

The Importance of Solvent Internal Pressure and Cohesion to Solution Phenomena

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1 Introduction

Intermolecular forces give a liquid its cohesion. The attractive forces mainly comprise hydrogen bonding, dipole-dipole, multipolar, and dispersion interactions. Repulsive forces, acting over very small intermolecular distances, play a minor role in the cohesion process under normal circumstances. Cohesion creates a pressure within a liquid of between 10^3 and 10^4 atmospheres. Dissolved solutes experience some of this pressure, and the amount of pressure on the solutes increases whenever they interact with solvent through hydrogen bonding, charge-transfer, coulombic, or van der Waals interactions. Thus a solute in solution is subject to a 'structural pressure' from the solvent and a 'chemical pressure' from interactions with the solvent. The solution exists under a higher internal pressure than the pure solvent.

This concept of internal pressure provides an excellent basis for examining solution phenomena. The first review of the subject by Richards¹ appeared in 1925, but the full potential of internal pressure as a structural probe did not become apparent until Hildebrand's^{2,3} work a decade later.

A liquid undergoing a small, isothermal volume expansion does work against the cohesive forces which causes a change in the internal energy, U . The function $(\partial U/\partial V)_T$ is known as the *internal pressure*, P_1 . Hildebrand showed that for non-polar liquids, $(\partial U/\partial V)_T = n\Delta U_{vap}/V$, where ΔU_{vap} represents the energy of vaporization of the liquid and V its molar volume. The quantity, n , approaches unity for non-polar liquids, and so P_1 can be equated to $\Delta U_{vap}/V$, the *cohesive energy density*. For polar liquids, however, n ranges from 0.32—1.62.⁴ Internal pressure and cohesive energy density (c.e.d.), evidently, do not reflect the same physical property of these liquids. Many workers have failed to discriminate between P_1 and c.e.d. One of the aims of this Review is to analyse the physical significance of P_1 and c.e.d. and to demonstrate the usefulness of both properties in the light of their differences.

We also intend to show the ability of the pressure concept⁵ to explain many

¹ T. W. Richards, *Chem. Rev.*, 1925, 2, 315.

² J. H. Hildebrand and R. L. Scott, 'Solubility of Non-Electrolytes', 3rd Edn., Reinhold, New York, 1950.

³ J. H. Hildebrand and R. L. Scott, 'Regular Solutions', Prentice-Hall, Englewood Cliffs, New Jersey, U.S.A., 1962.

⁴ G. Allen, G. Gee, and G. J. Wilson, *Polymer*, 1960, 1, 456.

⁵ G. Tammann, *Z. phys. Chem.*, 1893, 11, 676.

observations in solution. The approach successfully predicted isothermal compressibilities and coefficients of thermal expansion for dilute aqueous solutions in 1929,⁶ and it related internal pressure to the electrostatic field of dissolved ions as early as 1894.⁷ Interest in P_1 and c.e.d. has increased in recent years. Thus, we feel that the time is appropriate to examine such topics as solvent structure, salt effects, conductivity, chemical reactivity, spectroscopy, molal volumes, and solubility with these properties in mind. The work cited below is illustrative rather than exhaustive, and the features discussed tend to be salient rather than detailed. In this way we hope that the reader will acquire more rapidly a feeling for this old, but newly rediscovered concept of solvent pressure.

2 Physical Significance of Internal Pressure and Cohesive Energy Density

A. Measurement of P_1 and C.E.D.—Cohesive energy densities are readily obtained from experimentally determined heats of vaporization, ΔH_{vap} , via the relationship

$$\text{c.e.d.} = \frac{\Delta U_{\text{vap}}}{V} = \frac{\Delta H_{\text{vap}} - RT}{M/\rho} \quad (1)$$

where M and ρ are the molecular weight and density, respectively, of a liquid at a temperature, T K. Heats of vaporization, mostly obtained from vapour pressure data, are unavailable for some liquids. Small⁸ has assembled existing heat of vaporization data for a large number of non-associated liquids and has assigned values for the molar attraction constant, $(\Delta U_{\text{vap}}V)^{\ddagger}$, to constituent groups in the liquids. Addition of the individual molar attraction constants enables an estimate to be made of the c.e.d. of new liquids or compounds. This method would not be able to predict the c.e.d. of liquids in which hydrogen bonding contributed to the cohesion. Table 1 contains the cohesive energy densities (cal cm⁻³) of a selection of common organic solvents at 25 °C obtained directly from ΔH_{vap} .

Internal pressure is obtained by using the so-called 'thermodynamic equation of state':²

$$P_1 = \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (2)$$

For most liquids, the thermal pressure coefficient, $(\partial P/\partial T)_V$, multiplied by the absolute temperature is many thousands of atmospheres, so that the atmospheric pressure, P , becomes negligible by comparison. Measurement of P_1 is thereby reduced to measurement of the thermal pressure coefficient. Apparatuses of various designs have been used in these measurements,⁹⁻¹⁴ but they all operate on

⁶ H. M. Evjen and F. Zwicky, *Phys. Rev.*, 1929, **33**, 860.

⁷ P. Drude and W. Nernst, *Z. phys. Chem.*, 1894, **15**, 79.

⁸ P. A. Small, *J. Appl. Chem.*, 1953, **3**, 71.

⁹ W. Westwater, H. W. Frantz, and J. H. Hildebrand, *Phys. Rev.*, 1928, **31**, 135.

¹⁰ H. E. Eduljee, D. M. Newitt, and K. E. Weale, *J. Chem. Soc.*, 1951, 3086.

¹¹ C. F. Lau, G. N. Malcolm, and D. V. Fenby, *Austral. J. Chem.*, 1969, **22**, 855.

¹² E. B. Bagley, T. P. Nelson, and J. M. Scigliano, *J. Paint Technol.*, 1971, **43**, 35.

¹³ A. F. M. Barton, *J. Chem. Educ.*, 1971, **48**, 156

¹⁴ D. D. Macdonald and J. B. Hyne, *Canad. J. Chem.*, 1971, **49**, 611.

Table 1 Internal pressures (P_1) and cohesive energy densities (c.e.d.) for selected organic solvents at 25 °C

Solvent	c.e.d. (<i>experimental</i>) (cal cm ⁻³)	c.e.d. (<i>experimental</i>) (atm)	P_1 (<i>measured directly</i>) (cal cm ⁻³)	P_1 (<i>calc.</i>) from $T\alpha/\beta$ (cal cm ⁻³)
Water	550.2 ^a	22 703	41.0 ^a	36 ^b
Formamide	376.4 ^b	15 530	131 ^c	130 ^b
Ethylene glycol	213.2 ^b	8675	128 ^a	120 ^b
Methanol	208.8 ^b	8615	70.9 ^e	68.1 ^f
Propylene carbonate	ca.182.3 ^g	ca. 7522	129 ^c	
Dimethyl sulphoxide	168.6 ^a	6955	123.7 ^{a,h}	120 ^b
Ethanol	161.3 ^b	6655		69.5 ^f
Nitromethane	158.8 ⁱ	6550		
1-Propanol	144.0 ^j	5941		68.8 ^f
Dimethylformamide	139.2 ^b	5743	114 ^c	
Acetonitrile	139.2 ^b	5743	96 ^c	93 ^b
2-Propanol	132.3 ^j	5457		67.0 ^f
1-Butanol	114.5 ^j	4724		71.7 ^f
Pyridine	112.4 ^k	4636		
t-Butylalcohol	110.3 ^j	4549		81 ^f
Nitrobenzene	108.2 ^k	4463		
Acetophenone	108.2 ^j	4463		
Carbon disulphide	100.0 ^l	4126	89.0 ^m	90.0 ^f
Methyl iodide	98.0 ^j	4044		89.5 ^f
Dioxan	94.7 ^k	3906		119.3 ^f
Acetone	94.3 ^k	3890	79.5 ⁿ	80.5 ^f
Tetrahydrofuran	86.9 ^k	3584		
Chloroform	85.4 ^k	3523		88.3 ^f
Benzene	83.7 ^k	3454	88.4 ^m	90.5 ^f
Ethyl acetate	81.7 ^k	3372		84.5 ^f
Toluene	79.4 ^k	3276		84.8 ^f
Carbon tetrachloride	73.6 ^l	3037	80.6 ^{h,m}	82.4 ^b
Cyclohexane	66.9 ^k	2761		77.8 ^f
Diethyl ether	59.9 ^k	2472		63.0 ^f
Hexane	52.4 ^k	2163		57.1 ^f

^a Ref. 14. ^b Ref. 40. ^c M. R. J. Dack, preliminary and unpublished results, 1974. ^d Ref. 35. ^e Ref. 39. (Ref. 12 gives a value of 68.5 cal cm⁻³) ^f Ref. 4 at 20 °C; values of P_1 at 25 °C will be approximately 1–2 cal cm⁻³ lower. ^g Calculated from data extrapolated to 25 °C in 'Propylene Carbonate Technical Bulletin', Jefferson Chemical Co. Inc., Houston, 1962. ^h Ref. 11. ⁱ Ref. 2. ^j Ref. 52. ^k Ref. 48. ^l Ref. 3. ^m Ref. 9. ⁿ Ref. 9 (Ref. 12 gives a value of 78.8 cal cm⁻³).

the same principle. A piezometer is filled to a known volume with the solvent or solution, and the temperature raised to cause expansion of the liquid. Pressure is then applied to restore the liquid to its original volume. The procedure is repeated many times.

The thermal pressure coefficient can be equated to α/β , where α is the coefficient of thermal expansion and β is the isothermal compressibility. Allen, Gee, and Wilson⁴ calculated P_1 for a large number of pure liquids from $T\alpha/\beta$, and although the values obtained are extremely useful, errors in the individual properties are compounded in the ratio. Direct measurement of $(\partial P/\partial T)_V$ is essential for accurate determinations of P_1 , especially when differences in P_1 between the solvent and very dilute solutions are being examined. Internal pressures (cal cm⁻³) for a number of solvents appear in Table 1. Multiplication of c.e.d. or P_1 by 41.29 converts the values to atmosphere units for an easier evaluation of the pressures involved.

B. Description of P_1 and C.E.D.—The energy of vaporization is the energy required to break all the forces associated with one mole of liquid during removal of that mole from the liquid to the vapour state. Assuming negligible interaction in the vapour, values of c.e.d. therefore measure *the total molecular cohesion per ml of the liquid*.

To understand the physical significance of internal pressure, one must consider a liquid undergoing a small, isothermal volume expansion. Total disruption of all the interactions associated with one mole of liquid will not occur. We might intuitively expect those interactions varying most rapidly near the equilibrium separation in the liquid to make the most significant contribution to P_1 . The statistical mechanical equation of state¹⁵ leads to an expression for P_1 which supports this view:

$$P_1 = -\frac{2\pi}{3} \rho^2 KT \int_0^\infty r^3 \frac{\partial \phi}{\partial r}(r) \frac{\partial g}{\partial T}(r) dr \quad (3)$$

The expression is derived from consideration of two-body interactions, where $\phi(r)$ is the potential energy between a pair of molecules separated by a distance, r , and $g(r)$ is the radial distribution function—the probability of finding a molecule at a distance, r , from the reference molecule. Summation of these functions for the system as a whole assumes an additivity of the pair potentials. The probability of finding a particle at a given point is given by the number density, ρ . An analysis of how the various components of equation (3) vary with intermolecular separation confirms the huge dependence of P_1 upon rapidly varying interactions (*i.e.* repulsion, dispersion, and polar interactions).

The statistical mechanical internal energy equation¹⁵ converts into the following expression for c.e.d.:

$$\text{c.e.d.} = 2\pi\rho \frac{N}{V} \int_0^\infty r^3 \phi(r) g(r) dr \quad (4)$$

where V is the molar volume. It is apparent from this treatment that P_1 is not strictly a component of c.e.d. However, a number of experimental observations

¹⁵ For a discussion of statistical mechanical treatments, see R. O. Watts, *Rev. Pure Appl. Chem. (Australia)*, 1971, 21, 167. The author is indebted to Dr. Watts for the derivation of equations (3) and (4).

indicate that it may still be possible to regard P_1 as measuring some part of c.e.d.

Values of P_1 approach those of c.e.d. in the case of non-polar liquids (see Table 1) where repulsion and dispersion interactions mainly occur. That is, the small volume expansion associated with P_1 totally disrupts these interactions. The two properties are also approximately equal for weakly polar liquids ($\mu < 2D$), so that P_1 successfully accounts for weak dipole-dipole interactions. Hamann¹⁶ has calculated the following values for liquid argon from the statistical mechanical data of Barker, Fisher, and Watts:¹⁷ $P_1 = 43.1 \text{ cal cm}^{-3}$ and c.e.d. = 41.8 cal cm^{-3} . These results agree excellently with experiment, and they illustrate the success of statistical treatments in explaining solution phenomena.

The presence of hydrogen bonding in liquids causes the very large c.e.d. values in Table 1. P_1 does not change in this way, and it appears that although hydrogen bonding varies rapidly with intermolecular separation, a localized and 'chemical' nature prevents its detection by a minute volume expansion. Thus, it may be concluded that P_1 measures the polar and non-polar (non-chemical) interactions within a liquid. The quantity (c.e.d. - P_1) measures the intermolecular bonding energy due to hydrogen bonding. Bagley, Nelson, and Scigliano¹² have also arrived at this conclusion. Further support for this hypothesis will be generated in Section 3.

C. Relationship between P_1 , C.E.D., and other Solvent Properties.—Coomber¹⁸ found that a linear relationship exists between the internal pressure of non-polar liquids and their dielectric constants at high temperatures. This observation was subsequently justified theoretically.¹⁹ Deviations from the relationship which occur at lower temperatures are ascribed to an increased contribution of repulsive forces to P_1 .²⁰ As the liquid contracts on cooling, intermolecular separations decrease and repulsion between molecules becomes intensified.

The sensitivity of P_1 to its repulsive component can be judged from values at high compression for diethyl ether.²¹ The internal pressure decreases very slightly on increasing the external pressure from 200 to 5000 atm. Further compression causes such a dramatic decrease in P_1 that it becomes highly negative. Clearly a point is reached in the intermolecular separation where repulsive forces completely dominate the attractive forces. Molar volumes reflect changes in the intermolecular separation as an external pressure is applied. Barton¹³ has discussed the relationship between P_1 and molar volumes in some depth, and has shown that maxima occur in internal pressure-volume plots which can be detected at moderate pressures and temperatures. Calculations of the attractive *versus* repulsive contributions to P_1 with respect to volume predict such behaviour.^{2,3,13} Attractive and repulsive forces both increase as the molar

¹⁶ S. D. Hamann, personal communication, 1974.

¹⁷ J. A. Barker, R. A. Fisher, and R. O. Watts, *Mol. Phys.*, 1971, **21**, 657.

¹⁸ D. I. Coomber, *Trans. Faraday Soc.*, 1939, **35**, 304.

¹⁹ G. H. Meeten, *Nature*, 1969, **223**, 827.

²⁰ J. R. Partington, 'An Advanced Treatise on Physical Chemistry', Vol. 5, Longmans, London, 1950, p. 444.

²¹ W. J. Moore, 'Physical Chemistry', 4th Edn., Longmans, London, 1965, p. 713.

volume (intermolecular separation) is decreased. Initially, the attractive component of P_1 predominates, and P_1 increases with decreasing volume. At smaller volumes, the repulsive component predominates, causing P_1 to decrease. The observations above concerning diethyl ether were made at this region of the curve.

It should be emphasized that intermolecular repulsion does not contribute greatly to P_1 at normal temperatures and at atmospheric pressure. This fact enabled Cammarata and Yau²² to express the internal pressure for fifty solvents of low polarity in the following manner:

$$P_1 = 2.65 \times 10^{48} \frac{I\alpha}{V^3} \quad (5)$$

where I and V are the molecular ionization potential (eV) and molar volume, respectively, and α is the molecular polarizability. The expression was derived from the simple London treatment²³ of dispersion energies between like molecules.

Equation 6 is claimed by Srivastava²⁴ to relate the internal pressures of sixty liquids to their boiling point temperature, T K, and molar volume, V .

$$P_1 = (24.5T - 1400) \frac{4.5}{V} \quad (6)$$

Hildebrand has pointed out that approximate heats of vaporization can be obtained from boiling point temperatures,² and so it is not too surprising that the internal pressures calculated by equation (6) approach c.e.d. values for hydrogen-bonded solvents like water, and for dipolar aprotic solvents like dimethyl sulphoxide. The sixty liquids used to establish equation (6) are all relatively non-polar; their internal pressures can therefore be equated to cohesive energy densities.

In his account of various methods for determining 'internal, molecular, or intrinsic pressure,' Lewis²⁵ recalled Young's²⁶ earlier suggestion that the attractive forces responsible for cohesion are also responsible for the surface tension of liquids. Hildebrand² later predicted a relationship between c.e.d. and $\gamma/V^{1/3}$, where γ is the surface tension and V the molar volume. The relationship is linear for non-polar liquids. It breaks down in polar solvents, but in a given class of polar solvent (e.g. alcohol, dipolar aprotic solvent), values of γ appear to run parallel to c.e.d. Gordon²⁷ used cohesion, as represented by $\gamma/V^{1/3}$, to estimate the cohesive nature of molten inorganic salts in relation to polar liquids of known cohesion. He also made use of the complex relation between viscosity and cohesion^{28,2f} for the same purpose. Viscous flow can be regarded as a rate process

²² A. Cammarata and S. J. Yau, *J. Pharm. Sci.*, 1972, **61**, 723.

²³ F. London, *Trans. Faraday Soc.*, 1937, **33**, 8.

²⁴ S. C. Srivastava, *Indian J. Phys.*, 1959, **33**, 503.

²⁵ W. C. M. Lewis, *Trans. Faraday Soc.*, 1911, **7**, 94.

²⁶ T. Young, *Phil. Trans.*, 1805, **1**, 65.

²⁷ J. E. Gordon, *J. Amer. Chem. Soc.*, 1965, **87**, 4347.

²⁸ C. V. Suryanarayana, *Indian J. Chem.*, 1972, **10**, 713.

²⁹ R. V. Gopala Rao and V. Venkata Seshiah, *Z. phys. Chem. (Frankfurt)*, 1972, **78**, 26.

in which molecules migrate into neighbouring holes in the liquid.³⁰ Thus, the energy of activation of this process becomes related to the energy required to create a hole—the molar energy of vaporization.

3 An Examination of Solvent Structure in Terms of P_1 and C.E.D.

A. General.—The term structure can mean different things to different people. Does it refer to the strength of intermolecular bonding within a liquid, or does it refer to the geometry of the molecules of the liquid? An answer to the question clearly depends on the problem in hand. For example, a dissolved solute may be small enough to rest within the tetrahedral skeleton of water molecules without substantially affecting the intermolecular bonding, but in a hydrocarbon, the same solute may have to break many bonds to create a hole for itself. Solvent structure is affected in both cases. In addition, does it matter whether we mean chemical (hydrogen bonding) or non-chemical (polar and non-polar) interactions when discussing the strength of structure? Water is always regarded as a highly structured solvent, and so it is from a geometrical and hydrogen-bonding viewpoint. However, contributions from non-chemical forces to water cohesion are much lower than for any other solvent. It should be pointed out that 'structure' can be rigorously defined in terms of $\phi(r)$ and $g(r)$ (Section 2B), both of which are measurable quantities. Nevertheless, much chemistry is still at the 'physical picture' stage, and so the remainder of the discussion adopts a non-rigorous approach.

Intermolecular bonding energies are not usually expressed in cal cm⁻³ units. Energies due to non-chemical interactions ($E^\circ = P_1$) and those due to chemical interactions ($E^C = \text{c.e.d.} - P_1$) are therefore presented in units of kcal mol⁻¹ in Table 2 for a selection of solvents. The fact that E° increases with solvent molecular polarizability—a property related to dispersion interactions³¹—supports the premise that P_1 depends heavily on such interactions. E^C increases with increasing dipole moment of the dipolar aprotic solvents ($\mu > 2D$). Large dipolar interactions appear to restrict the movement of molecules in a manner similar to hydrogen bonding; such action goes undetected by P_1 . Bagley *et al.*¹² believe that (c.e.d. - P_1) measures only hydrogen-bonding energies. This assumption does not seem reasonable since it would give the dipolar aprotic solvents an appreciable amount of hydrogen-bonded structure. Molecular orbital studies³² indicate intermolecular hydrogen bonding in formaldehyde dimers of less than 0.6 kcal mol⁻¹. Similar bonding in dipolar aprotic solvents possessing no acidic hydrogen must be insignificant.

It is encouraging to find that values of E^C for the alcohols agree with hydrogen bonding energies obtained by other means.³³ The E^C value of 9.8 kcal mol⁻¹ for formamide cannot be entirely due to hydrogen bonding because of contributions

³⁰ H. Eyring, *J. Chem. Phys.*, 1936, 4, 283.

³¹ Ref. 21, p. 715.

³² K. Morokuma, *J. Chem. Phys.*, 1971, 55, 1236.

³³ I. A. Wiehe and E. B. Bagley, *Amer. Inst. Chem. Engineers J.*, 1967, 13, 836.

from dipole-dipole interactions caused by the large dipole moment of the solvent ($\mu = 3.37$ D). A similar dipole moment for dipolar aprotic solvents yields $E^C \approx 2$ kcal mol⁻¹. The resulting hydrogen bonding energy for formamide of *ca.* 7.8 kcal mol⁻¹ agrees very well with values calculated by Dreyfus and Pullman³⁴ for the linear dimer (8 kcal mol⁻¹).

The solvents listed in Table 2 illustrate three classes of solvent: protic, dipolar

Table 2 Splitting of the intermolecular bonding energies of selected solvents into non-chemical (E°) and chemical (E^C) contributions at 25 °C (kcal mol⁻¹)

Solvent	$\alpha \times 10^{24}$ (ml at 20 °C) ^a	E° (dispersion, repulsion, dipole- dipole)	μ (Debye)	E^C (dipole- dipole, hydrogen bonding)
Water	1.48	0.67	1.84	9.2
Methanol	3.24	3.0	1.66	5.6
Formamide	4.22	5.2	3.37	9.8
Acetonitrile	4.45	5.1	3.84	2.3
Ethanol	5.12	4.1	1.68	5.7
Ethylene glycol	5.73	6.7	2.31	5.2
Acetone	6.41	6.0	2.88	1.0
Methyl acetate	6.96	7.0	1.61	0
Dimethylformamide	7.91	8.7	3.82	2.1
Dimethyl sulphoxide	7.97	8.6	4.49	3.3
Propylene carbonate	8.51	11.0	4.94	<i>ca.</i> 4.5
Dioxan	8.75	10.1	0.45	0
Ethyl acetate	8.82	8.3	1.88	0
Benzene	9.91	8.0	0	0
Carbon tetrachloride	10.47	8.0	0	0

^a Obtained from $\alpha = [(n^2 - 1)/(n^2 + 2)] (M/d) (3/4\pi N)$ for sodium D-line.³⁵

aprotic ($\mu > 2$),³⁵ and solvents of low polarity ($\mu < 2$). Hydrocarbons and solvents of low dipole moment have E° values of between 7 and 8 kcal mol⁻¹. Cohesion comes entirely from dispersion forces. The appearance of E^C values in the dipolar aprotic solvents shows the significant contribution of dipole-dipole interactions to cohesion.³⁶ Compared with the non-polar solvents, therefore, greater non-chemical interactions cause the dipolar aprotic solvents to be more rigid and less open. On the other hand, the protic solvents possess small E° values and chemical bonding energies which always exceed E° . Intermolecular hydrogen bonding gives these solvents a distinct geometrical structure in the form of chains or three-dimensional arrays. This structure prevents the effective operation of the non-chemical forces. The extreme solvent is water, where

³⁴ M. Dreyfus and A. Pullman, *Theor. Chim. Acta*, 1970, **19**, 20.

³⁵ A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

³⁶ G. F. Longster and E. E. Walker, *Trans. Faraday Soc.*, 1953, **49**, 228.

non-chemical forces comprise only 7% of the total cohesion at 25 °C. The relative lack of non-chemical forces gives the structure of the protic solvents an openness and/or a flexibility unmatched by other solvents.

In terms of non-chemical structuring, the dipolar aprotic solvents are the most structured of all solvents, while water is the least structured. The distinction between the non-chemical and chemical interactions in liquids should aid an understanding of phenomena in solution. Prausnitz,³⁷ Hansen,³⁸ and Bagley,¹² for example, have used this approach to find the best solvent for a given polymer. Working on the principle that 'like dissolves like', they sought the best match between solvent and polymer according to their component intermolecular bonding energies. Several empirical methods were developed which enable hydrogen bonding energies to be separated from the energies of non-chemical interactions. An application of the c.e.d./ P_1 approach to the structure of water and binary solvent mixtures is now discussed.

B. Water Structure.—The internal pressures of most liquids decrease with increasing temperature.^{9,39} Additional thermal motion of liquid molecules enhances the probability that two molecules will approach each other close enough for the repulsive component of P_1 to increase its magnitude. Water does not share this behaviour; values of P_1 rise with increasing temperature until reaching a maximum in the region of 150 °C. At the same time, c.e.d. for water decreases regularly with increasing temperature,⁴⁰ as do the values of E^c obtained from (c.e.d. - P_1).

Falling E^c values result from the destruction of water's three-dimensional skeleton as the temperature is raised. Hydrogen bonds bend or break, so that the open geometry of the molecules becomes distorted, and, depending on the water model chosen, monomeric species either fill sites in the distorted skeleton⁴¹ or join the dense monomeric fluid surrounding the Frank and Wen flickering clusters.⁴² The net result of these two processes is to bring an increasing number of water molecules to an intermolecular distance where attractive non-chemical forces operate. Thus, P_1 and E^c rise with increasing temperature until the effect of the rate of breakdown of the water skeleton on P_1 is insufficient to counteract the build-up of repulsive forces at 150 °C. It appears that water retains its uniqueness due to an open structure well past a temperature of 35–45 °C where properties like compressibility and heat capacity show discontinuities.⁴³ Ethylene glycol must also possess a certain amount of open structure since its P_1 rises

³⁷ R. F. Blanks and J. M. Prausnitz, *Ind. and Eng. Chem. (Fundamentals)*, 1964, 3, 1.

³⁸ C. M. Hansen, 'The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient', Danish Technical Press, Copenhagen, 1967.

³⁹ R. E. Gibson and O. H. Loeffler, *J. Amer. Chem. Soc.*, 1941, 63, 898.

⁴⁰ Values of P_1 and c.e.d. at various temperatures obtained from data in 'Organic Solvents', ed. J. A. Riddick and W. B. Bunger, 3rd Edn., Wiley-Interscience, New York, 1970.

⁴¹ O. Ya. Samoilov, *Zhur. fiz. Khim.*, 1946, 20, 12.

⁴² H. S. Frank and Wen Yang Wen, *Discuss. Faraday Soc.*, 1957, 24, 133.

⁴³ D. Eisenberg and W. Kauzmann, 'The Structure and Properties of Water', University Press, Oxford, 1969.

slightly with temperature.³⁹ Other protic solvents behave normally, reflecting the non-open nature of their structure.

Gibson and Loeffler³⁹ found that plots of P_1 for water vs. molar volume at various temperatures show a change of slope at about 40 °C. Lee and Hyne⁴⁴ discovered that plots of P_1 vs. temperature show anomalies at about 35 °C for aqueous potassium chloride solutions. Both experiments involve water in a compressed state, caused by either external compression or internal electrostriction by an electrolyte. P_1 is related to isothermal compressibility through the expression, $P_1 = T\alpha/\beta$. It must be supposed that P_1 for compressed systems is more sensitive to the anomalous behaviour of β at 35–45 °C than to changes in the coefficient of thermal expansion.

C. Binary Liquid Mixtures.—Early studies by Westwater *et al.*⁹ showed that P_1 for 50 mol% binary mixtures of several liquids of low polarity is approximately given by the mean of the individual values. More recently, Hyne and his co-workers^{14,45} found that certain compositions of alcohol–water and DMSO–water mixtures produced a P_1 value *higher* than that of either component. A maximum appears in the P_1 –composition curve for aqueous DMSO at 0.3–0.4 mole fraction of DMSO, and at very small concentrations of alcohol in water. In both types of mixture, c.e.d. decreases regularly from its high water value to the much lower value of the co-solvent. Calculated values of E^C also decrease with added co-solvent.

These maxima occur at mixture compositions possessing other anomalous properties.^{46,47} The addition of alcohols to water is accompanied by large negative excess entropies, a fact which points to a considerable structural enhancement.⁴⁶ A maximization of structure when DMSO is co-solvent has been attributed to the formation of complexes such as DMSO, 2H₂O.⁴⁷ However, much doubt exists about the exact nature of the structure-making effect of the co-solvents.

P_1 /c.e.d. results suggest that structure-making takes place *via* non-chemical rather than chemical interactions. An increased degree of hydrogen bonding interaction would reveal itself in c.e.d. or E^C . This does not happen in the systems being analysed. Small amounts of added alcohol or DMSO form hydrogen bonds with water molecules, a process in which the energy lost in the disruption of water structure is not totally replenished in the formation of bonds with the co-solvent. Once again, depending on the water model selected, molecules of water and/or co-solvent enter the disrupted skeleton or join the existing layers of water monomers around the clusters. In either case, compressibility decreases⁴⁶ (even though alcohols are more compressible than water), and non-chemical attractive interactions increase. P_1 rises to a value greater than that of the co-solvent before further addition of co-solvent totally destroys the three-

⁴⁴ I. Lee and J. B. Hyne, *Canad. J. Chem.*, 1973, **51**, 1885.

⁴⁵ D. D. Macdonald, J. B. Hyne, and F. L. Swinton, *J. Amer. Chem. Soc.*, 1970, **92**, 6355; D. D. Macdonald and J. B. Hyne, *Canad. J. Chem.*, 1971, **49**, 2336.

⁴⁶ F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.

⁴⁷ J. J. Lindberg and J. Kenttamaa, *Suomen Kem.*, 1960, **B33**, 104.

dimensional arrangement of water molecules. With no intimate sites in which to place themselves, or no clusters to separate the monomeric layers, the water molecules find themselves increasingly interacting with, and surrounded by, more and more co-solvent. P_1 falls to the value of the alcohol or DMSO.

This analysis of water and liquid mixtures depends entirely on the validity of assumptions made in Section 2B. The possibility always exists that P_1 contains contributions from hydrogen bonding which dictate the above phenomena. Clearly much more effort is required in this area before firm conclusions can be drawn and categorical statements can be made.

4 Relationship between P_1 , C.E.D., and Selected Solution Phenomena

A. Solubility.—Two liquids do not completely mix if one liquid has a much greater cohesion than the other. Conversely, molecules in liquids of similar cohesion are just as likely to interact and mix with each other as with their own kind. In this way we can rationalize the low miscibility of paraffins (low c.e.d.) in water (high c.e.d.), and the complete miscibility of acetonitrile and DMF. Any interaction between unlike molecules enhances the changes of miscibility. Thus, although water (c.e.d. = 550 cal cm⁻³) and acetone (c.e.d. = 94.3 cal cm⁻³) differ considerably in cohesion, hydrogen bonding between the two liquids overcomes the natural reluctance of water to link with the co-solvent. Hildebrand² has referred to the square root of c.e.d. as the *solubility parameter*, δ , because of its frequent use in solubility problems.

This approach explains why water becomes increasingly miscible with the normal paraffins as the chain length is increased. Cohesion rises with increasing chain length, resulting in δ_{paraffin} moving closer to δ_{water} . On the other hand, the complete miscibility of the lower alcohols with water falls off as the alkyl group is enlarged. Hydrogen bonded interactions lessen on transfer to the higher alcohols, and cohesion falls; δ_{alcohol} becomes less like δ_{water} .

The same conditions of relative cohesion apply to the solubility of solids in solvents. We have already referred to attempts at matching the contributing interactions to cohesion for polymers and solvents. C.e.d.'s for polymers of high molecular weight cannot be obtained directly from vaporization experiments. Values are therefore obtained experimentally *via* swelling measurements,⁴⁸ or empirically by Small's estimation.⁸ Allen *et al.*⁴⁹ investigated the possibility of using P_1 for polymers in place of c.e.d. They found that for all the polymers investigated P_1 was some 30—50% higher than c.e.d., and they concluded that c.e.d. may underestimate the cohesion of a polymer. It would appear that δ^2 is better represented by P_1 when being used for predicting polymer solubility.

Whenever a solute dissolves, a hole has to be created in the solvent to accommodate that solute. The energy required to make the hole depends on the cohesion of the solvent and on the volume of the hole. The effect is most noticeable in the solubility of large molecules. Tetraphenylarsonium tetraphenylboride,

⁴⁸ G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, 1958, **54**, 1731.

⁴⁹ G. Allen, G. Gee, D. Mangaraj, D. Sims, and G. Wilson, *Polymer*, 1960, **1**, 467.

for example, is a large organic salt in which the ions are often considered to be buried beneath the phenyl groups. In terms of its solubility product, the boride is 10^{13} times more soluble in DMSO than in water.⁵⁰ Although some of the increased solubility must be due to enhanced interaction of DMSO with the cationic part of the salt, the difficulty of creating a large enough hole in water for the salt must be the major factor in its relative insolubility. Deno and Berkheimer⁵¹ noticed the effect during their solubility measurements of a series of R_4NClO_4 salts in water, ethanol, and benzene. When R was small, the salt dissolved to advantage in water because of strong ion-water interactions. As R increased from CH_3 to CH_6H_{13} , the energy needed to make a hole rises much more rapidly in water than in ethanol or benzene, and becomes the solubility determining factor. Thus, a change from water to benzene enhanced the solubility of $(C_6H_{13})_4NClO_4$ two-thousand fold.

B. Electrolytes in Solution.—Dissolved electrolytes increase the internal pressure within a solvent.^{5,52} The increase is achieved through *electrostriction*—a volume-reducing process which involves polarization and attraction of solvent molecules around the ionic species; e.g., a 3M aqueous solution of sodium bromide exhibits a P_1 value of ca. 75 cal cm^{-3} ,⁵³ whereas the value for water at 25°C is only 41 cal cm^{-3} . Thus the change in internal pressure gives a measure of the electrostrictive effect of a certain concentration of dissolved electrolyte. As Gordon²⁷ points out, uncertainties about the intrinsic volumes of ions in solution make an estimation of their electrostriction abilities very difficult. Use of internal pressure for such estimations surmounts these difficulties, as illustrated in the following two examples of electrolyte behaviour in solution.

(i) *Salting out, Salting in, and Salt Effects on Chemical Reactivity.* Dissolved sodium chloride separates 1-butanol and water into two layers, and the ability of inorganic salts to separate other organic compounds from water is well known. McDevit and Long⁵⁴ explained this effect in terms of a changing internal pressure of the medium. Dissolved salts increase the internal pressure/electrostriction of the aqueous solutions to such an extent that the non-electrolyte is squeezed out (salting out). When the dissolved salt reduces the internal pressure/electrostriction of the solution, more of the non-electrolyte is able to dissolve (salting in).

The salting out/in process can be described by equation (7),

$$\log \gamma = k_s c_s \quad (7)$$

where γ is the activity coefficient of non-electrolyte in solution, k_s is the Setschenow constant, and c_s is the concentration of dissolved salt in mol l^{-1} . McDevit and Long's treatment leads to equation (8). The volume \bar{V}°_1 refers to the molar

$$k_s = \bar{V}^{\circ}_1(V_s - \bar{V}^{\circ}_s)/2.3RT \beta_0 \quad (8)$$

⁵⁰ R. Alexander and A. J. Parker, *J. Amer. Chem. Soc.*, 1967, **89**, 5549.

⁵¹ N. C. Deno and H. E. Berkheimer, *J. Org. Chem.*, 1963, **28**, 2143.

⁵² H. F. Herbrandson and F. R. Neufeld, *J. Org. Chem.*, 1966, **31**, 1140; A. P. Stefani, *J. Amer. Chem. Soc.*, 1968, **90**, 1694.

⁵³ Calculated from data in E. B. Freyer, *J. Amer. Chem. Soc.*, 1931, **53**, 1313.

⁵⁴ W. F. McDevit and F. A. Long, *J. Amer. Chem. Soc.*, 1952, **74**, 1773.

volume of the non-electrolyte, V_s and \bar{V}_s° are the intrinsic and apparent molar volumes of the salt, respectively, and β_0 is the compressibility of the solution. The Setschenow constant is positive for salting out and negative for salting in. Equation (8) shows that the effect is greatest for non-electrolytes of largest molar volume, and for salts that cause the most electrostriction, $V_s - \bar{V}_s^\circ$. The effect of inorganic salts on k_s values for benzene, naphthalene, and biphenyl in water appear in Table 3.^{54,55} All the electrolytes, except perchloric acid, cause electro-

Table 3 Setschenow constants at 25 °C for the salting out/in of benzene, naphthalene, and biphenyl from aqueous solutions of electrolytes.^{54,55} (Molar volumes appear in parentheses)

Electrolyte	Benzene (89.4 cm ³ mol ⁻¹)	Naphthalene (125 cm ³ mol ⁻¹)	Biphenyl (149 cm ³ mol ⁻¹)
NaCl	0.195	0.260	0.276
KCl	0.166	0.204	0.255
LiCl	0.141	0.180	0.218
NaBr	0.155	0.169	0.209
NaClO ₄	0.106	0.096	0.113
HCl	0.048	0.046	0.070
HClO ₄	-0.041	-0.081	-0.116

striction of water and a salting out of the organic species. It appears that the volume of the system is increased by perchloric acid to give a 'negative electrostriction'; salting in occurs. Other workers⁵⁶ have obtained satisfactory agreement between experimental results and those predicted from equation (8). However, until salting out/in effects in solvents other than water have been examined, the universality of the theory cannot be judged.

Clarke and Taft⁵⁷ examined the effect of added salts on the rates of chemical reactions in terms of internal pressures. A study of the solvolysis of t-butyl chloride in water convinced these authors that although internal pressure effects (induced by the salt) influence the activity coefficient of both the reactants and the activated complex, a cancellation of effects occurs during the reaction. Kinetic salt effects were adequately explained by Ingold's ion-atmosphere treatment.⁵⁸

(ii) *Conductivity*. Electrochemists have long asked: why does the equivalent conductance of a strong electrolyte decrease with increasing concentration? In an effort to solve the problem, theories of conductivity⁵⁹ have considered the dependence on concentration of degrees of dissociation, ionic mobility, ion

⁵⁶ M. A. Paul, *J. Amer. Chem. Soc.*, 1953, **75**, 2513.

⁵⁷ N. C. Deno and C. H. Spink, *J. Phys. Chem.*, 1963, **67**, 1347; E. Grunwald and A. F. Butler, *J. Amer. Chem. Soc.*, 1960, **82**, 5647.

⁵⁸ G. A. Clarke and R. W. Taft, *J. Amer. Chem. Soc.*, 1962, **84**, 2295.

⁵⁹ L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 1940, 979.

⁶⁰ R. M. Fuoss, in 'Chemical Physics of Ionic Solutions', ed. B. E. Conway and R. G. Barradas, Wiley, New York, 1966, p. 463.

pairing, dielectric constant, and viscosity. In 1959 Suryanarayana and Venkatesan⁶⁰ put forward a theory of conductance which overcame the apparent inability of theories then prevailing to explain the behaviour of concentrated solutions of electrolytes. They recognized that solvent internal pressure was closely related to all of the above parameters, and they proposed that a moving ion is subject to the structural pressure of the surrounding solvent. An increase in concentration of the electrolyte simply increases the work necessary to move an ion through a medium of enhanced internal pressure with a given electric field. Ionic mobility and the equivalent conductance of the electrolyte fall. As the authors mentioned, the effect is not just one of changing the viscosity of the solution, since classical experiments have already shown that the conductivity of an electrolyte in a jelly does not change appreciably when the jelly sets.

Although we have stated that the internal pressure of a solution rises with added electrolyte, only regions around the ions really experience the increased pressure. In 1966 Fuoss⁵⁹ speculated that any improvement of existing theories of conductivity must include 'the discrete structure of the solvent' in the neighbourhood of the ions. Electrostricted solvent enlarges the effective size of the moving ions. In a concentrated solution, therefore, the probability of an ion and its attendant solvent environment being hindered in its movement by other moving species becomes greater than in more dilute solutions.

Thus, the internal pressure concept leads to two explanations for the behaviour of strong electrolytes in solution. One explanation envisages ionic mobility to be related to the *internal pressure of the medium*, while the other relates ionic mobility to an electrostriction process which determines the *internal pressure in the vicinity of the ions*.

C. Apparent Molal Volumes of Dissolved Species.—Internal pressure, electrostriction, and apparent molal volumes are interconnected phenomena. Three factors determine the apparent molal volume of a dissolved solute: (i), the intrinsic size of the solute, (ii), the ability of the solute to cause electrostriction of the solvent, and (iii), the ability of solvent to prevent electrostriction. Electrostriction depends on the chemical and/or electrostatic affinity of solvent molecules for the solute. Although electrostriction increases as the internal pressure of a system increases, internal pressure monitors rather than creates the electrostrictive effect. Total collapse of solvent molecules around a charged solute, and the ability of a neutral solute to make a hole for itself, are affected by solvent compressibility and cohesion. Both properties are related to internal pressure, but the contribution of electrostriction to apparent molal volumes is usually so large that it demotes the internal pressure effect of a solvent to a minor role. That role might be expected to increase when the solute species do not interact with the solvent.

Millero⁶¹ has comprehensively reviewed the whole subject of apparent molal

⁶⁰ C. V. Suryanarayana and V. K. Venkatesan, *Acta Chim. Acad. Sci. Hung.*, 1959, **19**, 441.

⁶¹ F. J. Millero, *Chem. Rev.*, 1971, **71**, 147.

volumes; thus we make no attempt to do so here. We merely re-emphasise the connection between electrostriction and the internal pressure of solutions, and suggest that the effect of solvent internal pressure on apparent molal volumes might become evident in the absence of electrostriction. For a determined test of the relevance of internal pressure, measurements should be made in dipolar aprotic solvents and protic solvents of high dipole moment ($P_1 = 80\text{--}130$ cal cm^{-3}) as well as the solvents of low dipole moment that have hitherto been used ($P_1 = 70\text{--}80$ cal cm^{-3}).

D. Chemical Reactivity.—In 1929 Richardson and Soper⁶² noticed that reactions in which the products had greater cohesion than the reactants proceed faster in solvents of highest cohesion. The converse also applied. Reactions which undergo little change in cohesion of the species respond poorly to solvent change. Glasstone⁶³ later predicted the same results from theoretical considerations. This promising approach to solvent effects on chemical reactivity fell into disuse when Hughes and Ingold⁶⁴ formulated their theory based on the energetics of species. The Hughes–Ingold theory compares the relative solvation of reactants and transition state complex by different solvents, and examines the effect of differing degrees of solvation on the free energy of activation of a reaction. However, the theory cannot deal in detail with electro-neutral reactions. With no movement of charge occurring on passing from the ground state to the transition state of these reactions, a change of solvent should have no effect on their rates. Small rate changes are observed, and they warrant inclusion in any theory of solvent effects.

Dack⁶⁵ recently showed how a consideration of *volumes of activation*, instead of free energies of activation, gives rise to a more general account of solvent effects on reaction rates. In its simplest terms, the account proposes that solvent internal pressure acts on the volume of activation (ΔV^\ddagger) of a reaction like an externally applied pressure. If a change of solvent polarity alters ΔV^\ddagger in some way, the structural pressure of the new solvent acts on the changed ΔV^\ddagger . When this happens, the polarity effect should outweigh any pressure effect on the reaction rate. Such an approach thereby covers non-polar reactions, since changes in rate caused by solvent transfer will only depend on changes in the solvent internal pressure. The following predictions were made:⁶⁵

- (i) Solvent internal pressure acts on the rates of non-polar reactions, and on polar reactions in non-polar solvents, in the same direction as external pressures.
- (ii) Solvents which lower the value of the volume of activation of a reaction by electrostriction accelerate the rate of that reaction.
- (iii) Those solvents able to raise the value for the volume of activation of a reaction cause the rates to fall.

⁶² M. Richardson and F. G. Soper, *J. Chem. Soc.*, 1929, 1873.

⁶³ S. Glasstone, *J. Chem. Soc.*, 1936, 723.

⁶⁴ E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1935, 244; C. K. Ingold, 'Structure and Mechanism in Organic Chemistry', 2nd Edn., Cornell University Press, Ithaca, 1953.

⁶⁵ M. R. J. Dack, *J. Chem. Educ.*, 1974, 51, 231.

The scheme in Table 4 depicts passage of eight reaction types from ground state to transition state in terms of the volume of each state. Types 1 and 2 are non-polar unimolecular and bimolecular reactions respectively. Bond breaking occurs in the unimolecular reaction to give a positive ΔV^\ddagger , while reactants come together in the bimolecular reaction to give a negative ΔV^\ddagger . An increased solvent polarity has little effect on ΔV^\ddagger ; an increased solvent internal pressure decreases and increases the rates, respectively.

Electrostriction of solvent around species in the polar reactions (types 3—8) yields the signs of ΔV^\ddagger shown in Table 4. Solvents of increased polarity cause a greater increase of electrostriction (volume-reducing process) around charged species and around species with the greater concentration of charge. It is therefore possible to predict the effect of solvent transfer on the magnitude of ΔV^\ddagger . Rate increases occur if the new solvent lowers the value of the volume of activation. The reader is referred to the original paper⁶⁵ for a more detailed discussion and for illustrative data.

Some doubt has been cast on the relevance of solvent internal pressure to chemical reactivity.⁶⁶ Predictions made by the pressure/volume approach are based on the transition state theory, and on theories of regular solutions involving the solubility parameter, δ . However, a non-polar solute of a given volume will not experience the full internal pressure of its solvent⁶⁷ (Section 4F). Nevertheless, other workers believe that solvent internal pressure plays a large role in polar as well as non-polar reactions.⁵² When solvation of reactants and transition state complex occurs to a similar extent, polarity effects are thought to cancel out, thus promoting the structural pressure of the solvent to a new importance. Fleischmann and Kelm⁶⁸ have separated the 'intrinsic' and 'electrostrictive' components of ΔV^\ddagger for a cycloaddition reaction in a number of solvents. More work of this precise nature is needed before the quantitative usefulness of the pressure/volume approach to solvent effects can be evaluated.

E. Conformational Equilibria.—The pressure/volume approach to chemical reactivity considered the equilibrium between reactants and transition state complex in terms of volumes. For non-polar reactions, pressure exerted by a solvent (P_1 or c.e.d.) acted on the equilibria in the same manner as an external pressure. Ouellette and Williams⁶⁹ proposed the same principle for determining the relative population of non-polar conformers when the non-interacting solvent is changed. An increase in solvent pressure favours the conformer with the smaller molar volume. These workers supported their proposal by finding a linear correlation between conformational equilibrium constants for the *trans* \rightleftharpoons *gauche* equilibrium of 4,4-dimethyl-2-silapentane and 2,3-dimethyl-2-silabutane and P_1 for four non-polar solvents.


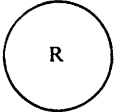
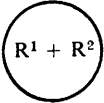
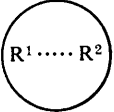



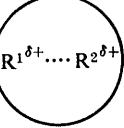



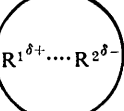



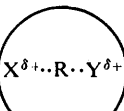
⁶⁶ R. G. Pearson, *J. Chem. Phys.*, 1952, **20**, 1478; A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, 1964, **68**, 651; R. C. Neuman, *J. Org. Chem.*, 1972, **37**, 495.

⁶⁷ P. J. Trotter, *J. Amer. Chem. Soc.*, 1966, **88**, 5721; *J. Chem. Phys.*, 1968, **48**, 2736.

⁶⁸ F. K. Fleischmann and H. Kelm, *Tetrahedron Letters*, 1973, **39**, 3773.

⁶⁹ R. J. Ouellette and S. H. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 466.

Table 4 Scheme for the pressure/volume approach to solvent effects on chemical reactivity.⁶⁴ (The effects of increased solvent polarity/internal pressure are discussed in text)

1		$\xrightarrow{+\Delta V^\ddagger}$		None	Decrease
2		$\xrightarrow{-\Delta V^\ddagger}$		None	Increase
3		$\xrightarrow{-\Delta V^\ddagger}$		More negative	Increase
4		$\xrightarrow{+\Delta V^\ddagger}$		More positive	Decrease
5		$\xrightarrow{-\Delta V^\ddagger}$		More negative	Increase
6		$\xrightarrow{+\Delta V^\ddagger}$		More positive	Decrease
7		$\xrightarrow{-\Delta V^\ddagger}$		More positive	Decrease
8		$\xrightarrow{-\Delta V^\ddagger}$		More positive	Decrease

Eckert⁷⁰ recognized the good correlation obtained by Ouellette and Williams, but lamented that no external pressure results were available for comparison. Earlier work by Le Noble⁷ has shown that equilibrium constants for the reaction

⁷⁰ C. A. Eckert, *Ann. Rev. Phys. Chem.*, 1972, **23**, 239.

of α to γ -methylalkyl azide in both solution and in the gas phase could be fitted to the same pressure curve if P_1 for the solvent (methylene chloride) was included in the total pressure. The dependence on P_1 of the dissociation of N_2O_4 in the gas and in solution has been known for many years.⁷¹ Thus, solvent pressure certainly affects chemical equilibria, but once again, it must be emphasized that its effect on conformer equilibria and other solution phenomena will be small in relation to the effect of any solute-solvent interactions.

F. Spectroscopic Observations.—Statistical mechanical calculations show that solvents exert a mechanical pressure (P_M) of 10^3 – 10^4 atm on dissolved molecules. P_M is the actual pressure that a molecule of a given size experiences and not just the internal pressure of the solvent. Trotter⁶⁷ has calculated P_M for a solute molecule with a 11.0 Å molecular diameter in a number of non-polar solvents at 25 °C: benzene, $P_M = 1550$ atm ($P_1 = 3631$ atm); CCl_4 , $P_M = 3320$ atm ($P_1 = 3342$ atm); CS_2 , $P_M = 1470$ atm ($P_1 = 3672$ atm). Such pressures are extremely pertinent to an analysis of the spectral data of weak molecular complexes on transfer of the complexes from the vapour to the condensed state.

Bonding in weak molecular complexes (charge-transfer, and to a lesser extent, hydrogen bonding) can be compressed by a pressure. Ample evidence exists⁷² to show that applied pressures of a few thousand atmospheres cause large red shifts and intensity enhancements (external compression of bonding) in the charge-transfer bands of molecular complexes. The complexes experience similar pressures when transferred from the vapour to the liquid (internal compression of bonding), and the question is asked: should the same spectral shifts be expected?

Trotter⁶⁷ believes that the internal compression effect of a non-polar solvent causes red shifts in weak charge-transfer complexes of between 1000–4000 cm^{-1} , and an intensity enhancement, when transferring the complexes from the vapour. Hydrogen bonds are much stronger than charge-transfer complexes and less compressible. Red spectral shifts of -20 – -40 cm^{-1} for O—H...O bonds might be expected from internal compression, plus a small downfield n.m.r. shift. As judged from existing experimental data, these predictions appear to be reasonable. Other solvent effects may contribute to the spectral shifts, but the ability of solvent pressure to change the bond lengths of molecular complexes must be a major factor.

G. Biological Observations.—Large biochemical molecules also experience internal compression from the surrounding medium, water. The mechanical pressure on a molecule like insulin (molecular diameter ≈ 50 Å) is thought⁶⁷ to be in the region of 500 atm at 25 °C. Any biological process which is sensitive to externally applied pressures (*e.g.* the unfolding of ribonuclease) may therefore be

⁷¹ W. J. Le Noble, *Progr. Phys. Org. Chem.*, 1967, **5**, 230.

⁷² J. R. Gott and W. G. Maisch, *J. Chem. Phys.*, 1963, **39**, 2229; A. H. Ewald, *Trans. Faraday Soc.*, 1968, **64**, 733.

affected by this type of solvent pressure, and the ability to alter the solvent pressure presents a possible mechanism for influencing that process.

Work by Ginzburg and Cohen⁷³ indicates that 'internal hydrostatic pressures' created in gels are responsible for squeezing out non-electrolytes from the gels. Proteins and carbohydrates are among those macromolecules able to form gels. Ginzburg and Cohen exemplified the biological implications of their observations as follows: 'it can be predicted that large molecules such as hemoglobin should be totally excluded from gels with an internal pressure of 10 atm,' while 'even molecules of low molecular volume (*e.g.* sucrose) should be excluded from gels having high internal pressures.' However, the relevance of solvent pressure to biological systems has not yet been established. It would be unwise to speculate further until connecting evidence is obtained.

5 Concluding Remarks

The aim of the Review has been to promote a wider awareness of the concept of solvent pressure. Internal pressure, mechanical pressure, or cohesion plays its largest role in non-interacting systems, and although its effect will be very small in many solution phenomena, it must always be present. It is possible that we have overstated the importance of solvent pressure. Many of the solution phenomena discussed can certainly be explained by other means. Maybe the legitimate place for solvent pressure is alongside steric effects in organic chemistry—to be invoked when all else fails. Only time and an appropriate amount of experimental effort can resolve the full importance of the concept.

It is a pleasure to acknowledge the helpfulness of several discussions held with Dr. R. O. Watts during the preparation of this Review. The advice and encouragement of Dr S. D. Hamann, Professor A. J. Parker, and Professor J. B. Hyne have been greatly appreciated.

⁷³ B. Z. Ginzburg and D. Cohen, *Trans. Faraday Soc.*, 1964, 60, 185.