of the formula for $\Delta_m S$ and $\Delta_m U$ we will obtain an expression for $\Delta_m F$, the molar free energy of mixing for a non-athermal mixture.

Assuming w to be zero, we may write the configurational partition function Ω , from equation (1.4.7) as

$$\Omega = e^{-2Q(swaa+twbb)} \sum_y g(N_A, N_B, Qy) \quad (1.5.1)$$

In determining the free energy of mixing, all the exponential terms will cancel, so we may write

$$\Omega = \sum_y g(N_A, N_B, Qy) \quad (1.5.2)$$

Now $\sum_y g(N_A, N_B, Qy)$ is the total number of ways of arranging N_A molecules of species A and N_B molecules of species B on a lattice of $N_A + N_B$ sites. Denoting this quantity by $g(N_A, N_B)$, then

$$\ln \Omega = \ln g(N_A, N_B) \quad (1.5.3)$$

and the free energy of mixing, ΔF , will be given from equation (1.3.3) by

$$-\Delta F/kT = (N_A + N_B) \ln g(N_A, N_B) - N_A \ln g(N_A, 0) - N_B \ln g(0, N_B) \quad (1.5.4)$$

We will now consider a mixture of N_1 molecules of monomer, N_A molecules of r_A -mer and N_B molecules of r_B -mer. If N_S is the total number of lattice sites to be filled, then

$$N_s = N_1 + r_A N_A + r_B N_B \quad (1.5.5)$$

Since the arrangement of molecules is random, the frequency of occupation of a chosen site by a monomer molecule will be

$$\frac{N_1}{N_1 + r_A N_A + r_B N_B} \quad (1.5.6)$$

If a site is occupied by a monomer molecule, then the chances that a given neighbouring site is occupied by another monomer molecule or by an element of an r_A -mer or r_B -mer are as N_1 to $(q_A N_A + q_B N_B)$. Then the frequency of occupation of a chosen pair of sites by two monomer molecules is given by

$$\frac{N_1}{N_1 + r_A N_A + r_B N_B} \quad \frac{N_1}{N_1 + q_A N_A + q_B N_B} \quad (1.5.7)$$

Now consider a group of r_A sites so interrelated that it is possible for them to be occupied by a single r_A -mer molecule. The frequency of occupation of a chosen one of these sites by any element of an r_A -mer molecule is

$$\frac{r_A N_A}{N_1 + r_A N_A + r_B N_B} \quad (1.5.8)$$

and the frequency of its occupation by a particular element of an r_A -mer molecule (regarding the individual elements as distinguishable) is

$$\frac{N_A}{N_1 + r_A N_A + r_B N_B} \quad (1.5.9)$$

Consequently the frequency of occupation of the group of r_A sites by a single r_A -mer molecule is proportional to

$$\frac{N_A}{N_1 + r_A N_A + r_B N_B} \quad (1.5.10)$$

By extension of equation (1.5.7) the frequency of occupation of the group entirely by monomer molecules is proportional to

$$\frac{N_1}{N_1 + r_A N_A + r_B N_B} \left(\frac{N_1}{N_1 + q_A N_A + q_B N_B} \right)^{r_A - 1} \quad (1.5.11)$$

An approximation has been made in the above argument in assuming that when two sites are not occupied by elements of the same molecule the probabilities of occupation of the two sites in any particular manner are independent. It can easily be shown that this assumption is at least sometimes false.

Consider a pair of neighbouring sites, P and Q. Let R denote another site neighbouring both P and Q. Let Q be occupied

by an element of a molecule. Then it has been assumed that all conceivable manners of occupation of site P, not prevented by the occupation of site Q, are equally probable. An error is made in not excluding those manners of occupation of site P such that some element of the molecule occupying site P is competing for site R with an element of the molecule occupying site Q. McGlashan³ has derived formulae for a mixture of dimers and monomers, considering groups of three and four sites, and has also derived formulae specifically excluding some of the "impossible" configurations referred to above. These higher approximations lead to values of thermodynamic functions very close to those derived for dimers and monomers using the treatment given above. It will be assumed that the errors arising from the "impossible" configurations are small, and they will be neglected in this work.

The equilibrium conditions between the molecules will now be derived by applying the principle of detailed balancing⁴ to the elementary processes of

- (a) the removal (evaporation) of an r_A -mer molecule from a selected group of r_A sites and its simultaneous replacement (condensation) on these sites by r_A monomer molecules from the gas phase and the inverse process of
- (b) the removal of r_A monomer molecules from the same set of sites and their simultaneous replacement by an r_A -mer molecule from the gas phase.

The rate of process (a) will be directly proportional to the r_A -th power of p_1 , the partial pressure of monomer in the gas phase, and to the frequency of occupation of the set of sites by an r_A -mer molecule. From equation (1.5.10) the rate will be proportional to

$$p_1^{r_A} \frac{N_A}{N_1 + r_A N_A + r_B N_B} \quad (1.5.12)$$

The rate of process (b) will similarly, from equation (1.5.11) be proportional to

$$p_A \frac{N_1}{N_1 + r_A N_A + r_B N_B} \left(\frac{N_1}{N_1 + q_A N_A + q_B N_B} \right)^{r_A - 1} \quad (1.5.13)$$

where p_A is the partial pressure of r_A -mer in the gas phase.

At equilibrium the rates of process (a) and process (b) must be equal and consequently

$$\frac{p_A}{p_1^{r_A}} = C_A^1 \frac{N_A}{N_1} (N_1 + q_A N_A + q_B N_B)^{r_A - 1} \quad (1.5.14)$$

where C_A^1 depends only on the geometrical properties of the molecules and is independent of N_1 , N_A and N_B . Now the relation between the partial pressure, p , of a perfect gas and its absolute activity, λ , is given by

$$\lambda = \frac{p}{RT} \Phi(T) \quad (1.5.15)$$

where $\Phi(T)$ is the partition function of the gaseous molecule with the volume factor removed. Hence the ratio λ/p is independent of p . Equation (1.5.14) may therefore be written

$$\frac{\lambda_A}{\lambda_1^{r_A}} = C_A \frac{N_A}{N_1} (N_1 + q_A N_A + q_B N_B)^{r_A - 1} \quad (1.5.16)$$

where C_A , like C_A^1 , is independent of N_1 , N_A and N_B .

Similarly, by considering r_B monomer molecules and an r_B -mer, on r_B selected sites, it can be shown that

$$\frac{\lambda_B}{\lambda_1^{r_B}} = C_B \frac{N_B}{N_1} (N_1 + q_A N_A + q_B N_B)^{r_B - 1} \quad (1.5.17)$$

Then eliminating λ , between equation (1.5.16) and equation (1.5.17) we have

$$\frac{\lambda_B^{r_A}}{\lambda_A^{r_B}} = C \frac{N_B^{r_A}}{N_A^{r_B}} (N_1 + q_A N_A + q_B N_B)^{r_B - r_A} \quad (1.5.18)$$

If N_1 is now put equal to zero (i.e., we are now considering a mixture of N_A molecules of r_A -mer and N_B molecules of r_B -mer) then

$$\frac{\lambda_B^{r_A}}{\lambda_A^{r_B}} = C \frac{N_B^{r_A}}{N_A^{r_B}} (q_A N_A + q_B N_B)^{r_B - r_A} \quad (1.5.19)$$

We now change to the variables N_S , ϕ , where

$$N_S = r_A N_A + r_B N_B, \quad \phi = r_B N_B / N_S, \quad 1 - \phi = r_A N_A / N_S$$

Equation (1.5.19) now becomes

$$\frac{\lambda_B^{r_A}}{\lambda_A^{r_B}} = C^1 \frac{\phi^{r_A}}{(1-\phi)^{r_B}} \left(\frac{q_A}{r_A} - \phi \left(\frac{q_A}{r_A} - \frac{q_B}{r_B} \right) \right)^{r_B - r_A} \quad (1.5.20)$$

where C^1 is independent of ϕ .

Now for a mixture of N_A molecules of r_A -mer and N_B molecules of r_B -mer at constant temperature and volume, the Helmholtz free energy is given by

$$dF = \mu_A dN_A + \mu_B dN_B \quad (1.5.21)$$

but as $\mu = kT \ln \lambda$, equation (1.5.21) may be written

$$dF/kT = \ln \lambda_A dN_A + \ln \lambda_B dN_B \quad (1.5.22)$$

or changing to the variables N_S, ϕ ,

$$dF/N_S kT = \frac{1}{r_A r_B} \ln \frac{\lambda_B r_A}{\lambda_A r_B} d\phi \quad (1.5.23)$$

We may regard the free energy as a function of N_S and ϕ ,

hence the free energy of mixing, ΔF , is given by

$$\Delta F = F(N_S, \phi) - (1 - \phi) F(N_S, 0) - \phi F(N_S, 1) \quad (1.5.24)$$

Comparing equation (1.5.24) with equation (1.5.23) we see ΔF is given by

$$\Delta F/N_S kT = \frac{1}{r_A r_B} \int_0^\phi \ln \frac{\lambda_B r_A}{\lambda_A r_B} d\phi - \frac{\phi}{r_A r_B} \int_0^1 \ln \frac{\lambda_B r_A}{\lambda_A r_B} d\phi \quad (1.5.25)$$

Equation (1.5.25) gives the free energy of mixing of a mixture containing N_A molecules of r_A -mer and N_B molecules of r_B -mer. To obtain the molar free energy of mixing, $\Delta_m F$,

ΔF must be divided by the total number of molecules, namely $(\frac{1-\phi}{r_A} + \frac{\phi}{r_B})$, and multiplied by Avogadro's number, $N = \frac{R}{k}$. Then

$$\Delta_m F/RT = \frac{1}{r_B + \phi(r_B - r_A)} \left(\int_0^\phi \ln \frac{\lambda_B r_A}{\lambda_A r_B} d\phi - \phi \int_0^1 \ln \frac{\lambda_B r_A}{\lambda_A r_B} d\phi \right) \quad (1.5.26)$$

Substituting for $\ln \frac{\lambda_B r_A}{\lambda_A r_B}$ in equation (1.5.26) from equation (1.5.20) and performing the integrations we obtain, after reverting to the variables N_A, N_B

$$\begin{aligned} (N_A + N_B) \Delta_m F/RT &= N_A \ln \frac{r_A N_A}{r_A N_A + r_B N_B} + \frac{1}{2} z q_A N_A \ln \frac{q_A (r_A N_A + r_B N_B)}{r_A (q_A N_A + q_B N_B)} \\ &+ N_B \ln \frac{r_B N_B}{r_A N_A + r_B N_B} + \frac{1}{2} z q_B N_B \ln \frac{q_B (r_A N_A + r_B N_B)}{r_B (q_A N_A + q_B N_B)} \end{aligned} \quad (1.5.27)$$

Then by differentiating with respect to temperature, we

obtain for $\Delta_m S$ the molar entropy of mixing,

$$\begin{aligned} - (N_A + N_B) \Delta_m S/R &= N_A \ln \frac{r_A N_A}{r_A N_A + r_B N_B} + \frac{1}{2} z q_A N_A \ln \frac{q_A (r_A N_A + r_B N_B)}{r_A (q_A N_A + q_B N_B)} \\ &+ N_B \ln \frac{r_B N_B}{r_A N_A + r_B N_B} + \frac{1}{2} z q_B N_B \ln \frac{q_B (r_A N_A + r_B N_B)}{r_B (q_A N_A + q_B N_B)} \end{aligned} \quad (1.5.28)$$

1.5. Determination of the Heat of Mixing of Non-Athermal Mixtures.

We will now make the assumption that for systems with

small heats of mixing (i.e., w is small) the arrangement of molecules is random. Thus the entropy of mixing is given correctly by equation (1.5.28), although equation (1.5.27) no longer gives the free energy of mixing. Guggenheim¹ has derived formulae for a model which allows for preferred configurations, due to the finite energy of interaction, but it has been shown¹ that the differences in the values of derived thermodynamic functions for the two models are very small. These differences are less than the experimental errors in the determination of thermodynamic functions in the systems to be considered later, so this work will be confined to mixtures whose entropy of mixing is given by equation (1.5.28).

Table 1.3, analogous to Table 1.1, may now be constructed for a completely random arrangement of N_A molecules of r_A -mer and N_B molecules of r_B -mer, using the same notation as before.

Table 1.3.

Kind of Contact	Energy per Contact	Number of Contacts	Energy of All such Contacts
aa	$2w_{aa}/z$	Qs^2	$2Qs^2w_{aa}/z$
ab	$(w_{aa}+w_{bb}+w)z$	$2Qst$	$2Qst(w_{aa}+w_{bb}+w)/z$
bb	$2w_{bb}/z$	Qt^2	$2Qt^2w_{bb}/z$
All		Q	$2Q(sw_{aa}+tw_{bb}+stw)/z$

From Table 1.3 it is seen that the configurational energy, U_c , for a random distribution is given by

$$\begin{aligned}
 U_c &= 2Q (sw_{aa} + tw_{bb} + stw)/z \\
 &= (q_{aA}N_A + q_{bB}N_B)w_{aa} + (q_{aA}tN_A + q_{bB}tN_B)w_{bb} \\
 &\quad + \frac{(q_{aA}N_A + q_{bB}N_B)(q_{aA}tN_A + q_{bB}tN_B)}{q_{aA}N_A + q_{bB}N_B} w \quad (1.6.1)
 \end{aligned}$$

Then the molar total energy of mixing, $\Delta_m U$, is given by

$$\Delta_m U = \frac{q_{aA}q_{bB}}{(N_A+N_B)(q_{aA}+q_{bB})} (s_{aB}+s_{bA}-s_{aA}-s_{bB}) Nw \quad (1.6.2)$$

Now combining equation (1.5.28) for the molar entropy of mixing with equation (1.6.2) for the molar energy of mixing we obtain for $\Delta_m F$, the molar free energy of mixing.

$$\begin{aligned}
(N_A + N_B) \Delta_{mF}/RT &= N_A \ln \frac{r_A N_A}{r_A N_A + r_B N_B} + \frac{1}{2} z q_A N_A \ln \frac{q_A (r_A N_A + r_B N_B)}{r_A (q_A N_A + q_B N_B)} \\
&+ N_B \ln \frac{r_B N_B}{r_A N_A + r_B N_B} + \frac{1}{2} z q_B N_B \ln \frac{q_B (r_A N_A + r_B N_B)}{r_B (q_A N_A + q_B N_B)} \\
&+ \frac{q_A N_A q_B N_B}{q_A N_A + q_B N_B} (s_{AtB} + s_{BtA} - s_{AtA} - s_{BtB}) \frac{w}{kT} \quad (1.6.3)
\end{aligned}$$

1.7. The Nature of the Parameter w.

We will define w such that equation (1.6.3) gives the correct value of the free energy of mixing to the approximation used during the treatment. So defined w is rather a complicated average energy. Consider a neighbouring pair of sites in a system both occupied by a elements, and another neighbouring pair of sites both occupied by b elements. Let W_1 denote the intermolecular energy of the whole system when the two pairs of sites are occupied as described while all other sites are occupied in all conceivable ways, and the average over all physically possible configurations, attaching the relevant Boltzmann factor to each configuration, is taken. Now suppose each of the given pairs of sites to be occupied by two elements, one a and one b , and let W_2 denote the intermolecular energy of the system, averaged in a similar manner to that used to define W_1 . Then the quantity w , defined by equation (1.6.3) may be regarded as being given by

$$2w = W_2 - W_1 \quad (1.7.1)$$

Then $2w$ may be loosely described as the average work required to interchange the manner of occupation of two pairs of sites isothermally, or still more loosely as the increase in the intermolecular free energy when the manner of occupation of the two pairs of sites is changed as described. Then w so defined is independent of the composition of the mixture. This is in fact the basic approximation on which the treatment rests.

The whole of the above argument applies only to one temperature, but nothing in the argument requires that w should be temperature independent. We will now consider the

effect of allowing w to be temperature dependent.⁵

Defining w by equation (1.6.3) we obtain $\Delta_m U$, the molar energy of mixing from

$$\Delta_m U = \frac{\delta(\Delta_m F/T)}{\delta(1/T)} \quad (1.7.2)$$

$$= \frac{q_A N_A q_B N_B}{(N_A + N_B)(q_A N_A + q_B N_B)} (s_A t_B + s_B t_A - s_A t_A - s_B t_B) \left(Nw - T \frac{d(Nw)}{dT} \right) \quad (1.7.3)$$

If we define a quantity u by

$$u = w - T \frac{dw}{dT} \quad (1.7.4)$$

equation (1.7.3) becomes

$$\Delta_m U = \frac{q_A N_A q_B N_B}{(N_A + N_B)(q_A N_A + q_B N_B)} (s_A t_B + s_B t_A - s_A t_A - s_B t_B) Nu \quad (1.7.5)$$

Equation (1.7.5) correctly gives the molar energy of mixing. Equation (1.6.2) on the other hand, gives $\Delta_m U$ only for the case when dw/dT is equal to zero and hence u is equal to w .

We may then call w the co-operative free energy of formation of a single ab contact and u the co-operative total energy of formation of such a contact.

1.8. Values for Comparison with Experiment.

We will now derive from equation (1.7.5) expressions for $\Delta_m U$ for the mixtures studied experimentally.

(a) Carbon tetrachloride: Chloroform and Carbon tetrachloride: Cyclohexane.

In these mixtures we will assume that each molecule occupies one lattice site, and that the molecules are energetically different. Then for the various parameters in equation (1.7.5) we have the following values.

$$r_A = 1, q_A = 1, s_A = 1, t_A = 0$$

$$r_B = 1, q_B = 1, s_B = 0, t_B = 1$$

Then equation (1.7.5) reduces to

$$\Delta_m U = \frac{N_A N_B}{(N_A + N_B)^2} Nu \quad (1.8.1)$$

If we denote by x the mole fraction of species B in the mixture, equation (1.8.1) becomes

$$\Delta_m U = x(1-x) Nu \quad (1.8.2)$$

Equation (1.8.2), which gives the energy of mixing according to the zeroth approximation, is independent of z , the co-ordination number of the lattice. Equations for regular mixtures derived from the zeroth approximation can be obtained from the first approximation for regular mixtures by putting z equal to infinity.¹ In the two regular solutions considered here the differences between the values derived by the two approximations are negligible compared to the experimental errors, so only the zeroth approximation will be used.

(b) Benzene: Diphenyl.

It has been shown⁶ that for mixtures of hydrocarbons the extent of agreement between theory and experiment is insensitive to the value chosen for the co-ordination number z , the agreement being comparable for $z = 4$ and $z = 8$. Hydrocarbon mixtures are more complicated examples of non-athermal mixtures than are benzene:diphenyl mixtures, and we will assume that the value chosen for z makes only a trivial difference to the extent of agreement between theory and experiment for benzene:diphenyl mixtures, and we will use the value $z = 6$ as the smallest likely to occur. Then assuming each benzene molecule (species A) occupies one lattice site and each diphenyl molecule (species B) occupies two lattice sites and the C_6H_6 and C_6H_5 - elements are energetically different, we have

$$r_A = 1, q_A = 1, s_A = 1, t_A = 0$$

$$r_B = 2, q_B = \frac{5}{3}, s_B = 0, t_B = 1$$

Then equation (1.7.5) reduces to

$$\Delta_m U = \frac{5N_A N_B}{(N_A + N_B)(3N_A + 5N_B)} N u \quad (1.8.3)$$

The quantity measured experimentally is, however, the energy of dilution and not the energy of mixing. Consider a mixture containing N_A moles of benzene and N_B moles of diphenyl, diluted by the addition of ΔN_A moles of benzene.

If ΔU_1 is the energy of mixing of N_A moles of benzene and N_B moles of diphenyl, then

$$\Delta U_1 = \frac{5N_A N_B}{3N_A + 5N_B} N u \quad (1.8.4)$$

If ΔU_2 is the energy of mixing of $(N_A + \Delta N_A)$ moles of benzene and N_B moles of diphenyl, then

$$\Delta U_2 = \frac{5(N_A + \Delta N_A)N_B}{3(N_A + \Delta N_A) + 5N_B} Nu \quad (1.8.5)$$

If $\Delta_D U$ is the energy of dilution of N_A moles of benzene and N_B moles of diphenyl with ΔN_A moles of benzene, then

$\Delta_D U$ is given by

$$\Delta_D U = \Delta U_2 - \Delta U_1 \quad (1.8.6)$$

$$= \frac{25 \Delta N_A N_B^2}{(3N_A + 3\Delta N_A + 5N_B)(3N_A + 5N_B)} Nu \quad (1.8.7)$$

Then the molar energy of dilution, $\Delta_{Dm} U$, is given by

$$\Delta_{Dm} U = \frac{25 \Delta N_A N_B^2}{(N_A + \Delta N_A + N_B)(3N_A + 3\Delta N_A + 5N_B)(3N_A + 5N_B)} Nu \quad (1.8.8)$$

If we denote the initial mole fraction of diphenyl by x_1 , and the final mole fraction of diphenyl by x_2 , then equation

(1.8.8) reduces to

$$\Delta_{Dm} U = \frac{25 x_2 (x_1 - x_2)}{(3 + 2x_2)(3 + 2x_1)} Nu \quad (1.8.9)$$

(c) Hexane: Decane.

As the extent of agreement between theory and experiment is insensitive to the value chosen for z , we will arbitrarily chose the value $z = 8$ of a body centered cubic lattice. We shall regard the hydrocarbon molecules as comprised of two kinds of elements, namely CH_2 - middle groups and CH_3 - end groups. Tompa⁶ has given geometrical reasons for assuming the elements to be $-\text{CH}_2-\text{CH}_2-$ middle and $-\text{CH}_2-\text{CH}_3$ end groups, and Van der Waals⁷ has given stronger reasons for choosing as elements $-\text{CH}_2-\text{CH}_2-$ middle and CH_3 - end groups. However, both these proposals lead to molecules containing half integral numbers of elements, which can have no geometrical interpretation. Moreover, the extent of agreement between theory and experiment is comparable for all the above choices, so we will use the simple choice specified above, assuming that the CH_2 - and CH_3 - groups each occupy one lattice site. Then for the various parameters in equation (1.7.5) we have the following values, denoting decane as species B and hexane as

species A.

$$r_A = 6, q_A = \frac{10}{4}, s_A = \frac{24}{38}, t_A = \frac{14}{38}$$

$$r_B = 10, q_B = \frac{31}{4}, s_B = \frac{48}{62}, t_B = \frac{14}{62}$$

Substitution of the above values in equation (1.7.5)

gives for $\Delta_m U$ the expression

$$\Delta_m U = 0.2496 \frac{x(1-x)}{1.5222 + x} Nu \quad (1.8.10)$$

where x is the mole fraction of hexane in the mixture.

1.9. Correction to Constant Volume.

Theories that have been developed to predict equilibrium properties of liquid mixtures yield expressions for the free energy and energy of mixing at constant total volume, but experimental determinations of vapour pressures and heats of mixing give values for the free energy and energy of mixing at constant pressure. A theory has been developed by Scatchard⁸ to correct the experimental constant pressure values to constant volume. Following is a treatment⁹ of the problem which makes clear the various assumptions that must be made to apply the theory.

It will be assumed that the elements of the components are such that these elements all lie on lattice sites, the lattice being similar for the pure components and the mixture, the lattice having a fixed and unalterable volume of V_e per mole of sites at all temperatures. The value of the free energy derived from theory is then given by

$$\Delta_m F(T, x, V_e) = F_m(T, x, V_e) - (1-x)F_m(T, 0, V_e) - xF_m(T, 1, V_e) \quad (1.9.1)$$

where $\Delta_m F$ is the molal free energy of mixing per mole of mixture at temperature T , and $F_m(T, x, V_e)$ is the molal free energy of a mixture of mole fraction x occupying a volume V_e per mole, at a temperature T . From equation (1.9.1) $\Delta_m F$ can be calculated as a function of T and x , $\Delta_m F$ being independent of V_e .

The experimental determination of vapour pressures leads to values of the free energy given by

$$\begin{aligned}\Delta_m G (T, x, P_a) &= G_m (T, x, P_a) - (1-x)G_m(T, 0, P_a) - xG_m (T, 1, P_a) \\ &= G_m [T, x, V(T, x, P_a)] - (1-x)G_m [T, 0, V(T, 0, P_a)] \\ &\quad - xG_m [T, 1, V(T, 1, P_a)]\end{aligned}\quad (1.9.2)$$

where P_a is the experimental pressure, usually one atmosphere, and

$$V = V (T, x, P)$$

is the molar volume of a mixture of mole fraction x at temperature T and pressure P .

Now as

$$G_m [T, x, V (T, x, P_a)] = F_m [T, x, V (T, x, P_a)] + P_a V (T, x, P_a)\quad (1.9.3)$$

then

$$\begin{aligned}\Delta_m G (T, x, P_a) &= F_m [T, x, V (T, x, P_a)] - (1-x)F_m [T, 0, V(T, 0, P_a)] \\ &\quad - xF_m [T, 1, V (T, 1, P_a)] + P_a \{V (T, x, P_a) - (1-x)V(T, 0, P_a) \\ &\quad - xV (T, 1, P_a)\}\end{aligned}\quad (1.9.4)$$

The compressibility, κ , of a liquid is defined by

$$\kappa = - \frac{1}{V} \left(\frac{dV}{dP} \right)_T \quad (1.9.5)$$

Then the pressure, P , exerted by a liquid in undergoing a volume change from $V (T, x, P_a)$ to $V (T, x, P)$ is given by

$$P = P_a - \int_{V (T, x, P_a)}^{V (T, x, P)} \frac{1}{\kappa V} dV \quad (1.9.6)$$

and as at a given temperature

$$dF_m = - P dV \quad (1.9.7)$$

then

$$dF_m = - (P_a - \int_{V (T, x, P_a)}^{V (T, x, P)} \frac{1}{\kappa V} dV) dV \quad (1.9.8)$$

Integration of equation (1.9.8) gives

$$\begin{aligned}F [T, x, V (T, x, P_a)] &- F (T, x, V_e) \\ &= - \int_{V_e}^{V (T, x, P_a)} (P_a - \int_{V (T, x, P_a)}^{V (T, x, P)} \frac{1}{\kappa V} dV) dV \quad (1.9.9) \\ &= P_a [V_e - V (T, x, P_a)] + \int_{V_e}^{V (T, x, P_a)} \int_{V (T, x, P_a)}^{V (T, x, P)} \frac{1}{\kappa V} dV dV\end{aligned}\quad (1.9.10)$$

Substitution of equation (1.9.10) into equation (1.9.4) gives

$$\begin{aligned}\Delta_m G (T, x, P_a) \\ &= F_m (T, x, V_e) - (1-x) F_m (T, 0, V_e) - x F_m (T, 1, V_e)\end{aligned}$$

$$\begin{aligned}
& + \int_{V_e}^{V(T,x,P_a)} \int_{V(T,x,P_a)}^{V(T,x,P)} \frac{1}{\mathcal{K}} V \, dV dV - (1-x) \int_{V_e}^{V(T,x,P_a)} \int_{V(T,x,P_a)}^{V(T,x,P)} \frac{1}{\mathcal{K}} V \, dV dV \\
& - x \int_{V_e}^{V(T,x,P_a)} \int_{V(T,x,P_a)}^{V(T,x,P)} \frac{1}{\mathcal{K}} V \, dV dV
\end{aligned} \tag{1.9.11}$$

where \mathcal{K} is given by

$$\mathcal{K} = \mathcal{K} [T, x, V(T, x, P_a)] \tag{1.9.12}$$

Then

$$\begin{aligned}
& \Delta_m F(T, x, V_e) - \Delta_m G(T, x, P_a) \\
= & - \int_{V_e}^{V(T,x,P_a)} \int_{V(T,x,P_a)}^{V(T,x,P)} \frac{1}{\mathcal{K}} V \, dV dV + (1-x) \int_{V_e}^{V(T,x,P_a)} \int_{V(T,x,P_a)}^{V(T,x,P)} \frac{1}{\mathcal{K}} V \, dV dV \\
& + x \int_{V_e}^{V(T,x,P_a)} \int_{V(T,x,P_a)}^{V(T,x,P)} \frac{1}{\mathcal{K}} V \, dV dV
\end{aligned} \tag{1.9.13}$$

which is the required equation.

From equation (1.9.13) by differentiation with respect to temperature at constant pressure, formulae for the quantities

$$\Delta_m S(T, x, V_e) - \Delta_m S(T, x, P_a) \tag{1.9.14}$$

$$\text{and } \Delta_m U(T, x, V_e) - \Delta_m H(T, x, P_a) \tag{1.9.15}$$

may be obtained.

Formulae (1.9.13) (1.9.14) and (1.9.15) are exact, but cannot be applied unless knowledge of the volume, temperature and composition dependence of \mathcal{K} is available. If it is assumed that \mathcal{K} is independent of volume, as in Scatchard's treatment, equation (1.9.13) can be integrated to give

$$\begin{aligned}
& \Delta_m F(T, x, V_e) - \Delta_m G(T, x, P_a) \\
= & - \frac{1}{\mathcal{K}(T,x)} \left[V_e \ln \frac{V(T,x,P_a)}{V_e} + V_e - V(T,x,P_a) \right] \\
& + \frac{1-x}{\mathcal{K}(T,0)} \left[V_e \ln \frac{V(T,0,P_a)}{V_e} + V_e - V(T,0,P_a) \right] \\
& + \frac{x}{\mathcal{K}(T,1)} \left[V_e \ln \frac{V(T,1,P_a)}{V_e} + V_e - V(T,1,P_a) \right]
\end{aligned} \tag{1.9.16}$$

Differentiation of equation (1.9.16) with respect to temperature at constant volume gives

$$\begin{aligned}
& \Delta_m S(T, x, V_e) - \Delta_m S(T, x, P_a) \\
= & \frac{\alpha(T,x)}{\mathcal{K}(T,x)} \left[V_e - V(T,x,P_a) + \ln \mathcal{K}(T,x) \right] \frac{d\mathcal{K}(T,x)}{dT} \left[V_e \ln \frac{V(T,x,P_a)}{V_e} + V_e - V(T,x,P_a) \right]
\end{aligned}$$

$$\begin{aligned}
 & -\frac{(1-x)\alpha(T,0)}{\mathcal{K}(T,0)} \left[V_e - V(T,0,P_a) + \ln \mathcal{K}(T,0) \frac{d\mathcal{K}(T,0)}{dT} \left\{ V_e \ln \frac{V(T,0,P_a)}{V_e} + V_e - V(T,0,P_a) \right\} \right] \\
 & -\frac{x\alpha(T,1)}{\mathcal{K}(T,1)} \left[V_e - V(T,1,P_a) + \ln \mathcal{K}(T,1) \frac{d\mathcal{K}(T,1)}{dT} \left\{ V_e \ln \frac{V(T,1,P_a)}{V_e} + V_e - V(T,1,P_a) \right\} \right]
 \end{aligned}
 \tag{1.9.17}$$

where the coefficient of thermal expansion, α , is defined by

$$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_p \tag{1.9.18}$$

Combination of equations (1.9.16) and (1.9.17) leads to an expression for

$$\Delta_{mH}(T,x,V_0) - \Delta_{mH}(T,x,P_a) \tag{1.9.19}$$

To apply equation (1.9.19) the dependence of α , \mathcal{K} , and the molar volume on the composition and temperature must be known. Wood and Gray¹⁰ have experimentally determined the composition and temperature dependence of the molar volumes of mixtures of carbon tetrachloride and cyclohexane, and by assuming that α and \mathcal{K} for the mixtures were additive in the volume fraction have obtained numerical results to apply to experimentally determined values of the free energy¹¹ and energy¹² of mixing of these liquids. Some calculations have been carried out using the same numerical values as Wood and Gray for the molar volumes and for α and \mathcal{K} , but assuming that $1/\mathcal{K}$ and α/\mathcal{K} were additive in the mole fraction. It was found that the results differed appreciably from those of Wood and Gray, and as both treatments assume that \mathcal{K} is independent of pressure it is seen that little can be gained in applying corrections obtained in such an arbitrary manner. Precise knowledge of the composition, pressure and temperature dependence of α and \mathcal{K} is necessary before the experimentally determined values of the free energy and heat of mixing at constant pressure can be corrected to constant volume.

The results of Wood and Gray and the results of the author, show that the heat of mixing at constant volume is approximately temperature independent. The application of the correction makes little difference in the extent of agreement between theory and experiment for the carbon tetrachloride: cyclohexane system, as the form of the heat of mixing versus mole fraction plots is not appreciably changed, even though

the magnitude of the value of Nu at each temperature is. As will be seen later, an arbitrary constant is introduced to compare the experimental free energy and energy of mixing values, and this constant will include the corrections to constant volume. Sufficient data was not available to carry out calculations for correction to constant volume of the other systems studied, and as it seems likely that the corrections play no part in the comparison of theory with experiment, except for the hydrocarbon systems, the constant pressure results obtained in this work will be directly compared to the values derived from theory.

1.10. Theory Allowance for Orientation.

Barker¹³ has developed a theory applicable to mixtures containing weakly polar molecules. The quasi-crystalline model is used, but allowance is made for the dependence of the interaction energies of neighbouring asymmetrical molecules upon their relative orientation. Good agreement between theory and experiment is obtained for the systems methanol:carbon tetrachloride and methanol:benzene, and qualitative agreement is obtained for the system ethanol:chloroform.

1.11. Conformal Solution Theory.

Longuet-Higgins¹⁴ has developed a theory for a class of mixtures defined as conformal. No model of state is used in the treatment, which applies equally well to mixtures of liquids and to mixtures of imperfect gases. By assuming that the mutual potential energy of a pair of molecules is a particular function of the distance between them, the mutual potential energy between all pairs of molecules in the mixture is found (c.f. the quasi-crystalline treatment, where only the mutual potential energy between neighbouring pairs of molecules is considered). From the expression for the potential energy of the whole system, the thermodynamic functions of mixing are found. The results are similar to those obtained from the quasi-crystalline treatment and in addition the theory predicts

some equilibrium properties which are not found by the quasi-crystalline treatment. Agreement between theory and experiment is obtained for the heats, entropies and volumes of mixing of several binary mixtures.

1.12. Application of "Cell" Method.

Prigogine and Mathot¹⁵ have applied the "cell" method of Leonard-Jones and Devonshire¹⁶ to mixtures of liquids. It is assumed that the distance between neighbouring molecules in the mixture is the same as between neighbouring molecules in both pure components, which is equivalent to the quasi-crystalline model, and that the mutual potential energy of a pair of molecules is given by a particular function of the distance between them (c.f. Longuet-Higgins' treatment). By consideration of the motion of a molecule in a "cell" formed by its nearest neighbours, expressions for the thermodynamic functions of mixing are found. The results are similar to those obtained from the quasi-crystalline model, and agreement between theory and experiment for the system carbon-tetrachloride:neopentane is obtained.

2. PREVIOUS DETERMINATIONS OF HEATS OF MIXING.

Hirobe¹⁷ measured the heats of mixing of a large number of binary mixtures at 25° C. The calorimeter consisted of a double walled copper vessel, having a graduated capillary tube communicating with the space between the walls. The space and a portion of the capillary tube were filled with xylene, the whole acting as a sensitive thermometer. The calorimeter was contained in a thermostated Dewar flask and partially filled with water. The liquids to be mixed were contained in a "U" tube and separated by mercury, the limbs of the tube being sealed off. The "U" tube was placed in the water in the calorimeter and the liquids mixed by inverting the "U" tube; the temperature change being compensated for by addition of mercury to the calorimeter. The heat effect on mixing was calculated from the weight and temperature of the added mercury. The accuracy of the results is not high as an appreciable vapour space existed over the liquids, and no corrections were made for evaporation and condensation on mixing.

Many of the binary mixtures investigated contained a highly polar component, and are not suitable for comparison with the theory given before, but the systems carbon tetrachloride:chloroform, carbon tetrachloride:benzene and benzene; chloroform were investigated, and gave parabolic Δ_{mH} versus mole fraction plots, in agreement with the theory for regular mixtures.

Carroll and Mathews¹⁸ measured the heats of mixing of several binary mixtures of polar molecules at atmospheric pressure and the boiling point of the mixtures. The liquids were mixed in a thermostated brass calorimeter, one liquid being directly placed in the calorimeter, the other being contained in a glass ampoule. The temperature change on mixing was followed adiabatically by the thermostat, using a thermopile between the calorimeter and the thermostat as a

null instrument. Corrections were made for evaporation and condensation on mixing into the vapour space present, and calibration was carried out by electrical heating. Owing to the difficulty of maintaining adiabatic conditions during a process of short duration, the results are not of a high accuracy.

Vold¹⁹ measured the heats of mixing of several binary mixtures of Group IV tetrachlorides, benzene and N-heptane at 25° C. The calorimeter consisted of an air thermostated Dewar flask. One liquid was placed in the calorimeter, and after thermal equilibrium was attained the other liquid was poured in, the temperature change being followed by a platinum resistance thermometer. Calibration was carried out by electrical heating. As the vapour space was small compared to the volume of the mixture (330 ml) the correction for evaporation and condensation was negligible. Since about twenty seconds were required to mix the liquids, considerable uncertainty in the temperature change on mixing existed, and the results cannot be regarded as accurate.

Parabolic $\Delta_m H$ versus mole fraction plots were obtained for the systems studied, in agreement with the theory for regular mixtures.

Van der Waals⁷ has measured the heats of mixing of several binary mixtures of hydrocarbons between 20 and 73° C. The calorimeter consisted of one of a pair of "twin" Dewar flasks, the liquids to be mixed being placed in "wells" in a mixing vessel mounted in the calorimeter. Inversion of this vessel mixed the liquids, the temperature change being followed by means of a thermopile between the Dewars. Calibration was carried out by electrical heating, and corrections were made for evaporation and condensation on mixing. The results show a considerable scatter, and as the correction for evaporation and condensation was sometimes as high as 30% of the total heat measured, the results cannot be regarded as highly accurate. Discussion of the results will be postponed to a later section.

Whitaker and Cheeseman²⁰ have measured the heat of mixing of the systems carbon tetrachloride:chloroform, carbon tetrachloride:methylene chloride, chloroform:methylene chloride, benzene:carbon tetrachloride and benzene:ethylene dichloride between 15 and 30° C. The calorimeter consisted of a vacuum jacketed and thermostated mixing vessel, in which the liquids to be mixed were separated by a tinfoil diaphragm, there being no vapour space. Mixing was effected by breaking the diaphragm, the temperature change being followed by means of a thermopile between the calorimeter and the thermostat. Calibration was carried out by electrical heating. Owing to the absence of a vapour phase, the results are of a high accuracy.

The results for all the systems studied except the benzene:ethylene dichloride system show that a Δ_{mH} versus mole fraction plot is parabolic, in agreement with the theory for regular mixtures. The temperature coefficient of the heat of mixing of some of the mixtures studied will be discussed in a later section. The non-agreement of the results for the benzene:ethylene dichloride system is probably due to the polar nature of the ethylene dichloride molecule.

Tompa²¹ has measured the heats of dilution of some high polymer solutions. The calorimeter consisted of a single Dewar flask, similar in design to that used in this work. The temperature change on mixing was followed by means of a thermistor, and calibration was carried out by electrical heating. The accuracy of the results is comparable to the accuracy obtained in this work.

Scatchard, Ticknor, Goates and McCartney¹² have measured the heat of mixing of the systems benzene:carbon tetrachloride, carbon tetrachloride:cyclohexane, benzene:cyclohexane and n-hexane:n-hexadecane, and also the heats of mixing of several binary mixtures containing methanol, at 20° C. The calorimeter consisted of an air thermostated "U" tube containing the liquids, which were separated by mercury. Cork stoppers closed the ends of the tube. The liquids were mixed by

inversion of the "U" tube, the temperature change being followed by means of a thermopile between the calorimeter and water at room temperature. The change in heat content was calculated from the change in temperature and the heat capacity of the calorimeter and liquids. No corrections were made for evaporation and condensation on mixing, or for absorption of liquid by the cork stoppers. Corrections of up to 20% of the total heat of mixing were applied to correct for heat exchange with the surroundings. The results cannot be considered to be accurate, as too many uncertainties exist in the corrections for heat exchange with the surroundings, and no further purification of the commercial liquids used was carried out. As can be seen in Graph 6 the results for the system carbon tetrachloride:cyclohexane differ appreciably from the results of this work.

Ferry, Gee and Treloar²² have measured the heats of dilution of solutions of low molecular weight homologues of rubber with benzene, acetone, carbon disulphide, toluene, heptane, carbon tetrachloride and chloroform. The calorimeter consisted of one of a pair of thermostated Dewar flasks containing two concentric bulbs, the inner bulb being sealed at the bottom by a pool of mercury. The liquids were placed in each bulb, and mixing was carried out by lifting the end of the inner bulb out of the mercury. The temperature change was followed by a thermopile between the Dewars, while calibration was by means of electrical heating. A large vapour space was present, so the results cannot be regarded as highly accurate. Guggenheim¹ has analysed these results, together with the vapour pressure results of Gee and his collaborators^{23, 24} and finds reasonable agreement between theory and experiment.

3. DESIGN AND OPERATION OF APPARATUS.

3.1. The Calorimeter.

The calorimeter was designed to measure positive heats of mixing, down to heats of mixing of the order of 0.1 joule per milliliter of mixture; to contain up to one milliliter of either component; to have no vapour phase and to be suitable for measurements between 10 and 70° C. The calorimeter design was a modification of those of Tompa²¹ and Calvet,²⁵ and was constructed of pyrex glass and is shown in Figure 1.

The instrument was a twin calorimeter consisting of two identical vessels (C) each containing two inverted bells constructed as shown (B) and covered by two caps (A) joined by a tube carrying the thermopile (T). In one of the vessels, hereinafter referred to as the calorimeter, the heat absorption on mixing was compensated by electrical heating, while the other vessel acted as a reference bath for the thermopile. This was found to be necessary as the thermostat temperature showed variations of about 0.001° C. about the mean value. By placing the reference junctions in a separate vessel and not directly in the thermostat the influence of these variations was suppressed, as the heat capacities and heat transfer coefficients of the two vessels were approximately the same. B.50 ground glass joints (G₁) provided water tight seals for the caps and B.14 ground glass joints (G₂) vacuum tight seals for connection to the vacuum system. Dow Corning Co. high vacuum silicone grease was used on all ground glass joints.

3.2. The Thermopile.

A ten junction thermopile of 0.018 inch diameter copper and constantan wires, of length 19 centimeters, having a resistance of about six ohms was used. The ends of the thermopile were insulated with "Araldite" cement, and the thermopile and leads were held in the calorimeter by W. E.

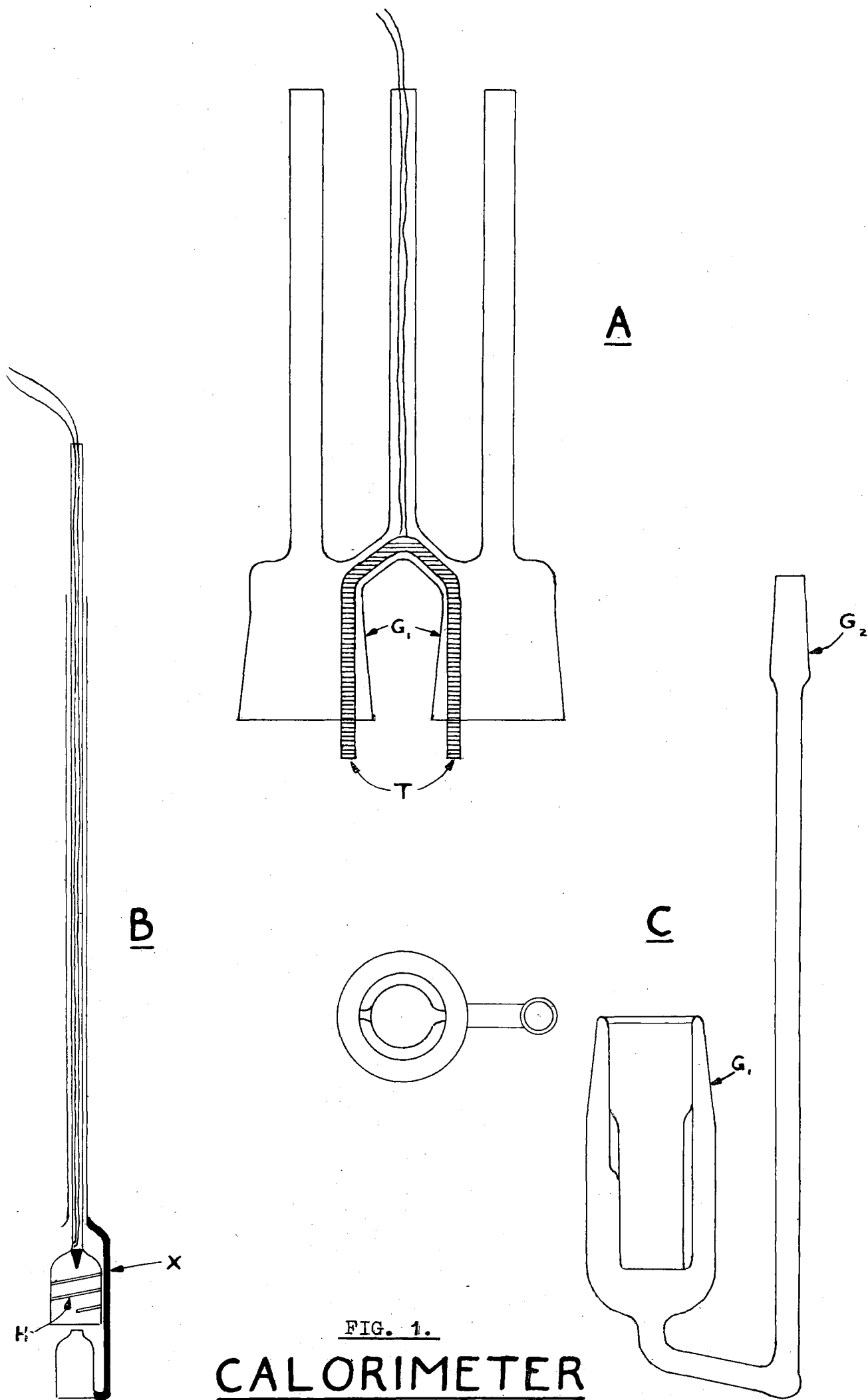


FIG. 1.

CALORIMETER

Scale: 1/2 size

Edwards and Co. W.40 wax.

3.3. The Galvanometer.

The thermal E.M.F. was fed directly to a Leeds and Northrup Co. type 2235a galvanometer, through mercury pool contacts mounted in the thermostat. Using a four meter light path, and about 340 grams of mercury in the calorimeter, the sensitivity was of the order of 80 millimeters deflection per 0.1 joule. The scale was read to the nearest millimeter.

3.4. The Heater.

The heating coil (H), having a resistance of approximately 30 ohms, was made from about 12 inches of enamelled constantan wire wound round the outside bell. The resistance of this was determined by comparison with standard resistances, using the potentiometer, to 0.001 ohm. A correction for the resistance of the leads was made. The heater was insulated from the mercury, and cemented to the bell, with clear lacquer.

3.5. The Potentiometer.

A Leeds and Northrup Co. type K.2 potentiometer was used in conjunction with a Cambridge Instrument Co. Weston Normal Cell and a Cambridge Instrument Co. type 41159 "spot" galvanometer to find the E.M.F. across the standard 50 ohm resistance to 0.00001 volt.

3.6. The Thermostat.

The thermostat was constructed of copper and was thermally lagged with wood fibre board on the bottom and sides and by wood on the top. It was about two feet square and contained two 200 watt immersion heaters, a mechanical stirrer, a copper cooling coil and a mercury toluene regulator. One heater was connected to the mains through a variable transformer and a relay actuated by the mercury toluene regulator, and the other through a variable resistance. The temperature was kept constant to better than 0.001° C.

between 10 and 45° C., and to better than 0.002° C. between 45 and 70° C.

The calorimeter was contained in a copper bath sunk into the thermostat and provided with a mechanical stirrer, as it was found that the small variations in the thermostat temperature as the relay operated heater went on and off caused variations in the calorimeter temperature. The inner bath acted as a buffer against these thermostat temperature variations.

3.7. The Vacuum System.

The jackets of the calorimeter and reference vessel were evacuated to provide thermal insulation with a mercury diffusion pump backed by an oil pump, through the B.14 ground glass joints (G₂). A vacuum of better than 10⁻³ millimeters of mercury was obtained, as shown by a vacuostat mounted in the vacuum system.

3.8. The Electrical Circuit.

The circuit to enable the E.M.F. across the calorimeter heater to be measured is shown in Figure 2.

H is the calorimeter heater; B a ballast resistance of approximately the same resistance as the calorimeter heater; S a standard 50 ohm resistance; V a variable resistance; A a two volt lead accumulator and X and Y are mercury pool switches.

3.9. Experimental Procedure.

A glass membrane across the top of the inside bell was made by breaking the solid rod at X (Figure 1) and then heating the top of the bell to redness and placing it against a thin 1.5 centimeter diameter bulb blown from 0.5 centimeter tubing. The rod was then rejoined, and to prevent premature rupture of the seal by the pointed "breaker" mounted in the outside bell, a strip of adhesive tape was wound around the tube carrying the outside bell, to give a clearance of about two millimeters

between the breaker and the membrane.

The calorimeter was filled to the top with clean mercury and the inside bell placed so that its lower edge was about 5 millimeters below the mercury surface. The bell was then completely filled with mercury by sucking the air out with a length of fine plastic tubing bent to a "U" shape. The lighter liquid was introduced into the inside bell, using a one milliliter hypodermic syringe with its needle bent to a "U" shape, the syringe being weighed before and after filling the bell, to the nearest 0.00001 gram. The bell assembly was then lowered until the lower edge of the outside bell was below the mercury surface, and the bell was then filled with mercury and the heavier liquid introduced as before. The whole bell assembly was then lowered, with the solid rod running down the slot going the full length of the calorimeter. Mercury was sucked off until about 5 millimeters remained above the top of the outside bell. The cap was then placed on, the thermopile fitting in the shorter slot. The reference vessel was filled with the same amount of mercury as in the calorimeter (about 340 grams). No seal was present in the reference vessel, and both bells were filled with mercury, as a series of blank runs with benzene in both bells of the reference vessel showed that a heating effect of less than 0.005 joule occurred on lowering the outside bell, but this effect was independent of the presence of benzene or a seal, and was therefore produced by stirring when the outside bell was lowered. When the bells in both vessels were lowered simultaneously a heating or cooling effect (referred to the calorimeter) of less than 0.002 joule was observed. The technique of lowering both bells together was followed throughout the work.

After filling, the calorimeter assembly was placed in the inside bath and connected to the vacuum system. When temperature equilibrium had been reached the vacuum was applied, and after a further hour the run was commenced. The minimum time from filling to the start of a run was about five hours.

The heating current, adjusted by the variable resistance to give a heating time of about ten seconds was switched on through the ballast resistance when the calorimeter was filled to ensure a steady current during the run.

Just before the run was commenced the galvanometer leads were disconnected and the "open circuit" galvanometer reading obtained. The leads were then reconnected and readings taken at fifteen second intervals for a period of two minutes before the seal was broken. The seal was then broken, and the heating current switched on as soon as possible for the calculated time for exact compensation. This procedure of compensating as soon as the liquids are mixed is similar to that employed by Van der Waals.⁷ For the carbon tetrachloride:chloroform and benzene:diphenyl systems a stop watch, reading to 0.1 second, was used, and for the carbon tetrachloride:cyclohexane and hexane:decane systems the pulses from an electrically maintained pendulum and the heating current giving parallel traces on a moving strip of paper were used to determine the time the heating current flowed. Galvanometer readings were taken at fifteen second intervals until temperature equilibrium was reached, as shown by constant, or uniformly changing, galvanometer readings. The galvanometer leads were then disconnected and the "open circuit" zero found to determine the zero shift of the galvanometer during the run.

An electrical calibration was carried out by observing galvanometer readings before and after the heating current was on for a known time. The "open circuit" zero was again checked, and the heating current determined by measuring the E.M.F. across the 50 ohm standard resistance while the current was flowing through the calorimeter heater. Before and after the run the E.M.F. across the 50 ohm standard was determined, with the ballast resistance in the circuit, to ensure that the current had remained steady during the run.

In the determination of the heat of mixing of the systems carbon tetrachloride:chloroform and carbon tetrachloride:

cyclohexane five two volt accumulators were used in series, with a voltage divider to the potentiometer and a 100 ohm resistance in series with the thermopile and galvanometer.

3.10. Typical Runs.

Details of two typical runs follow. Run (a) for carbon tetrachloride:chloroform is typical of this system and the system carbon tetrachloride:cyclohexane, and run (b) is typical of the systems benzene:diphenyl and hexane:decane.

(a) Carbon tetrachloride and chloroform at 25° C.

The galvanometer deflections given below are shown plotted against time in Graph 1.

Weight of chloroform = 0.75624 grams.

Weight of carbon tetrachloride = 1.12704 grams.

<u>Time</u> (minutes and Seconds)	<u>Deflection</u> (centi- meters)	<u>Time</u>	<u>Deflection</u>	<u>Time</u>	<u>Deflection</u>
0.00	26.0	7.15	26.3	10.00	32.3
3.00	26.0	7.30	26.2	10.15	37.5
5.00	26.0	7.45	26.1	10.30	40.5
5.15	23.8	8.00	26.1	10.45	41.1
5.30	24.1	8.15	26.1	11.00	41.1
5.45	26.6	8.30	26.1	11.15	40.9
6.00	27.4	8.45	26.1	11.30	40.7
6.15	27.3	9.00	26.1	11.45	40.5
6.30	26.9	9.15	26.1	12.00	40.3
6.45	26.7	9.30	26.1	12.15	40.1
7.00	26.4	9.45	27.2	12.30	39.8

Heating time during run (beginning at 5.05) = 10.3 seconds

Heating time during calibration (beginning at 9.30) = 11.9 seconds

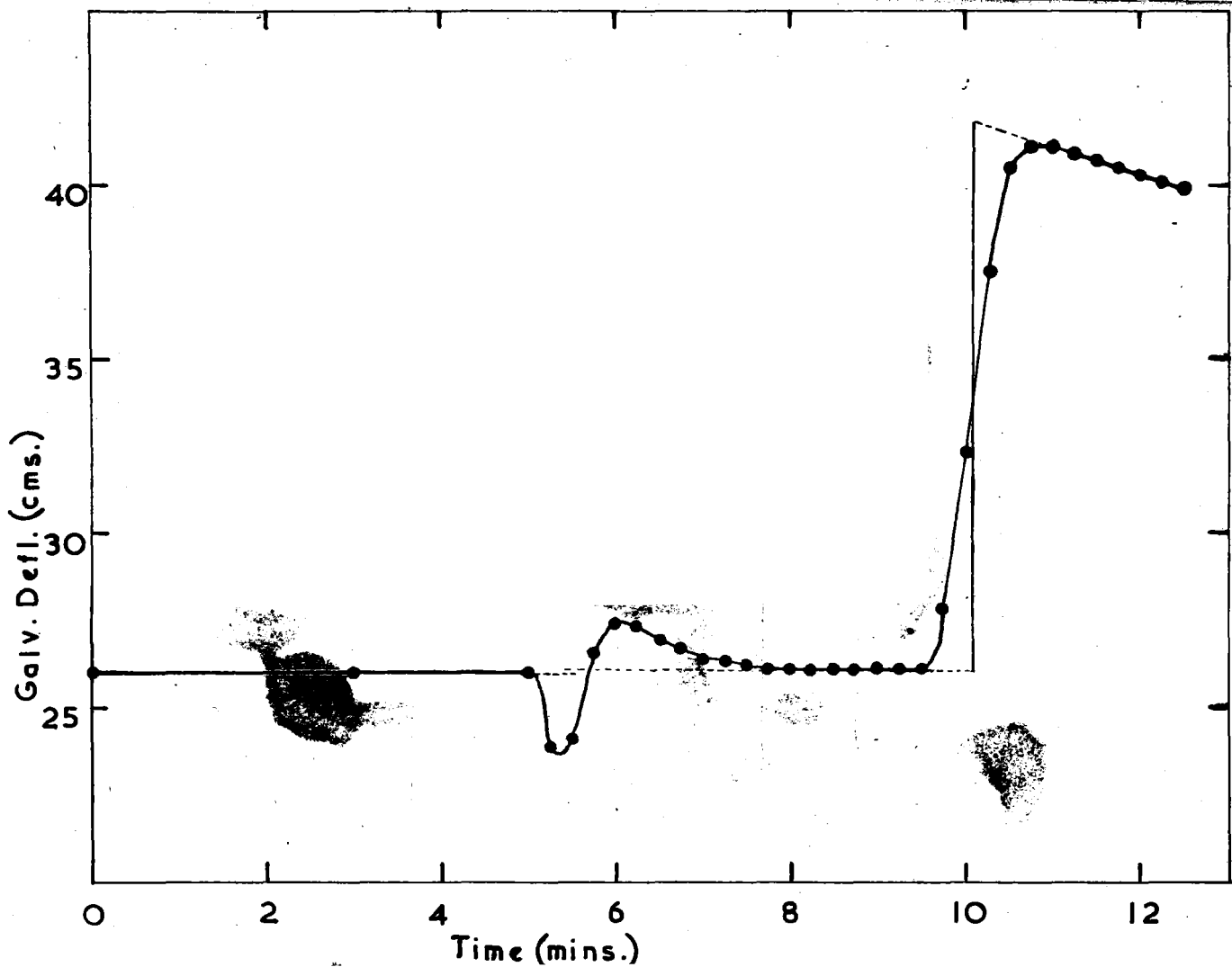
Seal broken at 5.00.

Open zero before run = 26.2 centimeters.

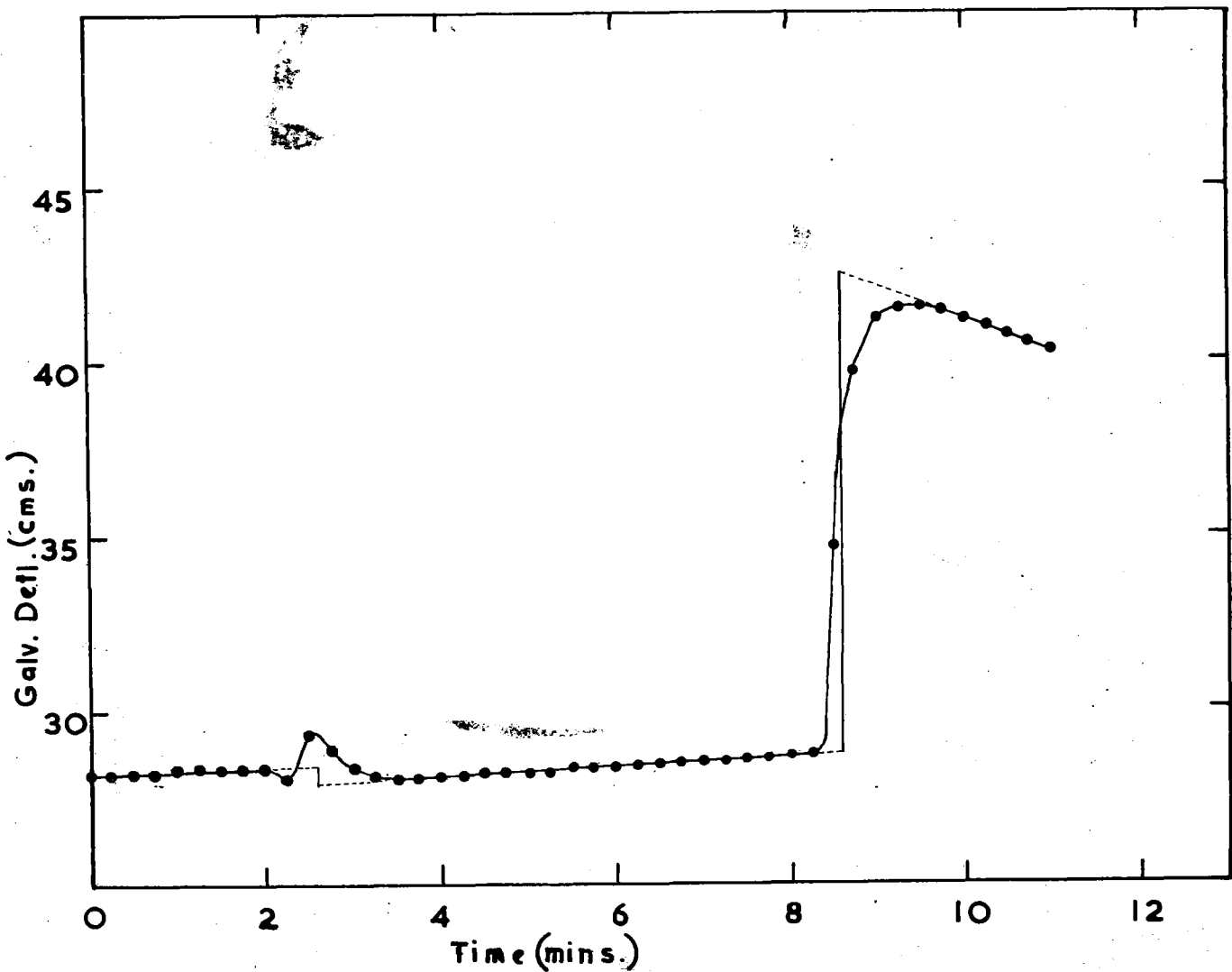
Open zero after run = 26.0 centimeters.

Open zero before calibration = 26.0 centimeters.

Open zero after calibration = 26.0 centimeters.



Graph 1. Typical Run.



Graph 2. Typical Run.

E.M.F. across 50 ohm standard with

calorimeter heater in circuit = 5.06981 volts.

Resistance of calorimeter heater = 29.525 ohms.

Then energy liberated during run

$$= \left(\frac{5.06981}{50}\right)^2 \times 29.525 \times 10.3 \text{ joules}$$

$$= 3.1266 \text{ joules}$$

and energy liberated during calibration

$$= \left(\frac{5.06981}{50}\right)^2 \times 29.525 \times 11.9 \text{ joules}$$

$$= 3.6123 \text{ joules.}$$

From Graph 1, and allowing for the zero correction, it is seen that the calorimeter has cooled by an amount corresponding to 0.1 centimeter deflection. The deflection caused by 3.6123 joules is seen to be 15.8 centimeters. Then the energy equivalent of a deflection of 0.1 centimeter is

$$\frac{0.1 \times 3.6123}{15.8} \text{ joules}$$

$$= 0.0229 \text{ joules.}$$

Then the heat of mixing is given by

$$\Delta H = 3.1266 + 0.0229 \text{ joules}$$

$$= 3.1495 \text{ joules.}$$

(b) Benzene and diphenyl solution at 45° C.

The galvanometer deflections given below are shown plotted against time in Graph 2.

Weight of benzene = 0.62282 grams.

Weight of diphenyl solution = 0.28967 grams.

Mole fraction of diphenyl in solution = 0.2870.

<u>Time</u> (minutes and seconds)	<u>Deflection</u> (centi- meters)	<u>Time</u>	<u>Deflection</u>	<u>Time</u>	<u>Deflection</u>
0.00	28.2	3.45	28.0	7.30	28.6
0.15	28.2	4.00	28.1	7.45	28.6
0.30	28.2	4.15	28.1	8.00	28.7
0.45	28.2	4.30	28.2	8.15	28.7
1.00	28.3	4.45	28.2	8.30	34.7
1.15	28.3	5.00	28.2	8.45	39.7
1.30	28.3	5.15	28.2	9.00	41.2
1.45	28.3	5.30	28.3	9.15	41.5
2.00	28.3	5.45	28.3	9.30	41.5
2.15	28.0	6.00	28.3	9.45	41.4
2.30	29.3	6.15	28.4	10.00	41.2
2.45	28.2	6.30	28.4	10.15	41.0
3.00	28.3	6.45	28.5	10.30	40.7
3.15	28.1	7.00	28.5	10.45	40.5
3.30	28.0	7.15	28.5	11.00	40.3

Heating time during run = 6.6 seconds
(beginning at 2.05)

Heating time during calibration = 10.0 seconds
(beginning at 8.15)

Seal broken at 2.00

Open zero before run = 25.0 centimeters.

Open zero after run = 24.8 centimeters.

Open zero before calibration = 24.8 centimeters.

Open zero after calibration = 25.0 centimeters.

E.M.F. across 50 ohm standard with

calorimeter heater in circuit = 1.21951 volts.

Resistance of heater = 33.445 ohms.

Then energy liberated during run

$$= \left(\frac{1.21951}{50} \right)^2 \times 33.445 \times 6.6 \text{ joules}$$

$$= 0.1313 \text{ joules}$$

and energy liberated during calibration

$$= \left(\frac{1.21951}{50} \right)^2 \times 33.445 \times 10.0 \text{ joules}$$

$$= 0.1990 \text{ joules.}$$

From Graph 2, and allowing for the zero correction, it is seen that the calorimeter has cooled by an amount corresponding to 0.7 centimeter deflection. The deflection caused by 0.1990 joule is seen to be 13.2 centimeters. Then the energy equivalent of a deflection of 0.7 centimeter is

$$\frac{0.7 \times 0.1990}{13.2} \text{ joule}$$

$$= 0.0106 \text{ joule.}$$

Then the heat of mixing is given by

$$\Delta H = 0.1313 + 0.0106 \text{ joule}$$

$$= 0.1419 \text{ joule.}$$

3.11. Purification and Storage of Materials.

(a) Mercury.

All mercury used was first towered through a solution of mercurous nitrate in 5% nitric acid and then distilled three times in vacuo. After mercury had been used in the calorimeter it was towered and redistilled in vacuo, and stored in stoppered flasks.

(b) Carbon tetrachloride.

Analytical Reagent quality carbon tetrachloride was fractionated four times, the middle fraction of each distillation being retained. The final product was stored over anhydrous sodium sulphate in a stoppered flask.

(c) Chloroform.

Six hundred milliliters of Analytical Reagent quality chloroform were shaken with five successive lots of six hundred milliliters of distilled water to remove alcohol, present as a stabiliser. The chloroform was then dried for 48 hours over anhydrous calcium chloride and then fractionated, the middle fraction being washed as before, dried over anhydrous calcium chloride and fractionated once again. The middle fraction was washed, dried over calcium chloride for a week, then fractionated from phosphorous pentoxide onto calcium carbonate. The middle fraction was filtered, degassed and sealed off into a storage flask.

(d) Cyclohexane.

Commercial quality cyclohexane was purified by Williamson³⁶ using the following method. The crude material was shaken for six hours with a nitrating acid consisting of five parts of concentrated nitric acid and nine parts of concentrated sulphuric acid, about 300 ml. of acid being used per liter of cyclohexane. The cyclohexane was then washed with distilled water and then with a 1% sodium hydroxide solution. After further washing with distilled water it was dried by standing over anhydrous calcium chloride for two days. The dry cyclohexane was then fractionated twice, the first and last quarter of each distillation being discarded. The product was stored over sodium wire in a stoppered flask.

(e) Hydrocarbons.

The hydrocarbons used were mass spectrograph standard samples obtained from the Department of Scientific and Industrial Research, Chemical Research Laboratory, Teddington, and were used without further purification.

(f) Benzene.

Analytical Reagent quality benzene was washed with successive lots of concentrated sulphuric acid until no yellow coloration of the acid was produced, then washed with distilled water and dried over anhydrous calcium chloride, then over sodium wire. It was then fractionated and the middle fraction was recrystallised seven times in a cryometer (Figure 3) similar in design to that of Timmermans.²⁷ The product was stored over sodium wire in a stoppered flask.

(g) Diphenyl.

Commercial quality diphenyl was recrystallised three times from purified alcohol and stored in a vacuum dessicator. Two runs were carried out with this product, then the diphenyl was again recrystallised. No significant difference was found in the results. The final product was stored in a vacuum dessicator.

(h) Solutions of diphenyl in benzene.

To make up and store the benzene:diphenyl solutions the storage flask shown in Figure 4 was used. The flask was weighed, the required amount of diphenyl introduced through the neck (A) and the flask reweighed. The side arm was filled with clean mercury, the flask reweighed, the benzene introduced through the neck (A) and then the neck was sealed off and the flask and detached neck reweighed.

To fill the hypodermic syringe a volume of clean mercury equal to the volume of solution to be taken was put in the syringe. The syringe was then fitted onto the ground glass joint (B) after the mercury in the side arm had been raised to B by warming the flask. The syringe was emptied of mercury, the flask tilted to empty the side arm and then the solution was drawn into the syringe. The flask was tilted to refill the side arm with mercury and the syringe removed and fitted with the bent needle.

2.12. Experimental Accuracy.

(a) Corrections for heat exchange.

The argument following is largely that of Van der Waals.⁷

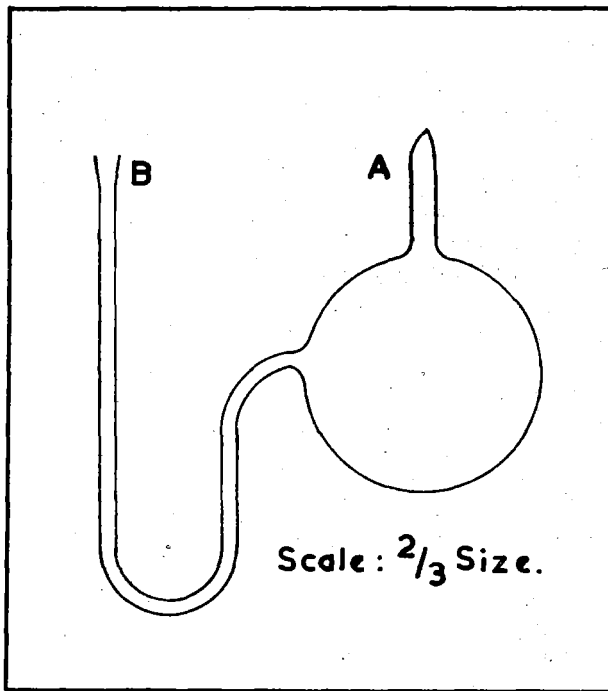


Fig. 4. Storage Vessel.

As the heat absorption on mixing and the electrical energy supplied never simultaneously balance one another, the calorimeter temperature shows small variations from the thermostat temperature during a run, and these variations are accompanied by heat transfer between the calorimeter and its surroundings. If the temperature of the thermostat is T_0 and the temperature of the calorimeter is T , there will be a flow of heat approximately proportional to $(T-T_0)$ from the surroundings to the calorimeter. As the galvanometer deflection G is proportional to $(T-T_0)$, then

$$dG/dt = -k (G-G_0)$$

where $(G-G_0)$ is the deviation of the galvanometer deflection from its value G_0 at temperature $T = T_0$, t the time and k a constant equal to the heat transfer coefficient of the calorimeter divided by its heat capacity. As k is small,

$$\Delta G / \Delta t = -k (G-G_0)_{AV}$$

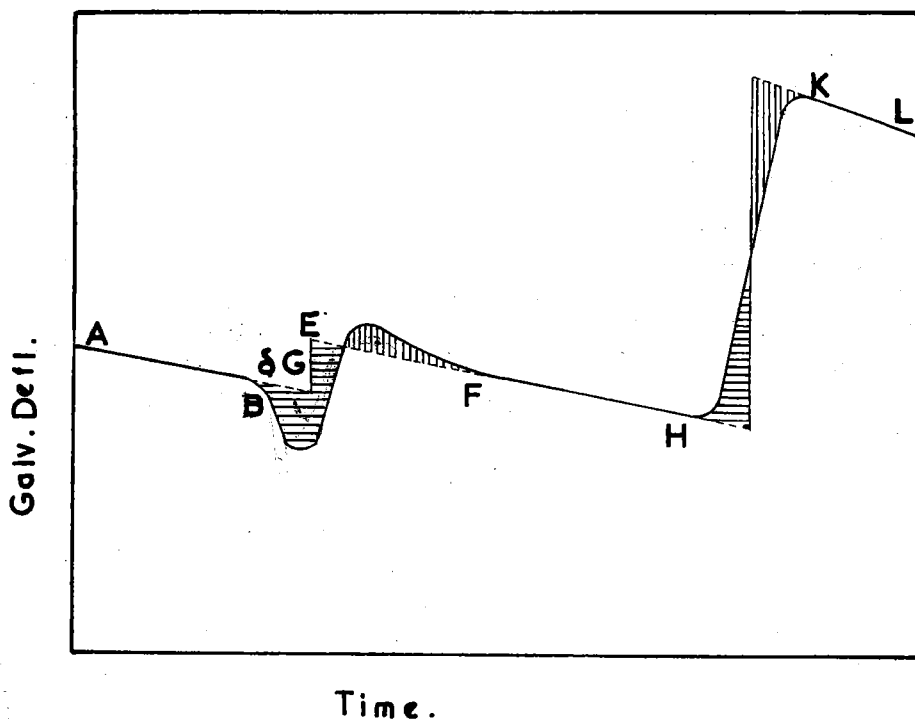
expressing that for a short time, Δt , the change in galvanometer deflection is proportional to Δt of the mean value of $(G-G_0)$ in that interval. This is represented by the straight lines AB, FH and KL in Graph 3. To apply a correction for inexact compensation, as shown by δG , a point E on the elongation of FH is found such that the vertically and horizontally hatched areas are equal. These areas represent heat loss and gain, respectively, and when they are equal the calorimeter has gained as much heat from its surroundings as it has lost to them, and δG then gives the amount of galvanometer deflection corresponding to the inexact compensation. The same procedure is applied to the calibration curve FHL, and from this curve the energy equivalent of δG is obtained. This energy equivalent is added to or subtracted from the energy supplied during the run.

The above argument is largely academic, as in nearly all the experiments the lines AB and FH were horizontal, and δG , the difference in galvanometer deflections before and after the run, was less than one centimeter. The errors introduced in reading the scale (to the nearest millimeter) and in the

extrapolations, in the value of the heat of mixing are estimated to be about $\frac{2}{3}$ of the heat measured.

(b) Other errors.

The value obtained for the heat of mixing is directly proportional to the time the heater is supplying energy, to the resistance of the heater and to the square of the current passing through the heater. The errors in making the electrical measurements will be regarded as negligible, so the only error to be considered in the above measurements is in the determination of the time. In the systems carbon tetrachloride:chloroform and benzene:diphenyl a stop watch reading to tenths of a second was used. In determining an interval of ten seconds a $\frac{2}{3}$ error may be made. Blank runs showed that the stirring effects accompanying the breaking of the seal caused the evolution or absorption (referred to the calorimeter) of 0.002 joule. The errors in weighing out the components are estimated to be less than 1%. Then the overall error in measuring 0.1 joule is $\frac{7}{8}$, and in measuring 1.0 joule, $\frac{5}{8}$. In measuring the heats of mixing of the systems carbon tetrachloride:cyclohexane and hexane:decane a pendulum operated relay was used, and it is estimated that in determining an interval of ten seconds an error of $\frac{1}{27}$ may be made. For these latter systems the error in measuring 0.1 joule is $\frac{6}{8}$, and in measuring 1.0 joule, $\frac{4}{8}$.



Graph 3. Hypothetical Run.

4. RESULTS.

The following are the results obtained in this investigation. All weights given are in grams, and have been corrected to vacuo. The heat of mixing is given in joules, and is the energy absorbed when the weights of components given are mixed.

4.1. Carbon tetrachloride:Chloroform.

All measurements were made at 25° C.

Weight CHCl ₃	Weight CCl ₄	Heat of Mixing	Weight CHCl ₃	Weight CCl ₄	Heat of Mixing
0.5272	1.3890	2.7085	0.5336	1.1617	3.5626
0.7602	1.1362	3.1215	1.1325	0.7202	2.9540
0.7533	1.1271	3.1438	1.1255	0.4101	2.0290
0.7239	1.1357	3.2416	1.2000	0.3299	1.7278
0.7926	1.1109	3.2335			

4.2. Benzene:Diphenyl.

Temperature (° C.)	Weight C ₆ H ₆	Weight Solution	Mole fraction of C ₁₂ H ₁₀ in Solution	Heat of Dilution
10	0.7980	0.1008	0.2492	0.0760
10	0.6255	0.2929	0.2492	0.1776
10	0.4061	0.4312	0.2492	0.1808
10	0.4022	0.4730	0.2492	0.1945
10	0.4017	0.4259	0.2492	0.1872
10	0.4025	0.4280	0.2492	0.1953
25	0.7332	0.1905	0.3037	0.1234
25	0.7390	0.1970	0.3037	0.1574
25	0.4430	0.4734	0.3037	0.2050
25	0.5327	0.3814	0.2370	0.2239
25	0.4432	0.4750	0.2372	0.2193
25	0.5317	0.3773	0.3037	0.2414
35	0.7005	0.2690	0.2492	0.1236
35	0.6444	0.3192	0.2492	0.1338
35	0.6022	0.3663	0.2492	0.1522
35	0.5667	0.4135	0.2492	0.1617
35	0.4429	0.4711	0.2492	0.1567
45	0.7940	0.1019	0.2370	0.0629
45	0.6212	0.2337	0.2370	0.1277
45	0.6223	0.2397	0.2370	0.1419
45	0.4412	0.4733	0.2370	0.1579
45	0.4447	0.4767	0.2370	0.1630
45	0.4470	0.4310	0.3037	0.1797
60	0.3614	0.5896	0.2492	0.1052
60	0.4057	0.4253	0.2492	0.1059
60	0.4025	0.4233	0.2492	0.0908
60	0.4459	0.4697	0.2492	0.1017
60	0.4023	0.4305	0.2370	0.1222

4.3. Carbon tetrachloride:Cyclohexane.

Temperature (° C.)	Weight C Cl ₄	Weight C ₆ H ₁₂	Heat of Mixing
10	0.9380	0.6362	1.0824
10	0.6531	0.4773	1.5160
10	1.1317	0.2401	1.2950
10	1.4216	0.0971	0.6197
25	0.2146	0.6809	0.7271
25	0.4134	0.5252	1.1437
25	0.6145	0.4949	1.3936
25	0.7991	0.3947	1.4503
25	1.0070	0.2960	1.3573
25	1.2053	0.2011	1.1030
25	1.3975	0.0538	0.3673
40	0.3306	0.6311	0.9313
40	0.6512	0.4729	1.3517
40	1.1313	0.2407	1.1697
40	1.4519	0.0863	0.5260
55	0.1966	0.6932	0.5827
55	0.3280	0.6269	0.8321
55	0.7129	0.3433	0.9616
55	1.0069	0.3000	1.2271

4.4. n-Hexane:n-Decane.

Temperature (° C.)	Weight C ₆ H ₁₄	Weight C ₁₀ H ₂₂	Heat of Mixing
10	0.1359	0.7328	0.1120
10	0.2024	0.7376	0.1743
10	0.2927	0.5513	0.1815
10	0.4011	0.4441	0.1929
10	0.4642	0.3699	0.1910
10	0.5252	0.2996	0.1922
25	0.2667	0.5911	0.1199
25	0.4023	0.4427	0.1399
25	0.4767	0.3733	0.1282

5. ANALYSIS OF RESULTS.

5.1. Carbon tetrachloride:Chloroform.

The molar volumes of carbon tetrachloride and chloroform at 25° C. are in the ratio of 1:1.2, but it has been shown²⁸ that for spherical molecules to be interchangeable on a lattice the ratio of the molar volumes may be as great as 1:2. Carbon tetrachloride and chloroform molecules may be regarded as spherical, so the assumptions made before (§ 1.2) are valid, and the molar heat of mixing should be given by

$$\Delta_{mH} = x (1-x) Nu \quad (5.1.1)$$

where x is the mole fraction of carbon tetrachloride in the mixture.

The results obtained in this work at 25° C., together with those of Hirobe¹⁷ at 25° C. and those of Whitaker and Cheeseman²⁰ at 24.7° C., are shown in Graph 4 plotted as Δ_{mH} versus the mole fraction of carbon tetrachloride in the mixture. Values of Nu were found by obtaining the best straight line through the origin to fit a Δ_{mH} versus $x (1-x)$ plot, by the method of least squares. These values are as follows:-

- (1) Whitaker and Cheeseman, $Nu = 923.6$ joules/mole.
- (2) Hirobe, $Nu = 939.3$ joules/mole.
- (3) This work, $Nu = 936.0$ joules/mole.

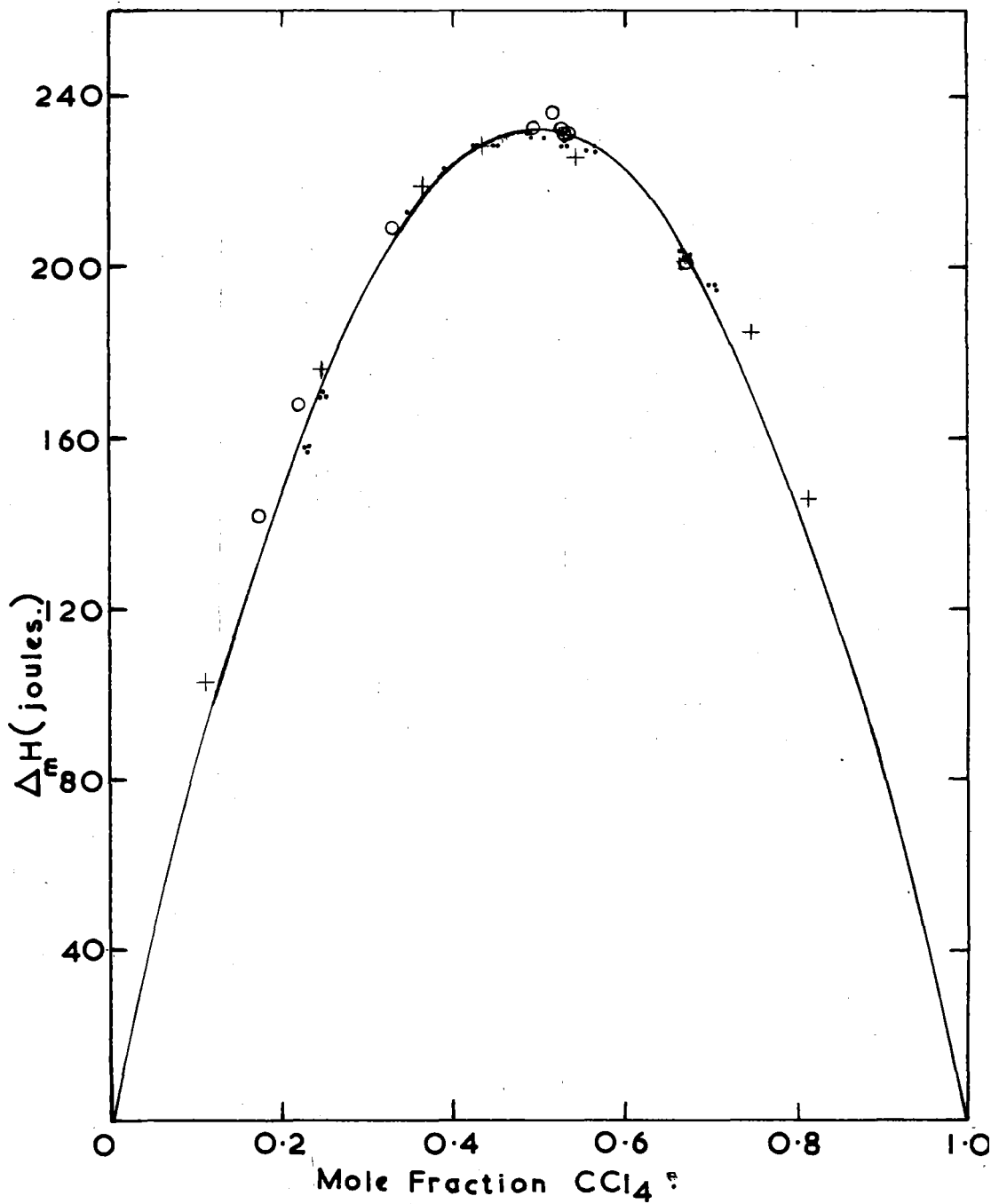
Combination of all the experimental data leads to a value of Nu of 923 joules/mole. Graph 4 shows that all the data is fitted, within experimental error, by the expression

$$\Delta_{mH} = x (1-x) 923 \text{ joules.} \quad (5.1.2)$$

Thus the molar heat of mixing is given correctly by the theory for regular mixtures.

Whitaker and Cheeseman found that the heat of mixing of equimolar mixtures was independent of temperature over the range 15 to 30° C., and thus Nu is independent of temperature. Now from equation (1.7.4) we have

$$Nu = Nw - T d (Nw)/dT \quad (5.1.3)$$



Graph 4. Results for the system CCl_4 - CHCl_3 .

•, Whitaker and Cheeseman;

+, Hirobe;

o, This work.

Then

$$N_w = - T \int (Nu)/T^2 dT \quad (5.1.4)$$

As Nu is independent of temperature integration of equation (5.1.4) gives

$$N_w = Nu + AT \quad (5.1.5)$$

where A is a constant, which may be zero, positive or negative. The molar free energy of mixing should thus be given by equation (1.6.3) with N_w given by equation (5.1.5). Unfortunately no vapour pressure data could be found to test this assumption.

5.2. Benzene:Diphenyl.

The molar volumes of benzene and diphenyl are in the approximate ratio of 1:1.7 over the experimental temperature range, but it will be assumed that the molecules pack on a lattice with each benzene molecule occupying one lattice site and each diphenyl molecule two lattice sites. The model will be applied, using a value $z = 6$ for the co-ordination number of the lattice, even though the molecules are not spherical but planar. Then the molar heat of dilution should be given, from equation (1.2.9) by

$$\Delta_{D_m}U = \frac{25 x_2 (x_1 - x_2)}{(3+2x_2)(3+2x_1)} Nu \quad (5.2.1)$$

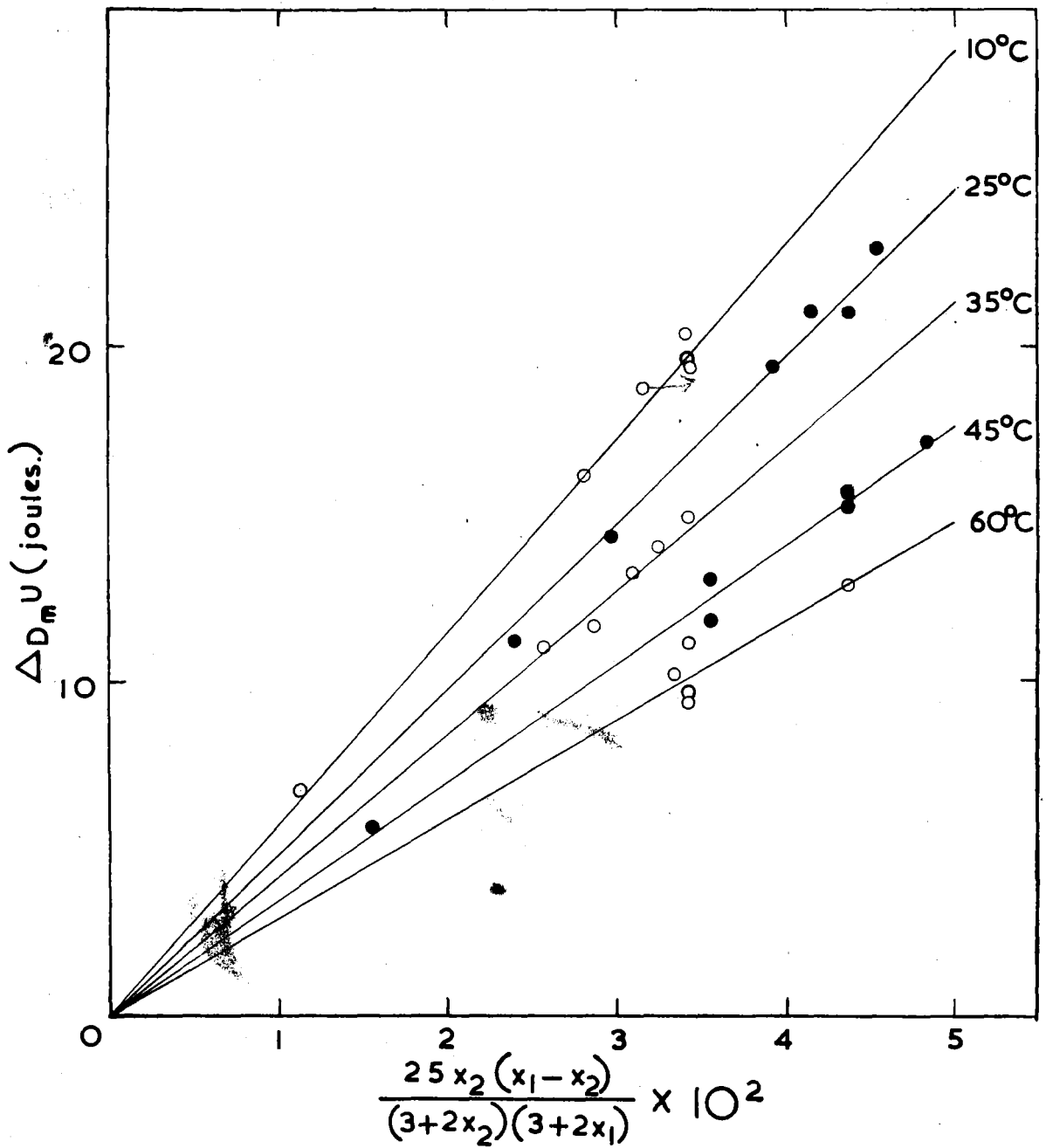
where x_1 and x_2 are the initial and final mole fractions of diphenyl in the mixture.

The results obtained in this work at 10, 25, 35, 45 and 60° C. are shown in Graph 5, plotted as $\Delta_{D_m}U$ versus $\frac{25 x_2 (x_1 - x_2)}{(3+2x_2)(3+2x_1)}$. The experimental points at one temperature all lie, within experimental error, on a straight line through the origin, showing that the results are in agreement with equation (5.2.1).

Values of Nu for each temperature were found by obtaining the best straight line through the origin to fit the above plots, by the method of least squares. These values are as follows:

10° C., Nu = 571 joules/mole.

25° C., Nu = 492 joules/mole.



Graph 5. Results for the system $C_6H_6-C_{12}H_{10}$.
 x_1 = Initial mole fraction $C_{12}H_{10}$;
 x_2 = Final mole fraction $C_{12}H_{10}$.

35° C., $N_u = 424$ joules/mole.

45° C., $N_u = 351$ joules/mole.

60° C., $N_u = 296$ joules/mole.

These values can be represented, within experimental error, by the equation

$$N_u = 2193 - 5.73T \text{ joules/mole} \quad (5.2.2)$$

where T is the temperature in degrees absolute.

From equation (5.1.4) we have

$$N_w = - T \int (N_u)/T^2 dT \quad (5.2.3)$$

and on substituting for N_u from equation (5.2.2) and performing the integration we have

$$N_w = 2193 + 13.19T \log_{10} T + \Lambda T \text{ joules/mole} \quad (5.2.4)$$

where Λ is a constant.

Vapour pressure measurements carried out on benzene: diphenyl mixtures by Everett and Penney²⁹ and by Baxendale, Enustun and Stern³⁰ over a temperature range of 15 to 75° C. have been analysed by Everett and McGlashan.¹ They found that the experimental results were in agreement with theory and that equation (1.6.3) correctly gave the molar free energy of mixing if N_w were given a temperature independent value of 636 ± 10 joules/mole. If we assume that equation (5.2.4) correctly gives the value of N_w at 35° C. (i.e., 636 joules/mole), equation (5.2.4) becomes

$$N_w = 2193 - 13.19T \log_{10} T - 37.88T \text{ joules/mole} \quad (5.2.5)$$

From equation (5.2.5) the following values of N_w are obtained:

25° C., $N_w = 631$ joules/mole.

35° C., $N_w = 635$ joules/mole.

45° C., $N_w = 643$ joules/mole.

55° C., $N_w = 649$ joules/mole.

The above values of N_w are in very good agreement with the constant value of N_w of 636 ± 10 joules/mole directly derived from vapour pressure measurements. However, if the problem of finding the relationship between N_u and N_w is approached in the reverse manner to that used above; that is if we try to find N_u , using the experimental values of N_w in

equation (1.7.4); it is found that the experimental accuracy in the determination of N_w is not sufficient to find an accurate value of $d(N_w)/dT$. More accurate determinations of vapour pressures than have hitherto been made are required before the value of N_u (and hence the heat of mixing) can be predicted from values of N_w derived from vapour pressure data.

The only previous determination of the heat of dilution of benzene:diphenyl mixtures that could be found was that of Tompa.³¹ He found a value of N_u of 740 joules/mole at 25° C. However, as Tompa made no corrections for the heat changes of evaporation and condensation on mixing, this figure cannot be regarded as accurate.

5.3. Carbon tetrachloride:Cyclohexane.

The molar volumes of carbon tetrachloride and cyclohexane are in the approximate ratio of 1:1.1 over the experimental temperature range. As in (§ 5.1) the molecules will be regarded as spherical, each molecule occupying one lattice site. Then the molar heat of mixing should be given by

$$\Delta_{mH} = x(1-x)N_u \quad (5.3.1)$$

where x is the mole fraction of carbon tetrachloride in the mixture.

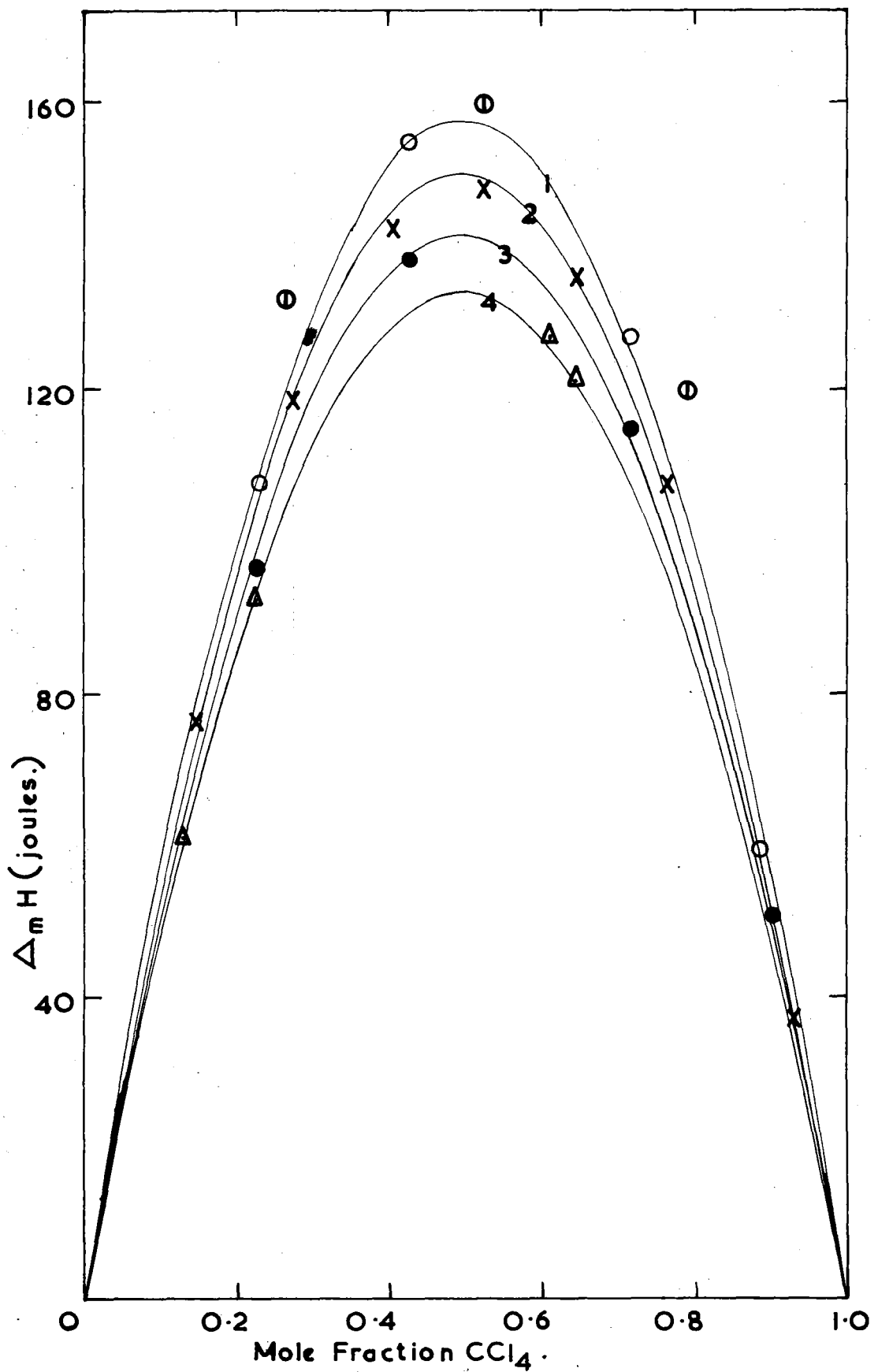
The results obtained in this work at 10, 25, 40 and 55° C., together with the results of Scatchard, Ticknor, Goates and McCartney¹² at 20° C. are shown in Graph 6, plotted as Δ_{mH} versus the mole fraction of carbon tetrachloride in the mixture. Values of N_u for each temperature were found by obtaining the best straight line through the origin to fit a Δ_{mH} versus $x(1-x)$ plot, by the method of least squares. Graph 6 shows that within experimental error, the data for each temperature fit equation (5.3.1) with the following values of N_u .

10° C., $N_u = 623$ joules/mole

25° C., $N_u = 593$ joules/mole

40° C., $N_u = 562$ joules/mole

55° C., $N_u = 532$ joules/mole



Graph 6. Results for the system CCl_4 - C_6H_{12} .
 Curve 1, 10°C ;
 Curve 2, 25°C ;
 Curve 3, 40°C ;
 Curve 4, 55°C ;
 O , Scatchard et al at 20°C .

These values can be represented, within experimental error, by the equation

$$N_u = 1198 - 2.03T \text{ joules/mole} \quad (5.3.2)$$

where T is the temperature in degrees absolute.

From equation (5.1.4) we have

$$N_w = - T \int (N_u)/T^2 dT \quad (5.3.3)$$

and on substituting for N_u from equation (5.3.2) and performing the integration we have

$$N_w = 1198 + 4.67T \log_{10} T + AT \text{ joules/mole} \quad (5.3.4)$$

where A is a constant.

Vapour pressure measurements carried out on carbon tetrachloride:cyclohexane mixtures by Scatchard, Wood and Nohel¹¹ have been analysed by Guggenheim.¹ He found that the experimental results were in agreement with theory; equation (1.6.3) giving the molar free energy of mixing for the values of N_w shown below in the third column of Table 5.1.

If it is assumed that equation (5.3.4) correctly gives the value of N_w at 40° C. (i.e., 264 joules/mole), equation (5.3.4) becomes

$$N_w = 1198 + 4.67T \log_{10} T - 14.64T \text{ joules/mole} \quad (5.3.5)$$

Values of N_w , derived from equation (5.2.5), together with the experimental values, are shown below in Table 5.1.

Table 5.1.

Temperature (° C.)	N_w from equation (5.2.5) (joules/mole)	Experimental N_w (joules/mole)
30	273	274
40	263	264
50	254	255
60	246	245
70	237	236

The above values are in excellent agreement, but as in (§ 5.2) values of N_u and hence the heat of mixing cannot be accurately found from the experimental N_w values available.

The only previous determination of the heat of mixing of carbon tetrachloride:cyclohexane mixtures that could be found

was that of Scatchard, Ticknor, Goates and McCartney¹² at 20° C. Their results are shown in Graph 6, and their accuracy has been discussed before (§ 2).

5.4. n-Hexane:n-Decane.

If it is assumed that the molecules are constructed of the elements $\text{CH}_2=$ and CH_3- , occupying a lattice with coordination number $z = 8$, then the molar heat of mixing should be given from equation (1.8.10) by

$$\Delta_{\text{m}}H = 0.2496 \frac{x(1-x)}{1.5833 + x} \text{Nu} \quad (5.4.1)$$

where x is the mole fraction of hexane in the mixture.

The results obtained in this work at 10 and 25° C. are shown in Graph 7, plotted as $\Delta_{\text{m}}H$ versus the mole fraction of hexane in the mixture. Values of Nu at each temperature were found by obtaining the best straight line through the origin to fit a $\Delta_{\text{m}}H$ versus $0.2496 \frac{x(1-x)}{1.5833+x}$ plot, by the method of least squares. The values are as follows:

$$10^\circ \text{ C.}, \text{Nu} = 843 \text{ joules/mole}$$

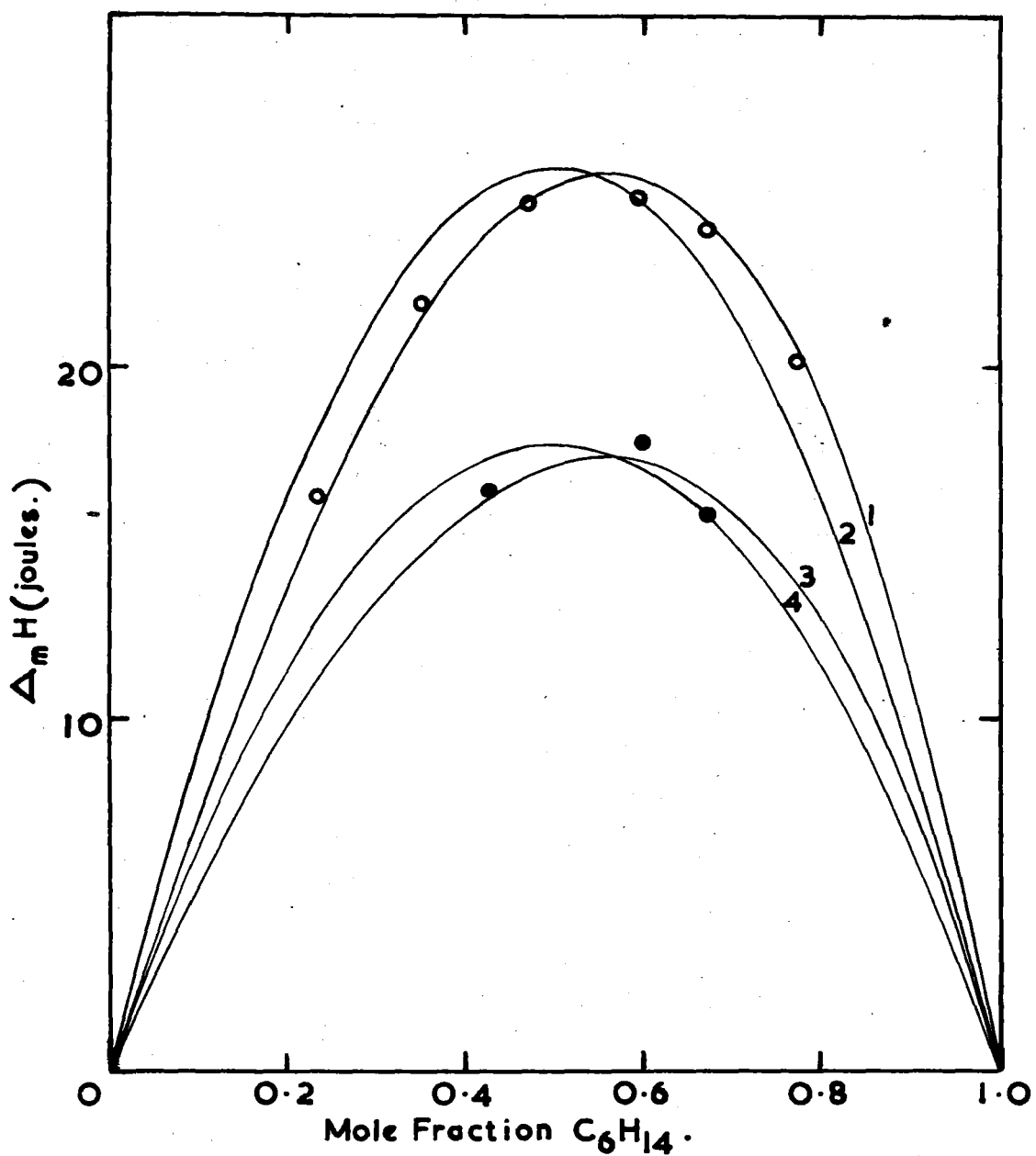
$$25^\circ \text{ C.}, \text{Nu} = 577 \text{ joules/mole.}$$

In Graph 7 curve (1) is given by equation (5.4.1) with Nu equal to 843 joules/mole, and curve (3) is given by equation (5.4.1) with Nu equal to 577 joules/mole. It is seen that within experimental error the points lie on the theoretical curves.

Van der Waals⁷ has measured the heats of mixing at 20° C. of mixtures of hexadecane with decane, octane, heptane and hexane. The results, which are not particularly accurate, show an appreciable scatter about the theoretical curves derived from equation (1.7.5). Van der Waals found that his results at 20° C. could be represented by the empirical expression

$$\Delta_{\text{m}}H = 5.1 (r_A - r_B)^2 x (1-x) \text{ joules/mole} \quad (5.4.2)$$

By finding the best parabolas to fit the results of this work, and interpolating between 10 and 25° C., it is found that for the system hexane:decane equation (5.4.2) correctly gives the heat of mixing at 20° C. Shown in Graph 7 are the



Graph 7. Results for the system $C_6H_{14}-C_{10}H_{22}$.
 Curves 1 and 2, $10^\circ C$;
 Curves 3 and 4, $25^\circ C$.

best parabolas to fit the data (curves (2) and (4)).

The scatter of the experimental results of Van der Waals about the theoretical curves derived from equation (1.7.5) is comparable to their scatter about the curve given by equation (5.4.2), but as is seen in Graph 7 the results of this work are better fitted by equation (1.7.5) than by equation (5.4.2). The values of Nu to give the best agreement of Van der Waals' results at 20° C. with theory were found by the method of least squares. The values are as follows:

Hexadecane:decane	, $Nu = 2463$ joules/mole
Hexadecane:octane	, $Nu = 1724$ joules/mole
Hexadecane:heptane	, $Nu = 1435$ joules/mole
Hexadecane:hexane	, $Nu = 1213$ joules/mole
Hexane:decane	, $Nu = 665$ joules/mole

The value for the system hexane:decane was found by interpolation between the values at 10 and 25° C. obtained in this work.

According to the theory given before all the above values should be equal since all the molecules are assumed to be constructed of the same elements, and Nu is the energy of formation of a mole of $CH_2=CH_2$ contacts. A different choice of elements to "build" the molecules from makes no appreciable difference to the extent of agreement in the Nu values given above.

Tompa⁶ has analysed the vapour pressure measurements of Bronstead and Koefoed³² on the systems hexadecane:hexane, hexadecane:heptane and hexane:dodecane. It was found that a value of Nw of 284 joules/mole, constant to $\pm 3\%$, fitted the experimental data for the three systems studied.

An explanation of the disagreement of the Nu values, and the agreement between the Nw values may lie in the fact that the results have not been corrected to constant volume. It is to be expected that the volume change on mixing will be greater the greater the difference in chain length between the component molecules of the mixture, and that the compressibilities and coefficients of thermal expansion for the mixtures will change in a regular manner with change in chain

length. The correction to be subtracted from the experimental heat of mixing values will thus be greater the greater the difference in chain length between the component molecules, and the constant volume values of Nu will be more nearly constant than the experimental constant pressure values. The correction to constant volume to be applied to the experimental vapour pressures is negligibly small, so the constancy of the experimental Nw values will not be affected. Until accurate volume, compressibility and thermal expansion data is available the results cannot be corrected to constant volume.

By integration of the Nu values over the experimental temperature range, agreement between the Nu and Nw values may be obtained, but there is little significance in the result as Bronstead and Koefoed only made measurements of vapour pressure at 20° C., and introduction of an integration constant ensures perfect agreement at one temperature.

6. SUMMARY.

A calorimeter has been built to measure the heats of mixing of binary liquid mixtures in the absence of a vapour phase. The operation of the calorimeter was checked by measuring the heat of mixing of the system carbon tetrachloride:chloroform at 25° C., and comparing the results with those obtained by other workers on the same system. Measurements were made over a temperature range of 10 to 60° C. on the systems benzene:diphenyl, carbon tetrachloride:cyclohexane and n-hexane:n-decane.

The results were found to be in good agreement with those predicted from a theory developed by Guggenheim and co-workers, based on the quasi-crystalline model of the liquid state, except that in the case of the hydrocarbon mixture, the results, when considered with results on the same type of system obtained previously, showed a discrepancy between theory and experiment. A suggested explanation of this discrepancy has been put forward.

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