Structure and Vapor Pressure of Aqueous Acid Solutions

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Heats of vaporization and relative partial vapor pressures for a few aqueous acid solutions have been calculated from available experimental data. Empirical relations have been established between those quantities and the molecular composition and the structure of the liquid. Those relations are discussed in terms of statistical methods developed for solutions which possess a lattice. Owing to lack of structure determinations on aqueous solutions, this discussion is limited to the dependence upon the number of nearest neighbors, while the dependence upon their geometrical arrangement cannot be treated.

The maximum number of nearest water molecule neighbors which can form bonds with an acid molecule is determined from the heat of vaporization of water. This number is 28 for H_2SO_4 , H_2SeO_4 and HClO_4 , 15 for HNO_3 , and 10 for HCl .

The relations found are compared with the degrees of dissociation of the acids which have been determined by independent methods.

In the classical theory of liquids, the liquids, like gases, have been treated as statistically disordered, even as continua. However, it has been shown experimentally that liquids possess a structure in which the constituent atoms or molecules occupy spatially more or less well-defined sites. Although this structural nature of liquids is now almost universally accepted, this has not led to the revision of the classical theory of aqueous solutions required by this new concept.

The object of this paper is to draw attention to some empirical relations of a bearing upon the structural properties of aqueous acid solutions.

Our knowledge of structures of aqueous acid solutions is largely due to the experimental work done by Finbak and coworkers¹⁻². The structure of aqueous solutions is characterized by three main features:

1. Each constituent molecule is surrounded by a characteristic number of nearest neighbors.
2. Those nearest neighbors are located at almost fixed coordinates relative to the molecule considered, and in a characteristic geometrical arrangement.
3. The structure is "ordered" in the sense that solute and solvent molecules are distributed on the lattice sites in a characteristic order.

Fig. 1. ΔE_{H_2O} for H_2SO_4 solutions.

The liquid structure differs, thus, from the solid structure by lacking a "long range order", the liquid structure being essentially confined to the nearest neighbors only. Further, the structure seems to be less rigidly defined than that of solids.

In a recent series of papers³ the author has shown that the dissociation of an acid in aqueous solution is a structural property which is very sharply quantitatively defined. It was concluded from those investigations that, within the experimental accuracy,

4. when the solution contains m molecules of water per molecule of acid on the average (and at not too great dilution), each single individual acid molecule is surrounded by m molecules of water;
5. this structural property is independent of the temperature.

A structure characterized by those five features should make itself particularly conspicuous in the partial vapor pressures of the solution. For that reason we will in the following discuss partial vapor pressures of some acid solutions on which experimental data are available.

A. HEATS OF VAPORIZATION

The heat of vaporization E of a constituent in a solution can be determined from its partial vapor pressure P by plotting $\ln P$ against $\frac{1}{T}$. The author has determined E and its dependence upon concentration for a few aqueous acid

Fig. 2. ΔE_{H_2O} for H_2SO_4 solutions.

solutions on which experimental data are available. Data employed and results arrived at are listed in Table 1. For water we have written

$$E_{H_2O} = E_w + \Delta E_{H_2O} \quad (1)$$

with $E_w = 10.54$ kcal/mole, the value of E for pure water.

Table 1.

Solute	Experimental data by	Range of $\Delta E_{H_2O} = 0$	ΔE_{H_2O}	E_{solute}
HNO_3	Taylor ⁴	all concentrations		
H_2SO_4	Collins ⁴	$m > 28$	Figs. 1, 2; eq. (2)	
HCl	Yannakis ⁴	$m > 10$	Figs. 3, 4; eq. (3)	
HCl	Zeisberg ⁴			Figs. 5, 6; eq. (4)
NaCl	Olnyk & Gordon ⁵	below saturation		
NaOH	Stock & Seelig ⁴	<30 % by weight	at 50 %, $\Delta E_{H_2O} = 6$	

Fig. 3 shows particularly conspicuously the sudden rise of ΔE_{H_2O} at a certain concentration, $c = 5$ N; $m = 10$.

From the plots in Figs. 2 and 4 we derive the empirical formulae for ΔE_{H_2O} in H_2SO_4 and HCl solutions, respectively,

$$\Delta E_{H_2O} = 3 \frac{2 - \alpha}{(m + 2)^2} E_w \quad (2)$$

$$\Delta E_{H_2O} = 4.4 \frac{10 - m}{(m + 1)^2} \text{ kcal/mole} \quad (3)$$

The symbol α in (2) stands for the degree of dissociation ⁶ given in Table 3.

Fig. 3. ΔE_{H_2O} for HCl solutions.

For E_{HCl} we find from Fig. 5 the formula

$$E_{HCl} = 19.97 - \frac{46.27}{m+1} \text{ kcal/mole} \quad (4)$$

in the range $m \leq 10$. The difference

$$\Delta E_{HCl} = E_{HCl} - \left(19.97 - \frac{46.27}{m+1}\right) \quad (5)$$

is shown in Fig. 6.

In a sufficiently dilute solution there are H_2O molecules which are bound to other H_2O molecules only, *i.e.* exactly as in pure water. Hence, $\Delta E_{H_2O} = 0$. At sufficiently high concentrations, however, there are no such H_2O molecules, all H_2O molecules present being bound to solute molecules too. Hence, ΔE_{H_2O} may or may not deviate from zero, depending upon the nature of the solute molecule.

According to Table 1 all solutions on which data are available show the first region $\Delta E_{H_2O} = 0$, more or less extended. From the data on H_2SO_4 and HCl solutions we may conclude that the H_2SO_4 molecule can form bonds with 28 H_2O molecules, and that the HCl molecule can form bonds with 10 H_2O molecules. At $m = 28$ the H_2SO_4 , and at $m = 10$ the HCl molecules are "saturated" with water. When $m < 28$ and $m < 10$, there are H_2O molecules missing which may be replaced by H_2O molecules already bound to another acid molecule or by acid molecules. We may, for convenience, speak of $28-m$ or $10-m$ holes in the structure.

Fig. 4. ΔE_{H_2O} for HCl solutions.

As a first step in the discussion of the empirical formulae we will consider the significance of the various empirical constants.

The HCl molecule is bound to H_2O molecules by Cl—H—O hydrogen bonds. The energy of such a bond in $o-C_6H_4OHCl$ is $E_{Cl-H-O} = 3.9$ kcal/mole⁷. It is also bound with the van der Waals energy $E_{v.d.w.}$ which we may estimate to the order of 0.5 kcal/mole. From considerations of the degree of dissociation as determined from Raman measurements⁸, from electrolytic conductivity⁹, and from the rates of dissolution of iron¹⁰ and aluminum¹¹ in HCl solutions it may be concluded that the HCl molecule can form 5 hydrogen bonds with neighbor H_2O molecules in the region where (4) is valid. Hence, we should have $E_{HCl} = E_{v.d.w.} + 5 E_{Cl-H-O}$. Putting this expression equal to the value given by (4) at infinite dilution we find $E_{v.d.w.} = 0.47$ kcal/mole. In H_2O (ice) and H_2O_2 , $E_{O-H-O} = 4.5$ kcal/mole⁷. Assuming that $E_{O-H-O} = 4.627$ kcal/mole in HCl solutions we have, thus, from (4)

$$E_{HCl} = E_{v.d.w.} + 5 E_{Cl-H-O} - \frac{10}{m+1} E_{O-H-O} \quad (6)$$

According to Finbak the structures of HCl and NaOH solutions are very similar. Hemily has determined the structure of solid $NaOH \cdot 4 H_2O$ and found the coordination number 5¹². At higher H_2O contents the coordination number increases to 6¹³. The same increase of the number of nearest neighbors in HCl solutions would lead to

$$E_{HCl} = \frac{6}{5} (E_{v.d.w.} + 5 E_{Cl-H-O}) = 23.96 \text{ kcal/mole} \quad (7)$$

in good agreement with a reasonable extrapolation of observed values (Fig. 5).

Fig. 5. E_{HCl} for HCl solutions.

The same values of $E_{\text{v.d.w.}}$ and $E_{\text{Cl-H-O}}$ inserted in (3) give

$$\Delta E_{\text{H}_2\text{O}} = \frac{10-m}{(m+1)^2} (E_{\text{v.d.w.}} + E_{\text{Cl-H-O}}) \quad (8)$$

In HCl solutions the total number of molecules, or sites occupied by molecules, is $m+1$. The probabilities of finding an HCl molecule, an H_2O molecule, or a hole on a given site are $\frac{1}{m+1}$, $\frac{m}{m+1}$, and $\frac{10-m}{m+1}$, respectively. The probability of the coincidence of an H_2O molecule and a hole is $\frac{m}{m+1} \cdot \frac{10-m}{m+1}$. It follows from the nature of the holes that an H_2O molecule filling a hole will form bonds with an HCl molecule with a corresponding change in its total binding energy. Dividing this change in bond energy equally between the m H_2O molecules we find an energy change per H_2O molecule proportional to $\frac{10-m}{(m+1)^2}$ as required by the empirical formula (3). However, if the number of nearest neighbors of the H_2O molecule filling the hole were unchanged, it would have to drop a bond with an H_2O molecule in order to form one with the HCl molecule. We find from (8) on the contrary that the energy of the H_2O —HCl bond is simply added to the energy of the bonds with the 4 H_2O neighbor molecules. Hence, the HCl molecule is simply added to the nearest neighbors and the number of nearest neighbors is effectively increased by $\frac{10-m}{(m+1)^2}$.

Fig. 6. ΔE_{HCl} for HCl solutions.

The same argument applied to the empirical formula (2) for H_2SO_4 solutions gives an effective increase of the number of nearest neighbors by

$$\Delta z = 4 \cdot 3 (2 - \alpha). \quad (9)$$

Since any one of the 10 H_2O molecules may be missing, the probability of the formation of a hole is $\frac{10}{m+1}$. We find thus from (6) that the formation of a hole leads to a decrease in the binding energy of the HCl molecule by the energy of an O—H—O bond. The total increase of E_{H_2O} corresponds to an almost equal total decrease of E_{HCl}

$$\frac{10}{m+1} E_{O-H-O} - m \Delta E_{H_2O} = \frac{10}{m+1} 4.6 - m \frac{10-m}{(m+1)^2} 4.4 = \sim 4.5 \text{ kcal/mole}$$

We find thus a redistribution of bond energies which is difficult to interpret without an intimate knowledge of the structure.

B. VAPOR PRESSURE.

The relative partial vapor pressure p of a constituent in a solution is its actual partial vapor pressure divided by that of the pure substance. In the following we will consider water vapor pressures only.

For an ideal solution, *i.e.* when the molecules are nearly equal and no hydrates are formed, p is equal to the mole fraction (Raoult's law). Thus,

$$p = \frac{m}{m+1}. \quad (10)$$

Fig. 7. Δp for HNO_3 solutions at 20° on the data of Taylor ($\odot$) and Wilson and Miles ($\times$).

We will consider this simple case in some detail. Vaporization and condensation may be looked upon as rate processes at equilibrium. If the vapor is an ideal gas, which is a good approximation at low pressures, the rate of condensation is independent of the solute. Hence, this process does not appear in the relative partial pressure p . The activation energy of vaporization is E . The activation entropy of vaporization is composed of a term which is independent of the solute and which therefore cancels, and the entropy of mixing ΔS . Hence,

$$p = e^{\frac{\Delta S}{R}} e^{-\frac{\Delta E}{RT}}. \quad (11)$$

For an ideal solution we have $\Delta E = 0$ and

$$\begin{cases} \Delta S = k \ln W \\ W = \left(\frac{m}{m+1}\right)^N. \end{cases} \quad (12)$$

As already pointed out we may consider a system of N identical aggregates consisting of one acid molecule and m water molecules. Hence, the probability of finding an H_2O molecule on a given site is $\frac{m}{m+1}$ and the total probability

is $W = \left(\frac{m}{m+1}\right)^N$. With $\Delta E = 0$ and ΔS from (12), (11) gives (10).

The condition $\Delta E = 0$ is fulfilled for HNO_3 solutions. Although HNO_3 and H_2O molecules are far from equal, we may expect (10) to be valid with the modifications required by the differences in shape and size of the two species.

From a plot of p against $\frac{1}{m+1}$ we find, in fact, at low concentrations,

$$p = \frac{m-1}{m+1}, \quad m > 15. \quad (13)$$

Although $\Delta E = 0$, the simple formula (13) does not hold at higher concentrations.

For other acids $\Delta E = 0$ at low concentrations only. However, for the time being we will disregard this fact and merely present the data and the empirical formulae derived for p as a function of m at constant temperature, viz. room temperature. The data are listed in Table 2.

Table 2

Eq.	Fig.	Solute	Empirical formula	Experimental data by
(14)	7	HNO ₃	$p = \frac{m-1}{m+1}(1 - \frac{1-\alpha}{m-1})$; $m > 3$	Taylor ⁴ , Wilson & Miles ¹⁴
(15)	8	H ₂ SO ₄	$p = \frac{m}{m+2}(1 - 3\frac{2-\alpha}{m})$; $m > 4$	Collins ⁴ , Shankman & Gordon ¹⁵ , Harned & Hamer ¹⁶
(16)	8		$p = \frac{m}{m+2}(1 - \frac{m+2}{2m})$; $2 < m < 4$	
(15)			$p = \frac{m}{m+2}(1 - 3\frac{2-\alpha}{m})$; $m > 4$	
(16)	9	H ₂ SeO ₄	$p = \frac{m}{m+2}(1 - \frac{m+2}{2m})$; $2 < m < 4$	Macalpine & Sayce ⁴
(17)			$p = 0$; $m < 2$	
(15)	10	HClO ₄	$p = \frac{m}{m+2}(1 - 3\frac{2-\alpha}{m})$; $m > 4$	Robinson & Baker ¹⁷ , Pearce & Nelson ⁴
(18)		HCl	$p = \frac{m-2}{m+1}$; $m > 26$	Yannakis ⁴ , Wrewsky, Savaritsky & Scharloff ⁴
(19)	11		$p = \frac{m-2}{m+1}(1 - \frac{1}{2}\frac{26-m}{m}\frac{\alpha}{m+1})$; $m < 26$	

The symbols α are defined in Table 3.

Table 3

HNO ₃	H ₂ SO ₄ , H ₂ SeO ₄ , HClO ₄	HCl
$\alpha = \frac{m}{9}$; $3 \leq m \leq 6$	$\alpha = \frac{m}{4}$; $m \leq 4$	$\alpha = \frac{m}{5}$; $m \leq 5$
$\alpha = \frac{12+m}{27}$; $6 \leq m \leq 15$	$\alpha = 1 + \frac{m-4}{24}$; $4 \leq m \leq 28$	$\alpha = 1$; $m \geq 5$
$\alpha = 1$; $m \geq 15$	$\alpha = 2$; $m \geq 28$

Fig. 8. Δp for H_2SO_4 solutions at 20° on the data of Collins ($\odot$), Shankman and Gordon ($\times$), and Hamred and Hamer ($+$).

For HNO_3^{18} and H_2SO_4^6 and H_2SeO_4 , α is the degree of dissociation. For HClO_4^9 the degree of dissociation is $\alpha = \frac{m}{4}$, $m \leq 4$; $\alpha = 1$, $m \geq 4$; thus, in this case α is merely a structure variable for $m > 4$. For HCl no direct measurements of the degree of dissociation have been made. From the considerations mentioned earlier in this paper we feel safe in concluding that $\alpha = 1$ for $m > 5$. The rate of dissolution of aluminum¹¹ in HCl solutions seems to indicate that for $m < 5$, $\alpha = \frac{m}{5}$ is the degree of dissociation of HCl .

The figures listed in Table 2 show the functions Δp defined as

$$\Delta p = \frac{m-1}{m+1} - p \text{ for } \text{HNO}_3 \quad (20)$$

$$\Delta p = \frac{m}{m+2} - p \text{ for } \text{H}_2\text{SO}_4, \text{H}_2\text{SeO}_4, \text{HClO}_4 \quad (21)$$

$$\Delta p = \frac{m-2}{m+1} - p \text{ for } \text{HCl} \quad (22)$$

Before turning to a discussion of the details of those empirical formulae we will consider the role of ΔE in the basic formula (11).

The empirical formulae are all of the same general form whether $\Delta E = 0$ (HNO_3) or $\Delta E \neq 0$. In the case of H_2SO_4 , $\Delta p = 0$ and $\Delta E = 0$ in the same range, $m > 28$, in the case of HCl , however, $\Delta p = 0$ for $m > 26$ and $\Delta E = 0$ for $m > 10$, whereas in the case of HNO_3 $\Delta p = 0$ for $m > 15$ and $\Delta E = 0$ for all m . Hence, there is no obvious connection between Δp and ΔE , i.e. the deviations from the limiting formulae (m large) do not follow ΔE .

Fig. 9. Δp for H_2SeO_4 solutions at 25° . $\times \Delta p = f\left(\frac{2-\alpha}{m+2}\right)$, $\circ \Delta p = f\left(\frac{\alpha}{m+2}\right)$.

The activation entropy ΔS consists of two parts, the configurational entropy $\Delta S_{\text{conf.}}$ and the thermal entropy $\Delta S_{\text{th.}}$. If we put

$$\Delta S_{\text{th.}} = \frac{\Delta E}{T_0} \quad (23)$$

in (11), we obtain

$$p = e^{\frac{\Delta S_{\text{conf.}}}{R} - \frac{\Delta E}{RT_0} - \frac{\Delta E}{RT}} \quad (24)$$

Hence, at $T = T_0$ and $\Delta E \neq 0$

$$p = e^{\frac{\Delta S_{\text{conf.}}}{R}} \quad (25)$$

Thus, at $T = T_0$ or $\Delta E = 0$, p depends on the configurational entropy $\Delta S_{\text{conf.}}$ only. We may then determine $\Delta S_{\text{conf.}}$ from (25).

Formulae similar to (24) have been derived previously from empirical and theoretical considerations. For the splitting of the entropy into $\Delta S_{\text{conf.}}$ and $\Delta S_{\text{th.}}$ reference is made to Gurney¹⁹, Moelwyn-Hughes²⁰ and Guggenheim²¹ arrive at a $\Delta S_{\text{th.}}$ for reaction rates in solution and vapor pressure, respectively, by way of a temperature-dependent activation energy. Cremer²² and Barrer²³ report that the logarithm of the entropy factor A in the Arrhenius rate expression is a linear function of the activation energy E . For catalysis, Cremer finds that E and $\log A$ are linear functions of the temperature at which the catalyst was prepared which intersect at a certain temperature. Barrer²³ finds that, for diffusion, viscosity, and gas reactions, T_0 is the average temperature in the temperature range of the experiment. Dienes^{24,25} finds that,

Fig. 10. $\Delta\rho$ for HClO_4 solutions at 25° on the data of Robinson and Baker ($\odot$) and Pearce and Nelson ($\times$).

in diffusion in metals, $\log A$ is a linear function of $\frac{E}{T_m}$, T_m being the melting point; $\frac{E}{T_m}$ is identified with the entropy of activation.

It is interesting to observe that the formula (25) is valid at room temperature when $\Delta E \neq 0$. This would seem to imply that T_0 is the temperature at which the solution was prepared. The same result has been obtained for electrolytic conductivities⁹. Preliminary measurements of conductivities of solutions prepared at different temperatures do not support that view.

The thermodynamic interpretation of (23) seems to be a theoretical problem which still remains to be solved.

At sufficiently low concentrations the formulae of Table 2 are of the type (10). Denoting by m^* the effective number of H_2O molecules we have $m^* = m - 1$ for HNO_3 , $m^* = m$ for H_2SO_4 , and $m^* = m - 2$ for HCl . According to Chédin and coworkers^{26,27}, when H_2O is added to HNO_3 , all H_2O molecules added are bound within the HNO_3 molecules to form the monohydrate

not be expected to contribute to the vapor pressure of H_2O . It was also mainly from the very low value of p in the region $m < 1$ as well as from spectroscopic evidence that Chédin concluded on this structure. It has been shown by Luzzati that this structure does not occur in the solid mono-²⁸ and tri-hydrates²⁹. However, it is difficult to conclude from the structure of the solid hydrate upon that of the liquid hydrate. In the X-ray investigations by Finbak and Lunde this structure was not found at $m = 3$ and $m = 6$, nor do structural considerations on the degree of dissociation admit of this structure in that region.

Fig. 11. Δp for HCl solutions at 20° on the data of Yannakis (○) and Wreusky, Savaritsky and Scharloff (×).

In order to account for all this evidence we are led to assume that the monohydrate of Chédin is not actually present in the dilute solution but that there is such a strong tendency towards its formation that one of the m H_2O molecules should be excluded when computing the probability of H_2O vaporization. The limiting formulae thus lead us to conclude upon the ultimate formation of the hydrates $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $\text{HCl} \cdot 2\text{H}_2\text{O}$.

Applying the same argument to the range of incomplete dissociation we find $m^* = m - 1 - (1 - \alpha)$ for HNO_3 and $m^* = m - 3(2 - \alpha)$ for H_2SO_4 . The latter formula should be compared with the formula (9) for the number of nearest neighbors. When $\Delta m = m - m^* = 3(2 - \alpha)$ is the decrease of the number of nearest neighbors, the theory of regular solutions²¹ gives a decrease of E by the amount

$$\Delta E = \frac{3(2-\alpha)}{m} \frac{m}{m+2} \frac{1}{m+2} \cdot \frac{1}{4} E_w \quad (26)$$

Comparing (2) and (26) we have

$$\Delta E_{\text{H}_2\text{O}} = -4 \Delta E. \quad (27)$$

Hence, the vapor pressure shows an effective decrease of the number of H_2O molecules by $\Delta m = 3(2 - \alpha)$ whereas the heat of vaporization shows an effective increase of the number of nearest neighbors by $\Delta z = 4 \cdot 3(2 - \alpha)$,

or, inserting $2 - \alpha = \frac{28 - m}{24}$,

$$\begin{cases} \Delta m = -\frac{1}{8}(28 - m) \\ \Delta z = \frac{1}{2}(28 - m), \end{cases} \quad (28)$$

$28 - m$ being the number of missing H_2O molecules.

The curves of Δp for HNO_3 and for H_2SO_4 and H_2SeO_4 are fairly well approximated by the formulae given in Table 2. In particular, the curves drawn pass through the origin, i.e. $\Delta p = 0$ for $\alpha = 1$ and $\alpha = 2$, respectively. In the case of HNO_3 the data are not too reliable though, as shown by the great difference between the data of Taylor and of Wilson and Miles. At high concentrations the HNO_3 molecule is likely to decompose into N_2O_5 and H_2O . This would tend to increase p and reduce Δp .

The values of Δp for H_2SO_4 fall close to a straight line. However, the experimental data show a tendency towards a S-shaped curve. This is particularly conspicuous in the case of HClO_4 . The formulae for those acids give therefore a first approximation only. We may interpret the deviation as a random deviation from the structure.

The formula (19) for HCl has been derived as follows: Inserting for α the expressions given in Table 3 we have

$$\Delta p = \frac{1}{27} \frac{15-m}{m+1}; \quad m > 3, \text{ for } \text{HNO}_3 \quad (29)$$

$$\Delta p = \frac{1}{8} \frac{28-m}{m} \frac{m}{m+2}; \quad m > 4 \text{ for } \text{H}_2\text{SO}_4 \quad (30)$$

Trying for HCl an expression of a similar form

$$p = \frac{m-2}{m+1} \left[1 - A \frac{B-m}{m} \frac{1}{m+1} \right]; \quad m > 5 \quad (31)$$

we find $A = \frac{1}{2}$ and $B = 25$ or $B = 26$. At higher concentrations we have to add a factor $\frac{m}{5}$ to the second term.

Introducing a quantity α defined in Table 3 we have thus, at all concentrations,

$$p = \frac{m-2}{m+1} \left[1 - A \frac{B-m}{m} \frac{\alpha}{m+1} \right] \quad (32)$$

Trying various values of B we find that $B = 25$ and $B = 26$ give constant values of A , viz. $A = 0.517 \pm 0.004$ and $A = 0.491 \pm 0.004$ respectively. The constancy of A is, thus, the same for both values of B . We have taken in (19), somewhat arbitrarily, $B = 26$. The values of A calculated from (32) are given in Table 8. It is difficult to see the significance of $m = 26$. No other property of HCl solutions is known to show any change at that particular concentration.

According to Finbak³⁰ the structure of HCl solutions is not well defined. It is true that certain values of m , such as $m = 5$ and $m = 10$, are as conspicuously manifested in physical and chemical properties of the HCl solutions as are the corresponding values of m for HNO_3 and H_2SO_4 solutions. The comparatively complicated formula for p with

$$\Delta m = \frac{1}{2} \frac{m-2}{m+1} \frac{26-m}{m} \frac{\alpha}{m+1} \quad (33)$$

seems to indicate a certain lack of definition of the structure.

Fig. 11 shows Δp as a function of $\frac{1}{m+1}$. The form of the curve suggests an error function for Δp . Fig. 12 shows $\ln(\Delta p \cdot 10^3) = f \left[\left(\frac{1}{m+1} - \frac{1}{5} \right)^2 \right]$. This gives us

$$\Delta p = 0.175 e^{-3.6 \left(\frac{m-4}{m+1} \right)^2} \quad (34)$$

and

$$\Delta m = \frac{1}{\sqrt{\pi h}} e^{-\frac{x^2}{h}} \quad (35)$$

with

$$\begin{cases} h = \frac{10}{(m+1)^2} \\ x = 6 \frac{m-4}{(m+1)^2} \end{cases} \quad (36)$$

It should be added that the representation (4) of E_{HCl} as a function of the molecular composition may as well, disregarding any physical significance of the formula, be substituted by a function of the normality of the acid. In fact, the formula

$$E_{\text{HCl}} = 20.3 - 0.89 c \text{ kcal/mole} \quad (37)$$

is valid in a still wider range of concentrations, viz. $c > 3 N$; $m < 17.4$, than is (4).

We may now look at the denominators of the empirical formulae from the same point of view as previously applied to the nominators. From the formulae for H_2SO_4 we may conclude that the H_2SO_4 molecule effectively occupies two sites. This is consistent with the formula for HNO_3 , because if one H_2O molecule is taken up by the HNO_3 molecule, this hydrate would be similar to the H_2SO_4

molecule and therefore cover two sites as does the H_2SO_4 molecule. Hence, the total number of occupied sites should be $(m-1) + 2 = m + 1$.

This result is somewhat surprising. We should, in fact, expect the H_2SO_4 molecule to occupy 5 and the HNO_3 molecule to occupy 4 times as many sites as does the H_2O molecule. However, it should be recalled that the atomic distances in the H_2SO_4 and HNO_3 molecules are much smaller than, about half, the distance between adjacent H_2O molecules. The result is therefore altogether reasonable.

From the data and from the discussion given above it may be concluded that the structural properties of aqueous acid solutions are conspicuously manifested in their heats of vaporization and vapor pressures. It may also be concluded that a simple approach to the theory of liquids may be based upon statistical methods developed for solid solutions. However, the structures are not sufficiently known as yet for a rigorous treatment along those lines. From the empirical data and relations presented in this paper we may only conclude upon the number of nearest neighbors but not upon their geometry. Due to this lack of data we can not interpret the significance of the change of "effective" number of neighbors. For that purpose we need not only the structural positions of the O, S, N etc. atoms but also those of the H atoms. Another difficulty pointed out is the significance of the constant temperature T_0 found in various connections. This seems to be a problem of theoretical thermodynamics.

Although it is hard to believe that the vapor pressure should depend upon the degree of dissociation, those two quantities are undoubtedly related, probably owing to their both being dependent upon the structure. For that reason experimental determinations of degrees of dissociation may be expected to contribute to our knowledge of the structure and, therefore, facilitate the study of vapor pressures.

Acknowledgement. The work reported in this paper was done in the Research Laboratory of Avesta Jernverks AB, Avesta, Sweden. I am indebted to the Management of Avesta Jernverks AB for permission to publish this report.

APPENDIX

The calculated values are given in the following Tables 4–11. At low concentrations where $\Delta p = 0$ and $\Delta E_{\text{H}_2\text{O}} = 0$, the small deviations actually observed and which are of the order of experimental errors, can not be represented to the scale of the curves of Δp and $\Delta E_{\text{H}_2\text{O}}$. This is apparent from an examination of the data given in the tables. However, in some cases, notably for HClO_4 , there is a tendency towards increasing values of Δp in the range where, according to the text, Δp should be zero. This tendency would not show up properly in the graphical representation of Δp .

In calculating $\Delta E_{\text{H}_2\text{O}}$ for HCl , we have not employed the data given by Yannakis at 6 and 10 % HCl by weight because the spread of the data is so large that no estimate of $\Delta E_{\text{H}_2\text{O}}$ can be made. At 14 % HCl by weight the data seemed to allow the determination of $\Delta E_{\text{H}_2\text{O}}$; the value given in Table 11

Table 4. Relative partial vapor pressure of water in HNO_3 solutions at 20°

% HNO_3 by weight	m	a	$\frac{m-1}{m+1}$	$\frac{1-a}{m+1}$	p	$4p$
	Taylor		%	%	%	%
20	13.9911	0.9626	86.66	0.25	86.66	0.00
25	10.4933	0.8331	82.60	1.45	80.96	1.64
30	8.1615	0.7467	78.16	2.77	75.26	2.90
35	6.4958	0.7218	73.32	3.71	68.42	4.90
40	5.2467	0.3830	67.98	6.68	61.57	6.41
45	4.2751	0.4750	62.08	9.96	53.59	8.49
50	3.4978	0.3886	55.54	13.59	45.04	10.50
55	2.8618	0.3103	48.21	17.85	38.20	10.01
60	2.3319	0.2220	39.98	23.35	31.93	8.05
65	1.8834	0.1472	30.64	29.57	27.94	2.70
70	1.4991	0.0832	19.98	36.68	23.38	
Wilson and Miles						
50	3.4978	0.3886	55.54	13.59	44.47	11.07
60	2.3319	0.2220	39.98	23.35	27.65	12.33
70	1.4991	0.0832	19.98	36.68	16.53	3.45

Table 5. Relative partial vapor pressure of water in H_2SO_4 solutions at 25° .

% H_2SO_4 by weight	m	a	$\frac{m}{m+2}$	$\frac{2-a}{2+m}$	p	$4p$
	Collins		%	%	%	%
10	49.00	2	96.08	0.00	95.6	0.5
20	21.776	1.7407	91.59	1.09	88.0	3.6
25	16.3322	1.5318	89.09	2.65	82.5	6.6
30	12.7026	1.3628	86.40	4.33	75.2	11.2
35	10.1104	1.2546	83.49	6.15	66.3	17.2
40	8.1561	1.1732	80.31	8.14	56.5	23.8
45	6.6539	1.1106	76.89	10.28	46.1	30.8
50	5.4440	1.0602	73.13	12.63	35.7	37.6
55	4.4542	1.0189	69.01	15.20	25.8	43.2
60	3.6294	0.9074	64.47	19.41	16.6	47.9
65	2.9314	0.7329	59.44	25.70	9.7	49.7
70	2.3331	0.5833	53.84	32.70	3.7	50.1
Shankman and Gordon						
15.835	28.9346	2	93.535		91.74	1.79
18.005	24.7912	1.8663	92.535	0.499	89.95	2.58
26.410	15.1689	1.4654	88.351	3.114	80.48	7.87
27.025	14.6998	1.4458	88.024	3.319	79.64	8.38
29.265	13.1580	1.3816	86.806	4.080	76.27	10.54
29.560	12.9724	1.3739	86.642	4.182	75.86	10.78
29.850	12.7935	1.3664	86.481	4.283	75.39	11.09
32.67	11.2192	1.3008	84.870	5.289	70.62	14.25
34.85	10.1769	1.2574	83.575	6.098	66.79	16.78
36.39	9.5159	1.2298	82.633	6.688	63.79	18.84
39.55	8.3206	1.1800	80.621	7.945	57.43	23.19
42.51	7.3622	1.1401	78.637	9.185	51.10	27.54
45.12	6.6214	1.1092	76.802	10.332	45.42	31.38
47.97	5.9046	1.0794	74.698	11.646	39.34	35.36
49.85	5.4766	1.0615	73.250	12.552	35.37	37.88
52.42	4.9412	1.0392	71.187	13.842	29.93	41.26
55.51	4.3631	1.0151	68.569	15.478	24.04	44.53
59.73	3.6702	0.9176	64.728	19.089	16.67	48.16
66.95	2.6873	0.6718	57.332	28.336	7.20	50.13
68.94	2.4527	0.6107	55.083	31.201	5.38	49.70

Harned and Hamer

0.5 *	111.012	2	98.230		98.21	0.02
1	55.506	2	96.522		96.20	0.32
2	27.753	1.9897	93.278	0.035	91.36	1.92
3	18.502	1.6043	90.245	1.930	85.06	5.18
5	11.1012	1.2959	84.734	5.374	69.80	14.93
7	7.9295	1.1637	79.858	8.422	54.53	25.33

*) moles per 1 000 g of H₂O.Table 6. Relative partial vapor pressure of water in H₂SeO₄ solutions at 25° according to Macalpine and Sayer.

% H ₂ SeO ₄ by weight	<i>m</i>	<i>a</i>	$\frac{m}{m+2}$ %	$\frac{2-a}{2+m}$ %	<i>p</i> %	Δp %
23.93	25.580	1.8992	92.75	0.36	89.27	3.58
34.13	15.5306	1.4804	88.59	2.97	81.02	7.57
47.08	9.0452	1.2102	81.89	7.15	63.59	18.30
51.34	7.6270	1.1511	79.23	8.81	53.83	25.40
57.58	5.9284	1.0804	74.77	11.60	41.04	33.73
65.30	4.2761	1.0115	68.13	15.75	26.18	41.95
67.58	3.8604	0.9289	65.87	18.28	22.64	43.21
76.69	2.4459	0.6077	55.01	31.32	8.25	46.76
83.18	1.6272	0.4068	44.86	43.92	2.61	42.25
85.48	1.3669	0.3417	40.60	49.25	1.35	39.25
89.29	0.9652	0.2413	32.55	59.31	0.76	31.79
93.50	0.5594	0.1399	21.86	72.67	0.13	21.73

Table 7. Relative partial vapor pressure of water in HClO₄ solutions at 25°.

Moles of HClO ₄ per 1 000 g of H ₂ O	<i>m</i>	<i>a</i>	$\frac{m}{m+2}$ %	$\frac{2-a}{m+2}$ %	<i>p</i> %	Δp %
Robinson and Baker						
0.1	555.06	2	99.641	0	99.658	0.02
0.2	277.53	2	99.285	0	99.317	0.03
0.3	185.02	2	98.931	0	98.970	0.04
0.4	138.77	2	98.579	0	98.618	0.04
0.5	111.01	2	98.230	0	98.258	0.03
0.6	92.510	2	97.884	0	97.888	0.00
0.7	72.295	2	97.308	0	97.510	0.20
0.8	69.438	2	97.200	0	97.124	0.08
0.9	61.723	2	96.861	0	96.727	0.13
1.0	55.506	2	96.522	0	96.319	0.20
1.2	46.255	2	95.855	0	95.471	0.38
1.4	39.647	2	95.198	0	94.572	0.63
1.6	34.691	2	94.549	0	93.637	0.91
1.8	30.837	2	93.909	0	92.660	1.25
2.0	27.753	1.9897	93.278	0.0346	91.650	1.63
2.5	22.203	1.7585	91.737	0.9978	88.915	3.82
3.0	18.502	1.6043	90.245	1.9303	85.900	4.35
3.5	15.859	1.4941	88.801	2.8327	82.650	6.15

4.0	13.877	1.4115	87.403	3.7066	79.152	8.25
4.5	12.335	1.3473	86.048	4.5532	75.479	10.57
5.0	11.101	1.2959	84.734	5.3744	71.530	13.20
5.5	10.092	1.2538	83.460	6.1710	67.528	15.93
6.0	9.2510	1.2188	82.224	6.9434	63.430	18.79
6.5	8.5394	1.1891	81.024	7.6940	59.271	21.75
7.0	7.9295	1.1637	79.858	8.4224	55.081	24.78
7.5	7.4008	1.1417	78.725	9.0237	50.972	27.75
8.0	6.9438	1.1227	77.638	9.8090	46.872	30.77
8.5	6.5301	1.1054	76.554	10.487	42.888	33.67
9.0	6.1723	1.0905	75.527	11.129	39.043	36.48
10.0	5.5506	1.0646	73.512	12.388	31.950	41.56
11.0	5.0460	1.0436	71.615	13.574	25.651	45.96
12.0	4.6255	1.0261	69.814	14.699	20.296	49.52
13.0	4.2697	1.0112	68.101	15.771	15.825	52.28
14.0	3.9647	1.9912	66.469	16.913	12.234	54.24
15.0	3.7004	1.9251	64.915	18.857	9.310	55.61
16.0	3.4691	1.8673	63.431	20.711	7.024	56.41

Pearce and Nelson

0.10016	554.18	2	99.640	0	99.663	0.02
0.20064	276.646	2	99.282	0	99.331	0.05
0.40257	137.890	2	98.570	0	98.640	0.08
0.60655	91.511	2	97.861	0	97.903	0.04
0.81037	68.495	2	97.163	0	97.116	0.04
1.01589	54.638	2	96.469	0	96.287	0.18
2.0661	26.865	1.9527	93.071	0.1639	91.331	1.74
3.1512	17.614	1.5673	89.803	2.2051	85.012	4.79
4.2734	12.989	1.3745	86.657	4.1731	77.412	9.25
5.4347	10.2133	1.2589	83.624	6.0680	68.659	14.97
6.6372	8.3629	1.1818	80.700	7.8955	58.669	22.03
7.8719	7.0512	1.1271	77.903	9.6440	48.375	29.53
9.1723	6.0515	1.0855	75.360	11.358	37.969	37.20
10.513	5.2798	1.0533	72.527	13.005	28.789	43.74
11.905	4.6624	1.0276	69.981	14.595	20.975	49.01

Table 8. Relative partial vapor pressure of water in HCl solutions at 20°

% HCl by weight	<i>m</i>	$\frac{1}{m+1}$ %	P_{H_2O} mm Hg	<i>p</i> %	$\frac{m-2}{m+1}$ %	Δp %	$\frac{A}{m=25}$	$\frac{A}{m=26}$
Yannakis								
6	31.72	3.06	15.9	90.65	90.82	0.17	—	—
10	18.22	5.20	14.6	83.24	84.40	1.16	(0.710)	(0.619)
14	12.44	7.44	13.1	74.69	77.68	2.99	0.512	0.474
18	9.223	9.78	11.3	64.42	70.66	6.24	0.528	0.496
20	8.098	10.99	10.3	58.72	67.03	8.31	0.540	0.510
22	7.178	12.23	9.30	53.02	63.31	10.29	0.535	0.507
24	6.411	13.49	8.30	47.32	59.53	12.21	0.524	0.498
26	5.762	14.79	7.21	41.11	55.63	14.52	0.529	0.502
28	5.206	16.11	6.32	36.03	51.67	15.44	0.488	0.464
30	4.724	17.47	5.41	30.84	47.59	16.75	0.497	0.473
32	4.302	18.86	4.55	25.94	43.42	17.18	0.507	0.483
34	3.930	20.28	3.81	21.72	39.16	17.44	0.521	0.498
36	3.599	21.74	3.10	17.67	34.78	17.11	0.529	0.505
38	3.303	23.24	2.51	14.31	30.28	15.97	0.523	0.498
40	3.037	24.77	2.00	11.40	25.69	14.29	0.511	0.489
42	2.796	26.35	1.56	8.89	20.95	12.06	0.492	0.471

Wrewsky, Savaritsky and Scharloff

5.05	38.06	2.56	16.05	91.51	0.81		
10.00	18.22	5.20	14.5	82.67	1.73	1.060	0.924
16.03	10.60	8.62	12.2	69.56	4.59	0.529	0.495
18.05	9.192	9.81	11.8	67.27	3.29	0.276	0.256
20.9	7.662	11.54	10.0	57.01	8.36	0.490	0.463
24.1	6.376	13.56	8.2	46.75	12.58	0.536	0.509
24.98	6.080	14.12	7.65	43.61	14.02	0.554	0.526
30.05	4.713	17.51	5.1	29.08	18.40	0.546	0.520
32.97	4.116	19.55	4.3	24.52	16.84	0.499	0.476
36.89	3.463	22.40	2.9	16.53	16.26	0.514	0.491

Table 9. Relative partial vapor pressure (in %) of water in HNO_3 solutions at various temperatures according to Taylor.

t°C % HNO_3 by weight	0	5	10	15	20	25	30	35	40	45	50
20	89.52	87.16	86.86	85.22	86.66	86.70	86.74	86.53	85.86	86.26	86.48
25	82.97	82.57	82.52	80.53	80.96	80.81	80.77	80.13	79.54	79.99	81.07
30	78.60	76.45	77.09	75.84	75.26	74.92	74.80	73.73	74.11	73.73	74.59
35	72.05	70.34	70.58	69.59	68.42	66.18	68.20	67.09	68.15	66.78	68.10
40	65.50	64.22	62.98	62.55	61.57	61.45	61.28	60.46	60.56	59.82	60.53
45	56.77	55.05	54.29	53.95	53.59	53.45	53.11	52.87	52.96	52.87	53.51
50	45.85	45.87	45.60	45.35	45.04	45.03	45.25	45.05	45.19	45.21	45.94
55	39.30	38.23	38.00	38.31	38.20	38.30	38.34	38.17	38.50	38.95	39.24
60	32.75	32.11	32.57	32.06	31.93	32.41	32.37	32.24	32.72	32.97	33.51
65	28.38	27.52	28.23	27.37	27.94	27.78	27.66	27.50	28.08	27.82	28.10
70	24.02	24.46	23.89	23.46	23.38	23.15	23.26	23.23	23.14	23.23	23.56
80	—	—	13.03	13.29	13.68	13.47	12.57	13.04	12.65	13.22	12.97
90	—	—	—	—	—	4.21	4.09	4.27	4.34	4.17	4.32

Table 10. $\Delta E_{\text{H}_2\text{O}}$ for H_2SO_4 solutions calculated from data by Collins.

% H_2SO_4 by weight	m	α	$\frac{2-\alpha}{(m+2)^2} \cdot 10^3$	$\Delta E_{\text{H}_2\text{O}}$ kcal/mole	$\Delta E_{\text{H}_2\text{O}}$ $\frac{(m+2)^2}{2-\alpha}$
10	49.000	2	0	0	0
20	21.776	1.7407	0.4587	0	0
25	16.3322	1.5318	1.3932	0.0549	39.41
30	12.7026	1.3628	2.9477	0.101	34.26
35	10.1104	1.2546	5.0824	0.185	36.40
40	8.1561	1.1732	8.0158	0.281	35.06
45	6.6539	1.1106	11.8761	0.379	31.91
50	5.4440	1.0602	16.960	0.543	32.02
55	4.4542	1.0189	23.552	0.759	32.23
60	3.6294	0.9074	34.478	1.037	30.08
65	2.9314	0.7329	52.104	1.564	30.02
70	2.3331	0.5833	75.454	2.676	35.47
Mean value					33.69

Table 11. ΔE_{H_2O} and E_{HCl} for HCl solutions from data by Yannakis and Zeisberg, respectively.

% HCl by weight	m	$\frac{1}{m+1}$ %	ΔE_{H_2O} kcal per mole	ΔE_{H_2O} kcal per mole from (3)	$\frac{10-m}{(m+2)^2}$	E_{HCl} kcal per mole	E_{HCl} kcal per mole from (5)	ΔE_{HCl} kcal per mole
2	99.19	0.998				21.66	19.51	2.15
4	45.58	2.02				20.51	19.03	1.48
6	31.72	3.06				19.25	18.55	0.70
8	23.28	4.11				18.48	18.07	0.41
10	18.22	5.20				17.88	17.56	0.32
12	14.85	6.31				17.25	17.05	0.20
14	12.44	7.44	0.01*			16.64	16.53	0.11
16	10.63	8.60				16.07	15.99	0.08
18	9.223	9.78	0.0433	0.0328	0.00745	15.46	15.44	0.02
20	8.098	10.99	0.124	0.101	0.0230	14.86	14.88	-0.02
22	7.178	12.23	0.219	0.186	0.0422	14.33	14.31	0.02
24	6.411	13.49	0.284	0.288	0.0654	13.74	13.73	0.01
26	5.762	14.79	0.439	0.408	0.0928	13.12	13.12	0.00
28	5.206	16.11	0.525	0.547	0.1233	12.50	12.51	-0.01
30	4.724	17.47	0.662	0.709	0.1611	11.87	11.88	-0.01
32	4.302	18.86	0.842	0.893	0.203	11.25	11.24	0.01
34	3.930	20.28	1.048	1.10	0.250	10.61	10.58	0.03
36	3.599	21.74	1.341	1.33	0.302	10.19*	9.91	0.28
38	3.303	23.24	1.663	1.60	0.354	9.52*	9.22	0.30
40	3.037	24.77	1.962	1.88	0.427	8.63*	8.51	0.12
42	2.796	26.35	2.356	2.20	0.500			

* less accurate values.

is very rough, though. At very high concentrations the values of E_{HCl} are probably too high.

For H_2SO_4 (Table 10) the mean value of $\Delta E_{H_2O} \cdot \frac{(m+2)^2}{2-a}$ is 33.69.

This value is probably too high owing to the great influence of the values of ΔE_{H_2O} at 25 and 70 % H_2SO_4 by weight. A weighted average seems to be closer to 31.6, the value given in eq. (2).

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Received April 10, 1953.