720. *Thermodynamics of Hydrocarbon Mixtures. Part II.* The Heats of Mixing of the Binary Mixtures formed by Benzene,* cyclo*Hexane,* n-*Heptane, Toluene, and* n-*Hexane.*

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The heats of mixing at 20° of the binary systems formed by benzene, toluene, *cyclo*hexane, *n*-hexane, and *n*-heptane have been measured. The volume changes on mixing have also been measured for most of these systems. From these data, values have been calculated for solubility parameters and interaction parameters, and these values are considered in terms of the theories of liquid mixtures. Kirkwood's equation to correct for non-uniform distribution of molecules in a mixture has been found to be in good agreement with the results.

THE heats of mixing at 20° have been measured for seven binary mixtures formed by benzene, *cyclo*hexane, *n*-heptane, toluene, and *n*-hexane, the other three pairs having been reported in Part I. The volumes of mixing at 25° have also been measured for several of these binary mixtures.

EXPERIMENTAL

The volumes of mixing were measured by means of a single-stem pycnometer, which was fitted with a B7 joint and stopper to prevent evaporation. The technique involved was similar to that of previous workers.[1,2] The heats of mixing were measured as described in Part I.

Purity of Materials.—Toluene. B.P. grade was shaken repeatedly with concentrated sulphuric acid, washed with aqueous sodium carbonate, then water, and dried ($CaCl_2$). It was fractionated through a 1½ m. column packed with glass helices, and the fraction of boiling range 110·58—110·62° collected.

n-*Hexane.*[3] The spectroscopic grade was shaken at 45° with redistilled chlorosulphonic acid, washed with concentrated sulphuric acid, water, 10% sodium hydroxide solution, and water, and dried ($CaCl_2$). The fraction collected had b. p. 68·40°.

Benzene, *cyclo*hexane, and *n*-heptane were purified as described in Part I.

The properties of the first two liquids are summarised below, values reported by Rossini *et al.*[4] being given in parentheses.

	B. p. (760 mm.)	n^{25}	d_4^{25}
Toluene	110·60° (110·623°)	1·4940 (1·49405)	0·86121 (0·86220)
n-Hexane	68·40 (68·742)	1·3738 (1·37226)	0·65892 (0·65481)

RESULTS

For convenience, the five hydrocarbons are allotted subscripts : benzene, 1 ; *cyclo*hexane, 2 ; *n*-heptane, 3 ; toluene, 4 ; *n*-hexane, 5. Then ΔH_{14} is the heat of mixing per mole of the mixture

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* Part I, *J.*, 1955, 4141.

[1] Wood and Brasie, *J. Amer. Chem. Soc.*, 1943, **65**, 1891.

[2] Wood and Austin, *ibid.*, 1945, **67**, 480.

[3] Shepard, Midgely, and Henne, *ibid.*, 1931, **53**, 1948.

[4] Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 129.

benzene and toluene, and x_1, ϕ_1 are the mole fraction and volume fraction of benzene. Table 1 shows the heat of mixing of seven of the ten possible binary mixtures; the results for the other three binary mixtures have been given in Part I.

TABLE 1. *Heats of mixing at* 20°.

Benzene–Toluene (ΔH_{14})

x_1	0·199	0·390	0·560	0·665	0·780
ΔH_{14} (J/mole) ...	43·5	64·0	67·8	61·5	48·1
ϕ_1	0·175	0·348	0·514	0·624	0·748
ΔH_{14} (J/ml.)	0·42	0·64	0·70	0·65	0·51

Benzene–n-*Hexane* (ΔH_{15})

x_1	0·175	0·301	0·310	0·403	0·470	0·563	0·667	0·788	0·866
ΔH_{15} (J/mole) ...	452	657	669	795	841	866	837	628	469
ϕ_1	0·128	0·229	0·238	0·318	0·385	0·471	0·581	0·720	0·818
ΔH_{15} (J/ml.)	3·64	5·56	5·69	6·99	7·49	8·08	8·12	6·40	4·94

cyclo*Hexane–Toluene* (ΔH_{24})

x_2	0·250	0·300	0·340	0·435	0·516	0·570	0·708	0·733
ΔH_{24} (J/mole)......	460	523	531	590	594	611	536	485
ϕ_2	0·253	0·303	0·344	0·438	0·520	0·573	0·711	0·736
ΔH_{24} (J/ml.)	4·27	4·85	4·98	5·48	5·52	5·65	4·94	4·48

n-*Heptane–Toluene* (ΔH_{34})

x_3	0·220	0·395	0·498	0·648	0·658
ΔH_{34} (J/mole) ...	397	531	561	498	498
ϕ_3	0·279	0·473	0·576	0·717	0·727
ΔH_{34} (J/ml.)	3·77	4·44	4·31	3·68	3·72

cyclo*Hexane*–n-*Hexane* (ΔH_{25})

x_2	0·254	0·275	0·290	0·301	0·499	0·511	0·615	0·810	0·835
ΔH_{25} (J/mole) ...	119	145	138	145	215	220	211	149	126
ϕ_2	0·223	0·242	0·258	0·267	0·457	0·468	0·574	0·782	0·810
ΔH_{25} (J/ml.)	0·95	1·16	1·11	1·17	1·80	1·84	1·80	1·32	1·12

Toluene–n-*Hexane* (ΔH_{45})

x_4	0·254	0·290	0·320	0·477	0·522	0·614	0·785
ΔH_{45} (J/mole) ...	360	402	427	456	469	427	326
ϕ_4	0·218	0·253	0·278	0·430	0·472	0·567	0·740
ΔH_{45} (J/ml.)	2·89	3·26	3·47	3·81	3·93	3·68	2·93

n-*Heptane*–n-*Hexane* (ΔH_{35})

x_3	0·396	0·420	0·720	0·821
ΔH_{35} (J/mole) ...	15·5	23·4	9·2	5·0
ϕ_3	0·428	0·459	0·765	0·839
ΔH_{35} (J/ml.)	0·11	0·17	0·06	0·03

The volumes of mixing are shown in Table 2; ΔV_{14} is the volume change per mole of mixture, and $V_0 = x_1V_1 + x_4V_4$, where V_1 and V_4 are the molar volumes of the pure components at 25°.

TABLE 2. *Volumes of mixing at* 25°.

Benzene–Toluene (ΔV_{14})

x_1	0·446	0·557	0·604
$100\Delta V_{14}/V_0$	0·152	0·148	0·140
ϕ_1	0·402	0·512	0·560

Benzene–n-*Hexane* (ΔV_{15})

x_1	0·266	0·325	0·567	0·576	0·588	0·834
$100\Delta V_{15}/V_0$	0·255	0·289	0·433	0·433	0·422	0·315
ϕ_1	0·204	0·250	0·475	0·486	0·497	0·777

cyclo*Hexane–Toluene* (ΔV_{24})

x_2	0·416	0·571
ϕ_2	0·420	0·576
$100\Delta V_{25}/V_0$...	0·546	0·550

Toluene–n-*Hexane* (ΔV_{45})

x_2	0·401
ϕ_2	0·357
$100\Delta V_{45}/V_0$	0·221

Toluene–n-*Heptane* (ΔV_{43})

x_3	0·477	0·510
ϕ_3	0·555	0·586
$100\Delta V_{43}/V_0$	0·193	0·189

cyclo*Hexane*–n-*Hexane* (ΔV_{25})

x_2	0·433	0·528	0·673
ϕ_2	0·392	0·486	0·636
$100\Delta V_{25}/V_0$	0·182	0·198	0·168

cyclo*Hexane*–n-*Heptane* (ΔV_{23})

x_2...............	0·501	0·590
ϕ_2	0·426	0·516
$100\Delta V_{23}/V_0$	0·261	0·274

Benzene–n-*Heptane* (ΔV_{13})

x_1	0·430	0·604	0·813
ϕ_1	0·314	0·481	0·725
$100\Delta V_{13}/V_0$	0·479	0·521	0·449

Benzene–cyclo*Hexane* (ΔV_{12})

x_1	0·175	0·242	0·254	0·339	0·462	0·475	0·508	0·512
ϕ_1	0·148	0·208	0·219	0·296	0·414	0·426	0·459	0·464
$100\Delta V_{12}/V_0$	0·368	0·436	0·462	0·618	0·633	0·631	0·633	0·654
x_1	0·559	0·577	0·580	0·620	0·769	0·808	0·860	0·881
ϕ_1	0·508	0·529	0·532	0·573	0·732	0·776	0·835	0·859
$100\Delta V_{12}/V_0$	0·648	0·651	0·664	0·611	0·506	0·546	0·329	0·298

The results for the heats and volumes of mixing (Tables 1 and 2) are best represented by the following equations :

Benzene–Toluene

$$\Delta H_{14} = x_1x_4[272 - 18{\cdot}8(x_1 - x_4) - 5{\cdot}4(x_1 - x_4)^2] \tag{1}$$
$$\Delta H_{14} = \phi_1\phi_4[2{\cdot}76 - 0{\cdot}04(\phi_1 - \phi_4) + 0{\cdot}04(\phi_1 - \phi_4)^2] \tag{2}$$

*Benzene–*n-*Hexane*

$$\Delta H_{15} = x_1x_5[3431 + 781(x_1 - x_5) + 245(x_1 - x_5)^2] \tag{3}$$
$$\Delta H_{15} = \phi_1\phi_5[32{\cdot}60 + 1{\cdot}12(\phi_1 - \phi_5) + 1{\cdot}12(\phi_1 - \phi_5)^2] \tag{4}$$
$$100\Delta V_{15}/V_0 = x_1x_5[1{\cdot}66 + 0{\cdot}80(x_1 - x_5) + 0{\cdot}07(x_1 - x_5)^2] \tag{5}$$
$$100\Delta V_{15}/V_0 = \phi_1\phi_5[1{\cdot}72 + 0{\cdot}23(\phi_1 - \phi_5) + 0{\cdot}10(\phi_1 - \phi_5)^2] \tag{6}$$

cyclo*Hexane–Toluene*

$$\Delta H_{24} = x_2x_4[2385 - 201(x_2 - x_4) - 212(x_2 - x_4)^2] \tag{7}$$
$$\Delta H_{24} = \phi_2\phi_4[22{\cdot}13 + 0{\cdot}08(\phi_2 - \phi_4) + 3{\cdot}61(\phi_2 - \phi_4)^2] \tag{8}$$

n-*Heptane–Toluene*

$$\Delta H_{34} = x_3x_4[2218 - 44{\cdot}8(x_3 - x_4) + 145(x_3 - x_4)^2] \tag{9}$$
$$\Delta H_{34} = \phi_3\phi_4[17{\cdot}4 + 1{\cdot}8(\phi_3 - \phi_4) + 3{\cdot}6(\phi_3 - \phi_4)^2] \tag{10}$$

cyclo*Hexane–*n-*Hexane*

$$\Delta H_{25} = x_2x_5[862 + 279(x_2 - x_5) - 256(x_2 - x_5)^2] \tag{11}$$
$$\Delta H_{25} = \phi_2\phi_5[7{\cdot}36 + 1{\cdot}34(\phi_2 - \phi_5) - 1{\cdot}76(\phi_2 - \phi_5)^2] \tag{12}$$

*Toluene–*n-*Hexane*

$$\Delta H_{45} = x_4x_5[1841 - 123(x_4 - x_5) + 201(x_4 - x_5)^2] \tag{13}$$
$$\Delta H_{45} = \phi_4\phi_5[15{\cdot}41 - 0{\cdot}04(\phi_4 - \phi_5) + 4{\cdot}01(\phi_4 - \phi_5)^2] \tag{14}$$

n-*Heptane–*n-*Hexane*

$$\Delta H_{35} = x_3x_5(62{\cdot}8) \tag{15}$$
$$\Delta H_{35} = \phi_3\phi_5(0{\cdot}33) \tag{16}$$

*Benzene–*n-*Heptane*

$$\Delta H_{13} = \phi_1\phi_3[33{\cdot}81 + 0{\cdot}67(\phi_1 - \phi_3) + 1{\cdot}34(\phi_1 - \phi_3)^2] \tag{17}$$
$$100\Delta V_{13}/V_0 = x_1x_3[2{\cdot}03 + 0{\cdot}82(x_1 - x_3) + 0{\cdot}57(x_1 - x_3)^2] \tag{18}$$
$$100\Delta V_{13}/V_0 = \phi_1\phi_3[2{\cdot}11 + 0{\cdot}05(\phi_1 - \phi_3) + 0{\cdot}72(\phi_1 - \phi_3)^2] \tag{19}$$

*Benzene–*cyclo*Hexane*

$$\Delta H_{12} = \phi_1\phi_2[33{\cdot}53 + 3{\cdot}81(\phi_1 - \phi_2) - 3{\cdot}59(\phi_1 - \phi_2)^2] \tag{20}$$
$$100\Delta V_{12}/V_0 = x_1x_2[2{\cdot}57 + 0{\cdot}34(x_1 - x_2) + 0{\cdot}26(x_1 - x_2)^2] \tag{21}$$
$$100\Delta V_{12}/V_0 = \phi_1\phi_2[2{\cdot}56 - 0{\cdot}26(\phi_1 - \phi_2) + 0{\cdot}34(\phi_1 - \phi_2)^2] \tag{22}$$

cyclo*Hexane–n-Heptane*

$$\Delta H_{23} = \phi_2\phi_3[8{\cdot}87 + 0{\cdot}21(\phi_2 - \phi_3) - 2{\cdot}0(\phi_2 - \phi_3)^2] \tag{23}$$
$$100\Delta V_{23}/V_0 = x_2x_3[1{\cdot}07 + 0{\cdot}22(x_2 - x_3) + 0{\cdot}18(x_2 - x_3)^2] \tag{24}$$
$$100\Delta V_{23}/V_0 = \phi_2\phi_3[1{\cdot}09 + 0{\cdot}12(\phi_2 - \phi_3) - 0{\cdot}27(\phi_2 - \phi_3)^2] \tag{25}$$

DISCUSSION

The results for ΔH_m and 100 $\Delta V/V_0$ can always be represented in terms of a power series (equations 1—25), in every case no more than three terms being required to express the results satisfactorily. For *n*-heptane–*n*-hexane the first term only is needed to represent the results to the degree of accuracy obtainable for this system.

It has been found that where the molar volumes of the components of the binary mixture differ by less than 10%, the experimental results generally fall on a curve with its maximum at, or very near to, 0·5, when plotted with respect to mole fraction or to volume fraction. However, where the molar volumes differ considerably the position of the maximum value alters in the case of mole fraction, but remains near to 0·5 for the volume fraction plots, and this is especially noticeable in the case of benzene–*n*-hexane and

TABLE 3.

	(a) *Solubility parameters*			(b) *Interaction parameters*			
System	$\Delta\delta$ (from ΔH_m)	$\Delta\delta$ (from $\Delta E_m{}^V$)	$\Delta\delta$ (from H. & S.)	$\Delta H/x_1x_2$	$\Delta V/x_1x_2$	d_{12} (from ΔH)	d_{12} (from ΔV)
Benzene–Toluene	0·82	0·54	0·25	65	0·60	−0·0080	−0·0107
Benzene–*cyclo*Hexane	2·85	2·46	0·95	800	2·57	−0·0983	−0·0714
Benzene–*n*-Hexane	2·78	2·50	1·85	820	1·66	−0·1007	−0·0415
Benzene–*n*-Heptane	2·84	2·44	1·70	918	2·03	−0·1128	−0·0477
Toluene–*n*-Hexane	1·94	1·66	1·60	440	+ve *	−0·0482	−ve *
Toluene–*n*-Heptane	2·07	1·58	1·45	530	0·93	−0·0581	−0·0204
Toluene–*cyclo*Hexane	2·29	1·96	0·70	570	2·20	−0·0625	−0·0574
*cyclo*Hexane–*n*-Hexane	1·32	1·13	0·90	206	0·78	−0·0259	−0·0182
*cyclo*Hexane–*n*-Heptane	1·46	1·26	0·75	268	1·09	−0·0337	−0·0242
n-Heptane–*n*-Hexane	0·33	0·26	0·15	15	—	−0·0020	—
Benzene–Carbon tetrachloride	1·06	0·91	0·55	100	0·06	−0·0122	−0·0017

* Since only one value of the volume of mixing was observed for this system, no value could be calculated for $\Delta V/x_1x_2$ when $x_1 = 0{\cdot}5$. The only conclusion that may be drawn is that, since a volume increase occurs on mixing, then the sign of the interaction parameter will be negative. This is of the same sign as that of the parameter calculated from $\Delta H/x_1x_2$.

benzene–*n*-heptane where the molar volumes of the components in each mixture differ by about 40% and 50% respectively.

The energy of vaporisation per millilitre is a factor which has an important rôle in Hildebrand's theory of regular mixtures. The relation is expressed by the equation

$$\delta_1 = (\Delta E_1/V_1)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

where δ_1 is called the solubility parameter, ΔE_1 is the energy of vaporisation, and V_1 is the molar volume of component 1. Also

$$\Delta\delta_{12} = \delta_1 - \delta_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

The factor $\Delta\delta_{12}$ can be calculated from a knowledge of the heat of mixing of the binary mixture 1, 2. This, however, assumes that the heat of mixing at constant pressure (ΔH_m) is equivalent to the energy of mixing at constant volume ($\Delta E_m{}^V$). Because of the volume change frequently observed on mixing, this relation between the heat of mixing and the energy of mixing is not strictly true. Scatchard,[5] by considering mixing to be a two-step process involving (i) the mixing of the two components at constant volume followed by (ii) expansion (or contraction) of the mixture to return to its original internal pressure, and Hildebrand and Scott,[6] by means of a Taylor expansion series, have related the thermodynamic functions at constant pressure to those at constant volume. Both obtain, to a first approximation, the equation

$$\Delta H_m = \Delta E_m{}^V\,(1 + \alpha T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where α is the coefficient of thermal expansion.

For many liquids at room temperature ($T \sim 300°$ K), α is about $1{\cdot}2 \times 10^{-3}$, so that

$$\Delta H_m \approx 1{\cdot}36\Delta E_m{}^V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

This represents a substantial correction that has to be made to ΔH_m when calculating the quantity $\Delta\delta_{12}$ by means of Scatchard's equation : [7]

$$\Delta E_m/(x_1V_1 + x_2V_2) = \phi_1(1 - \phi_1)(\Delta\delta_{12})^2 \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Table 3(a) shows values of $\Delta\delta$ calculated (i) from ΔH_m data, (ii) from $\Delta E_m{}^V$ by use of equation (30), (iii) from values of the individual solubility parameters at 25° calculated by Hildebrand and Scott.[8] It can be seen that agreement between the calculated values of $\Delta\delta$ and the experimental values is much improved when equation (29) is used but, even so,

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[5] Scatchard, *Trans. Faraday Soc.*, 1937, **33**, 160.

[6] Hildebrand and Scott, " The Solubility of Non-electrolytes," Reinhold, New York, 1950, 136.

[7] Scatchard, *Chem. Rev.*, 1931, **8**, 321.

[8] Hildebrand and Scott, *ibid.*, p. 436.

agreement is poor generally. In every case the experimental value of $\Delta\mathcal{S}$ is higher than the calculated value, in agreement with the results of Vold,[9] Cheesman and Whitaker,[10] and Cheesman and Canning.[11]

For the ten systems studied, only in one case, that of benzene (1), toluene (2), and *cyclo*-

$$\Delta\mathcal{S}_{13} = \Delta\mathcal{S}_{23} + \Delta\mathcal{S}_{12} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (31)$$

hexane (3), does the relation (31) hold to better than 5%. For the other systems, up to 50% deviation from equation (31) is observed. This is in accord with the results of Cheesman and Whitaker, and of Cheesman and Canning, but not with those of Vold.

By means of the theory of conformal solutions developed by Longuet-Higgins,[12] the thermodynamic properties of this type of solution can be calculated in terms of the thermodynamic properties of one of the pure components and a difference function. In this theory, which is based upon no definite model for the liquid state, a binary solution may be characterised by only one parameter, the difference function d_{12}.

The difference function (or the interaction parameter) d_{12} may be calculated separately from heat-of-mixing data, and from volume-of-mixing data, by means of equations (32) and (33). This affords a means of comparison of the values of the parameter when calculated from two sources :

FIG. 1.

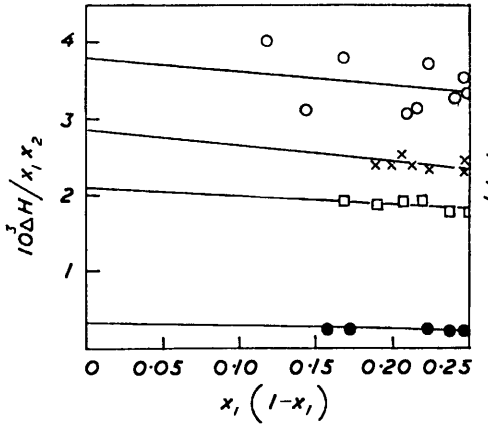
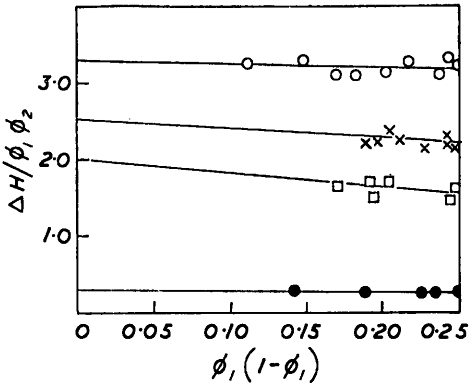


FIG. 2.



○, Benzene–*n*-Hexane. ×, *cyclo*Hexane–Toluene. □, Toluene–*n*-Hexane. ●, Benzene–Toluene.

$$d_{12} = \Delta H/x_1x_2(T \,.\, \mathrm{d}E_0/\mathrm{d}T - E_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (32)$$

$$d_{12} = \Delta V/[x_1x_2(-T\alpha_0) \,.\, V_0{}^1] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (33)$$

where $V_0{}^1$ = molar volume, α_0 = coefficient of thermal expansion and E_0 = latent heat of vaporisation of either of the pure components.

The values obtained for the interaction parameter d_{12}, calculated from both sets of data, are given in Table 3(b). In every case the sign of the parameter is the same whether calculated from ΔH_{m} or from ΔV_{m}, and the values are approximately of the same magnitude. The actual numerical differences are relatively unimportant, since d_{12} represents the difference between quantities close to unity.

Prigogine and Mathot [13] have recently developed a theory of solutions based upon a lattice model, where the mean cell-field is represented by a smoothed potential, that is, by

[9] Vold, *J. Amer. Chem. Soc.*, 1937, **59**, 1515.
[10] Cheesman and Whitaker, *Proc. Roy. Soc.*, 1952, *A*, **212**, 406.
[11] Cheesman and Canning, *J.*, 1955, 1230.
[12] Longuet-Higgins, *Proc. Roy. Soc.*, 1951, *A*, **205**, 247.
[13] Prigogine and Mathot, *J. Chem. Phys.*, 1952, **20** 49.

a potential well with a flat base and vertical walls. By this means, equations may be obtained to express the thermodynamic functions in terms of three parameters Λ_{11}, Λ_{12}, and Λ_{22} which are measures of the intermolecular attractions and are related to the molecular energies of vaporisation. In this treatment an equation may be obtained for the excess volume of mixing. This equation predicts that when $\Lambda_{12} = (\Lambda_{11}\Lambda_{22})^{\frac{1}{2}}$ then a contraction will be observed when components 1 and 2 are mixed. No contractions on mixing have been observed in this work, although several such cases have been reported.[14, 15]

The series expansion derived by Kirkwood [16] to correct for the non-uniform distribution of the molecules in a mixture can be reduced to the following form if the higher terms are neglected :

$$\frac{\Delta H_{\mathrm{m}}}{x(1-x)} = \frac{Nw}{z}\left[1 - \frac{x(1-x)w}{kT}\right] \quad . \; . \; . \; . \; . \; . \; . \quad (34)$$

where N is Avogadro's number, z is the co-ordination number of the quasi-lattice, and w is the interchange energy. The experimental results have been plotted so as to test this equation and in most cases an excellent linear relation is observed between $\Delta H_{\mathrm{m}}/x(1-x)$ and $x(1-x)$. In cases where there is a scatter of the experimental points (always in cases where the molar volumes of the components differ appreciably), then representation of the results is very much improved by plotting $\Delta H/\phi_1(1-\phi_1)$ against $\phi_1(1-\phi_1)$. This is extremely well illustrated for the mixture benzene–*n*-hexane, Figs. 1 and 2 showing some of these results.

Values of $\Delta H/x_1x_2$ in Table 3(b) represent the values of the interchange energies of the binary mixtures expressed in calories per mole of mixture.

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[14] Mathot and Desmyter, *J. Chem. Phys.*, 1953, **21**, 782.

[15] Rowlinson and Thacker, *ibid.*, p. 2242.

[16] Kirkwood, *ibid.*, 1938, **6**, 70.