

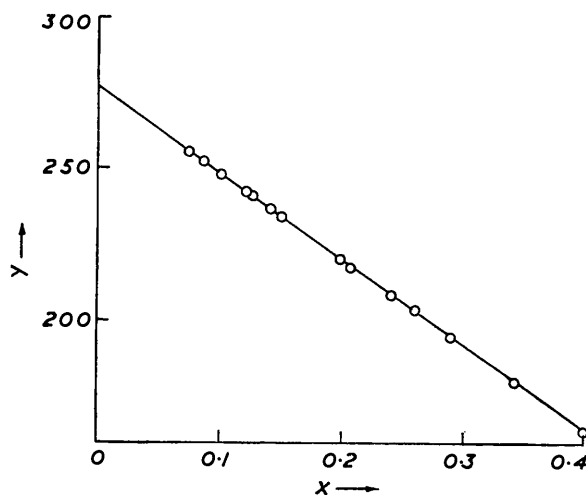
549. *The Ionisation Functions of Cyanoacetic Acid in Relation to the Structure of Water and the Hydration of Ions and Molecules.*

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Dissociation constants of cyanoacetic acid in aqueous solution have been measured at 5° intervals between 5° and 45°, with an accuracy in $\ln K$ of the order of 0.005%. Fifteen interpolation equations have been tested by statistical methods, and three of these have been found to be capable of expressing the dependence of $\ln K$ upon temperature within experimental error. These three equations, and graphical interpolation, show that the heat-capacity loss accompanying the ionisation of cyanoacetic acid passes through a minimum at 20–30°. This is very likely to be due to the effects of temperature upon the structure of water, the hydration of molecules, and the hydration of ions. Present knowledge of these topics is reviewed. The strength of cyanoacetic acid is shown to depend on an entropy effect, as well as on the normally accepted influence of a polar substituent. The results are discussed in relation to recent data on the halogenoacetic acids.

THE heat-capacity change accompanying the ionisation of a weak electrolyte in aqueous solution (ΔC_p , cal. mole⁻¹ deg.⁻¹) is potentially of great value in relation to the study of the ionisation process. Its experimental determination is, however, so difficult that there

FIG. 1.



is at present only agreement about its magnitude in a number of cases, but no information on its variation with temperature. The present work was undertaken in order to supply such information in one favourable case.

The potentialities of the conductance method for evaluating the thermodynamic functions of ionisation have recently been demonstrated¹ for aqueous solutions of monohalogenoacetic acids, but these substances are not suitable for very accurate measurements over the wide temperature range essential to obtain significant information about ΔC_p . We chose cyanoacetic acid as solute since it is stable in aqueous solution and is of suitable strength to give optimum accuracy. The methods employed, except for certain refinements described in the Experimental section, were as used in the earlier investigation.¹ Three samples of cyanoacetic acid were used to prepare fourteen solutions, the conductances of which were measured at nine temperatures over the range 5–45°. Dissociation

¹ Ives and Pryor, *J.*, 1955, 2104.

constants were evaluated by extrapolation² as before. The application of this method is illustrated in Fig. 1, for one temperature (5°). It can be seen that the relation

$$y = \Lambda_0 - x/K \quad \dots \dots \dots (1)$$

where $y = \Lambda + aC_i^{1/2}$ and $x = \Lambda^2 C \times 10^{-2AC_i^{1/2}} / (\Lambda_0 - aC_i^{1/2})$,

where a and A are the Onsager and Debye-Hückel coefficients and C and C_i are the concentrations (moles/l.) of total and ionised solute, does not deviate from strict linearity. This procedure should be more accurate than the usual one involving sodium salt solubility, which in any case is not applicable here because of the possibility of amic acid formation.

The results are given in Table 1.

TABLE 1. *Equivalent conductances of cyanoacetic acid solutions.*

10 ⁴ C (moles/l. at 25°) =	Temp.	47·7082	33·0766	23·3394	19·0834	16·6513	12·8735	12·1358
5°	159·71	176·15	191·66	200·45	205·77	215·61	217·86	
10	176·51	194·68	211·91	221·66	227·43	238·36	240·84	
15	192·76	212·78	231·70	242·06	249·09	260·83	263·49	
20	208·61	230·40	250·97	262·28	269·89	282·77	285·77	
25	223·76	247·35	269·55	281·93	290·15	304·05	307·39	
30	238·29	263·53	287·56	300·75	309·64	324·72	328·43	
35	251·94	278·91	304·55	318·74	328·24	344·54	348·50	
40	264·86	293·53	320·81	335·93	346·09	363·62	367·82	
45	276·79	307·14	336·07	352·16	362·98	381·67	385·61	

10 ⁴ C (moles/l. at 25°) =	Temp.	7·9565	7·3034	6·1734	5·9368	4·6651	3·7920	3·2012
5°	232·12	234·72	239·59	240·63	246·22	250·68	253·65	
10	256·64	259·57	265·02	266·02	272·83	277·18	280·49	
15	280·90	284·13	290·08	291·29	298·78	303·71	307·24	
20	304·78	308·33	314·81	316·14	324·34	329·91	333·64	
25	328·09	331·91	339·27	340·45	349·91	355·47	359·60	
30	350·80	354·29	362·65	364·15	374·10	380·53	386·02	
35	372·65	377·13	385·49	387·07	397·92	404·98	410·95	
40	393·81	398·60	407·62	409·43	421·23	428·72	435·30	
45	414·06	419·24	428·88	431·10	443·41	451·66	458·61	

Values of dissociation constants and of equivalent conductances at zero concentration, with their probable errors, are collected in Table 2. The probable errors were obtained by an application of Bessel's relation to equation (1) which involved a shift of the origin to the "centre of gravity" of the x, y points.

TABLE 2.

Temp.	5°	10°	15°	20°	25°
10 ⁵ K	359·20 ± 0·06	357·45 ± 0·07	352·93 ± 0·07	346·94 ± 0·06	338·76 ± 0·09
Λ ₀	275·87 ± 0·04	305·32 ± 0·05	334·77 ± 0·05	364·06 ± 0·04	393·23 ± 0·06
Temp.	30°	35°	40°	45°	
10 ⁵ K	329·78 ± 0·06	319·52 ± 0·06	308·51 ± 0·06	296·40 ± 0·06	
Λ ₀	421·97 ± 0·04	450·21 ± 0·04	478·10 ± 0·04	505·48 ± 0·04	

Many interpolation equations have been proposed to express the variation of acid strength with temperature, the simplest and most striking being Harned and Embree's parabolic relation:³

$$\ln K = \ln K_{\max.} - 5 \cdot 0 \times 10^{-5}(t - \theta)^2 \dots \dots \dots (2)$$

where θ is the temperature at which the dissociation constant attains its maximum value, $K_{\max.}$ For a wide variety of weak acids, the plot of $\ln (K/K_{\max.})$ against $(t - \theta)$ is so nearly

² Ives, J., 1933, 731.

³ Harned and Embree, *J. Amer. Chem. Soc.*, 1934, **56**, 1050.

a single parabola as to leave no doubt that this relation is an excellent approximation. The more generalised parabolic law

$$\ln K = a + bT + cT^2 \quad \dots \quad (3)$$

was found by Ives and Pryor¹ to fit their results within experimental error. This equation, however, requires ΔC_p to vary as a function of temperature according to the expression:

$$\Delta C_p = 2bRT + 6cT^2 \quad \dots \quad (4)$$

In contrast, it has been asserted that all the available data can⁴ be equally well expressed by formulations based upon the supposition that ΔC_p does not vary with temperature; these all reduce to the basic form:

$$\ln K = a/T + b \ln T + c \quad \dots \quad (5)$$

Harned and Robinson⁵ concluded that no definite statement could be made about the variation of ΔC_p with temperature, as has been re-affirmed.⁶

For the present investigation it was of the utmost importance to avoid injecting any predetermined form into the relationship between ΔC_p and temperature by use of an oversimplified or unsuitable interpolation equation. No *a priori* means of choosing between the more likely forms was available, so a wide range of equations was tested on an equal basis, each one being independently fitted to the experimental results by the method of least squares. All the equations concerned are assembled in Table 3.

TABLE 3.

	Ref.
3. $-\ln K = a + bT + cT^2$	1, 5
3a. $-\ln K = a + bT + cT^2 + dT^3$	
3b. $-\ln K = a + bT + cT^2 + dT^3 + eT^4$	
3c. $-\ln K = a + bT + cT^2 + dT^3 + eT^4 + fT^5$	
6a. $-\ln K = a + bT + cT \ln T$	
6b. $-\ln K = a + bT + cT \ln T + dT^2$	
6c. $-\ln K = a + bT + cT \ln T + dT^2 + eT^3$	
7a. $-\ln K = a/T + b + cT$	5, 7
7b. $-\ln K = a/T + b + cT + dT^2$	
5a. $-\ln K = a/T + b/T \ln T + c/T \ln^2 T + d$	8
2a. $-\ln K = -\ln K_{\max} + 0.05 \times 10^{-5} (t - \theta)^2$	3
8a. $\Delta G = a + bT + cT \ln T + dT^2 + eT^3$	
8b. $\Delta G = a + bT + cT \ln T + dT^2$	
8c. $\Delta G = a + bT + cT \ln T$	
9. $\Delta G = a + bT + cT^2 + dT^3 + eT^4 + fT^5$	
Since $\Delta G = -RT \ln K$, equations 8a—9 are equivalent to	
8a'. $-\ln K = A/T + B + C \ln T + DT + ET^2$	9, 10
8b'. $-\ln K = A/T + B + C \ln T + DT$	
8c'. $-\ln K = A/T + B + C \ln T$	4, 11, 12, 13
9'. $-\ln K = A/T + B + CT + DT^2 + ET^3 + FT^4$	

All the other equations are simple extensions of those for which references are quoted.

The labour of fitting each equation independently to the experimental results was eased by the use of matrix and determinant algebra;¹⁴ for the six-term equations it was necessary to redefine the temperature scale in terms of $\phi = (T - 298.16)/5$. In all cases observed and calculated values of $\ln K$ were compared by tabulating residuals and applying statistical tests for randomness where necessary.¹⁵

⁴ Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380.

⁵ Harned and Robinson, *ibid.*, 1940, **36**, 973.

⁶ Harned and Owen, "Electrolytic Solutions," Reinhold, New York, 1950, p. 510.

⁷ Harned and Done, *J. Amer. Chem. Soc.*, 1941, **63**, 2579.

⁸ Jenkins, *Trans. Faraday Soc.*, 1945, **41**, 138.

⁹ Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, **55**, 652.

¹⁰ Harned and Hamer, *ibid.*, 1933, **55**, 2194.

¹¹ Lewis and Randall, "Thermodynamics," McGraw-Hill, New York, 1923, p. 104.

¹² Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.

¹³ Briegleb and Bieber, *Z. Elektrochem.*, 1951, **55**, 250.

¹⁴ Aitken, "Determinants and Matrices," Oliver, Edinburgh, 1954.

¹⁵ Bond, "Probability and Random Errors," Arnold, London, 1935, p. 103.

Only equations 3*b*, 3*c*, and 9 were found to be capable of expressing the observed values of $\ln K$ as a function of temperature with fully random deviations not exceeding those to be expected from the standard error in the dissociation-constant determinations. Some examples are quoted in Table 4, in terms of residuals, $10^5 (\ln K_{\text{obs.}} - \ln K_{\text{calc.}})$, or in the case of equation 9, $\Delta G_{\text{obs.}} - \Delta G_{\text{calc.}}$.

TABLE 4.

Temp.	Equation	3	3 <i>a</i>	3 <i>b</i>	3 <i>c</i>	6 <i>c</i>	7 <i>b</i>	9
5°		+162	-34	-5	-8	-419	+591	+0.20
10		+125	+61	+9	+19	-118	+170	+0.06
15		+101	-15	-41	-45	+39	-396	+0.12
20		+116	+34	+42	+46	+232	-1307	-0.39
25		-76	-76	-33	-33	+299	-77	+0.08
30		-91	-9	+56	+21	+440	+1331	-0.06
35		-110	+9	-19	-15	+252	+391	+0.21
40		+3	+67	+15	+4	-9	-41	-0.12
45		+89	-38	-8	-5	-116	-661	-0.08
Mean deviation		±97	±38	±28	±22	±280	±550	±0.15
%		—	—	0.0049	0.0039	—	—	0.0045

The standard error in the dissociation constants, arrived at by means of Bessel's equation and assuming x to be free from error [cf. eqn. (1)], is consistent with a mean deviation of ± 0.00021 in $\ln K$, or 0.005%. It is clear from the examples given that these calculations unambiguously select equations 3*b*, 3*c*, and 9 as capable of expressing, without distortion, the experimental accuracy of the measurements. These equations are expressed in Table 5, which shows, in order, the coefficients of ϕ^0 to ϕ^5 .

TABLE 5.

Function	<i>a</i>	10 ² <i>b</i>	10 ³ <i>c</i>	10 ⁴ <i>d</i>	10 ⁵ <i>e</i>	10 ⁶ <i>f</i>
$-\ln K$	+5.68730	+2.52289	+2.14013	-0.75968	+1.393	—
$-\ln K$	+5.68730	+2.53440	+2.14013	-1.045	+1.393	+1.37
ΔG	+3368.61	+7127.70	+1496.25	+55.653	+818.28	-892.09

The three equations were used to calculate ΔH , the enthalpy change of ionisation, and the results are shown in Table 6, together with the mean values obtained from independent, very large-scale, graphical evaluations.

TABLE 6. *Enthalpy changes, ΔH (cal. mole⁻¹).*

Temp.	5°	10°	15°	20°	25°	30°	35°	40°	45°
Equation 3 <i>b</i>	-27.8	-281.6	-505.4	-705.9	-891.4	-1072	-1257	-1462	-1700
„ 3 <i>c</i>	-44.1	-278.1	-501.2	-706.8	-895.1	-1072	-1253	-1458	-1720
„ 9	-24.2	-287.3	-515.0	-703.7	-881.9	-1074	-1260	-1472	-1696
Graphical ...	—	-286.7	-490.9	-703.7	-883.9	-1079	-1252	-1470	—

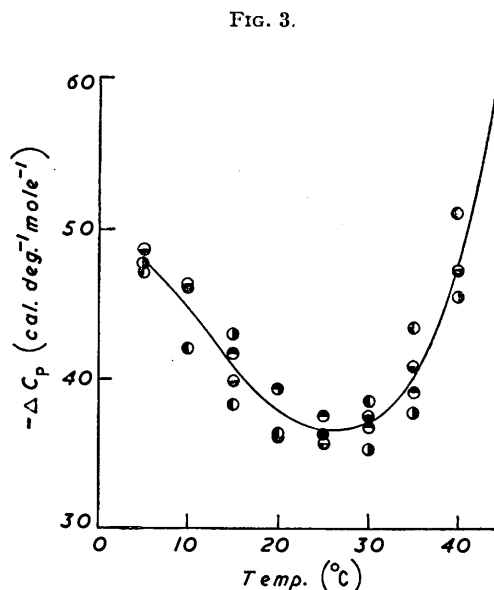
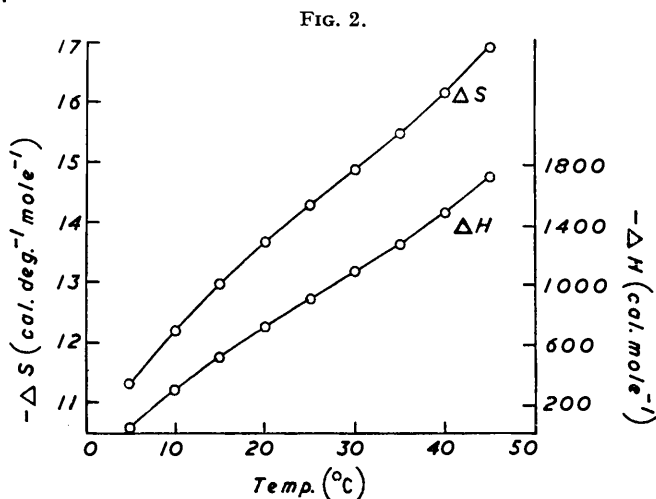
It will be seen that the four solutions for ΔH are in reasonable agreement. Gibbs free energy changes, mean enthalpy changes, and entropy changes are collected in Table 7, together with over-all assessments of probable errors.

TABLE 7.

Temp.	5°	10°	15°	20°	25°
ΔG (cal. mole ⁻¹)	3110.37	3169.02	3232.24	3298.29	3368.68
ΔH (cal. mole ⁻¹)	-32	-283	-502	-705	-888
ΔS (cal. deg. ⁻¹ mole ⁻¹)	-11.30	-12.19	-12.96	-13.66	-14.28
Temp.	30°	35°	40°	45°	
ΔG (cal. mole ⁻¹)	3441.34	3517.47	3596.36	3679.10	±0.14
ΔH (cal. mole ⁻¹)	-1074	-1255	-1465	-1705	±5
ΔS (cal. deg. ⁻¹ mole ⁻¹)	-14.89	-15.49	-16.16	-16.92	±0.02

ΔH and ΔS are plotted as functions of temperature in Fig. 2, in which it can be seen that both curves are sigmoid, and that, with a larger scatter of points, or a narrower temperature range, these plots might easily have been mistaken for straight lines. This implies that $-\Delta C_p$ passes through a minimum with rising temperature, which is a result

of such interest as to merit the closest examination. For this reason independent calculations have been made based upon the four independent sets of ΔH values. The result are assembled in Table 8 and shown graphically in Fig. 3, where the curve passes through the mean values.



○ Equation 3b. ◐ Equation 3c. ● Equation 9. ● Graphical.

TABLE 8. Values of $-\Delta C_p$ (cal. deg.⁻¹ mole⁻¹).

Temp.	5°	10°	15°	20°	25°
Equation 3b	47.2	42.0	38.3	36.3	36.2
" 3c	47.7	46.1	43.0	39.3	36.2
" 9	48.6	46.2	39.9	36.1	35.7
Graphical	—	—	41.7	39.3	37.5
Mean	47.8 ± 0.5	44.7 ± 1.8	40.7 ± 1.3	37.7 ± 1.5	36.4 ± 0.5
Temp.	30°	35°	40°	45°	
Equation 3b	38.5	43.4	51.0	62.3	
" 3c	35.2	37.7	45.5	60.7	
" 9	37.5	40.8	47.2	60.5	
Graphical	36.8	39.1	—	—	
Mean	37.0 ± 1.0	40.2 ± 1.8	47.9 ± 2.0	61.1 ± 0.7	

Although the uncertainty in ΔC_p is not much less than 2 cal. deg.⁻¹ mole⁻¹, it is evident that the conclusion that $-\Delta C_p$ in this case passes through a minimum between 20° and 30° is valid and can hardly be ascribed to experimental error, nor to the use of an arbitrary interpolation formula. The assumption of a constant ΔC_p of about -40 cal. deg.⁻¹ mole⁻¹ would allow us to interpret the dependence of K upon temperature within an accuracy of about 0.5%, which is not much less than the experimental accuracy of data hitherto available. It is interesting that a re-examination of Harned and Robinson's tests⁵ of five interpolation equations by means of the results for formic acid of Harned and Embree¹⁶ shows that in every case there is a sigmoid distribution of residuals about 35°. Any suggestion that the dependence of ΔC_p upon temperature which has been found for cyanoacetic acid is general must be made with caution. It is, however, a result of considerable interest, with implications that are followed in the Discussion.

Comparisons of the new data for cyanoacetic acid with results previously recorded are confined to 25° and are shown in Table 9.

TABLE 9.

	Δ_0	$K \times 10^5$
Ostwald (<i>Z. phys. Chem.</i> , 1889, 3 , 170)	362	373
Whiteman and Jones (<i>Amer. Chem. J.</i> , 1911, 46 , 56)	—	363
Kendall (<i>J.</i> , 1912, 101 , 1275), recal. by MacInnes (<i>J. Amer. Chem. Soc.</i> , 1926, 48 , 2068)	386	349
Saxton and Darken (<i>ibid.</i> , 1940, 62 , 847)	392	336
Ives and Sames (<i>J.</i> , 1943, 513)	387	342
Present investigation	393.2	338.8

The new values are to be preferred, since the acid used was of considerably higher m. p. than any previously recorded and technique has been improved in several ways compared with that of earlier work.

DISCUSSION

The change in any extensive thermodynamic property which accompanies the ionisation of a weak electrolyte is properly regarded as the difference between the values of the property for one mole of completely ionised solute and for one mole of non-ionised solute in their respective standard states. In both cases, these standard states are hypothetical ideal solutions of unit concentration at the fixed temperature concerned. Ideality, however, is defined in the sense of Henry's law, and postulates that solute-solute interactions are absent. The properties of the initial and final states are therefore determined not only by the properties of the ions and molecules, but also by the properties of the solvent and by solute-solvent interactions. Ionisation may be viewed as occurring in steps, involving the destruction of molecule-solvent interactions, the ionisation of the solute in the gaseous state, and the generation of a different set of interactions between the ions and the solvent. All the interactions depend fundamentally upon the properties of the solvent and must vary with temperature in a manner defined by the variation of these properties themselves with temperature. For water as solvent, the problem becomes especially complex. The new results emphasise this complexity, and can be discussed at present only in qualitative terms after a basis for discussion has been laid down by assembling evidence upon the structure of water, and upon the interactions of molecular and ionic solutes with water, under appropriate headings.

(a) *The Properties and Structure of Water.*—Bernal and Fowler's¹⁷ theory of the quasi-crystalline structure of water encountered difficulties. One of these arose from later X-ray scattering experiments¹⁸ which showed the "second shell peak" to be so diffuse as to suggest a very restricted continuity of order. The conclusion that a given water molecule is, at a given instant, bonded only to two or three neighbours, supported by Raman spectrum evidence,¹⁹ suggested that any degree of "crystalline" order must be vanishingly

¹⁶ Harned and Embree, *J. Amer. Chem. Soc.*, 1934, **56**, 1042.

¹⁷ Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515.

¹⁸ Morgan and Warren, *ibid.*, 1938, **6**, 670; Katzoff, *ibid.*, 1934, **2**, 841.

¹⁹ Cross, Burnham, and Leighton, *J. Amer. Chem. Soc.*, 1937, **59**, 1134.

small. This opened the way for a revival of the old idea of the presence of definite polymeric entities in liquid water²⁰ by Eucken,²¹ who, by invoking "octomers" involving considerable "hohlraum," was able to elaborate and apply his theory to a remarkable extent.^{22, 23} In spite of attempts to reconcile the two theories,²⁴ the radical difference remains that in one of them the order which is postulated is essentially co-operative, and in the other it is not. There is evidence that discrete molecular aggregates have no real existence in liquid water^{25, 26} and it may be assumed²⁷ that the polymers of Eucken's semi-empirical treatment have only the status of convenient computational parameters.

The fact that liquid water has an open structure in which the molecules are held apart, rather than packed together, by intermolecular attractions makes it easy to believe that a high degree of co-operative order is involved in its structure. That this is in fact so has been confirmed in Pople's modification of Bernal and Fowler's theory,²⁸ which disposes of the difficulties previously mentioned. The new theory is based upon the indications of molecular-orbital treatment that the outer electrons in the water molecule occupy four tetrahedrally directed orbitals, two of which are associated with O-H bonds, and the other two with lone pairs of electrons. Each molecule then tends to form four hydrogen bonds (better regarded as "lone-pair attractions") in tetrahedral directions, very much as proposed earlier.^{17, 29} The important innovation consists in the establishment of the fact that the bending of hydrogen bonds without breaking, provides a means for the extensive absorption of energy and entropy. The force constant for bending was evaluated from the same radial distribution function, from X-ray scattering, that had previously been a source of difficulty. These calculations lead to the view that water differs from ice mainly because the hydrogen bonds are able to bend independently rather than co-operatively, and dispose of the necessity for over-extensive bond-breaking to explain the high heat capacity of water. A mandate is given³⁰ for considering that, in water, there is "a network of bonds extending throughout the whole liquid, which is, in a sense, one large molecule." The full success of Pople's theory is realised in its application by Harris and Alder³¹ to a remarkably accurate calculation of the dielectric constant of water from 0° to 83°.

Any characteristic changes in the structure and properties of water over the temperature range within which the minimum in $-\Delta C_p$ for the ionisation of cyanoacetic acid has been observed would be of great significance. The view that liquid water is quasi-crystalline implies that one or more "quasi-Curie points" may be looked for, giving rise to directly observable, or second- and third-order, changes of properties over a range of temperatures.³² There is considerable evidence that such a change does occur in liquid water between 30° and 40°: the list of properties revealing this, assembled and discussed by Magat,³³ can be considerably extended from the literature. Such evidence, however, is inconclusive and may be misinterpreted. Thus the minimum in the isothermal compressibility of water³⁴ at about 35° is due simply to the opposed temperature coefficients of structural and molecular compressibilities.³⁵ The internal latent heat of evaporation and the volume coefficient of internal energy show no sign whatever of second- or third-order changes both being perfectly smooth functions of temperature over the whole range. Since neither of these quantities need be directly affected by changes of structure, these facts do not exclude

²⁰ Sutherland, *Phil. Mag.*, 1900, **50**, 460.

²¹ Eucken, *Z. Elektrochem.*, 1948, **52**, 255.

²² *Idem*, *Z. phys. Chem.*, 1950, **195**, 1.

²³ Eigen and Wicke, *Z. Elektrochem.*, 1951, **55**, 354.

²⁴ Gierer and Wirtz, *Z. Naturforsch.*, 1950, **5a**, 577.

²⁵ Wang, *J. Amer. Chem. Soc.*, 1951, **73**, 4181.

²⁶ Collie, Hasted, and Ritson, *Proc. Roy. Soc.*, 1948, *B*, **60**, 145.

²⁷ Wang, *J. Phys. Chem.*, 1954, **58**, 686.

²⁸ Pople, *Proc. Roy. Soc.*, 1951, *A*, **205**, 163.

²⁹ Verwey, *Rec. Trav. chim.*, 1941, **60**, 887.

³⁰ Lennard-Jones and Pople, *Proc. Roy. Soc.*, 1951, *A*, **205**, 155.

³¹ Harris and Alder, *J. Chem. Phys.*, 1953, **21**, 1031.

³² Staveley, *Quart. Rev.*, 1949, **3**, 65.

³³ Magat, *J. Phys. Radium*, 1934, [7], **5**, 347; 1935, [7], **6**, 179; *Trans. Faraday Soc.*, 1937, **33**, 114.

³⁴ Smith and Keys, *Proc. Amer. Acad.*, 1934, **69**, 285.

³⁵ Hall, *Phys. Rev.*, 1948, **73**, 775.

the possibility of such changes but indicate that, if they occur, they are unaccompanied by a parallel loss of cohesion.

Two features in the behaviour of liquid water provide unequivocal evidence for the occurrence of a structural "melting" between 30° and 40°. The very accurate measurements of heat capacity at constant pressure by Ginnings and Furukawa³⁶ confirm that there is a well-marked minimum near 35°. Although the effect is small compared with the total heat capacity (<1%), it suggests the onset of a new mode of order-depleting heat absorption at this temperature. The effects of high pressures on the viscosity of water³⁷ provide more compelling evidence. The viscosity-pressure isotherm for liquid water at 0° shows a marked minimum at above 10³ kg. cm.⁻², which is well-known as evidence for the existence of expanded ice-like structures, the effect being consistent with the destruction of these structures on compression. In isotherms for successively higher temperatures the minimum becomes shallower and has vanished at 30°, where, however, there are still signs of a corresponding curvature, showing that a remnant of a viscosity-reducing pressure effect remains. It may be safely concluded that at some slightly higher temperature the structure-breaking effect of pressure vanishes. It is also of interest that the conductance of dilute solutions of strong electrolytes increases with rising pressure and that the pressure coefficient of conductance $\left(\frac{1}{\kappa} \cdot \frac{\partial \kappa}{\partial P}\right)$ shows a maximum rate of decline with temperature at about 35°. ³⁸

We suggest that the balance of evidence favours the existence in liquid water of a high degree of quasi-crystalline, co-operative structure, which is, however, vulnerable to increasing thermal agitation and suffers at least a partial collapse between 30° and 40° by an order-disorder transition which does not involve extensive breaking of hydrogen bonds. This statement, which can be reasonably adopted as a hypothesis, receives no direct confirmation from the temperature-dependence of the dielectric constant of water, which is perfectly smooth. The very high dielectric constant, however, is a function of a "correlation parameter," g , which is unity in cases where no short-range association occurs, *i.e.*, when the interaction between a dipolar molecule and its surroundings is just that which would exist if the surroundings were replaced by any material of the same macroscopic dielectric constant.³¹ For water, g is 2.60 at 0°, falling smoothly to 2.46 at 83°. These values, calculated by Harris and Alder³¹ on the basis of the tetrahedral unit of water structure, are not as high as they could be, for the structure does not permit all the dipoles to have parallel alignment. When this structure is broken down isothermally by increase of pressure, there is a considerable increase of dielectric constant³⁹ which must be predominantly due to an increase in g . Thus, high pressures increase the abnormalities of water,⁴⁰ perhaps increasing its resemblance to liquid hydrogen cyanide ($g = 3.6$). The effect of rising temperature on the dielectric constant of water (giving a curve convex towards the temperature axis) is therefore partly due to a randomisation of structure which will allow configurations of higher g to become relatively more probable, and partly to the general effect of thermal agitation to reduce g . This appears to provide a reasonable basis for the insensitivity of dielectric constant to changes of the kind envisaged.

(b) *Interactions between Molecular Solutes and Water.*—Frank⁴¹ and Frank and Evans⁴² have greatly clarified the problem of solute-solvent interactions in terms of the free-volume treatment of entropy, the results of which appear to be of fundamental importance in all discussions of aqueous solutions. The great loss of entropy to be expected when a gas molecule enters the confined state of solution in a liquid is normally offset by the loosening effect, due to relaxation of intermolecular restraints, on the solvent. Correspondingly, the entropy of evaporation, ΔS_2 , is smaller than would be expected for the removal of the solute from the condensed to the gaseous phase, an anomaly which is resolved

³⁶ Ginnings and Furukawa, *J. Amer. Chem. Soc.*, 1953, **75**, 552.

³⁷ Bridgman, "The Physics of High Pressures," Bell, London, 1949, p. 346.

³⁸ Körber, *Z. phys. Chem.*, 1909, **67**, 212.

³⁹ Dorsey, "The Properties of Ordinary Water Substance," Reinhold, New York, 1940, p. 367.

⁴⁰ Smith and Lawson, *J. Chem. Phys.*, 1954, **22**, 351.

⁴¹ Frank, *ibid.*, 1945, **13**, 378, 393.

⁴² Frank and Evans, *ibid.*, p. 507.

in terms of an excess of entropy of the solvent due to the loosening effect. Water is unique as a solvent in that the values of ΔS_2 for non-polar solutes are, on the contrary, far "too large" to the extent of 10 e.u. per mole of solute. This implies that the "excess of entropy" of the solvent is large and negative. To explain this, each solute molecule is regarded as surrounded by an "iceberg," of greater extent the larger the solute molecule. This "freezing" of the water causes more heat and entropy to be lost during dissolution than expected; ΔH , otherwise small, becomes large, and $-\Delta S$ remarkably large. With rising temperature, the "melting" of the icebergs accounts for the enormous partial molar heat capacities found for the inert gases and other non-polar solutes in aqueous solution. Because of this melting, this very abnormal "solvent reaction," peculiar to water, is supplanted at higher temperatures by the normal one, and water then behaves little differently from other solvents. It may be noted that, although this cannot be taken as evidence of marked structural change with rising temperature in water itself, it indicates unambiguously a radical change in the response of water to foreign molecules. This is no doubt the basis for minima which have been found in the partial molar volumes⁴³ and solubilities⁴⁴ of hydrocarbons in water on a rising temperature scale, together with other similar phenomena noted by Magat.³³

Independent evidence for the hydration of non-polar solutes is convincing. Claussen's⁴⁵ intuitive ideas on the clathrate nature of inert gas hydrates have been confirmed by X-ray structure determinations⁴⁶ and have a clear relation with the "icebergs" of Frank and Evans. There can be little doubt that these authors have drawn attention to, and clarified, a property of water of outstanding importance which, now realised, appears relevant in most unexpected fields.⁴⁷

Other kinds of hydration are likely to be active in relation to the undissociated molecules of weak acids and bases, for all must contain at least one centre for the formation of a hydrogen bond with one or more solvent molecules. The presence of any other polar group in the molecule may lead to dipole-dipole interactions sufficiently strong to be classed as hydration.¹ These considerations show that no undissociated molecule in aqueous solution is likely to escape extensive hydration of some kind. This means that, in considering the thermodynamics of the ionisation of a weak electrolyte in aqueous solution, it must be recognised that hydration plays a major part in determining, *inter alia*, the entropy and heat capacity of the *initial* system. Unless these effects are substantially unchanged in the final, ionised system, which appears to be most unlikely, they will also largely affect the values of ΔS and ΔC_p for the ionisation and, perhaps to a less extent, all the other thermodynamic functions. Since molecules do not, like ions, possess integral charge, it appears to be impossible to develop a general theoretical treatment of their hydration; each case must be considered as a special problem.

(c) *Interactions between Ionic Solutes and Water.*—The hydration of ions, so extensively studied, can be regarded as part of the wider problem concerned with all the effects which operate between the ions and the solvent. These effects, which are not independent, can be classified in order of decreasing intensity of interaction, or of increasing distance from the centre of an ion. The strongest interaction can give rise to what is known as primary hydration,⁴⁸ in which water molecules become attached to the ion with loss of their own translational freedom, but remain in activated exchange equilibrium with the rest of the solvent.⁴⁹ Steric limitations, and the screening effect⁵⁰ which causes a sharp decrease in the strength of the ionic field just outside the first hydration shell,⁵¹ restrict the primary hydration to a small number of molecules. Since coulombic forces are of long range, the residual field outside the primary hydration shell will set up a zone of

⁴³ Masterton, *J. Chem. Phys.*, 1954, **22**, 1830.

⁴⁴ Bohon and Claussen, *J. Amer. Chem. Soc.*, 1951, **73**, 4181.

⁴⁵ Claussen, *J. Chem. Phys.*, 1951, **19**, 259, 662, 1425.

⁴⁶ Stackelburg and Müller, *J. Chem. Phys.*, 1951, **19**, 1319.

⁴⁷ Grahame, *ibid.*, 1955, **73**, 1725.

⁴⁸ Bockris, *Quart. Rev.*, 1949, **3**, 179.

⁴⁹ Journet and Vadon, *Bull. Soc. chim. France*, 1955, 593.

⁵⁰ Fuoss, *Trans. Faraday Soc.*, 1934, **30**, 970.

⁵¹ Azzam, *Z. Elektrochem.*, 1954, **58**, 889.

secondary hydration in which there is a rapidly changing population of water molecules which retain some translational freedom, but are oriented by the ionic field with loss of rotational freedom. It is, however, likely that the water molecules in the first shell will exert an ordering effect upon the outer molecules by hydrogen bonding⁵² but it is reasonably certain that there is a wide difference in firmness of binding, and in average time of residence, between the water molecules in primary and secondary hydration shells. It seems desirable to define the secondary hydration shell as that containing all water molecules which, without substantial loss of translational freedom, experience an order-producing effect exerted by the ionic field. This definition differs somewhat from that due to Bockris,⁴⁸ but is more precise.

Outside the hydration zones there is a region in which a condition of maximum disorder prevails where the incompatible ordering influences of the central ionic field and of the external quasi-crystalline water structure largely annul one another. The evidence for this disordered zone is compelling. Frank and Evans⁴² observed that the entropies of evaporation of ionic and of non-ionic solutes from aqueous solution are closely similar. Thus, although the ionic charge has a very large effect upon the heat of evaporation, it has little effect upon the entropy. Since the hydration of ions in solution must produce a large entropy defect, it appears that the ionic solutes have "too much" entropy, an anomaly that can be resolved by supposing that the excess of entropy resides in a disordered zone, in which the residual ionic field breaks down the water structure without being able to impose its own centrosymmetrical order. With reasonable assumptions, Frank and Evans⁴² calculated a "structural entropy" which represents the influence of the ions, excluding polarisation, on the structure of the water beyond the first shell of primary hydration. This term makes a positive contribution to the entropy of evaporation if the *net* effect of the ions is structure-promoting, but for most ions the reverse is true, indicating predominance of the structure-breaking effect.

The evidence of the structural entropy is supported by the smooth relationship existing between ionic elevation of fluidity⁵³ and ionic entropy of evaporation, from which it is clear that ions which have the largest structure-breaking effect enhance fluidity the most. These effects appear to be expressible⁵⁴ in terms of the *B* coefficient of Jones and Dole's equation⁵⁵ for the viscosities of electrolytic solutions. Values of *B* run parallel with structural entropies, and it is noteworthy that negative values of *B*, corresponding with ionic structure-breaking, are found only for aqueous solutions.

The large, negative partial molar heat capacities of ions in solution are due to the loss of kinetic freedom imposed upon solvent molecules by the ionic field. This effect is not, as might be expected, a maximum for the smallest ions of a given charge.⁵⁶ Since, however, the high heat capacity of water is a function of its structure, the breaking of the structure by means other than increase of temperature will reduce the heat capacity, and this will in turn make the partial molar heat capacities of ions more negative. There is indeed a parallel between this effect and the structure-breaking properties of ions, which are not directly related to ionic radius.

There is much other evidence suggesting that the effect of ions upon water is akin to that of raising the temperature, thus allowing the conception of a "structural temperature" for each solution. This evidence is based upon *X*-ray scattering,⁵⁷ dielectric absorption,⁵⁸ infrared absorption⁵⁹ and self-diffusion.²⁷

This summary of ion-water interactions makes it clear that there may be three zones about an ion in which the properties of the solvent undergo radical changes, all of which will contribute to the partial thermodynamic properties of the ion. How these effects will vary with temperature is almost entirely unknown, for even evidence upon the change

⁵² Verwey, *Rec. Trav. chim.*, 1942, **61**, 127.

⁵³ Bingham, *J. Chem. Phys.*, 1941, **45**, 885.

⁵⁴ Gurney, "Ionic Processes in Solution," McGraw-Hill, New York, 1953, pp. 172, 249.

⁵⁵ Jones and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 2950.

⁵⁶ Rossini, *J. Res. Nat. Bur. Stand.*, 1931, **7**, 47.

⁵⁷ Stewart, *Phys. Rev.*, 1931, **37**, 9; *J. Chem. Phys.*, 1939, **7**, 689.

⁵⁸ Mansel Davies, *Quart. Rev.*, 1954, **8**, 250.

⁵⁹ Ganz, *Ann. Physik*, 1937, **28**, 445.

of ionic hydration with temperature is very scarce. It is also evident that a problem of equal complexity is presented by the interaction, considered as a function of temperature, between a polar, multifunctional molecule and water. Under these conditions, it is obvious that no general physical treatment, based upon Born-Webb continuum physics or upon ion-dipole models, has much prospect of success in relation to this problem, which must therefore be discussed as a special case, with use of all available specific evidence.

(d) *Specific Properties of Cyanoacetic Acid Ions and Molecules.*—The distribution of charge between the oxygen atoms of the carboxylate anion is such as to make the occurrence of ordinary primary solvation improbable, but the presence of lone pairs on these atoms will undoubtedly lead to hydrogen bonding with water molecules, reinforced by the anionic field. It is important to know whether this hydration can be concerned in the temperature dependence of the thermodynamic functions. Limiting anionic mobilities have been calculated by using hydrogen ion mobilities selected by Robinson and Stokes,⁶⁰ and Gurney's modification of Walden's rule⁶¹ has been applied to them. If no change occurs in primary solvation, ηl , where η and l are viscosity and mobility, should be constant. The data relating to this test for the cyanoacetate ion are shown in Table 10.

TABLE 10.

Temp.	η (centipoises)	l_+	l_-	ηl_-
0°	1.792	—	21.6 *	38.7
5	1.519	250.1	25.8	39.2
15	1.140	300.6	34.2	39.0
25	0.8937	349.8	43.4	38.8
35	0.7225	397.0	53.2	38.5
45	0.5988	441.4	64.1	38.4

* Extrapolated.

Since a three-fold mobility range is covered, this test is reasonably satisfactory in excluding any significant change in the cyanoacetate ion, as a kinetic entity, over the temperature range. The same test cannot be applied to the hydrogen ion because of its special mechanism of transport in aqueous solution, but the lithium ion responds very well, and because it appears to be almost identical with the hydrogen ion in osmotic activity⁶² it is likely to have similar constitution and dimensions. The hydronium ion is firmly joined to three water molecules by reinforced hydrogen bonds;⁶³ a hydration number of 4 for the proton is not inconsistent with assessments by old⁶⁴ or recent⁶⁵ methods, and is supported by the views of Darmois.⁶⁶ It may also be relevant that the test seems best satisfied by order-promoting ions, of which the hydrogen ion is one. It is therefore established with reasonable certainty that no changes in primary solvation need be considered.

Evidence on secondary hydration is confined to that available from measurements of viscosities of cyanoacetic acid solutions.⁶⁷ With allowance for incomplete dissociation, Jones and Dole's B coefficient for the fully ionised acid is $+0.172$ at 35° . The value⁶⁴ for the hydrogen ion is $+0.07$ at 25° . The difference in temperature being ignored, it is reasonable to assess the B coefficient for the cyanoacetate ion at about $+0.10$; it is therefore structure-promoting, but less so than the acetate ion itself ($B = +0.245$). It may be concluded that, since both of the ions of cyanoacetic acid are structure-promoting, considerable secondary hydration is involved at ordinary temperatures.

The nitrogen atom of the highly polar nitrile group carries a lone pair of electrons; the strong interaction of this group with water consequently expected is confirmed by the complete, endothermic mixing of acetonitrile with water.⁶⁸ This effect will no doubt

⁶⁰ Robinson and Stokes, "Electrolytic Solutions," Butterworths, London, 1954, p. 454.

⁶¹ Ref. 54, p. 69.

⁶² MacInnes, "Principles of Electrochemistry," Reinhold, New York, 1939, p. 173.

⁶³ Wicke, Eigen, and Ackermann, *Z. phys. Chem.* (Frankfurt), 1954, **1**, 340.

⁶⁴ Ulich, *Z. Elektrochem.*, 1930, **36**, 497.

⁶⁵ Glueckauf and Kitt, *Proc. Roy. Soc.*, 1955, *A*, **223**, 322.

⁶⁶ Darmois, *Compt. rend.*, 1955, **240**, 1341.

⁶⁷ Srinivasan and Prasad, *J. Indian Chem. Soc.*, 1939, **16**, 371.

⁶⁸ Vierk, *Z. anorg. Chem.*, 1950, **261**, 283.

confer upon cyanoacetic acid molecules a hydration, in addition to that normally centred on the carboxyl group, of a short-range, stable nature. This is supported by the evidence adduced in relation to the cyanoacetate ion, where similar nitrile hydration must occur. The strong hydration of the cyanoacetic acid molecules provides an immediate explanation for the comparatively small entropy loss accompanying the ionisation of the acid (-14.3 cal. deg. $^{-1}$ mole $^{-1}$) compared with that (-22.1 cal. deg. $^{-1}$ mole $^{-1}$) for acetic acid. It is unlikely that for such polar molecules any hydration of the Frank and Evans type should occur.

(e) *The Heat-capacity Change on Ionisation of Cyanoacetic Acid.*—The observed variation of ΔC_p with temperature must be considered in terms of the heat capacities of the final and initial systems. These, in turn, are largely dependent upon solute-solvent interactions which are no doubt variously sensitive to rise of temperature. In the preceding sections it has been established with reasonable certainty that there are three kinds of interaction, and related kinds of order, involved in the present problem, and that they have the following characteristics: (1) the short-range forces of hydrogen bonding, producing the long-range, co-operative order of the quasi-crystalline structure of water, (2) the short-range forces of molecule-solvent interaction, producing short-range, non-co-operative order, and (3) the long-range forces of ion-solvent interaction, producing long-range, non-co-operative order.

Of these interactions, (1) is the most vulnerable to rise of temperature, and, of the remainder, (3) is more widespread in effect. It is therefore natural to suppose that, with rising temperature, (3) may replace (1) in predominance. If this is the case, secondary hydration of the ions should, above a certain temperature, increase with further rise of temperature. Evidence in favour of this novel suggestion is available from the heat-capacity measurements made with the high-precision adiabatic calorimeter of Eucken and Eigen.⁶⁹ The apparent heat capacities of ions at infinite dilution in aqueous solution, together with apparent ionic volumes, pass through well-defined maxima with rising temperature.^{23, 63} Within the restricted range of available data, the tendency of these functions to assume negative temperature coefficients runs roughly parallel with the order-promoting properties of the ions concerned, measured in terms of their B viscosity coefficients. Since ionic hydration powerfully reduces heat capacity, these effects are entirely consistent with our suggestion, as also is the general tendency of B coefficients to rise with temperature.⁷⁰ A different interpretation is given by the Göttingen school, but there is some agreement in the postulation of the joint action of hydration forces and the

“solvent medium effect.”

With this indication, it is possible to interpret the problem tentatively in some detail. For the ionisation (Fig. 2) $-\Delta S$ increases smoothly with rising temperature, but remains abnormally low over the whole range, compared with its values for other monocarboxylic acids. It may be concluded that no rapid collapse of the molecular hydration takes place, and that no sudden, *uncompensated* change in order-disorder relations occurs in either the initial or the final system, within the temperature range, so it is suggested that C_p for the initial system rises smoothly with temperature, as indicated purely formally, by curve I in Fig. 4. At each low temperature, C_p is regarded as being depressed by the degree of “freezing” of the solvent produced by the action of the polar solute molecules upon it. At each higher temperature, the magnitude of C_p is enhanced by an amount depending upon the degree of disorder generated in the preceding temperature rise, and by an amount depending upon the extent to which “melting” occurs at the temperature concerned.

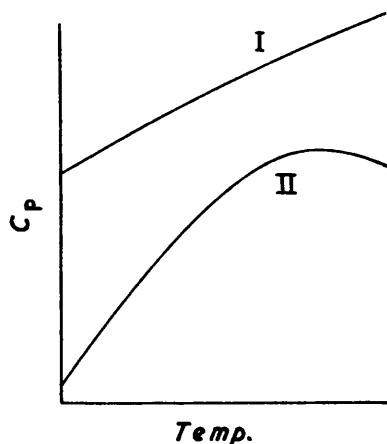


FIG. 4.

⁶⁹ Eucken and Eigen, *Z. Elektrochem.*, 1951, **55**, 343.

⁷⁰ Ref. 54, p. 162.

It will become clear why the curvature has been made similar to, but much slighter than, that of curve II, which relates to the final system.

At a low temperature, the heat capacity of the initially un-ionised system is largely reduced when ionisation occurs, since the long-range, ionic forces which are generated produce extensive secondary hydration, in which many water molecules suffer loss of rotational freedom. With rising temperature (within the range for which C_p for pure water is decreasing), thermal agitation will increasingly overcome the centrosymmetrical orienting force, and the zone of disorder surrounding that of secondary hydration will move inwards. This may cause a rather rapid increase of C_p for the final system because of the comparatively large number of water molecules simultaneously involved, the restoration of whose rotational freedom requires a "latent heat." For this reason, the left-hand branch of curve II has been made quite steep.

With further rise of temperature, the peculiar vulnerability of the water structure comes into play. Since water is the common solvent for both initial and final systems, any direct effects upon C_p (which have not been taken into account in Fig. 4) will be cancelled out of ΔC_p , which will therefore record only the indirect effects of the change in water structure. As already indicated, the main effect depends upon the fact that the order of the quasi-crystalline water structure is co-operative, whilst the order of ion-controlled orientation is not. If then, over quite a narrow temperature range, the opposition which the "water structure forces" offer to the ionic ordering forces suffers a partial collapse, there will be a swing of the balance between them in favour of the ionic forces. Thus, the initial recession of the zone of secondary hydration is arrested and replaced by an expansion. The C_p curve for the final system then passes through a maximum and assumes a negative slope as the "freezing" process is resumed, accompanied by liberation of "latent heat." A similar set of occurrences, on a much restricted scale, may give curve I, for the initial system, the curvature that has been assigned to it.

It is not known how far these considerations may be generally applicable. As a special case of an electrolyte providing order-promoting ions, the ionisation in aqueous solution, containing dissolved nitrogen, has been found to involve a heat-capacity change with a characteristic temperature dependence which calls for an explanation of the sort that has been given. No similar data exist with which comparison can be made. Even if practicable, it would be premature to try to strengthen the theory by quantitative or mathematical treatment; over-simplified attempts to do so might well obscure the issues in a problem of complexity.

(f) *General Discussion of Ionisation Functions.*—A comparison of cyanoacetic acid with its relatives is of interest. The data, all relating to 25°, are shown in Table 11.

TABLE 11.

	CH ₃ ·CO ₂ H	CH ₂ F·CO ₂ H	CH ₂ Cl·CO ₂ H	CH ₂ Br·CO ₂ H	CH ₂ I·CO ₂ H	CH ₂ CN·CO ₂ H	Ref.
ΔG (cal. mole ⁻¹) ...	6487	3527	3911	3958	4330	3368	<i>a</i>
ΔH (cal. mole ⁻¹) ...	-112	-1390	-1123	-1239	-1416	-888	<i>a</i>
ΔS (cal. deg. ⁻¹ mole ⁻¹)	-22.1	-16.5	-16.9	-17.4	-19.3	-14.3	<i>a</i>
ΔC_p (cal. deg. ⁻¹ mole ⁻¹)	-33.9	-32.6	-46.4	-38.1	-32.9	-35.6	<i>a</i>
Dipole moment (CH ₃ ·X)	—	1.81	1.87	1.80	1.64	3.94	<i>b</i>
Field strength, <i>E</i> ...	—	0.197	0.190	0.177	0.153	0.174	<i>c</i>
Bond refractivity, C-X (c.c.)	1.69	1.72	6.53	9.37	14.55	5.3	<i>d</i>
$\Delta pK/E$	—	11.0	10.0	10.5	10.3	13.0	<i>e</i>
$\Delta(-\Delta H)/E \times 10^3$	—	6.4	5.3	6.4	8.6	4.5	<i>e</i>

References: (*a*) For acetic acid, Harned and Ehlers;⁹ for halogenoacetic acids, Ives and Pryor.¹ (*b*) For CH₃F, Smyth and McAlpine, *J. Chem. Phys.*, 1934, 2, 499; for halides and cyanide, Groves and Sugden, *J.*, 1937, 158. (*c*) Ives and Sames.⁷¹ (*d*) Syrkin and Dyatkina, "The Structure of Molecules," Butterworths, London, 1950, p. 201. (*e*) For halogenoacetic acids, Ives and Pryor.¹

It is remarkable that whilst cyanoacetic acid is stronger than any of the halogenoacetic acids, its enthalpy decrease on ionisation is the least. This is counterbalanced by the

⁷¹ Ives and Sames, *J.*, 1943, 513.

fact that the entropy loss is also the least. The implication of this is that cyanoacetic acid owes its strength substantially to the fact that its ionisation is less disfavoured than normal by a large entropy loss, but at the same time the undissociated acid is stabilised by its rather stable hydration. This can also be seen from the values of $\Delta pK/E$, indicating the acid to be stronger than is to be expected, and of $\Delta(-\Delta H)/E$, which shows that the total energy change is less than would be expected on the same grounds. The polarisability of the nitrile group, as measured by bond refractivity, can hardly be significant, as in the case of the halogenoacetic acids, for the group is small, and is further removed from the seat of ionisation. Change in heat capacity for ionisation at a single temperature loses much significance according to the previous discussion, but the value of ΔC_p for the cyano-acid at 25° is in line with the tentative treatment previously given.¹

The maximum dissociation of cyanoacetic acid occurs at $4.3^\circ \pm 0.1^\circ$ (from equations 3b, 3c, or 9) and the value of K_{\max} is $(359.3 \pm 0.1) \times 10^{-5}$, yielding values for ΔG of 3103 cal. mole⁻¹ and for ΔS of -11.18 cal. deg.⁻¹ mole⁻¹ at this temperature. It is evident that the condition for ΔH to be zero at the temperature of maximum dissociation is

$$\Delta H_0 = - \int_0^\theta \Delta C_p dT$$

from which it can be seen that the factors determining θ and K_{\max} , vary from case to case, robbing these constants of any clear or simple significance.

EXPERIMENTAL

The apparatus and procedure were essentially as described by Ives and Pryor.¹ All solutions were prepared from independent, directly weighed samples of solute, and for a given solution all the measurements over the temperature range were carried out without interruption. Before each set of measurements, the contacts of the standard resistance box were cleaned with "Microid" polishing γ -alumina (Griffin and Tatlock Ltd.) moistened with thiophen-free benzene, and a stream of dry nitrogen was passed through the box throughout the measurements. This procedure was found to be very advantageous in eliminating errors due to variable contact resistances, which were particularly important in relation to the platinum thermometry. The mean deviation between platinum and mercury-in-glass (N.P.L.) thermometers was 0.003°, and in no case was there a deviation greater than the tolerance of the N.P.L. calibration (0.005°).

Cyanoacetic Acid.—Three samples of purified acid were prepared. A fractionally distilled sample of ethyl cyanoacetate (b. p. 105°/22 mm.) was refractionated through a column 60 cm. long packed with Fenske helices (b. p. 68°/1.5 mm.). The ester (50 ml.) and 0.5N-nitric acid ("AnalaR") (100 ml.) were heated at 60° for 2 hr. with constant stirring whereupon miscibility was complete. Heating was continued for a further 2 hr.; the cold mixture was then kept for 72 hr., and reduced to 25 ml. by evaporation *in vacuo* at 50°. On cooling, fine white needles separated; they were washed with redistilled absolute ethanol, collected on a sintered glass filter, and dried *in vacuo* (yield 20 g.). The crude product was recrystallised four times in all-glass apparatus from 40 : 60 benzene-acetone, prepared from intensively purified and dried solvents (Sample A). Two further samples from independent commercial sources were repeatedly crystallised from the same solvent; five recrystallisations were needed in each case to obtain material of constant m. p. and conductance of equimolar solutions (Samples B and C). Equivalents of these samples were determined by comparison with 99.96% benzoic acid ("Calorimetric Standard") and with 99.98% potassium hydrogen phthalate, by titration with baryta, with precautions to ensure maximum volumetric accuracy. M. p.s were determined in thin-walled glass tubes, attached to a high-vacuum apparatus, immersed in a mechanically stirred water bath, the temperature of which was raised at 0.05° per minute. A totally immersed N.P.L. thermometer, (in 0.02°) was used. The constants for the three samples were: Sample A; equiv., 85.06 ± 0.04 ; m. p. 70.8—71.0°. Sample B; equiv., 85.12 ± 0.05 ; m. p. 70.9—71.0°. Sample C; equiv., 85.06 ± 0.03 ; m. p. 70.9—71.1°. Calc.: equiv., 85.0656.

The new m. p. is higher than any previously recorded (68—68.5°⁵¹; 68°⁷²); this, together with the stringent test that all three samples gave the same conductance results within experimental error, justifies the claim that material with properties independent of its history had been obtained.

The interesting observation was made that cyanoacetic acid is unstable to intensive desiccation with phosphoric oxide. It decomposes with formation of a brown, deliquescent,

⁷² Letch and Linstead, *J.*, 1932, 443.

highly acidic material, thought to be a polymerised poly(cyano-acid). For this reason high-vacuum sublimation was discarded as a method of purification. Samples of acid were stored over silica gel, which cannot produce this effect, and were intensively desiccated for only a short period before use. The stability of the acid in solution was tested by repeated measurement of conductance at 5° after a set of measurements, occupying 12 hr., in which the temperature had been raised to 45°. Reproducibility of the conductance was always within experimental error.

Calculations.—The fundamental constants of Birge⁷³ were used, together with Wyman's dielectric-constant data⁷⁴ and Bingham and Jackson's viscosity data.⁷⁵ Values of the Debye-Hückel constant, A , and the Onsager slopes, a , used in the calculations are shown in Table 12.

TABLE 12.

Temp.....	5°	10°	15°	20°	25°	30°	35°	40°	45°
A	0.49274	0.49633	0.50028	0.50457	0.50908	0.51405	0.51925	0.52486	0.53070
a {	0.22146	0.22308	0.22485	0.22678	0.22883	0.23104	0.23338	0.23590	0.23853
.....	+35.069	+40.829	+46.942	+53.418	+60.252	+67.466	+75.019	+82.922	+91.174

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⁷⁴ Wyman, *Phys. Rev.*, 1930, **35**, 623.

⁷⁵ Bingham and Jackson, *Bull. Bur. Stand.*, 1918, **14**, 75.