898. *The Relationship between the Excess Heat and Volume of Mixing.*

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Equations are derived for binary liquid mixtures relating the heat of mixing to the excess volume and compressibility, and the excess compressibility to the excess volume and vapour pressure. The equations are applied to the systems *cyclo*hexane–carbon tetrachloride, benzene–toluene, benzene–carbon tetrachloride, benzene–*cyclo*hexane and ethanol–water, and it is shown that for the non-polar mixtures it is possible to calculate the heat of mixing from density measurements and the compressibilities of the pure components where the excess vapour pressure is always very small. For systems with larger excess vapour pressures these need to be known also. The theoretical significance of the equations is discussed, and comparison is made with recent theories of non-electrolyte solutions.

THE variation of the excess thermodynamic functions of mixing with concentration for many binary liquid mixtures can be represented by equations of the same form in mole fraction (x) or volume fraction (ϕ). In particular, the excess heat (ΔH_{m}) and excess volume (ΔV_{m}) at constant pressure and temperature can frequently be expressed by equations of the form

$$\Delta H_{\mathrm{m}} = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2] \quad . \quad . \quad . \quad . \quad (1)$$

$$\Delta V_{\mathrm{m}} = x_1x_2[D + E(x_1 - x_2) + F(x_1 - x_2)^2] \quad . \quad . \quad . \quad . \quad (2)$$

where x_1, x_2 are the mole fractions of the two components and A, B, C, D, E, F are constants. Equations of the same form hold for ϕ. This has been demonstrated for the ten binary mixtures formed from benzene, toluene, *n*-hexane, *n*-heptane, and *cyclo*hexane,[1,2] and for binary mixtures of benzyl acetate with chloroform, *m*-cresol, dioxan, and aniline.[3] In other cases where investigators have expressed their results differently, (1) and (2) often describe the results as well. For benzyl acetate–aniline it is striking how similar is the form of the variation of ΔH_{m} and ΔV_{m} with x, each showing a maximum and a minimum at almost the same values of x^3. The variations with x of ΔH_{m} and ΔV_{m} seem to be related, and Newitt and Weale,[4] who studied mixtures containing hexane, heptane, and octane, and mixtures of alcohols, suggested that a relationship must exist between the excess heat of mixing, the molar volume, and the compressibility. Such a relationship might be useful if it enabled heats of mixing, which are tedious to measure, to be calculated from simpler measurements such as that of density, and would have important theoretical implications.

Theoretical.—Equations relating the excess heat and volume of mixing. A thermodynamic

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[1] Brown, Mathieson, and Thynne, *J.*, 1955, 4141.
[2] Mathieson and Thynne, *J.*, 1956, 3708.
[3] Moore and Styan, *Trans. Faraday Soc.*, 1956, **52**, 1556.
[4] Newitt and Weale, *J.*, 1951, 3092.

relationship can be obtained giving the differential of the excess heat content with concentration in terms of the excess compressibility, the excess volume and its differentials with temperature and concentration, and a constant volume term.

The heat content is a function of the four variables $H = F(P, V, T, x)$ and the pressure of the three

$$P = G(V, T, x) \qquad \ldots \ldots \ldots \quad (3)$$

Partial differentiation gives dH in terms of the two sets of variables V, T, x and P, V, T as

$$\begin{aligned} \mathrm{d}H &= \left(\frac{\partial H}{\partial V}\right)_{T,x}\mathrm{d}V + \left(\frac{\partial H}{\partial T}\right)_{V,x}\mathrm{d}T + \left(\frac{\partial H}{\partial x}\right)_{V,T}\mathrm{d}x \\ &= \left(\frac{\partial H}{\partial V}\right)_{P,T}\mathrm{d}V + \left(\frac{\partial H}{\partial T}\right)_{P,V}\mathrm{d}T + \left(\frac{\partial H}{\partial P}\right)_{V,T}\mathrm{d}P \end{aligned}$$

At constant T, then,

$$\left(\frac{\partial H}{\partial V}\right)_{T,x} = \left(\frac{\partial H}{\partial V}\right)_{P,T} + \left(\frac{\partial H}{\partial P}\right)_{V,T}\left(\frac{\partial P}{\partial V}\right)_{T} - \left(\frac{\partial H}{\partial x}\right)_{V,T}\left(\frac{\partial x}{\partial V}\right)_{T} \quad \ldots \quad (4)$$

Partial differentiation also gives

$$\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_{T,x}\mathrm{d}V + \left(\frac{\partial P}{\partial T}\right)_{V,x}\mathrm{d}T + \left(\frac{\partial P}{\partial x}\right)_{V,T}\mathrm{d}x$$

which at constant T yields

$$\left(\frac{\partial P}{\partial V}\right)_{T} = \left(\frac{\partial P}{\partial V}\right)_{T,x} + \left(\frac{\partial P}{\partial x}\right)_{V,T}\left(\frac{\partial x}{\partial V}\right)_{T} \qquad \ldots \ldots \quad (5)$$

Combining (5) with (4), we have

$$\left(\frac{\partial H}{\partial V}\right)_{T,x} = \left(\frac{\partial H}{\partial V}\right)_{P,T} + \left(\frac{\partial H}{\partial P}\right)_{V,T}\left(\frac{\partial P}{\partial V}\right)_{T,x} + \left(\frac{\partial x}{\partial V}\right)_{T}\left[\left(\frac{\partial H}{\partial P}\right)_{V,T}\left(\frac{\partial P}{\partial x}\right)_{V,T} - \left(\frac{\partial H}{\partial x}\right)_{V,T}\right] \quad . \quad (6)$$

Since the following hold for these functions

$$\left(\frac{\partial H}{\partial x}\right)_{V,T} = \left(\frac{\partial H}{\partial P}\right)_{V,T}\left(\frac{\partial P}{\partial x}\right)_{V,T} \qquad \ldots \ldots \quad (7)$$

$$\left(\frac{\partial H}{\partial V}\right)_{T,x} = \left(\frac{\partial H}{\partial P}\right)_{T,x}\left(\frac{\partial P}{\partial V}\right)_{T,x}; \quad \left(\frac{\partial H}{\partial V}\right)_{P,T} = \left(\frac{\partial H}{\partial x}\right)_{P,T}\left(\frac{\partial x}{\partial V}\right)_{P,T} \quad \ldots \quad (8)$$

and (7) shows that the last term in (6) is zero, combination of (7) and (8) with (6) gives

$$\left(\frac{\partial H}{\partial P}\right)_{T,x}\left(\frac{\partial P}{\partial V}\right)_{T,x} = \left(\frac{\partial H}{\partial x}\right)_{P,T}\left(\frac{\partial x}{\partial V}\right)_{P,T} + \left(\frac{\partial H}{\partial P}\right)_{V,T}\left(\frac{\partial P}{\partial V}\right)_{T,x}$$

Rearranging, we have

$$\left(\frac{\partial H}{\partial x}\right)_{P,T}\left(\frac{\partial x}{\partial V}\right)_{P,T} = \left(\frac{\partial P}{\partial V}\right)_{T,x}\left[\left(\frac{\partial H}{\partial P}\right)_{T,x} - \left(\frac{\partial H}{\partial P}\right)_{V,T}\right] \quad \ldots \quad (9)$$

For these functions also,

$$\left(\frac{\partial H}{\partial P}\right)_{V,T} = \left(\frac{\partial H}{\partial x}\right)_{V,T}\left(\frac{\partial x}{\partial P}\right)_{V,T}; \quad \left(\frac{\partial x}{\partial P}\right)_{V,T} = -\left(\frac{\partial V}{\partial P}\right)_{T,x}\left(\frac{\partial x}{\partial V}\right)_{P,T} \quad \ldots \quad (10)$$

and combination with (9) gives

$$\left(\frac{\partial H}{\partial x}\right)_{P,T} = \left(\frac{\partial V}{\partial x}\right)_{P,T}\left(\frac{\partial P}{\partial V}\right)_{T,x}\left(\frac{\partial H}{\partial P}\right)_{T,x} + \left(\frac{\partial H}{\partial x}\right)_{V,T} \quad \ldots \quad (11)$$

Equation (11) can be applied to the process of mixing the two components, for which $\Delta H_{\mathrm{m}} = H_{\mathrm{m}} - H_0$ and $\Delta V_{\mathrm{m}} = V_{\mathrm{m}} - V_0$, where H_{m}, V_{m} are the heat content and molar volume of the mixture, and H_0, V_0 are the corresponding additive functions for the separated components. Then,

$$\left(\frac{\partial \Delta H_{\mathrm{m}}}{\partial x}\right)_{P,T} = \left(\frac{\partial \Delta V_{\mathrm{m}}}{\partial x}\right)_{P,T}\left(\frac{\partial P}{\partial \Delta V_{\mathrm{m}}}\right)_{T,x}\left(\frac{\partial \Delta H_{\mathrm{m}}}{\partial P}\right)_{T,x} + \left(\frac{\partial \Delta H_{\mathrm{m}}}{\partial x}\right)_{\Delta V_{\mathrm{m}},T} \quad . \quad (12)$$

On introduction of

$$\left(\frac{\partial \Delta H_{\mathrm{m}}}{\partial P}\right)_{T,x} = \Delta V_{\mathrm{m}} - T\left(\frac{\partial \Delta V_{\mathrm{m}}}{\partial T}\right)_{P,x} \quad . \; . \; . \; . \; . \quad (13)$$

and

$$\left(\frac{\partial \Delta V_{\mathrm{m}}}{\partial P}\right)_{T,x} = (\beta_0 V_0 - \beta_{\mathrm{m}} V_{\mathrm{m}})_{T,x} \quad . \; . \; . \; . \; . \; . \; . \quad (14)$$

where β_{m}, β_0 are respectively the isothermal compressibilities of the mixture and the corresponding additive function for the separated components, equation (12) becomes

$$\left(\frac{\partial \Delta H_{\mathrm{m}}}{\partial x}\right)_{P,T} = \left(\frac{\partial \Delta V_{\mathrm{m}}}{\partial x}\right)_{P,T}\left(\frac{1}{\beta_0 V_0 - \beta_{\mathrm{m}} V_{\mathrm{m}}}\right)_{T,x}\left[\Delta V_{\mathrm{m}} - T\left(\frac{\partial \Delta V_{\mathrm{m}}}{\partial T}\right)_{P,x}\right] + \left(\frac{\partial \Delta H_{\mathrm{m}}}{\partial x}\right)_{\Delta V_{\mathrm{m}},T} \quad . \; . \; . \; . \quad (15a)$$

The corresponding equation for volume fraction is

$$\left(\frac{\partial \Delta H_{\mathrm{m}}}{\partial \phi}\right)_{P,T} = \left(\frac{\partial \Delta v_{\mathrm{m}}}{\partial \phi}\right)_{P,T}\left(\frac{1}{100(\beta_0 V_0 - \beta_{\mathrm{m}} V_{\mathrm{m}})}\right)_{T,\phi}\left[\Delta V_{\mathrm{m}} - T\left(\frac{\partial \Delta V_{\mathrm{m}}}{\partial T}\right)_{P,\phi}\right] + \left(\frac{\partial \Delta H_{\mathrm{m}}}{\partial \phi}\right)_{\Delta V_{\mathrm{m}},T} \quad . \; . \; . \; . \quad (15b)$$

where $\Delta v_{\mathrm{m}} = 100\Delta V_{\mathrm{m}}/V_0$ and ΔH_{m} is expressed per ml. instead of per mole as in equation (15*a*). Application of these equations to the calculation of ΔH_{m} requires knowledge of the density over a small range of temperature and of the compressibility together with some information regarding the quantity $(\partial \Delta H_{\mathrm{m}}/\partial x)_{\Delta V_{\mathrm{m}},T}$. There is reason to believe that this term is zero or negligible, at least for non-polar mixtures. The regular-solution approximation as applied by Scott [5] makes ΔH_{m} constant at constant ΔV_{m}, and the smoothed-potential cell model of Prigogine and Mathot [6] leads to the conclusion that ΔV_{m} is proportional to the other excess functions for non-polar mixtures. This is elaborated in the Discussion where the equations presented here are compared with several theories of mixtures. Experimental confirmation that $(\partial \Delta H_{\mathrm{m}}/\partial x)_{\Delta V_{\mathrm{m}},T}$ is zero or negligible has been obtained for the non-polar mixtures examined.

Equations relating excess compressibility and vapour pressure. Knowledge of β_{m} is required for the practical application of equations (15) to the calculation of heats of mixing. For systems which depart sufficiently from ideality for the approximation $\beta_{\mathrm{m}} = \beta_0$ to be invalid, β_{m} can be calculated from the vapour pressure.

Let $\Delta p = p_{\mathrm{m}} - p_0$ where p_{m}, p_0 are the vapour pressure of the mixture and the additive vapour pressure of the separated components (the "ideal" vapour pressure). Then $\Delta p = \mathrm{f}''(P, \Delta V_{\mathrm{m}}, T, x)$ and analogous treatment to that for ΔH_{m} leads to

$$\left(\frac{\partial \Delta p}{\partial x}\right)_{P,T} = \left(\frac{\partial \Delta V_{\mathrm{m}}}{\partial x}\right)_{P,T}\left(\frac{\partial P}{\partial \Delta V_{\mathrm{m}}}\right)_{T,x}\left(\frac{\partial \Delta p}{\partial P}\right)_{T,x} + \left(\frac{\partial \Delta p}{\partial x}\right)_{\Delta V_{\mathrm{m}},T} \quad . \; . \quad (16)$$

$(\partial \Delta p/\partial x)_{\Delta V_{\mathrm{m}},T}$ may be zero or negligible for non-polar mixtures, which is virtually the same assumption as for $(\partial \Delta H_{\mathrm{m}}/\partial x)_{\Delta V_{\mathrm{m}},T}$. It holds when ΔF_{m} (the excess free energy) is proportional to ΔV_{m}, which is predicted theoretically for non-polar mixtures.[5, 6] This assumption agrees with experiment for two non-polar mixtures.

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[5] Scott, *Discuss. Faraday Soc.*, 1953, **15**, 44.

[6] Prigogine and Mathot, *J. Chem. Phys.*, 1952, **20**, 49.

If we put

$$\left(\frac{\partial \Delta p}{\partial P}\right)_{T,x} = \frac{d}{d_m - d} - \frac{d}{d_0 - d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where d_m, d_0, d are the densities of the mixture, the additive density of the separated components, and the density of the vapour, assumed ideal, (16) becomes, with (14), for non-polar mixtures,

$$\beta_0 V_0 - \beta_m V_m = \left(\frac{\partial \Delta V_m}{\partial \Delta p}\right)_{P,T}\left[\frac{d}{d_m - d} - \frac{d}{d_0 - d}\right] \quad . \quad . \quad . \quad . \quad (18)$$

Equation (18) permits the calculation of β_m from the densities, and the compressibilities of the pure components.

Application of the Equations to Specific Mixtures.—Equations (15) and (18) were used to calculate the heat of mixing for different types of binary mixture and the results were compared with experimental values. Three groups of mixtures were considered and representatives taken from each. (1) Mixtures showing very small departures from ideality, for which $\beta_m = \beta_0$ (*cyclo*hexane–carbon tetrachloride, benzene–toluene). (2) Mixtures showing larger departures from ideality, for which $\beta_m \neq \beta_0$ (benzene–carbon tetrachloride, benzene–*cyclo*hexane). (3) Polar mixtures, for which $\beta_m \neq \beta_0$ and $(\partial \Delta H_m/\partial x)_{\Delta V_m, T}$ is probably not zero (ethanol–water).

For group (1), ΔH_m can be calculated from (15) with $\beta_m = \beta_0$, and for group (2), from (15) and (18). This test of the equations is necessary to show whether normal experimental measurements of density and compressibility are sufficiently accurate for a useful calculation, and to show empirically that $(\partial \Delta H_m/\partial x)_{\Delta V_m, T}$ and $(\partial \Delta p/\partial x)_{\Delta V_m, T}$ are negligible.

cyclo*Hexane–carbon tetrachloride.* For the heat of mixing at 20° Scatchard, Ticknor, Goates, and McCartney [7] give

$$\Delta H_m = \phi_1 \phi_2 V_0[1{\cdot}49 + 0{\cdot}49(\phi_1 - \phi_2)^2]$$

where ϕ_1, ϕ_2 are the volume fractions of carbon tetrachloride and *cyclo*hexane, respectively, and ΔH_m is in cal./mole. Heats of mixing can also be interpolated at 20° from the results of Adcock and McGlashan.[8] Wood and Gray [9] measured the density of the mixture accurately from 15° to 75° and expressed their results as

$$100\Delta V_m/V_0 = \phi_1 \phi_2[0{\cdot}6763 - (0{\cdot}04362 + 0{\cdot}01335t)\phi_1]$$

where t is in °C. The vapour pressure of this mixture is almost ideal [10] and so $\beta_m \approx \beta_0$. Scatchard, Wood, and Mochel [10] use, at 25°,

$$\beta_m = 1{\cdot}10(1 + 0{\cdot}009\phi_2) \times 10^{-4}$$

The variation of β_m with concentration is so small that it may safely be neglected, and a constant value of $\beta_m = 1{\cdot}05 \times 10^{-4}$ has been employed for 20°.

Δv_m being expressed by an equation of the form of (2), $(\partial \Delta v_m/\partial \phi_1)_{P,T}$ was obtained for three values of ϕ_1, and $(\partial \Delta H_m/\partial \phi_1)_{P,T}$ calculated from (15*b*). With ΔH_m expressed in the form of (1),

$$(\partial \Delta H_m/\partial \phi_1)_{P,T} = A(1 - 2\phi_1) + B(6\phi_1 - 6\phi_1^2 - 1) + C(1 - 10\phi_1 + 24\phi_1^2 - 16\phi_1^3)$$

permitting evaluation of A, B, and C. Fig. 1 shows ΔH_m calculated in this way compared with the experimental results.[7, 8] The agreement is excellent and justifies the neglect of

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[7] Scatchard, Ticknor, Goates, and McCartney, *J. Amer. Chem. Soc.*, 1952, **74**, 3721.

[8] Adcock and McGlashan, *Proc. Roy. Soc.*, 1954, *A*, **226**, 266.

[9] Wood and Gray, *J. Amer. Chem. Soc.*, 1952, **74**, 3729.

[10] Scatchard, Wood, and Mochel, *ibid.*, 1939, **61**, 3206.

$(\partial \Delta H_m/\partial \phi_1)_{\Delta V_m, T}$ in (15*b*). Clearly also, the data employed permit an accurate calculation to be made. Table 1 show the parameters of (15*b*) where χ has been written for

$$\left[\frac{1}{100(\beta_0 V_0 - \beta_m V_m)}\right]_{T,\phi} \times [\Delta V_m - T(\partial \Delta V_m/\partial T)_{P,\phi}].$$

TABLE 1. *Parameters of equation* (15b) *for* cyclo*hexane–carbon tetrachloride* (20°).

ϕ_1	0·25	0·50	0·75
Δv_m	0·12351	0·16028	0·11693
$10^5(\partial \Delta V_m/\partial T)_{P.\phi}$	8·90	2·16	−4·66
χ (J)	7·72	9·28	10·77
$(\partial \Delta v_m/\partial \phi_1)_{P.T}$	0·3595	0·01758	0·3513

Benzene–toluene. This system has a very small heat of mixing which has been measured at 20° by Cheesman and Canning[11] and Mathieson and Thynne[2] and the results are in very good agreement. The latter give $\Delta H_m = x_1 x_2[272 - 18{\cdot}8(x_1 - x_2) - 5{\cdot}4(x_1 - x_2)^2]$,

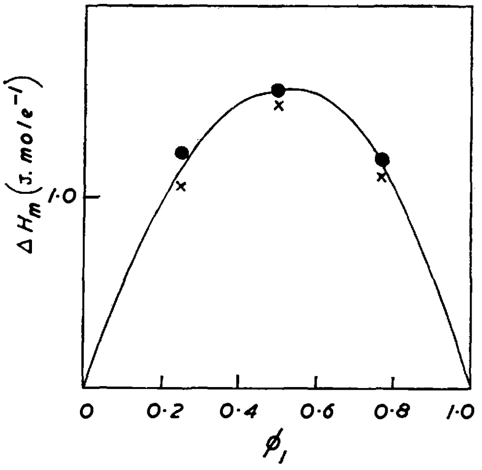

FIG. 1. *Carbon tetrachloride*—cyclo*hexane at* 20°.
● Results of Scatchard, Ticknor, Goates, and McCartney.
× Interpolated results of Adcock and McGlashan.
Full curve, calculated values from (15).

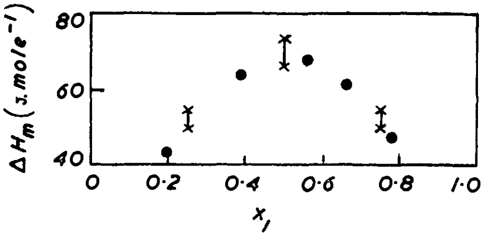

FIG. 2. *Benzene–toluene at* 20°.
● Results of Mathieson and Thynne.
× Calculated values showing limits of accuracy, from (15).

where ΔH_m is in J/mole, and x_1 is the mole fraction of benzene. Thynne[12] gives $100\Delta V_m/V_0 = x_1 x_2[0{\cdot}60 + 0{\cdot}06(x_1 - x_2) - 0{\cdot}13(x_1 - x_2)^2]$ at 20°. The variation of ΔV_m with T can be calculated from the results of Kremann, Meingast, and Gugl[13] provided that only their values for 10°, 20°, and 30° are employed. Their results at higher temperatures, and the more recent determinations of Rastogi and Rama Varma[14] at 30°, are not sufficiently self-consistent to be used. The constant value of $\beta_m = \beta_0 = 0{\cdot}92 \times 10^{-4}$ was used since benzene, toluene, and their mixtures all show the same isothermal compressibility.[15] The values of $(\partial \Delta V_m/\partial T)_{P,x}$ are not so accurate as for the other systems

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[11] Cheesman and Canning, *J.*, 1955, 1230.

[12] Thynne, Thesis, Nottingham, 1956.

[13] Kremann, Meingast, and Gugl, *Monatsh.*, 1907, **28**, 831.

[14] Rastogi and Rama Varma, *J.*, 1957, 2257.

[15] Gabrielli and Poiani, *Koninkl. Vlaam. Acad. Wetenschap.*, letter, en Schone Kunsten België, Colloquium, Ultrasonore, Trillingen, Brussels, 1951, 234; *Chem. Abs.*, 1952, **46**, 10,741.

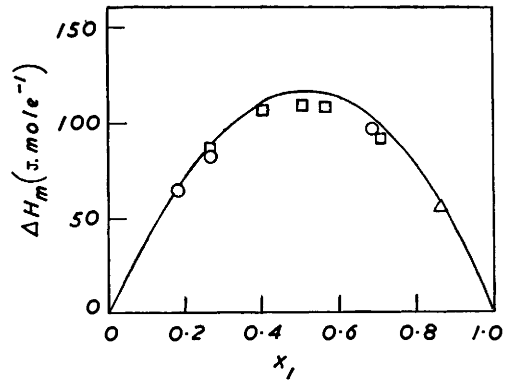
considered, and the limits so set to the accuracy of the calculation are shown in Fig. 2, in which ΔH_m calculated from (15*a*) is compared with the experimental results.[2] The values predicted are in accord with the experiments, and again $(\partial \Delta H_m/\partial P)_{\Delta V_m, T}$ is negligible. The parameters of (15*a*) are shown in Table 2. For this system and for ethanol–water and benzene–carbon tetrachloride, $\chi = [1/(\beta_0 V_0 - \beta_m V_m)][\Delta V_m - T(\partial \Delta V_m/\partial T_{P,x}]$.

TABLE 2. *Parameters of equation* (15a) *for benzene–toluene at* 20°.

x_1	0·25	0·50	0·75
ΔV_m	0·110	0·146	0·108
$10^4(\partial \Delta V_m/\partial T)_{P,x}$	5·5	7·0	5·5
χ(J)	510	460	540

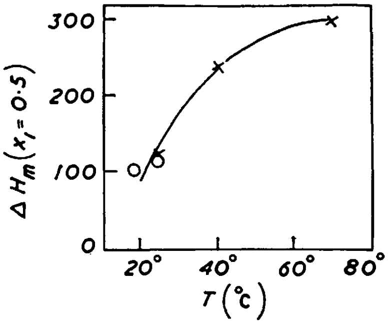
Carbon tetrachloride–benzene. This system has small heats[1,16,17] and volumes[18] of mixing but the vapour pressure deviates by about 4% from ideality at 25°.[22] Since ΔV_m is so small the difference between β_m and β_0, though small, is significant and β_m was calculated from (18) by using the vapour-pressure data of Scatchard, Mochel, and Wood,[22] specific volumes of vapour of 326 and 146 for benzene and carbon tetrachloride respectively at N.T.P., specific volumes of the liquid mixtures at various temperatures determined by Wood and Brusie,[18] and the values of β_0 employed by the latter. Calculations were made for 25°, 40°, and 70° (Table 3). When $\beta_m - \beta_0$ is known accurately, uncertainty of a few units % in β_0 has negligible effect on (15*a*). Fig. 3 shows values of ΔH_m calculated from (15*a*) at 25° compared with the experimental results.[1,16,17] Agreement is very good. For this system, $\Delta V_m - T(\partial \Delta V_m/\partial T)_{P,x}$ is independent of temperature, having values of −0·385, −0·442, and −0·467 for x = 0·25, 0·50, and 0·75, respectively, for 25°, 40°, and 70°. The effect of temperature on ΔH_m is shown in Fig. 4, where values calculated from

FIG. 3. *Carbon tetrachloride–benzene.*



○ Results of Brown, Mathieson, and Thynne (25°).
□ Results of Cheesman and Whitaker (24·7°).
△ Result of Hirobe (25°).
Full curve, calculated values (25°).

FIG. 4. *Effect of temperature for carbon tetrachloride – benzene (equimolar mixtures).*



○ Results of Cheesman and Whitaker.
× Calculated values.

TABLE 3. *Parameters of* (15a) *for carbon tetrachloride–benzene.*

x_1 (CCl$_4$)	0·25	0·50	0·75	ΔV_m at 25°	0·0106	0·0144	0·0110
10^6 $(\beta_m - \beta_0)$ at 25°	0·040	0·043	0·044	,, 40°	0·0324	0·0373	0·350
,, 40°	0·023	0·028	0·024	,, 70°	0·0688	0·0867	0·0796
,, 70°	0	0	−0·015	χ (J) at 25°	8400	8130	8770
				,, 40°	6610	6310	7110
$(\partial \Delta V_m/\partial T)_{P,x}$ at 25—70°	0·00133	0·00153	0·00160	,, 70°	3860	3400	4330

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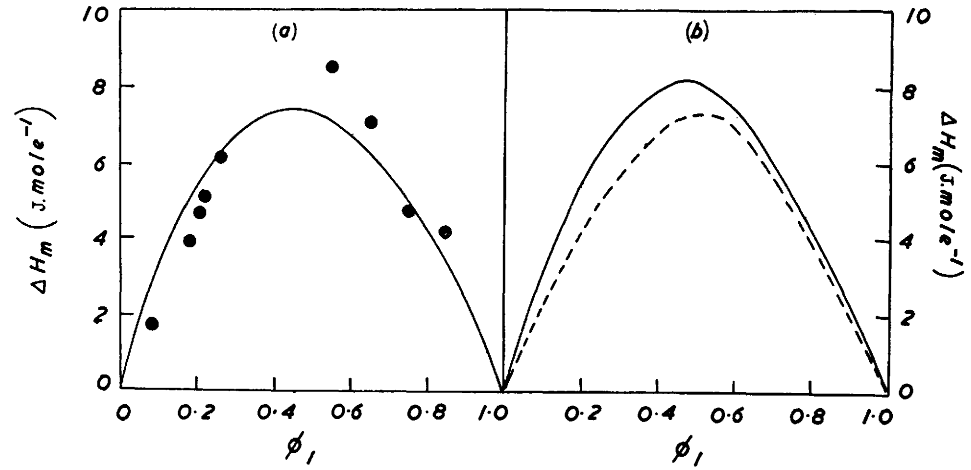
[16] Cheesman and Whitaker, *Proc. Roy. Soc.*, 1952, *A*, **212**, 406.
[17] Hirobe, *J. Fac. Sci. Tokyo Univ.*, 1925, **1**, 155.
[18] Wood and Brusie, *J. Amer. Chem. Soc.*, 1943, **65**, 1891.

(15*a*) are compared with Cheesman and Whitaker's results.[16] The calculated values suggest that ΔH_m is not linear in T, but experimental determinations at higher temperatures would be desirable for confirmation.

Benzene–cyclo*hexane.* This system is far from ideal[19] and has a relatively large heat of mixing.[1] β_m was calculated from (18) by using the vapour-pressure data from Scatchard, Wood, and Mochel,[19] specific volumes of vapour of 326 and 302 for benzene and *cyclo*hexane respectively at N.T.P., specific volumes of the liquid mixtures at various temperatures determined by Scatchard, Wood, and Mochel,[19] Wood and Austin,[20] Mathieson and Thynne,[2] and some new measurements, and values of β_0 calculated[21] from $\beta_0 = 1{\cdot}02(1 + 0{\cdot}12\phi_2) \times 10^{-4}$ at 30° and $\mathrm{d}\ln\beta/\mathrm{d}T = 0{\cdot}0076$, where ϕ_2 is the volume fraction of *cyclo*hexane. The values of β_m fall on a convex-upwards curve with ϕ and are up to 2·5% greater than β_0 (Table 4). All the data being considered, the excess volume was expressed as

FIG. 5. *Benzene*–cyclo*hexane.*



(*a*) 20°. ● Results of Brown, Mathieson and Thynne. Full curve, calculated values from (15).
(*b*) 40°. Broken curve, values calculated from vapour pressure. Full curve, calc. values from (15).

$$100\Delta V_m/V_0 = \phi_1\phi_2[3{\cdot}28 - 0{\cdot}587(\phi_1 - \phi_2) - 0{\cdot}174(\phi_1 - \phi_2)^2] \quad (40^\circ)$$
$$100\Delta V_m/V_0 = \phi_1\phi_2[2{\cdot}32 - 0{\cdot}481(\phi_1 - \phi_2) - 0{\cdot}427(\phi_1 - \phi_2)^2] \quad (20^\circ)$$

ΔH_m was calculated from (15*b*), the parameters of which are shown in Table 4. Fig. 5*a* shows the calculated values compared with the experimental results of Brown, Mathieson, and Thynne[1] at 20°. Agreement is good, though not so good as for benzene–carbon tetrachloride and carbon tetrachloride–*cyclo*hexane, but the experimental results are more scattered for the present system. ΔH_m calculated at 40° can only be compared with the values calculated by Scatchard, Mochel, and Wood[22] from vapour-pressure measurements

TABLE 4. *Parameters of equation* (15b) *for benzene*–cyclo*hexane.*

ϕ_1	0·25	0·50	0·75	ΔV_m (40°)	0·700	0·823	0·523
$10^6\beta_m$ (20°)	103·9	101·3	98·5	$(\partial\Delta V_m/\partial T)_{P,\phi}$ (20°, 40°)	0·0108	0·0137	0·0092
$10^6\beta_m$ (40°)	120·8	117·9	114·2	χ (20°) (J)	10·84	12·52	13·22
ΔV_m (20°)	0·483	0·550	0·340	χ (40°) (J)	9·71	9·86	10·40

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[19] Scatchard, Wood, and Mochel, *J. Phys. Chem.*, 1939, **43**, 119.
[20] Wood and Austin, *J. Amer. Chem. Soc.*, 1945, **67**, 480.
[21] International Critical Tables, Nat. Acad. Sci., U.S.A., 1928.
[22] Scatchard, Mochel, and Wood, *J. Amer. Chem. Soc.*, 1940, **62**, 712.

and this comparison is shown in Fig. 5*b*. The calculation of heats of mixing from vapour-pressure measurements is uncertain owing to the variation of the heat of mixing with temperature,[1, 23] but nevertheless the two sets of values are in reasonable accord.

Ethanol–water. Many accurate data are available for this system, for which the form of the variation of ΔH_m and ΔV_m with x indicates that $(\partial \Delta H_m/\partial x)_{\Delta V_m, T}$ is not zero. Isothermal compressibilities were calculated from Giacomini's sound velocities (u),[24] the coefficients of expansion (a) calculated from the densities (d_m),[21] and the specific heats at constant pressure (C_p) [21] by using

$$\alpha = 1/d_m u^2 \text{ and } \beta = \alpha + aT/C_p d_m$$

where α is the adiabatic compressibility. The results (Table 5) have minima between $x_1 = 0{\cdot}05$ and 0·11 corresponding to the maxima of the sound velocities. At values of x_1 greater than those corresponding to the minima, β_m increases with T but it decreases with T at lower values of x_1. ΔV_m and $(\partial \Delta V_m/\partial T)_{P, x}$ were calculated from the density compilation [21] and are shown with the other parameters of (15*a*) in Table 6.

TABLE 5. *Isothermal compressibilities of ethanol–water.*

Mole fraction of EtOH (x_1)	$10^6\beta_m$ 10°	20°	30°	40°
0·0000	47·39	45·66	44·66	44·00
0·0416	42·52	41·92	41·80	42·08
0·0890	39·57	40·65	41·86	43·15
0·144	40·89	42·77	44·91	47·27
0·207	45·63	48·02	50·81	53·70
0·281	52·92	54·35	57·86	61·77
0·370	59·97	62·82	66·04	70·07
0·477	67·21	71·39	75·49	79·36
0·610	75·53	80·22	85·31	90·69
0·779	86·08	92·24	98·61	105·41
1·000	102·11	109·82	118·16	127·36

TABLE 6. *Parameters of equation* (15a) *for ethanol–water.*

x_1	0·0416	0·0891	0·144	0·207	0·281	0·370	0·447	0·610	0·778
$-\Delta V_m$ at 20°	0·1884	0·4600	0·7250	0·9170	0·0372	1·0976	1·0935	0·9919	0·7114
,, 30°	0·1972	0·4563	0·7004	0·8812	0·9995	1·0629	1·0627	0·671	0·6943
$T(\partial \Delta V_m/\partial T)_{P,x}$ at 20°	−0·288	0·119	0·810	1·174	1·211	1·114	0·957	0·762	0·467
,, 30°	−0·242	0·108	0·681	0·990	1·056	0·994	0·906	0·758	0·523
χ (J) at 20°	−75·2	235	494	658	690	757	809	645	510
,, 30°	−36·2	256	616	688	744	740	853	633	541

Clearly, $(\partial \Delta H_m/\partial x_1)_{\Delta V_m, T}$ is not zero, so ΔH_m cannot be calculated from (15*a*). However, plots of $\chi.(\partial \Delta V_m/\partial x_1)_{P, T}$ against x_1 at 20° and 30° give curves of similar shape to plots of ΔH_m against x_1 constructed from Bose's data [25] at the same temperature. Both sets of curves rise to a maximum at $x_1 = 0{\cdot}15$ and then fall gradually, showing the same minor inflexion between $x_1 = 0{\cdot}55$ and 0·85. This striking similarity implies that, to a first approximation,

$$\chi(\partial \Delta V_m/\partial x_1)_{P, T} = k_1.\Delta H_m + k_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where $k_1 = 3{\cdot}7$ (20°) and 5·7 (30°) and $k_2 = 2000$ J. Fig. 6 shows plots of $\chi(\partial \Delta V_m/\partial x_1)_{P, T}$ and $k_1.\Delta H_m + k_2$ against x_1. Equation (19) makes it possible to calculate values of ΔH_m for any concentration from measurements of density and compressibility provided ΔH_m is known experimentally at a single concentration. Its theoretical significance is obscure. By combination with (15*a*),

$$k_1.\Delta H_m + k_2 = (\partial \Delta H_m/\partial x_1)_{P, T} - (\partial \Delta H_m/\partial x_1)_{\Delta V_m, T} \quad . \quad . \quad . \quad (20)$$

It is not yet known whether (19) and (20) are peculiar to this system, or are applicable to polar mixtures in general.

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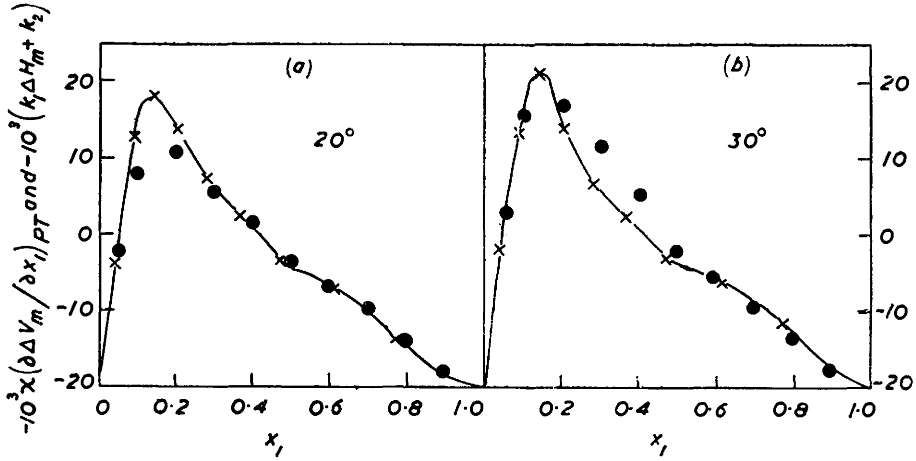
[23] Cheesman and Ladner, *Proc. Roy. Soc.*, 1955, *A*, **229**, 337.
[24] Giacomini, *J. Acoust. Soc. Amer.*, 1947, **19**, 701.
[25] Bose, *Z. phys. Chem.*, 1907, **58**, 585.

Discussion.—The excess heat and volume of mixing are related *via* their differentials with concentration by expressions involving the change of excess volume with temperature and the excess compressibility. Provided the mixtures chosen can be regarded as typical of their groups of mixtures, it may be concluded that for binary mixtures which depart from ideality (as determined by their vapour pressure) by less than ~2% it is possible to calculate the heat of mixing from density measurements and the compressibilities of the pure components. For binary mixtures which show greater positive departures from ideality the compressibility of the mixtures needs also to be known, or it can be calculated from the vapour pressures. For ethanol-water a value of ΔH_m at a single concentration is also required. Conversely, in the last two cases if the heats of mixing are known the compressibilities of the mixtures can be calculated.

FIG. 6. *Ethanol-water.*



—×— $x(\partial\Delta V_m/\partial x_1)_{P,T}$.
● $k_1\,\Delta H_m + k_2$.

(*a*) 20°.
(*b*) 30°.

The equations presented here may be compared with the various theories of mixtures. Scatchard [26] and Hildebrand and Scott [27] concluded that ΔH_m and ΔV_m were interdependent for non-polar solutions. The extension of the treatment of regular solutions by Scott [5] to include volumes of mixing led to equations for $\Delta V_m/V_m$ and $\Delta H_m/\mathbf{N}$ ($\mathbf{N}$ = Avogadro's number) which when combined yield

$$\Delta H_m/\mathbf{N} = \frac{\Delta V_m}{\beta_m V_m}\left[T(\partial V_m/\partial T)_p - \frac{\varepsilon\beta_m V_m}{T(\partial V_m/\partial T)_p}\right] \quad . \quad . \quad . \quad . \quad (21)$$

where ε is the molecular interaction energy. When (15*a*) is applied to regular solutions, ΔH_m and ΔV_m may be written for $(\partial\Delta H_m/\partial x)_{P,T}$ and $(\partial\Delta V_m/\partial x)_{P,T}$ since ΔH_m and ΔV_m are proportional functions of x. Equation (21) is evidently related to (15*a*) and predicts proportionality of ΔH_m and ΔV_m. The first-order conformal solution treatment of Longuet-Higgins [28] gives equations for $\Delta V_m/V_m$ and $\Delta H_m/\mathbf{N}$ which on combination yield

$$\Delta H_m/\mathbf{N} = \Delta V_m \cdot \frac{1}{T}\left(\frac{\partial T}{\partial V_0}\right)\left[T\left(\frac{\partial\varepsilon_0}{\partial T}\right) - \varepsilon_0\right] \quad . \quad . \quad . \quad (22)$$

where ε_0, V_0 refer to the reference substance. This also predicts proportionality of ΔH_m and ΔV_m. Prigogine and Mathot's [6] " smoothed potential " (square-well potential) cell

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[26] Scatchard, *Trans. Faraday Soc.*, 1937, **33**, 160.
[26] Hildebrand and Scott, " Solubility of Non-electrolytes," Reinhold, New York, 1950, pp. 138—143.
[28] Longuet-Higgins, *Proc. Roy. Soc.*, 1951, *A*, **205**, 247.

model gives ΔV_{m} proportional to the other excess functions of mixing for non-polar mixtures, and for other mixtures also provided second-order terms are neglibible. Sarolea[29] considered that non-random mixing (excluded from the original theory) would not affect the conclusions. Pople,[30] employing the cell field of Lennard-Jones and Devonshire[31] and allowing for non-random mixing, found ΔV_{m} a function of ΔF_{m} for first-order interactions. All these theories agree that, for first-order interactions, ΔV_{m} is a function of ΔH_{m}, which is equivalent to setting $(\partial \Delta H_{\mathrm{m}}/\partial x)_{\Delta V_{\mathrm{m}}, T} = 0$ in (15*a*). With this condition, (15*a*) is applicable to four non-polar solutions but not to ethanol–water, and it may well hold for first-order interactions in general. It is tempting to suggest that $(\partial \Delta H_{\mathrm{m}}/\partial x)_{\Delta V_{\mathrm{m}}, T}$ may account for second- and higher-order interactions.

Recently, some more general corresponding-states treatments of non-electrolyte solutions have appeared.[32,33] Scott, for two types of cell (the "two-liquid" approach, equivalent to that of Prigogine *et al.*), gives expressions for ΔH_{m} in terms of the excess energy of vaporisation $(\bar{E}')$, $(\partial \bar{E}'/\partial T)$, and $(\partial^2 \bar{E}'/\partial T^2)$, molecular parameters and difference functions, and for ΔV_{m} in terms of V_{m}, $(\partial V_{\mathrm{m}}/\partial T)$, $(\partial^2 V_{\mathrm{m}}/\partial T^2)$, molecular parameters, and difference functions. By treating $\bar{E}'$ as an excess internal latent heat at constant zero pressure, relationships between $\bar{E}'$ and V_{m}, and the corresponding temperature derivatives, can be established involving ΔV_{m}, $\Delta(\beta V)$, a, and their temperature derivatives. In this way it can be shown that the theory leads to

$$\Delta H_{\mathrm{m}} = \Delta V_{\mathrm{m}} \left(\frac{1}{\beta_0 V_0 - \beta_{\mathrm{m}} V_{\mathrm{m}}} \right) \left[\Delta V_{\mathrm{m}} - T \left(\frac{\partial \Delta V_{\mathrm{m}}}{\partial T} \right)_P - T^2 \left(\frac{\partial \Delta V_{\mathrm{m}}}{\partial T} \right)_P^2 \right] j + \Delta V_{\mathrm{m}} - x_1 x_2 \mathrm{f}(V_{\mathrm{m}}, \beta_{\mathrm{m}}, a, T, j') \quad . \quad . \quad (23)$$

where j, j' have been written for different combinations of the molecular parameters and difference functions. Equation (23) is more closely related to (15*a*) than the earlier theoretical equations, (21) and (22). Part of the last term in (23) is independent of ΔV_{m} and so corresponds to $(\partial \Delta H_{\mathrm{m}}/\partial x)_{\Delta V_{\mathrm{m}}, T}$. The expressions of Prigogine *et al.* are in such a form as not to lend themselves so readily to comparison with the present theory.

EXPERIMENTAL

Experimental.—The densities of benzene–*cyclo*hexane mixtures were measured at 35° ± 0·02° and 45° ± 0·02°, and the excess volumes calculated (Table 7). The results are in good agreement with earlier determinations.[2, 19, 20] The liquids were purified as already described, and their properties have been listed.[1] A 20 ml. pyknometer, of dilatometer pattern, viewed through a cathetometer, was employed. It was calibrated with water.

TABLE 7. *Densities and excess volumes of benzene–*cyclo*hexane.*

35°			45°		
x_1	d_{m}	ΔV_{m}	x_1	d_{m}	ΔV_{m}
0·0	0·76522	—	0·0	0·75456	—
0·28792	0·78566	0·674	0·28792	0·77486	0·724
0·54978	0·80930	0·775	0·54801	0·79780	0·891
0·78761	0·83550	0·434	0·78576	0·83275	0·594
1·00000	0·86182	—	1·00000	0·85172	—

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[29] Sarolea, *J. Chem. Phys.*, 1953, **21**, 182.
[30] Pople, *Trans. Faraday Soc.*, 1953, **49**, 591.
[31] Lennard-Jones and Devonshire, *Proc. Roy. Soc.*, 1937, *A*, **163**, 63.
[32] Prigogine, Bellemans, and Englert-Chwoles, *J. Chem. Phys.*, 1956, **24**, 518.
[33] Scott, *ibid.*, 1956, **25**, 193.