The methyl–methyl contacts are indicated by the heavy white lines in Fig. 5. In this figure the C atoms, designated 1, 2 and 3, lie in a plane parallel to the base of the unit cell, while atoms 4 and 5 are above and below this plane, respectively. The distances C_1–C_2 and C_1–C_3 are both 3.98 Å.; C_1–C_4 and C_1–C_5 are both 4.15 Å. These distances are about the same as the methyl–methyl distances in many other organic crystals.

The distances between CH_3 and the O and N atoms of adjacent molecules are shown in Fig. 6. In this figure the distance between the methyl C atom of molecule B to the O atom of molecule D is 4.07 Å.; the distance to the N atom of molecule E is 3.74 Å.; and the distance to the O atom of molecule F is 3.54 Å.; the last distance probably represents a CH_3–O contact—the other distances are probably too large.[14]

Acknowledgment.—One of the authors, Frederic Senti, wishes to express his gratitude to the American Can Company for their financial assistance without which this work would not have been possible. The authors are also indebted to Alice Senti for the painstaking assistance she has given in performing the lengthy calculations, to Dr. Edward R. Blanchard of this department for the use of his calculating machine, to Mr. John Graham for preparing the photographs for Figs. 5 and 6, and to Dr. S. B. Hendricks for the use of his set of Beevers and Lipson sine and cosine strips.

Summary

The crystal structure of acetamide has been determined. Its space group is C_{3v}^6—R3c; $a_0 = 11.44 \pm 0.03$ Å., $c_0 = 13.49 \pm 0.03$ Å. referred to the smallest hexagonal unit cell which contains eighteen molecules of CH_3CONH_2. The structure is completely determined by stating the coördinates of the atoms in one molecule.

$X_O = 0.225 \pm 0.004$ $Y_O = -0.004 \pm 0.004$
$X_{CH_3} = 0.477 \pm 0.005$ $Y_{CH_3} = 0.123 \pm 0.005$
$X_{NH_2} = 0.333 \pm 0.004$ $Y_{NH_2} = -0.090 \pm 0.004$
$X_C = 0.333 \pm 0.004$ $Y_C = 0.005 \pm 0.004$
($Z_O = 0.000$)
$Z_{CH_3} = 0.033 \pm 0.023$
$Z_{NH_2} = 0.096 \pm 0.004$
$Z_C = 0.034 \pm 0.004$

This structure leads to the conclusions (a) that the length of the N–H–O bridge is 2.86 ± 0.05 Å., (b) the molecule of acetamide is planar, (c) the molecule exists in the keto form, and (d) the N–H bonds lie in the plane of the molecule. The intramolecular distances are C–CH_3 = 1.51 ± 0.05 Å., C–NH_2 = 1.38 ± 0.05 Å., C–O = 1.28 ± 0.05 Å., and the bond angles are CH_3–C–NH_2 = 109 ± 5°, CH_3–C–O = 129 ± 5°, and NH_2–C–O = 122 ± 5°.

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[14] The distances taken by L. Pauling, ("The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 177) to represent intermolecular contacts are CH_2–CH_2 = 3.96, CH_2–O = 3.32, 3.33, CH_2–N = 3.55, 3.69 in diketopiperazine, and CH_2–CH_2 = 4.05, CH_2–O = 3.38, 3.52 in glycine.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Ionic Entropies and Free Energies and Entropies of Solvation in Water–Methanol Solutions

BY WENDELL M. LATIMER AND CYRIL M. SLANSKY[1]

Sufficient thermodynamic data are now available for the calculation of the partial molal entropies of a number of ions in water–methanol solutions whose compositions range from pure water to pure alcohol. This paper will present these calculations and discuss the entropy and free energy of solvation with reference to the general picture of the solvation process.

Ionic Entropies.—The calculation of partial molal ionic entropies in any solvent will follow the method used in aqueous solutions by Latimer and co-workers.[2] In short it involves the calculation of the entropy of solution of a substance MX from the heat and free energy of solution by the equation $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$. All of the calculations in this paper are at 298.1°K. The process of solution is written

$$MX = M^+ \text{ (soln.)} + X^- \text{ (soln.)}$$

From the ΔS° of solution and the entropy of MX, one obtains the sum of the positive and negative ionic entropies.

$$\bar{S}^\circ_{M^+} + \bar{S}^\circ_{X^-} = \Delta S^\circ + S^\circ_{MX}$$

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[1] Shell Research Fellow in chemistry, academic year 1939–1940. Present address, The Dow Chemical Co., Midland, Michigan.

[2] W. M. Latimer and R. M. Buffington, THIS JOURNAL, **48**, 2297 (1926).

The heats of solution of hydrogen chloride gas and a number of alkali halide salts in water-methyl alcohol solutions have been determined.[3] The free energy of solution of hydrogen chloride gas was determined from electromotive force data[4,5,6] on the cell whose net reaction is:

$$AgCl(s) + {}^1/_2H_2 = Ag(s) + Cl^-(soln.) + H^+(soln.)$$

The data were extrapolated to zero concentration to obtain $E°_{298.1}$. Then

$$\Delta F°_{298.1} = -23066nE°_{298.1} = \Delta F°_{AgCl} - \Delta \overline{F}°_{H^+(soln.)} - \Delta \overline{F}°_{Cl^-(soln.)}$$

Using for $\Delta F°_{AgCl}$ the value −26220 cal./mole,[7] one has the free energy of formation of hydrogen ion and chloride ion in the corresponding solution of water-methyl alcohol. The free energy of solution of hydrogen chloride gas is obtained by subtracting the free energy of formation[8] of hydrogen chloride gas, −22740 cal., from the free energy of formation of hydrogen and of chloride ions.

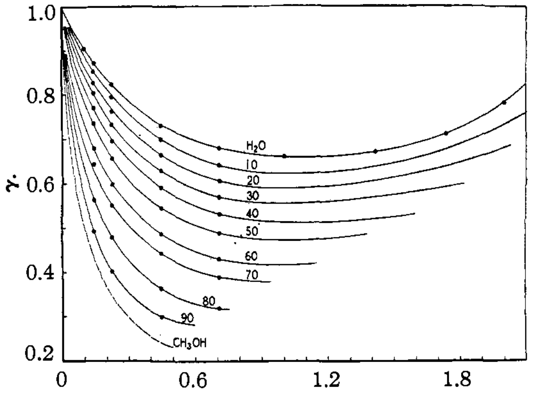

Fig. 1.—Activity coefficients of sodium chloride in water-methyl alcohol solutions. Curves are labeled in weight per cent. methyl alcohol and are extrapolated to saturated solutions.

The standard free energy of solution at 298.1°K. of a uniunivalent salt is given by

$$\Delta F°_{298.1} = -1364.9 \log (m\gamma)^2$$

where m is the solubility in moles per 1000 g. of solvent and γ is the activity coefficient of the salt in the saturated solution. The solubilities of sodium chloride, potassium chloride, potassium bromide, and potassium iodide in water–methanol solutions have been determined.[9]

Activity coefficients of salts in water–methanol solutions were available for only sodium, potassium, lithium and hydrogen chlorides.[4] These data were extrapolated to saturated solutions. A typical set of curves for sodium chloride is shown in Fig. 1. The curve for absolute methanol was unavailable and had to be approximated by comparing the data for sodium chloride with complete data for hydrochloric acid.

The activity coefficients of saturated solutions of potassium bromide were taken from the curves for sodium chloride since the solubilities of the two are similar and the activity coefficients in pure water are nearly the same over a wide range of concentrations.

Uncertainties in the values of γ for saturated solutions will probably not exceed 15% of the free energy of solution.

From the foregoing data it is possible to calculate the entropy of solution of hydrogen chloride, sodium chloride, potassium chloride, and potassium bromide in water–methanol solutions. The entropies of these four compounds are 44.66, 17.3, 19.75, and 22.5 calories per mole per degree, respectively.[7] By adding the entropy of the compound to the entropy of solution one obtains the entropy of the corresponding pair of ions. The results in water–methanol solutions at intervals of 10% methyl alcohol by weight are given in Tables I and II. Heats and free energies are given in calories per mole and are positive when heat is absorbed. Entropies are in calories per mole per degree.

The data in Tables I and II are plotted in Fig. 2.

Partial relative ionic entropies for Na^+, K^+, Cl^- and Br^- may be obtained by assuming that $\overline{S}°_{H^+}$ is zero. These values are shown in Fig. 3. The curves are labeled with the hydrogen ion added or subtracted to the various ions in order to emphasize the fact that the values are relative to hydrogen ion as zero.

Entropy of Solvation of Gas Ions.—The entropies and free energies of solvation of alkali and halide gas ions have been studied in aqueous solutions.[10,11]

The data for water–methanol solutions are insufficient to calculate the entropy and free energy

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[3] C. M. Slansky, THIS JOURNAL, **62**, in press (1940).

[4] G. Åkerlöf, *ibid.*, **52**, 2353 (1930).

[5] H. S. Harned and H. C. Thomas, *ibid.*, **57**, 1666 (1935).

[6] G. Nonhebel and H. Hartley, *Phil. Mag.*, **50**, 729 (1925).

[7] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

[8] W. F. Giauque and R. Overstreet, THIS JOURNAL, **54**, 1731 (1932).

[9] G. Åkerlöf and H. E. Turck, *ibid.*, **57**, 1746 (1935).

[10] W. M. Latimer, *Chem. Rev.*, **18**, 349 (1936).

[11] W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

TABLE I

PARTIAL MOLAL IONIC ENTROPIES OF $Na^+ + Cl^-$, $K^+ + Cl^-$, AND $K^+ + Br^-$ AT 298.1°K. IN WATER–METHANOL SOLUTIONS

Wt. % CH_3OH	Mole % CH_3OH	Soly. m	γ	Solution ΔF°	Solution ΔH°	Solution ΔS°	$\bar{S}^\circ_{(cation)} + \bar{S}^\circ_{(anion)}$
				$Na^+ + Cl^-$			
0	0.0	6.162	1.00	−2156	920	10.3	27.6
10	5.88	5.10	0.826	−1705	1400	10.4	27.7
20	12.32	4.14	.687	−1238	1680	9.8	27.1
30	19.41	3.30	.600	− 810	1750	8.6	25.9
40	27.25	2.55	.530	− 370	1720	7.0	24.3
50	36.08	1.91	.485	90	1590	5.1	22.4
60	45.74	1.325	.420	696	1375	2.3	19.6
70	56.73	0.882	.376	1310	1030	− 0.9	16.4
80	69.41	.566	.315	2040	500	− 5.2	12.1
90	83.50	.362	.281	2710	− 350	−10.3	7.0
100	100.0	.239	.234	3420	−2000	−18.2	0.9
				$K^+ + Cl^-$			
0	0.0	4.826	0.599	−1258	4120	18.1	37.9
10	5.88	3.77	.550	− 866	4430	17.8	37.6
20	12.32	2.83	.514	− 423	4610	16.9	36.7
30	19.41	2.10	.504	− 67	4620	15.7	35.5
40	27.25	1.476	.490	383	4540	13.9	33.7
50	36.08	0.960	.480	920	4280	11.3	31.1
60	45.74	.630	.385	1680	3870	7.3	27.1
70	56.73	.375	.285	2650	3400	2.5	22.2
80	69.41	.205	.216	3690	2790	− 3.0	16.8
90	83.50	.110	.137	4960	2060	− 9.7	10.1
100	100.0	.0707	.090	6000	1080	−16.5	3.3
				$K^+ + Br^-$			
0	0.000	5.78	0.680	−1620	4780	21.4	43.9
10	5.88	4.70	.600	−1230	5050	21.0	43.5
20	12.32	3.75	.550	− 860	5230	20.4	42.9
30	19.41	2.94	.530	− 526	5150	19.0	41.5
40	27.25	2.22	.500	− 120	4950	17.0	39.5
50	36.08	1.64	.450	360	4550	14.1	36.6
60	45.74	1.17	.400	900	4070	10.6	33.1
70	56.73	0.756	.310	1725	3530	6.1	28.6
80	69.41	.460	.220	2720	2820	0.3	22.8
90	83.50	.262	.140	3920	2020	− 6.4	16.1
100	100.0	.1805	.105	4700	870	−12.8	9.7

TABLE II

$\bar{S}^\circ_{H^+} + \bar{S}^\circ_{Cl^-}$ AT 298.1°K. IN WATER–METHANOL SOLUTIONS

Wt. % CH_3OH	Mole % CH_3OH	Solution $-\Delta F^\circ$	Solution $-\Delta H^\circ$	Solution $-\Delta S^\circ$	$\bar{S}^\circ_{H^+} + \bar{S}^\circ_{Cl^-}$
0	0.000	8605	17880	31.1	13.6
10	5.88	8450	17550	30.6	14.1
20	12.32	8300	17320	30.3	14.4
30	19.41	8180	17200	30.3	14.4
40	27.25	8020	17240	31.0	13.7
50	36.68	7815	17440	32.3	12.4
60	45.74	7580	17740	34.2	10.5
70	56.73	7250	18030	36.2	8.5
80	69.41	6770	18500	39.5	5.3
90	83.50	5915	19030	44.0	0.7
100	100.0	3250	19700	55.2	−10.5

of solvation of individual ions but one can calculate these quantities for three pairs of alkali halide ions and hydrogen chloride gas.

The entropy of solvation of a pair of gas ions, M^+ and X^-, is given by the equation

$$\Delta S^\circ_{\text{solvation}} = \bar{S}^\circ_{M^+} + \bar{S}^\circ_{X^-} - S^\circ_{M^+(g)} - S^\circ_{X^-(g)}$$

The entropies of the gas ions were calculated from the Sackur equation and corrected from 1 mole in 24.46 liters to 1 mole in the volume occupied by 1000 g. of solvent. From the Sackur equation the entropies of monatomic H^+, Na^+, K^+, Cl^-, and Br^- are 26.0, 35.4, 36.9, 36.7, and 39.1 entropy units, respectively. The entropy correction for volume change is R ln (24.46/Sp. vol.) for any solution and varies from 6.36 in water to 5.89 e. u. in absolute methanol. The specific volumes of water–methanol solutions at 298.1°K. have been determined by Gibson.[12] In Fig. 4 the

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[12] R. E. Gibson, THIS JOURNAL, **57**, 1551 (1935).

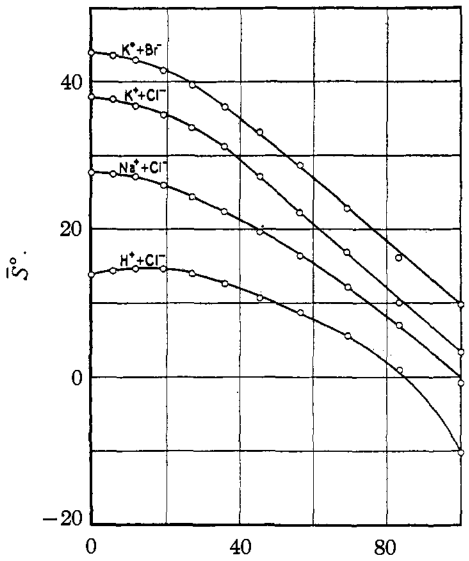


Fig. 2.—Partial molal entropies of pairs of ions at 25° in water–methyl alcohol solutions. Values in calories per degree per mole.

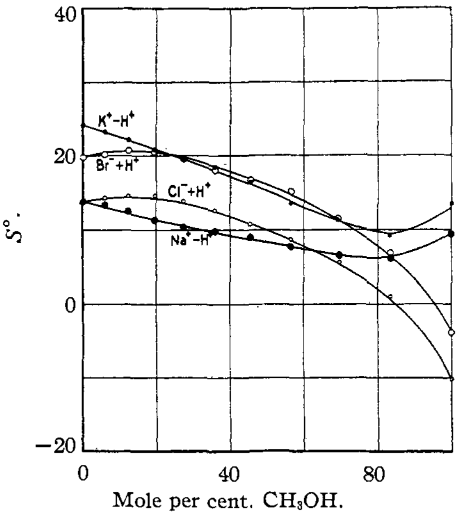


Fig. 3.—Partial molal relative ionic entropies at 25° in water–methyl alcohol solutions. Calories per degree per mole.

entropies of solvation of the four pairs of gas ions are plotted against mole per cent. methyl alcohol.

Free Energy of Solvation of Gas Ions.—The free energy of solvation of a pair of gas ions may be calculated from the entropy and heat of solvation.[11] This was done for sodium chloride, potassium chloride and potassium bromide. The crystal energy in kcal. at 298.1°K. for sodium chloride, potassium chloride, and potassium bromide is 184.1, 168.4 and 161.6, respectively.[11] The crystal energies, combined with the heats of solution, give the heat of solvation. Results are given in Table III.

Discussion

It may be observed that the free energies of solvation of a pair of ions decrease in the range from pure water to pure methanol in approximate agreement with the change in the dielectric constant as predicted by the Born equation

$$-\Delta F_{\text{solv.}} = [1 - 1/D]Ne^2/2r$$

where D is the dielectric constant and r the effective radius of the ion. The predicted effect in going from a dielectric constant of 78.5 to 31.5 is 2% and the observed decrease is about 4%. The change in the effective radii of the two ions is unknown but in general it may be stated that the agreement with the Born equation is about what could be expected.

On the other hand, the entropies of solvation present quite a different picture. In spite of the fact that the energies of solvation in methanol are less than in water, the corresponding entropies are much larger; in the case of potassium chloride, for example, the increase is almost 30 entropy units. This may be explained in terms of the

TABLE III

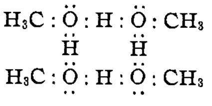
HEATS, ENTROPIES, AND FREE ENERGIES OF SOLVATION OF NaCl, KCl, AND KBr IN WATER–METHANOL SOLUTIONS

Wt. % CH_3OH	$Na^+(g) + Cl^-(g)$			$K^+(g) + Cl^-(g)$			$K^+(g) + Br^-(g)$		
	$-\Delta H°$ kcal.	$-\Delta S°$ e. u.	$-\Delta F°$ kcal.	$-\Delta H°$ kcal.	$-\Delta S°$ e. u.	$-\Delta F°$ kcal.	$-\Delta H°$ kcal.	$-\Delta S°$ e. u.	$-\Delta F°$ kcal.
0	183.2	31.7	173.7	164.3	22.9	157.5	156.8	19.3	151.0
10	182.7	32.1	173.1	164.0	23.4	157.0	156.5	19.9	150.6
20	182.4	32.4	172.7	163.8	24.3	156.6	156.4	20.5	150.3
30	182.3	33.6	172.3	163.8	25.5	156.2	156.4	21.9	149.9
40	182.4	35.4	171.9	163.9	27.5	155.7	156.6	24.1	149.4
50	182.5	37.3	171.4	164.1	30.1	155.1	157.0	27.0	149.0
60	182.7	40.3	170.7	164.5	34.3	154.3	157.5	30.7	148.3
70	183.1	43.5	170.1	165.0	39.2	153.3	158.1	35.2	147.6
80	183.6	48.0	169.3	165.6	44.8	152.2	158.8	41.2	146.5
90	184.5	53.1	168.7	166.3	51.5	150.9	159.6	47.9	145.3
100	186.1	61.2	167.9	167.3	58.5	149.9	160.7	54.5	144.5

larger entropy of the alcohol molecules, so that there is a greater decrease in entropy when the alcohol molecules are tied up about an ion even though the total energy of the process is slightly less. Another way of expressing the same idea is to say that in water the continuous hydrogen bonding gives a tetra-coördinated structure to the liquid and as a consequence the entropy of the water molecules is very much less than it would be if the liquid were normal.

It may also be noted in Fig. 4 that although the entropies of solvation increase in methanol the spread of the values for the different salts and hydrochloric acid is only about one-third as large as in water. It would seem that the effect of the size of the ion, which is very marked in water solution, is much less in pure methanol. We have no data on the absolute entropies of the ions in methanol, but if we assume the absolute value for hydrogen ion is about zero, as it is in water,[11] we obtain for the entropies of solvation of the individual ions in entropy units per mole: H^+, 20; Na^+, 19; K^+, 19; Cl^-, 41; and Br^-, 37. In order to have the entropies of solvation of the small positive ions greater than those of the large negative ions, as they are in water, it would be necessary to assume a value of about -20 for the absolute entropy of H^+. Some such very low value for hydrogen ion may of course be correct but it is rather difficult to imagine the hydrogen ion tying up a large number of methanol molecules and we would like to suggest the possibility of another explanation.

One may postulate that methyl alcohol contains a large number of molecular aggregates such as



$$\begin{array}{c} H_3C:\ddot{O}:H:\ddot{O}:CH_3 \\ \ddot{H}\qquad\ddot{H} \\ H_3C:\underset{..}{\ddot{O}}:H:\underset{..}{\ddot{O}}:CH_3 \end{array}$$

or even larger with additional molecules attached to the oxygens above and below the plane of the paper through hydrogen bonds. If now the small positive ions are able to go into the center cavity of such a complex, the resulting change in entropy would be small since the solvent molecules are already greatly restricted in their motion. Also the effect of the size of the positive ion would be small provided, of course, it was not too large to enter the cavity. The large negative ions being unable to get into such a cavity because of the repulsion of the oxygens, would tend to bind a number of unassociated alcohol molecules.

The binding of unassociated solvent molecules would thus produce a much larger entropy of solvation. This effect should be dependent upon the size of the ion and would account for the observed difference in chloride and bromide.

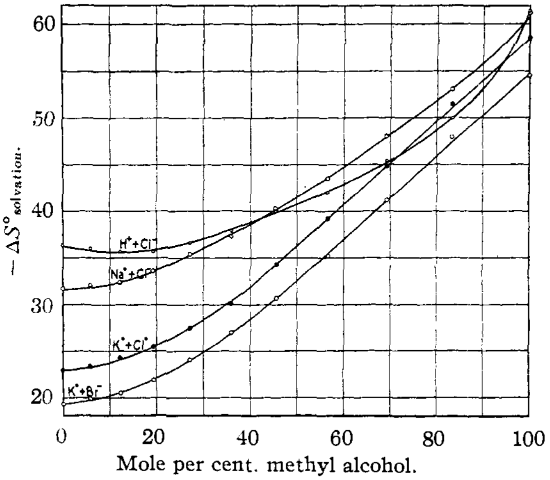


Fig. 4.—Entropies of solvation of pairs of gas ions in water–methyl alcohol solutions. Calories per degree per mole at 25°.

Such a picture appears to be consistent with the data[13,14] on conductances in water–methanol mixtures. However, until additional values for ionic entropies in methanol, especially absolute values, are obtained, these attempts to explain the apparent anomaly in the entropies of solvation of the positive and negative ions must be considered as merely suggestions to direct future investigations.

Summary

Ionic entropies, free energies, and entropies of solvation for the pairs of ions: $H^+ + Cl^-$, $K^+ + Cl^-$, and $K^+ + Br^-$ have been calculated for water–methanol mixtures whose compositions range from pure water to pure methanol. These values are discussed with reference to the nature of the solvation process.

BERKELEY, CALIF. RECEIVED MAY 28, 1940

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(13) Longsworth and MacInnes, *J. Phys. Chem.*, **43**, 239 (1939).

(14) Kraus, "Properties of Electrically Conducting Systems," Chem. Catalog Co., New York, N. Y., 1922.