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Energy, Enthalpy, and Volume Change of Hydrogen-Bond Formation in Large, Charged, Water Vapor Clusters, $H^+(H_2O)_c$, Determined from Mass Spectral Distributions

G. E. Walrafen*

Chemistry Department, University of Kansas, 2010 Malott Hall, Lawrence, Kansas 66045-0046

Y. C. Chu

Chemistry Department, Howard University, Washington, D.C. 20059

H. R. Carlon

1904 Norwood Court, Fallston, Maryland 21047

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Thermodynamic analysis via simultaneous equations of previously reported mass spectra obtained from water vapor at 99 °C yielded ΔE, ΔH, and ΔV values for H-bond formation in large, ion-induced, charged, water clusters, $H^+(H_2O)_c$, ranging from $C \approx 20$ to $C \approx 45$ H_2O. An average ΔE value of -2190 ± 15 cal/mol H-bond was calculated for formation at pressures from ≈0.39 to ≈0.56 bar, as well as an approximate ΔH of -2540 ± 70 cal/mol H-bond. However, van't Hoff treatment of mass spectral data between 41 and 90 °C at a constant partial pressure of 0.038 bar yielded a more accurate ΔH of -2425 ± 25 cal/mol H-bond. Both ΔH's are in close agreement with H-bond ΔH's from Raman, infrared, and viscosity data for liquid water, despite the fact that they refer to charged water clusters. A ΔV value of $-31\,300 \pm 1000$ cm^3/mol H-bond also resulted from the simultaneous equations. This ΔV compares favorably with a limiting ΔV value of $-30\,790$ cm^3/mol H-bond corresponding to the condensation of steam to liquid water at 0.5 bar and 373.15 K. The ΔE, ΔH, ΔV, and ΔS values involved here demonstrate that the condensation of monomeric water onto large, *charged*, clusters in the vapor is analogous to the condensation of steam.

Introduction

Monomeric water molecules constitute the overwhelmingly dominant species in the vapor above liquid water at, or near, the normal boiling point.[1,5] Nevertheless, a small amount of the vapor (order of magnitude ≈1%) is thought to be composed of large clusters, both neutral and charged, and broadly distributed, ranging in size from, e.g., 20 to 45 H_2O, at pressures of roughly 0.5 bar at 99 °C.[1]

Carlon and Harden[1] designated this distribution of large clusters as water's "hidden phase" because of the difficulty of its characterization in the presence of severe monomer interference.

Ordinary Raman spectroscopic examination of saturated water vapor at 100 °C using a spectral resolution of several cm^{-1} mainly reveals the intense symmetric stretching monomer peak near 3657 cm^{-1}.[5,6] Infrared spectroscopic analysis of the vapor near 3 μm is, unfortunately, so rich in fine structure, e.g., rotational, that any hope of seeing clusters, clearly and separately, is virtually nil.[7] Other infrared regions may be more useful, but the experiments are difficult.[8]

Mass spectroscopy, in contrast, is ideal for studying large, ion-induced, charged, water vapor clusters, $H^+(H_2O)_c$, because it simply reveals a series (broad distribution) of sharp, well-defined, mass "spikes" at integral multiples of the H_2O mass. Specifically, if one examines the region from about 20 to 45 H_2O masses at 99 °C and $P \approx 0.5$ bar, one sees a broad distribution of peaks whose maximum signal occurs between 28 and 34 H_2O masses.

In this article we employed mass spectrometric data reported in 1980[1] but never analyzed by thermodynamic methods. We demonstrate that the mass distribution from large, charged, water clusters in the vapor may be analyzed by standard thermodynamics to yield ΔE, ΔH, and ΔV values for H-bond formation. We strongly emphasize that all thermodynamic quantities obtained here refer solely to positively charged clusters, *not* to neutral clusters, because only positively charged clusters are detected.

Our method is statistical in nature, and as such is devoid of specific structural information about the clusters. For example, a cluster on the low-mass tail of the distribution, involving say 20 water molecules, might have dangling OH groups, etc., but its contribution to the most probable cluster size, is very small. Hence, a structural inference, e.g., that the most probable cluster size involves extensive H- bonding, cannot be extended to describe the tails of the distribution. Moreover, it would be improper to use chemical equations involving specific structures—only a general description that involves condensation of monomers onto the surface of charged clusters may be invoked.

Our first procedure was to obtain the most probable cluster size, $\hat{C}$, of the mass distribution, as described below, and then to use this most probable cluster size in thermodynamic calculations. The thermodynamic calcluations involved simultaneous equations of the form $\ln \hat{C} = A/T + BP$, from which we extracted ΔE and ΔV values for the condensation of monomeric water molecules onto the large, positively charged, clusters.

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We next compared the cluster ΔE values with H-bond ΔH values obtained from Raman and infrared studies of water (because of their availability and reliability). This comparison clearly indicated that the cluster ΔE values refer to single H-bond processes. Comparison of the ΔV values with the corresponding values for the condensation of steam, recalculated to a per mole of H-bond basis, was also made, and indicated very close agreement. The thermodynamic agreements suggested that large, charged, water clusters having sizes near the most probable size are extensively H-bonded.

The simultaneous equations were converted into a new form involving an equilibrium constant, by including an entropy change obtained from the condensation of steam on a per mole of H-bond basis. This allowed us to calculate the ratio of the mass of the most probable clusters to the mass of the monomers, and this ratio was found to be in good agreement with Carlon's results.[1]

In summary, three agreements, (1) between the cluster ΔE (and ΔH values, see below) and the Raman and infrared H-bond ΔH values, (2) between the ΔV and the volume change for the condensation of steam on a per mole of H-bond basis, and (3) between the calculated equilibrium constant and the measurements of Carlon and Harden,[1] constitute basic tenets of this work, which indicate a similarity between the condensation of monomers on charged clusters and the condensation of steam.

The thermodynamic methods employed here are described in the following sections.

Thermodynamic Analysis of Mass Spectral Data Using Simultaneous Equations

We designate the cluster size, that is, the number of water molecules in a specific cluster by the integer C. The cluster size corresponding to the "apparent peak" of the mass distribution is designated by $\hat{C}$, whereas the average cluster size is $\bar{C}$.

We determined $\hat{C}$ as follows.

The signal heights, S, of the mass peaks were accurately measured for a given mass distribution, e.g., 20−45 H_2O. These S values were then multiplied by the corresponding integral C values, giving CS. We designate $CS = Y$ and the corresponding C's as X. The file of the Y,X values constitutes the corrected distribution.

We next subjected a given Y,X distribution to nonlinear least-squares analysis, as one would do with continuous functions. The result was a nearly symmetric bell- shaped curve, whose equation corresponded to a high-degree least squares polynomial in X. The X corresponding to the maximum Y value determined analytically is $\boldsymbol{\hat{C}}$.[9]

Our high-degree polynomial Y versus X curves are essentially symmetric about the peak, and thus the X value corresponding to the peak is essentially the average X, i.e., $\hat{C} \approx \bar{C}$. High-signal "magic number" clusters at $C = 21$ or $C = 28$ were averaged by the least-squares analysis as if they were points having positive error.

We emphasize that the mass spectra refer, for example, to the charged species $H^+(H_2O)_c$, which is formed by the intense β ionization source in the mass spectrometer. Hence, the H-bond ΔE, ΔH, and ΔV values to follow correspond to large, *charged*, water-containing clusters. No statement may be made about the neutral clusters from the mass spectral data, because neutral clusters were not detected. Moreover, although the charged clusters were produced by the β source in the spectrometer, this process occurred near the entrance, leaving ample time for the charged clusters to attain equilibrium structures prior to detection.

We found that the $\hat{C}$ values corresponding to a given T and P may be described by

$$\ln \hat{C} = A/T + BP \tag{1}$$

From thermodynamics it follows that

$$[\partial \ln K/\partial(1/T)]_P = -\Delta H/R = -\Delta E/R - P\Delta V/R \tag{2}$$

However, if

$$\ln K = -\Delta E/RT - P\Delta V/RT + \Delta S/R \tag{3}$$

operation on both sides of (3) by the operator $[\partial/\partial(1/T)]_P$ yields (2) when ΔE, ΔV, and ΔS are constants.

Next, compare coefficients of like power in the variables $1/T$ and P, between (1) and (3). This comparison gives $\Delta E = -AR$ and $\Delta V = -BRT$, and identifies $\ln K = \ln \boldsymbol{\hat{C}} + \Delta S/R$, or $K = \hat{C}e^{\Delta S/R}$. K, the equilibrium constant, equals $\hat{C}e^{\Delta S/R} = (\Pi_{\text{liquid}}/\Pi_{\text{vapor}})$. We designate the ratio of Π's as the reaction probability ratio. K calculated from $\hat{C}e^{\Delta S/R}$ corresponds to an ≈3% water cluster content, cf. ref 1. Details related to calculation of ΔS, as well as about the form of the equilibrium constant which allowed us to calculate the percentage of the water cluster content, are discussed in a subsequent section.

A and B are readily obtained from solutions of simultaneous equations. For two pressures, P_1 and P_2, at fixed T, one obtains

$$\ln \hat{C}_2 = A/T + BP_2 \tag{4}$$

and

$$\ln \hat{C}_1 = A/T + BP_1 \tag{5}$$

Subtraction of (5) from (4) yields

$$(\ln \hat{C}_2 - \ln \hat{C}_1)/(P_2 - P_1) = \Delta \ln \hat{C}/\Delta P = \text{B} \tag{6}$$

Moreover, if data at widely separated temperatures were available at constant P (near 0.5 bar), we could obtain A directly from

$$(\ln \hat{C}_2 - \ln \hat{C}_1)/(1/T_2 - 1/T_1) = \Delta \ln \hat{C}/\Delta(1/T) = A \tag{7}$$

but such data were lacking. Therefore, our procedure was to obtain B via (6), and then to determine A from substitution in either (4) or (5).

Three sets of A and B values may be obtained from the three pairs of simultaneous equations that result from the three different pressures at 99 °C.[1] These three equations are designated E, F, and G.

$\hat{C}$ values are $\hat{C}_E = 33.94$, $\hat{C}_F = 31.08$, and $\hat{C}_G = 28.56$. The corresponding pressures are $P_E = 0.5560$ bar, $P_F = 0.4733$ bar, and $P_G = 0.3853$ bar.

We carried a large number of figures in our calculations to prevent round-off error, but we finally rounded off the ΔE, ΔH, and ΔV values to three significant figures.

An example of our calculation method is given using the E and G data. Simultaneous solution of the E and G equations yields $B = 1.011$ and $A = 1102$. Because $\Delta E = -AR$, $\Delta E = -2190$ cal/mol. $\Delta V = -BRT$, which gives $\Delta V = -31\,300$ cm^3/mol. $\bar{P} = (0.5560 + 0.3853)/2 = 0.4707$ bar, giving $\bar{P}\Delta V = -350$ cal/mol. $\Delta H \approx \Delta E + \bar{P}\Delta V = -2190 - 350$ cal/mol ≈ -2540 cal/mol.

Table 1 lists ΔH, ΔE, ΔV, $\bar{P}$, and $\bar{P}\Delta V$ values. We emphasize once more that all thermodynamic quantities were calculated

TABLE 1: Thermodynamic Quantities Calculated from Simultaneous Equations for Large, *Charged*, Clusters in Water Vapor

pair	$\approx\Delta H$, cal/mol	ΔE, cal/mol	ΔV, cm^3/mol	$\bar{P}$, bar	$\bar{P}\Delta V$, cm^3 bar/mol
E,G	−2540	−2190	−31 300	0.4707	14 700
F,G	−2510	−2200	−29 700	0.4293	12 800
E,F	−2570	−2170	−32 900	0.5147	17 000
average	−2540	−2190	−31 300		

from most probable $\hat{C}$ values, corresponding to a given temperature and pressure. Hence, the thermodynamic values are properties averaged over the entire mass distribution, and cannot refer to specific structures and chemical reactions involving specific structures.

An important conclusion from Table 1 is that the ΔE and ΔV values are nearly constant (some deviations from exact constancy would be expected from experimental error).

We made one further calculation using one 100 °C data set, designated 1, with the 99 °C, E, data.[1] We used $\hat{C}_1 = 24.68$ and $P_1 = 0.3120$ bar. This yielded $\Delta E = -2190$ cal/mol and $\Delta V = -39\,500$ cm^3/mol. $\bar{P} = 0.4340$ bar and $\bar{P}\Delta V = -410$ cal/mol; hence $\Delta H \approx -2490$ cal/mol.

Two other 100 °C data sets were not sufficiently accurate to be used here.[1]

Comparisons with Raman Data

Numerous Raman measurements of liquid water give ΔH values for H-bond formation which occur in the vicinity of −2.5 kcal/mol H-bond.[2] An infrared determination gives $\Delta H = -2.4$ kcal/mol H-bond,[3] and thermodynamic analysis of viscosity data for liquid water gives −2.4 kcal/mol H-bond.[4]

$\Delta H \approx \Delta E$ for liquid water. Hence, we must compare the water ΔH values with the current ΔE values, i.e., −2.4 to −2.5 kcal/mol H-bond versus −2.2 kcal/mol, Table 1.

The agreement is close enough to indicate that the current ΔH, ΔE, and ΔV values refer to 1 mol of H-bonds.

Van't Hoff Treatment of Mass Spectral Data at Constant Partial Pressure of Water

Carlon and Harden[1] reported average, i.e., $\bar{C}$ values for a series of temperatures from 41 to 90 °C at a constant water partial pressure of 28.4 mmHg. These data were recast in terms of a van't Hoff plot, i.e., ln $\bar{C}$ versus $1/T$, and then treated by least squares. Ln K should be plotted versus $1/T$, instead of ln $\bar{C}$, but the partial derivative of $\ln(\bar{C}e^{\Delta S/R})$ with respect to $1/T$ at constant P gives the same ΔH as the corresponding derivative of K, when ΔS is a constant.

The van't Hoff plot is shown in Figure 1, where the slope corresponds to a ΔH of −2425 cal/mol H-bond, a value in excellent agreement with Raman,[2] with infrared,[3] and especially with viscosity, −2431 cal/mol H-bond,[4] data. We also emphasize that ΔH, *not* ΔE, is obtained in this case, as opposed to the simultaneous equation method which gives ΔE directly.

The Volume Change, ΔV

If ΔE refers to 1 mol of H-bonds, it follows that the corresponding ΔV must also refer to 1 mol of H-bonds. However, the ΔV values are large, $\approx -31\,300$ cm^3/ mol, and negative. Hence, an explanation of such large negative volume changes is required.

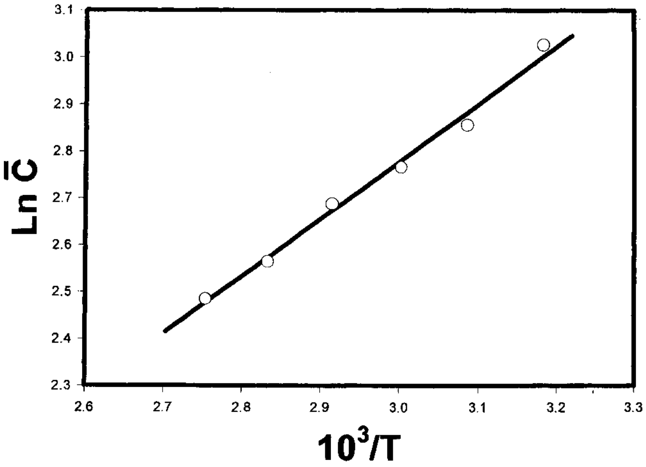

Figure 1. ln $\bar{C}$ versus l/T at constant pressure of 0.0379 bar taken from the data of Carlon and Harden;[1] see their Figure 10. The solid line is a least-squares fit of the data, the slope of which corresponds to an enthalpy change of −2431 cal/mol H-bond.

The H-bond volume change for formation in liquid water at 100 °C obtained from Raman data between 1 and 23 000 bar is $\Delta V = -1.2$ cm^3/mol H-bond.[4] Hence, the volume change for H-bond formation in the liquid is obviously not involved here. The ideal gas volume at 100 °C and 0.5 bar is 62 049 cm^3/mol, giving a ΔV of − 31 025 cm^3/mol H-bond, if we neglect the liquid volume, and divide the volume by 2; see below. Hence, the $\Delta V = -31\,300$ cm^3/mol H-bond obtained from the simultaneous equations must be related to (dominated by) condensation of gas monomers onto *charged* clusters.

A *measured* value for the volume of steam at 0.5 bar and 373.15 K is available, namely, 61 591 cm^3/mol H_2O.[10] The volume of liquid water at 373.15 K is about 18.8 cm^3/mol H_2O. Hence, $\Delta V = 18.8 - 61\,591 = -61\,572$ cm^3/mol H_2O, for condensation.

To put the ΔV of −61 572 cm^3/mol H_2O onto a per mole of H-bond basis, we ask the following question. What is the *maximum* number of moles of hydrogen bonds that 1 mol of monomeric water molecules can form from the gas phase, if they condense to a hypothetically completely hydrogen-bonded tetrahedral network as the condensed state? The answer is readily shown to be 2, since each of the four H-bonds surrounding a fully H-bonded water molecule is shared by another molecule. Hence, the ΔV of condensation must be divided by 2 to obtain the *limiting* value per mole of H-bond, namely, $\Delta V = -30\,790$ cm^3/mol H-bond.

The above ΔV refers to *maximum* H-bonding, but at 100 °C. We could use supercooled water or ice volumes, since many H-bonds are broken in the 100 °C liquid. If we use the density of ice, ≈19.7 cm^3/mol, we obtain a ΔV of −61 571 cm^3/mol H_2O, or $\Delta V = -30\,786$ cm^3/mol H-bond. The condensed state volume is clearly not very important when the ΔV is dominated by the gas volume.

The ΔV of this work is −31 300 ± 1000 cm^3/mol H-bond. The agreement with the calculated steam value of −30 790 cm^3/mol H-bond is excellent, and well within the accuracy of the mass spectral data. This agreement indicates that the condensation of water molecules from the vapor (at pressures from ≈0.385 to ≈0.556 bar at 372.15 K) onto large, *charged*, water clusters is closely related to the condensation of steam to the liquid, and it further suggests, when combined with the agreement between the cluster ΔE values and the Raman and infrared ΔH values, that the *most probable charged clusters* are extensively H-bonded.

We emphasize that the above statement about most probable clusters does not preclude the possibility of dangling OH bonds, and broken H-bonds, in small-mass clusters at the low-mass tail of the distribution. The following condensation reaction characterizes the thermodynamic quantities of this work:

$$H_2O_{(\text{monomeric gas})} = H_2O_{(\text{charged,H}-\text{bonded cluster})} \tag{8}$$

All thermodynamic quantities refer to eq 8, and all are on a (limiting) per mole of H-bond basis. In addition, all thermodynamic quantities refer, exclusively, to most probable cluster sizes.

Reaction Probability Ratio and Cluster Concentrations

The heat of vaporization of water at 100 °C and 1.0132 bar is 9717.5 cal/mol.[1] We use this value to approximate the entropy of condensation, roughly, at 99 °C and 0.5560 bar before calculating the equilibrium constant from $K = \hat{C}e^{\Delta S/R}$, using $\hat{C}_E = 33.94$. The ΔS of condensation (corrected to 0.5 bar) is ≈ -27.42 cal/deg·mol H_2O, or after division by 2 (as done previously for ΔV), $\Delta S \approx -13.71$ cal/deg·mol H-bond. The reaction probability ratio is thus $e^{\Delta S/R} = 1.01 \times 10^{-3}$, which when multiplied by 33.94 gives $K = 0.034$, i.e, $\approx 3\%$. This result gives the correct magnitude for the cluster concentration, as stated in the Introduction and in ref 1.

The exponential term $e^{\Delta S/R}$ equals $\Pi_{\text{liquid}}/\Pi_{\text{vapor}}$, where the subscript "liquid" here refers to the charged clusters. This probability ratio is the concentration of charged clusters (moles of most probable sized clusters/liter) divided by the monomer concentration. When the probability ratio is multiplied by the ratio, e.g., $M_{H_2O}C_E/[M_{H_2O}(C_1=1)]$, where M is the molecular weight, it gives the mass of the charged clusters for the most probable species divided by the mass of the monomers in the vapor. This is so because $C_E \times$ (concentration, moles per liter, of charged clusters) gives the number of moles per liter on a monomer basis for the water in the charged clusters. K so calculated is 0.034 for $\hat{C}_E = 33.94$.

The β source increases the charged cluster concentration above the value before ionization; hence, we conclude that the neutral cluster condensation in steam at 99 °C is less than 3%, in agreement with ref 1.

The ΔV and ΔS values used thus far, taken from ref 10, for steam and water refer to the condensation of the vapor to the liquid to form 1 mol of H-bonds; i.e., both values per mole of H_2O were divided by 2.

Let us now apply the same type of thermodynamic formulation, used for water vapor and *charged* water clusters, to steam and pure liquid water. This is a *new application* to saturated steam; it has absolutely *no* bearing, whatsoever, on the case of monomeric water condensing on charged clusters, discussed above.

It is easily shown from $\Delta H/T = \Delta S$, $\Delta H = \Delta E + P\Delta V$, and $P_{HB} = P_{\text{cond}}$, that

$$\ln K = \Delta E_{\text{cond}}/RT - \Delta E_{HB}/RT \tag{9}$$

or that

$$K = \exp(\Delta E_{\text{cond}}/RT)/\exp(\Delta E_{HB}/RT) \tag{10}$$

where "cond" refers to the energy change of condensation, "HB" refers to formation of H-bonds, P_{HB} is the pressure at which the H-bonds were formed, eq 1, and where both energy changes are on a *1 mol of H-bond* basis.

It is obvious from eq 10 that the low amount of water involved in *neutral* clustering at 99 °C [1] (again there is no reference, whatsoever, to monomers condensing on charged clusters, discussed above) results from the fact that the energy of condensation per mole of H-bond divided by RT is a larger negative number than the energy of H-bond formation divided by RT. However, the negative energy of condensation should decrease faster with rising temperature than the negative energy of H-bond formation, and must go to zero at the critical point, as the H-bond energy also goes to zero. This condition should lead to $K = C \approx 1$ at the critical point, in agreement with a recent conclusion.[11]

Relation of Charged Water Vapor Clusters to Liquid Water

The van't Hoff H-bond ΔH value of this work (see Figure 1) for charged water clusters, $\Delta H = -2425$ cal/mol H-bond, is in very close agreement with H-bond ΔH values obtained from liquid water. The water value from viscosity data, $\Delta H = -2431$ cal/mol H-bond,[4] is regarded by us to be more accurate than our Raman values, and it is virtually the same as the near-infrared value of Worley and Klotz.[3]

In addition to ΔH agreements, the large, charged, H-bonded water vapor clusters involved here would certainly sustain O−O−O bending, O−O restricted translations, and H_2O librations similar in frequency to those which occur in liquid water,[12] despite the fact that a proton is involved in the charged clusters.

Hence, there are similarities between the nearest-neighbor energy and frequency properties of large, charged, water vapor clusters and liquid water.

Two Caveats

(1) The stabilizaton, i.e., lowering of energy, involved in adding water molecules to a protonated water cluster containing, say, 24 water molecules, was measured here; in contrast, the energy change in adding water molecules to a *neutral* water cluster was definitely *not* measured. We strongly emphasize, therefore, that the latter should *not* be considered to be quantitatively the same as the former, despite the several close ΔE and ΔH comparisons described in the text. The presence of a proton in a water cluster of the sizes involved in this work should have the effect of strengthening the H-bonds throughout the cluster, a strengthening which cannot exist in a neutral water cluster of the same size.

(2) We divided H-bond energies per mole of H_2O by a factor of 2 to obtain the H-bond energy per mole of H-bond. This procedure yields a *limiting value*. This limit refers to the fact that a hypothetically perfect, and completely H-bonded, tetrahedral network composed of water molecules has two H-bonds per water molecule. (Liquid water under ambient conditions has less than two H-bonds per water molecule because some of the H-bonds are broken, e.g., at 25 °C and 1 atm pressure. However, this latter consideration is totally irrelevant as far as the limiting value is concerned.) We next observed that the ΔV values calculated in this work agree, within their experimental uncertainties, with the ΔV calculated from the condensation of the real water vapor, when divided by 2, for conversion to a per mole of H-bond basis. This suggests considerable H-bonding in the charged clusters. However, complete H-bonding (unlikely) could only be inferred if the two ΔV values were precisely identical, a condition which does not exist here because of the experimental uncertainties.

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