249. *The Solubility of Non-electrolytes. Part III. The Entropy of Hydration.*

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It has been shown in previous papers (J., 1935, 280, 952) that the free energy of hydration of aliphatic compounds, evaluated as $\Delta F = RT \log p/N$, is to a considerable extent an additive property of the various groups in the molecule, indicating some kind of additive interaction between the parts of the molecule and the surrounding water. In the discussion of these data it was assumed provisionally that the heats of hydration of a series of compounds run parallel with the free energies of hydration, *i.e.*, that the entropies of hydration are not significantly different. An examination of the existing data, and some new measurements, shows that this is not the case, and it appears that the variation of the entropy of hydration is a predominant factor in determining the free energies of a series of similar compounds.

The heat of hydration which corresponds to the free energy given above is $\Delta H = H^\circ - H_g^\circ$, where H° is the partial heat content of the solute in an infinitely dilute solution and H_g° its heat content in the vapour at 1 mm. pressure. This can be determined practically as $\Delta H = Q - \lambda$, where Q is the heat of solution of the solute as pure liquid or solid in an infinitely dilute solution, and λ its heat of vaporisation at the same temperature. These data for a number of compounds, obtained in most cases from I.C.T., Vol. V, are given in Table I, together with the values of ΔF recorded in the previous papers. It can be seen that, as the number of CH_2 groups in a homologous series increases, the changes of ΔF and ΔH, instead of being parallel as was anticipated, are *in the opposite directions.* The entropy of hydration, which is given by $\Delta S = (\Delta H - \Delta F)/T$, therefore increases numerically by a considerable amount between one compound and its immediate homologue.

The entropy of hydration can also be obtained from the temperature coefficient of the free energy, by $d(\Delta F)/dT = -\Delta S$. In order to extend the table, which was very incomplete in its original form, ΔS has been obtained for a number of compounds by determining ΔF at 25° and 35°. These results are marked * in the table.

Table I.

Entropy of Hydration of some Aliphatic Compounds.†

A. Aliphatic alcohols.

	Q_{25}.	λ_{25}.	$-\Delta H_{25}$.	ΔF_{25}.	ΔF_{35}.	$-T.\Delta S$.	$-\Delta S$.
Methyl	−2·0	9·24	11·24	3·09	—	14·33	48
Ethyl	−2·55	10·33	12·88	3·19	—	16·07	54
n-Propyl	−3·05	11·37	14·42	3·38	—	17·80	60
*iso*Propyl	−3·77	9·68	13·45	3·45	—	16·90	56
n-Butyl *	—	12·63	—	3·49	4·14	—	65
*iso*Butyl	−2·90	12·34	15·24	3·68	—	18·92	63
sec.-Butyl *	—	12·00	—	3·59	4·22	—	63
tert.-Butyl	−3·24	11·20	14·44	3·69	—	18·13	61
n-Amyl *	—	13·60	—	3·73	4·44	—	71
tert.-Amyl *	—	11·96	—	3·77	4·43	—	65

B. Other compounds.

	Q_{25}.	λ_{25}.	$-\Delta H_{25}$.	ΔF_{25}.	ΔF_{35}.	$-T.\Delta S$.	$-\Delta S$.
Ethylamine	−6·33	6·58	12·91	3·58	—	16·49	55
Ethyl acetate	−3·07	8·64	11·71	5·11	—	16·82	56
Acetone	−2·51	7·58	10·09	4·29	—	14·38	48
Acetone *	—	—	—	4·29	4·76	—	48
Glycerol	−1·51	23·22	24·73	−1·01	—	23·72	80
Glycerol *	—	—	—	−1·01	−0·21	—	80
Chloroform	−2·20	7·64	9·84	7·14	—	16·98	57

† Units in all columns except the last are kg.-cals.; ΔS is in cals./degree.

The solubility of gases is often expressed by the Ostwald coefficient $\gamma = c_l/c_g$, where c_l and c_g are the concentrations in mols./c.c. in the liquid and the vapour. In these units the free energy of hydration is $\Delta F_c = - RT \log \gamma$, and since for sufficiently dilute solutions

$p/N = 1{\cdot}7032 \times 10^7 Td/273{\cdot}1M_1$, where M_1 is the molecular weight and d the density of the solvent, it follows that the entropy of solution when these units of concentration are used is greater than that on the p/N system by 29·4 units at 25°, *i.e.*, $\Delta S_{(p/N)} + 29{\cdot}4 = \Delta S_{(c)}$. Table II gives the entropy of solution of a number of gases calculated from the solubility data.

TABLE II.

Entropy of Hydration of some Gases (in cals./degree at ca. *25°).*

	$-\Delta S_{(p/N)}$.		$-\Delta S_{(p/N)}$.		$-\Delta S_{(p/N)}$.		$-\Delta S_{(p/N)}$.
He............	40·0 [1] (38·6) [2]	Rn............	47·5 [1]	CO............	43·0	C_2H_6	48·6
Ne............	42·0 [1] (39·4) [2]	H_2	39·2 [3]	CO_2	43·8	C_2H_4	44·5
A	43·4 [1] (43·1) [2]	N_2	43·0	COS	48·3	C_2H_2	38·8
Kr............	45·5 [1]	O_2	44·5	CH_4	45·0	CH_3Cl	46·8
Xe............	46·8 [1]						

[1] From Valentiner's interpolation formulæ (*Z. Physik*, 1927, **42**, 253).

[2] Data from Lannung (*J. Amer. Chem. Soc.*, 1930, **52**, 73).

[3] Remainder from I.C.T., Vol. IV.

EXPERIMENTAL.

The methods used for the determination of the temperature coefficient of p/N were similar to those previously described, but a more efficient six-bulb bubbler was employed to saturate the gas. The experimental figures are given in Table III, where N is the molar fraction of the solute in the original solution and x its weight % in the condensate. The measurements at 25° were repeated to secure uniformity with those at 35° and, except in the case of glycerol, are in good agreement with the figures recorded previously.

TABLE III.

Temperature Coefficients of the Partial Pressures.

		$T = 25°$.			$T = 35°$.			
	$N \times 10^3$.	x.	p/N.	ΔF_{25}, mean.	x.	p/N.	ΔF_{35}, mean.	$-\Delta S_{30°}$.
n-Butyl alcohol	1·108	6·43	359		8·50	861		
	1·108	6·45	360		8·52	863		
	0·863	5·17	366	3490	6·79	866	4145	65
sec.-Butyl alcohol	0·821	5·71	427		7·19	969		
	0·821	5·69	425		7·18	968		
	0·821	5·69	425	3590	7·18	968	4220	63
n-Amyl alcohol	0·413	4·39	541		6·30	1400		
	0·413	4·37	537		6·29	1400		
	0·397	4·29	549	3730	6·19	1430	4440	71
tert.-Amyl alcohol	1·087	11·49	581		14·7	1380		
	1·087	11·47	578		14·7	1360		
	1·087	11·44	577	3770	14·6	1355	4430	65
Acetone	0·822	13·3	1380		13·0	2380		
	0·822	13·1	1360		13·0	2380		
	0·822	13·5	1400	4290	12·9	2370	4770	48
Glycerol	10·74	0·042	0·182		0·091	0·71		
	10·74	0·040	0·173		0·091	0·69		
	10·74	0·043	0·188	−1010	0·093	0·71	−213	80

DISCUSSION.

On the whole, the entropies of solution are strikingly independent of the chemical nature of the solute. This can be illustrated by the following examples :

C_2H_6.			$CH_3{\cdot}OH$.			CH_3Cl.		
$-\Delta H$.	ΔF.	$-\Delta S$.	$-\Delta H$.	ΔF.	$-\Delta S$.	$-\Delta H$.	ΔF.	$-\Delta S$.
4·43	10·05	49	11·24	3·09	48	6·30	7·65	47

Methyl alcohol, ethane, and methyl chloride all have nearly the same entropy of solution although their heats of solution and solubilities differ greatly. Although there do appear to be some minor constitutive effects, the entropy of solution seems to be mainly a function of the size of the solute molecule; *e.g.*, in the inert gases the entropy of solution increases from helium to radon. In a homologous series there is an increase of about 5 units in

— ΔS for each additional CH_2 group. This has a most important effect on the solubility of these compounds. If the entropy were a constant, the solubility of the vapour (N/p) would be determined by the heat of solution and would *increase* as the number of carbon atoms increased. The decrease in this ratio, which actually occurs and is one of the factors which produce the steady decrease of solubility of the *liquid* in going up the series, is due to this property of the entropy.

The origin of this effect is not obvious. If the entropy change on solution depends mainly on the size of the solute molecule it is reasonable to suppose that it is associated with the size of the cavity in the water which is required to hold it. Water is an abnormal liquid and its entropy of vaporisation is about 5 units less than that of a liquid which obey's Trouton's rule. This difference is due to orientational effects. Now at first sight we might expect that the introduction of solute molecules would tend to upset the orientation of the water molecules and therefore cause an increase in their entropy which might well be proportional to the size of the solute molecule. If this were the case the partial entropy of the solute in aqueous solution would be greater than its normal entropy in the dissolved state, and the decrease of entropy on solution would diminish as the size of the solute molecule increased.

This argument is, however, fallacious. The entropy of a system is a measure of the number of possible configurations having the given entropy, *i.e.*, of the probability of the given state. The entropy of water is abnormally low because the average energy at a given temperature corresponds to a certain degree of orientation, which decreases the probability of this state. The presence of molecular cavities within the liquid may also make the degree of orientation, which is required by the average energy, more improbable and therefore decrease the entropy. The partial entropy of the solute will then be abnormally low. The observed effect can thus be accounted for on the hypothesis that the solute molecules have a disorientating influence on the water, which increases with the size of the solute molecules. But it is important to notice that what is postulated is not so much an actual decrease in orientation, which would influence the energy of solution, as in the probability of an orientated state. If these conclusions are correct, the partial entropies of solutes in other " associated " liquids should also be abnormally small.

SUMMARY.

The entropies of hydration of a number of substances have been calculated from the heats and free energies of hydration, or determined from the temperature coefficient of the free energy. This quantity is little influenced by the constitution of the solute molecule, but it appears to be mainly dependent on its size. It is suggested that the solute molecules have a disorientating effect on water, increasing with their size, which gives the solute an abnormally low partial entropy in the solution.

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