

Modified Kelvin–Thomson equation considering ion-dipole interaction: Comparison with observed ion-clustering enthalpies and entropies

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The classical Kelvin–Thomson (CKT) equation does not consider the interaction of condensing molecules with the ions and hence is not able to treat polar and nonpolar molecules differently. The ion-clustering enthalpy and entropy changes predicted by CKT equation for small ions are known to be significantly less negative than those observed. In this paper, we derive a modified Kelvin–Thomson (MKT) equation, which considers the effect of dipole-ion interaction, by taking into account the kinetic energy change of condensing polar ligands as they approach the ions or the extra energy needed for dipole molecules to escape from the ion cluster. The clustering enthalpies and entropies for protonated clusters (H^+L_n , with $L=H_2O$, NH_3 , CH_3OH , and C_5H_5N) are calculated based on MKT equation and compared with experimental data. Our calculations indicate that enthalpy values given by MKT equation are in very good agreement with experimental results for small ions ($n \leq 5$) of all four species investigated. MKT predictions appear to be consistent with observed enthalpies for CH_3OH at $n \geq 6$ and for H_2O at $n=14-25$, however, MKT equation cannot reproduce the observed discontinuous transition in enthalpy changes at $n=6$ for NH_3 and at $n=7-13$ for H_2O which is probably associated with the formation of inner shell. The stepwise entropy changes for small ions are $5-15 \text{ cal mol}^{-1} \text{ K}^{-1}$ more negative when the effect of dipole-ion interaction is considered, which suggests that the ordered structure of the cluster ions can somewhat be accounted for by the dipole-ion interaction term. © 2005 American Institute of Physics. [DOI: 10.1063/1.1845395]

I. INTRODUCTION

Thomson¹ first showed that the presence of a charge on a droplet diminishes the evaporation tendency of the droplet because the electrostatic potential energy of the droplet increases as the droplet evaporates and more work has to be available to evaporate the charged droplet than it is neutral. The Thomson effect is opposite to the well-known Kelvin effect associated with surface tension which enhances the evaporation tendency of the droplet. Thomson² derived an equation describing the equilibrium vapor pressure over a charged droplet of given radius, which is widely known as Kelvin–Thomson equation (or Thomson equation) in the literature. The classical Kelvin–Thomson (CKT) equation has been the fundamental of the classical ion-induced nucleation theory²⁻⁶ as well as the basic theoretical tools used to analyze the experimental thermodynamic data of ion clusters.⁷⁻⁹

The thermodynamic data about the clustering of ligand molecules (including H_2O , NH_3 , CH_3OH , and C_5H_5N) with small ions have been used to assess the validity of the Kelvin–Thomson's charged liquid drop approximation of small ion clusters.⁸ It was found that, for small ion clusters, the experimental enthalpy values are up to 20 kcal mol^{-1} more negative than those predicted by CKT equation and the experimental entropy values are systematically $5-20 \text{ cal mol}^{-1} \text{ K}^{-1}$ more negative than the predicted ones.⁸ Holland and Castleman⁸ suggested that a fundamental incon-

sistency exists between the general form of the CKT expression and the properties of small cluster ions. To overcome the inconsistency, D'Auria and Turco¹⁰ applied a hybrid thermodynamical/kinetic model to study the ion cluster size distribution in the polar winter stratosphere. In the hybrid model, enthalpies and entropies are taken from experimental data for the smaller clusters but are derived from CKT equation for larger clusters.

Mäkelä *et al.*⁹ compared the diameters of ion clusters inferred from the measured mobility with the diameters calculated from CKT equation and found that Kelvin–Thomson diameters of ions are systematically smaller than the corresponding mobility equivalent diameters. It has been shown recently that this discrepancy is probably due to the dipole-charge interaction of ions with dipole ligands neglected in CKT equation.¹¹ Nadykto *et al.*¹¹ derived the dipole-charge interaction term by considering the forcing acting on the gaseous dielectric in the vicinity of the charge and the enhancement of the number concentration of polar molecules in the vicinity of the charged clusters due to dipole-charge interaction. More recently, Nadykto and Yu¹² applied a new ion nucleation model which considers the dipole-charge interaction effect to analyze the ion nucleation measurements reported by He and Hopke,¹³ and found that dipole-charge interaction term is critical to explain the observed dependence of reduced critical supersaturation on temperature.

In this paper, we demonstrate the effect of dipole-ion interaction and derive the modified Kelvin–Thomson (MKT) equation in an approach that is different from our earlier

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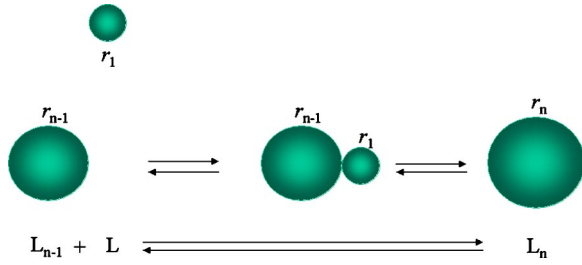


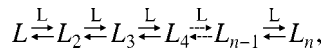
FIG. 1. A liquid droplet model representation of the clustering or dissociation processes between $(n-1)$ -mers and n -mers. L is the clustering ligand or monomer.

derivation.¹¹ We then apply the MKT equation to calculate the stepwise enthalpy and entropy changes for small ion-clustering reactions and compare them with the experimental results obtained in earlier ion-clustering investigations.

II. MODIFIED KELVIN–THOMSON EQUATION ACCOUNTING FOR ION-DIPOLE INTERACTION

A. Kelvin equation

The following series of clustering reactions lead to the formation of neutral clusters containing n ligands (n -mers):



where L represents the clustering ligand. In the liquid droplet model, n -mers ($n=1, 2, 3, \dots$) are treated as a liquid droplet of radius

$$r_n = \left(\frac{3nM}{4\pi N_A \rho} \right)^{1/3}, \quad (1)$$

where M and ρ are the molecular weight and the bulk density of the liquid. N_A is Avogadro's number. Figure 1 shows schematically a liquid droplet model representation of the clustering of monomers L with $(n-1)$ -mers to form n -mers or evaporation of monomer from n -mers to form $(n-1)$ -mers.

Based on the liquid droplet model, the Gibbs free energy change for monomers L clustering with $(n-1)$ -mers to form n -mers is

$$\begin{aligned} \Delta G_{n-1,n}^{\text{neutral}} &= -kT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \sigma(A_n - A_{n-1}) \\ &= -kT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \sigma 4\pi r_{n-1}^2 \left[\left(1 + \frac{1}{n-1} \right)^{2/3} - 1 \right], \end{aligned} \quad (2)$$

where p is the vapor pressure of the gas ligands (monomers) and p_{sat} is the gas saturation vapor pressure over the flat surface. σ is the surface tension of the liquid and A_n is the surface area of the n -mer droplet. k is Boltzmann's constant and T is the temperature.

The equilibrium vapor pressure over a cluster or the size of the critical cluster ($r^* = r_{n-1}$) can be decided by letting $\Delta G_{n-1,n}^{\text{neutral}} = 0$,

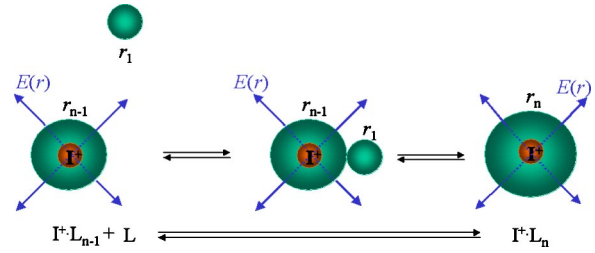


FIG. 2. A liquid droplet model representation of the clustering of a monomer L with a charged $(n-1)$ -mer to form a charged n -mer and the dissociation of a monomer L from a charged n -mer to form a charged $(n-1)$ -mer. Core ion I^+ has radius of r_0 . $E(r)$ is the electric field strength at a distance r from the center of the core ion.

$$-kT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \sigma 4\pi r_{n-1}^2 \left[\left(1 + \frac{1}{n-1} \right)^{2/3} - 1 \right] = 0. \quad (3)$$

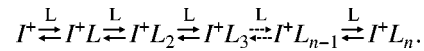
When $n \gg 1$, $[1 + 1/(n-1)]^{2/3} - 1 = 2/[3(n-1)] = M/[2\pi r_{n-1}^3 N_A \rho]$, then Eq. (3) becomes

$$-kT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \frac{2\sigma M}{N_A \rho r^*} = 0. \quad (4)$$

Equation (4) is the well-known Kelvin equation which is valid when the clusters are big ($n \gg 1$). For small clusters ($n \leq 10$), Eq. (3) is more accurate.

B. Classical Kelvin–Thomson equation

The following series of forward and reverse reactions lead to the formation of ion clusters containing n ligands (charged n -mers) from a core ion I^+ (or I^-):



In the liquid droplet model, charged n -mers ($n=1, 2, 3, \dots$) are treated as a liquid droplet of radius,

$$r_n = \left(r_0^3 + \frac{3nM}{4\pi N_A \rho} \right)^{1/3}, \quad (5)$$

where r_0 is the radius of core ion I^+ . Figure 2 illustrates schematically a liquid droplet model representation of the clustering of a monomer L with a charged $(n-1)$ -mer to form a charged n -mer and the dissociation of a monomer L from a charged n -mer to form a charged $(n-1)$ -mer.

A charged n -mer formed on a core ion of radius r_0 has an electrostatic potential energy of

$$P_n = \frac{(qe)^2}{8\pi\epsilon_0 r_n} + \frac{(qe)^2}{8\pi\epsilon_0 \epsilon_l} \left(\frac{1}{r_0} - \frac{1}{r_n} \right), \quad (6)$$

where e is the elementary charge and q is the number of charge carried by the ion. ϵ_0 is the vacuum permittivity and ϵ_l is the relative permittivity of bulk liquid. When a charged $(n-1)$ -mer become a charged n -mer after clustering with a monomer L , its electrostatic potential energy changes by

$$\Delta P_{n-1,n} = P_n - P_{n-1} = -\frac{(qe)^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_l} \right) \left(\frac{1}{r_{n-1}} - \frac{1}{r_n} \right). \quad (7)$$

Thus, the Gibbs free energy change to form a charged n -mer from a charged $(n-1)$ -mer is

$$\begin{aligned}\Delta G_{n-1,n}^{\text{charged}} &= \Delta G_{n-1,n}^{\text{neutral}} + \Delta P_{n-1,n} \\ &= -kT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \sigma 4\pi (r_n^2 - r_{n-1}^2) \\ &\quad - \frac{(qe)^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_l} \right) \left(\frac{1}{r_{n-1}} - \frac{1}{r_n} \right).\end{aligned}\quad (8)$$

The equilibrium vapor pressure over an ion cluster or the size of critical ion cluster ($r^* = r_{n-1}$) can be decided by letting $\Delta G_{n-1,n}^{\text{charged}} = 0$:

$$\begin{aligned}-kT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \sigma 4\pi r_{n-1}^2 \left[\left(\frac{r_n}{r_{n-1}} \right)^2 - 1 \right] \\ - \frac{(qe)^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_l} \right) \frac{1}{r_{n-1}} \left(1 - \frac{r_{n-1}}{r_n} \right) = 0.\end{aligned}\quad (9)$$

For relative large ion clusters (i.e., $n \gg 1$),

$$\left(\frac{r_n}{r_{n-1}} \right)^2 - 1 \approx \left(\frac{n}{n-1} \right)^{2/3} - 1 \approx \frac{2}{3(n-1)} = \frac{M}{2\pi r_{n-1}^3 N_A \rho},\quad (10)$$

$$1 - \frac{r_{n-1}}{r_n} \approx \frac{1}{3(n-1)} = \frac{M}{4\pi r_{n-1}^3 N_A \rho}.\quad (11)$$

Applying Eqs. (10) and (11) to Eq. (9) and noting $r^* = r_{n-1}$, we get

$$kT \ln \left(\frac{p}{p_{\text{sat}}} \right) = \frac{2\sigma M}{N_A \rho r^*} - \frac{(qe)^2 M}{32\pi^2 \epsilon_0 N_A \rho (r^*)^4} \left(1 - \frac{1}{\epsilon_l} \right).\quad (12)$$

Equation (12) is the well-known CKT equation² which is valid when the ion cluster is large ($n \gg 1$). When the ion clusters are small ($n \leq 10$), Eq. (9) is more appropriate as the change in the radius is discrete rather than continuous.

The total free energy change to form a charged n -mer from the core ion of radius r_0 is

$$\begin{aligned}\Delta G_{0,n}^{\text{charged}} &= \sum_{n=1}^n \Delta G_{n-1,n}^{\text{charged}} \\ &= -nkT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \sigma 4\pi (r_n^2 - r_0^2) - \frac{(qe)^2}{8\pi\epsilon_0} \\ &\quad \times \left(1 - \frac{1}{\epsilon_l} \right) \left(\frac{1}{r_0} - \frac{1}{r_n} \right).\end{aligned}\quad (13)$$

When $r_n \gg r_0$, Eq. (13) becomes

$$\begin{aligned}\Delta G_{0,n}^{\text{charged}} &= -nkT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \sigma 4\pi r_n^2 - \frac{(qe)^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_l} \right) \\ &\quad \times \left(\frac{1}{r_0} - \frac{1}{r_n} \right).\end{aligned}\quad (14)$$

Equation (14) is the widely used CKT equation for total Gibbs free energy change to form an ion cluster containing n ligands from a core ion.

C. Modified Kelvin–Thomson equation

In the derivation of CKT equation shown in Sec. II B it is implied that the kinetic energy of the monomer ligand (or ion-ligand system) does not change when it moves from a distance far away from ion clusters to the vicinity of ion clusters. This approximation is valid when the clustering ligand is nonpolar or the radius of the ion cluster is large. However, when a polar molecule approaches a small ion clusters, it experiences electric force in the strong electric field in the vicinity of small ion clusters and thus its kinetic energy may increase significantly. Since the collision of ligand with ion cluster is inelastic, the extra kinetic energy of the ligand-cluster system is converted to another form of energy upon collision. It is necessary to take into account this extra kinetic energy in calculating the free energy change for the formation of small charged clusters. The necessity to account for the ion-dipole interaction is also clear as extra energy is needed for a polar ligand to overcome the electric force and move away from the ion cluster (i.e., evaporation).

The electric force a polar molecule experienced in the electric field of an ion cluster (see Fig. 2) is

$$F = \vec{\mu}_p \cdot \frac{d\vec{E}}{dr} + \vec{\mu}_0 \cdot \frac{d\vec{E}}{dr} = \alpha E \frac{dE}{dr} + \mu_0 \cos \theta \frac{dE}{dr},\quad (15)$$

where $\vec{\mu}_p = \alpha \vec{E}$ is the induced dipole moment vector, α is the polarizability of the clustering specie. $E = qe / (4\pi\epsilon_0 r^2)$ is the electric field strength at a distance r from the center of ion cluster. μ_0 is the permanent dipole moment of the clustering molecule. θ is the angle between the electric field vector and the direction of the dipole.

The probability of a polar molecule forming an angle of θ between the direction of its dipole and the electric field vector depends on $\mu_0 E \cos \theta$ as well as the kinetic energy of agitation.¹⁴ The average value of $\cos \theta$ can be found as,¹⁴

$$\begin{aligned}\frac{\int_0^\pi \exp\left(\frac{\mu_0 E \cos \theta}{kT}\right) \cos \theta 2\pi \sin \theta d\theta}{\int_0^\pi \exp\left(\frac{\mu_0 E \cos \theta}{kT}\right) 2\pi \sin \theta d\theta} \\ = \frac{\exp(z) + \exp(-z)}{\exp(z) - \exp(-z)} - \frac{1}{z} = L(z),\end{aligned}\quad (16)$$

where $z = \mu_0 E / kT$ and $L(z)$ is the Langevin function.

We assume that the polar molecule has the average kinetic energy when it is one mean free path λ away from the ion cluster. The kinetic energy change of the polar molecule when it moves from $r = \lambda$ to $r = r_{n-1} + r_1$ [i.e., the surface of the charged $(n-1)$ -mer, see Fig. 2] is

$$\Delta U = \int_{\lambda}^{r_{n-1}+r_1} F dr = \left[\frac{1}{2} \alpha E^2 + kT \ln \left(\frac{\exp\left(\frac{\mu_0 E_{n-1}}{kT}\right) - \exp\left(-\frac{\mu_0 E_{n-1}}{kT}\right)}{2 \frac{\mu_0 E_{n-1}}{kT}} \right) \right]_{\lambda}^{r_{n-1}+r_1} = \Phi(r_{n-1} + r_1) - \Phi(\lambda), \quad (17)$$

where

$$\Phi(r) = \frac{1}{2} \alpha E^2 + kT \ln \left\{ \left[\exp\left(\frac{\mu_0 E_{n-1}}{kT}\right) - \exp\left(-\frac{\mu_0 E_{n-1}}{kT}\right) \right] / \left(2 \frac{\mu_0 E_{n-1}}{kT} \right) \right\}.$$

Under typical ambient pressure and for the ion radius of our interest $r_{n-1} + r_1 \ll \lambda$ and $\Phi(r_{n-1} + r_1) \ll \Phi(\lambda)$, and thus we have

$$\Delta U = \Phi(r_{n-1} + r_1) = \frac{1}{2} \alpha E_{n-1}^2 + kT \ln \left(\frac{\exp\left(\frac{\mu_0 E_{n-1}}{kT}\right) - \exp\left(-\frac{\mu_0 E_{n-1}}{kT}\right)}{2 \frac{\mu_0 E_{n-1}}{kT}} \right), \quad (18)$$

where

$$E_{n-1} = \frac{qe}{4\pi\epsilon_0(r_{n-1} + r_1)^2} \quad (19)$$

is the electric field strength at $r = r_{n-1} + r_1$ from the center of core ion.

It is clear that the polar molecules obtain extra kinetic energy when they approach the ion clusters as a result of the dipole-ion interaction. In other words, for a polar molecule to escape from the surface of ion clusters, extra energy is needed to overcome the electric force. Thus, dipole-charge interaction diminishes the tendency of the charged cluster (or droplet) to evaporate, which is opposite to the Kelvin surface tension effect.

When the effect of dipole-charge interaction is considered, the Gibbs free energy change to form a charged n -mer from a charged $(n-1)$ -mer becomes

$$\begin{aligned} \Delta G_{n-1,n}^{\text{dipole}} = \Delta G_{n-1,n}^{\text{charged}} - \Delta U = \Delta G_{n-1,n}^{\text{neutral}} + \Delta P_{n-1,n} - \Phi(r_{n-1} + r_1) = & -kT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \sigma 4\pi(r_n^2 - r_{n-1}^2) \\ & - \frac{e^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_l} \right) \left(\frac{1}{r_{n-1}} - \frac{1}{r_n} \right) - \frac{1}{2} \alpha E_{n-1}^2 - kT \ln \left(\frac{\exp\left(\frac{\mu_0 E_{n-1}}{kT}\right) - \exp\left(-\frac{\mu_0 E_{n-1}}{kT}\right)}{2 \frac{\mu_0 E_{n-1}}{kT}} \right). \end{aligned} \quad (20)$$

The total free energy change to form a charged n -mer from the core ion of radius r_0 is

$$\begin{aligned} \Delta G_{0,n}^{\text{dipole}} = \sum_{n=1}^n \Delta G_{n-1,n}^{\text{dipole}} = \Delta G_{0,n}^{\text{charged}} - \sum_{n=1}^n \Delta U = & -nkT \ln \left(\frac{p}{p_{\text{sat}}} \right) + \sigma 4\pi(r_n^2 - r_0^2) - \frac{e^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_l} \right) \left(\frac{1}{r_0} - \frac{1}{r_n} \right) \\ & - \sum_{n=1}^n \left\{ \frac{1}{2} \alpha E_{n-1}^2 + kT \ln \left[\frac{\exp\left(\frac{\mu_0 E_{n-1}}{kT}\right) - \exp\left(-\frac{\mu_0 E_{n-1}}{kT}\right)}{2 \frac{\mu_0 E_{n-1}}{kT}} \right] \right\}. \end{aligned} \quad (21)$$

Equation (21) contains four terms. The first term represents the change in the free energy as a result of the condensation of n ligands at supersaturation ratio p/p_{sat} . The second term is the work done in changing the surface area. The third term gives the change in electric potential energy of the ion due to the condensation of dielectric film about the ion. The final term accounts for the energy change associated with the interaction of the core ion with the condensing dipole molecules.

The size of critical ion cluster ($r^* = r_{n-1}$) or the equilibrium vapor pressure of dipole gas molecules over an ion cluster can be decided by letting $\Delta G_{n-1,n}^{\text{dipole}} = 0$,

$$kT \ln\left(\frac{p}{p_{sat}}\right) = \sigma 4\pi(r_n^2 - r_{n-1}^2) - \frac{e^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_l}\right) \\ \times \left(\frac{1}{r_{n-1}} - \frac{1}{r_n}\right) - \frac{1}{2}\alpha E_{n-1}^2 - kT \ln\left(\frac{\exp\left(\frac{\mu_0 E_{n-1}}{kT}\right) - \exp\left(-\frac{\mu_0 E_{n-1}}{kT}\right)}{2\frac{\mu_0 E_{n-1}}{kT}}\right). \quad (22)$$

Equation (22) is the MKT equation that takes into account the effect of dipole-ion interaction. When $n \gg 1$, $r^* = r_{n-1} \gg r_1$ (relative large ion clusters), Eq. (22) becomes

$$kT \ln\left(\frac{p}{p_{sat}}\right) = \frac{2\sigma M}{N_A \rho r^*} - \frac{(qe)^2 M}{32\pi^2 \epsilon_0 N_A \rho (r^*)^4} \left(1 - \frac{1}{\epsilon_l}\right) - \frac{\alpha(qe)^2}{32\pi^2 \epsilon_0^2 (r^*)^4} \\ - kT \ln\left(\frac{\exp\left(\frac{\mu_0 qe}{4\pi\epsilon_0 (r^*)^2 kT}\right) - \exp\left(-\frac{\mu_0 qe}{4\pi\epsilon_0 (r^*)^2 kT}\right)}{2\frac{\mu_0 qe}{4\pi\epsilon_0 (r^*)^2 kT}}\right). \quad (23)$$

It is obvious from Eq. (23) that the dipole-charge interaction reduces the supersaturation needed to maintain the equilibrium of an ion cluster of given size. Equation (23) is almost identical to the equation we derived earlier [Eq. (21) in Ref. 11] although they are derived in different approaches that are based on different physics. Equation (23) is valid at large n and for small clusters Eq. (22) should be used.

D. Enthalpy and entropy changes for ion-clustering reactions

Equation (20) gives the stepwise Gibbs free energy change per molecule. The stepwise Gibbs free energy change per mole under the standard pressure (i.e., $p=p^0=1$ atm) is given by

$$\Delta G_{n-1,n}^0 = RT \ln p_{sat} + N_A \sigma 4\pi(r_n^2 - r_{n-1}^2) \\ - N_A \frac{(qe)^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_l}\right) \left(\frac{1}{r_{n-1}} - \frac{1}{r_n}\right) - \frac{1}{2} N_A \alpha E_{n-1}^2 \\ - RT \ln\left(\frac{\exp\left(\frac{\mu_0 E_{n-1}}{kT}\right) - \exp\left(-\frac{\mu_0 E_{n-1}}{kT}\right)}{2\frac{\mu_0 E_{n-1}}{kT}}\right), \quad (24)$$

where p_{sat} is the saturation vapor pressure (in atm) of the condensing ligands at the temperature of the system (over flat surface). $R=kN_A$ is the gas constant.

Differentiation of Eq. (24) with respect to T gives an expression for the stepwise standard entropy change

$$-\Delta S_{n-1,n}^0 = \frac{d(\Delta G_{n-1,n}^0)}{dT} = \text{term1} + \text{term2} + \text{term3} + \text{term4} \\ + \text{term5}, \quad (25)$$

where

$$\text{term1} = R \ln p_{sat} + RT \frac{d(\ln p_{sat})}{dT}, \\ \text{term2} = 4\pi N_A (r_n^2 - r_{n-1}^2) \frac{d\sigma}{dT} - \frac{2\sigma M}{\rho^2} \left(\frac{n}{r_n} - \frac{n-1}{r_{n-1}}\right) \frac{d\rho}{dT}, \\ \text{term3} = -N_A \frac{(qe)^2}{8\pi\epsilon_0} \left[\left(\frac{1}{r_{n-1}} - \frac{1}{r_n}\right) \frac{1}{\epsilon_l^2} \frac{d\epsilon_l}{dT} + \left(1 - \frac{1}{\epsilon_l}\right) \right. \\ \left. \times \left(\frac{n-1}{r_{n-1}^4} - \frac{n}{r_n^4}\right) \frac{M}{4\pi N_A \rho^2} \frac{d\rho}{dT} \right], \\ \text{term4} = -\frac{1}{2} N_A E_{n-1}^2 \left[\frac{d\alpha}{dT} + \alpha \frac{(n-1)M}{\pi N_A r_{n-1}^2 (r_{n-1} + r_1) \rho^2} \frac{d\rho}{dT} \right], \\ \text{term5} = -R \ln\left(\frac{\exp(x) - \exp(-x)}{2x}\right) + RL(x)x - RTL(x) \\ \times \left[\frac{1}{\mu_0} \frac{d\mu_0}{dT} + \frac{(n-1)M}{2\pi N_A r_{n-1}^2 (r_{n-1} + r_1) \rho^2} \frac{d\rho}{dT} \right], \\ x = \frac{\mu_0 E_{n-1}}{kT}.$$

The stepwise standard enthalpy change can then be obtained with the following thermodynamic relation:

$$\Delta H_{n-1,n}^0 = \Delta G_{n-1,n}^0 + T\Delta S_{n-1,n}^0. \quad (26)$$

III. COMPARISONS WITH LABORATORY MEASUREMENTS

The stepwise free energy $\Delta G_{n-1,n}^0$, enthalpies $\Delta H_{n-1,n}^0$, and entropies $\Delta S_{n-1,n}^0$ for the ion-clustering reactions ($I^+L_{n-1} + L \rightarrow I^+L_n$) can be determined from the measured temperature dependence of reaction equilibrium constants (i.e., van't Hoff's analysis). Various experimental results on

TABLE I. Parameters used in calculating the stepwise enthalpy and entropy changes for water (H₂O), methanol (CH₃OH), ammonia (NH₃), and pyridine (C₅H₅N). α and μ_0 from *Handbook of Chemistry and Physics* (Ref. 26). All other parameters are from the table compiled by Holland and Castleman (Ref. 8).

Parameters	Water	Methanol	Ammonia	Pyridine
T (K)	313.15	293.15	233.15	353.15
M (g mol ⁻¹)	18.015	32.04	17.031	79.1
σ (ergs/cm ²)	69.56	22.61	35.46	29.3
$d\sigma/dT$	-0.1635	-0.086	-0.25	-0.1425
ε_l	73.15	33.7	22.1	10.6
$d\varepsilon_l/dT$	-0.335	-0.19	-0.1	-0.033
ρ (g/cm ³)	0.99224	0.7916	0.69	0.9211
$d\rho/dT$	-0.00038	-0.00094	-0.00097	-0.00103
$\ln(p_{sat})$ (p_{sat} in atm)	-2.62	-2.149	-0.34489	-1.1591
$d \ln(p_{sat})/dT$	0.053	0.05224	0.05357	0.03893
α (Å ³)	1.45	5.26	2.31	9.5
μ_0 (D)	1.854	1.69	1.46	2.19

the clustering thermochemistry of different ligand molecules about protonated molecules or metal ions have been reported in the literature.^{15–25} In this study, we focus on the protonated clusters H⁺L_{*n*} with L=H₂O, NH₃, CH₃OH, and C₅H₅N.

In order to calculate $\Delta S_{n-1,n}^0$ using the MKT equation (25), the data on the temperature dependence of p_{sat} , σ , ε_l , ρ , α , μ_0 have to be known. We use the values of p_{sat} , σ , ε_l , and ρ at a given temperature for H₂O, NH₃, CH₃OH, and C₅H₅N and the temperature dependence data of these parameters compiled by Holland and Castleman⁸ (Table I). We are not able to find the data about $d\alpha/dT$ and $d\mu_0/dT$. $d\alpha/dT$ values estimated based on Clausius–Mosotti equation are used in this study. $d\mu_0/dT$ term is not included in our calculation. The contribution of $d\mu_0/dT$ term to $\Delta S_{n-1,n}^0$ is likely to be small.

Figure 3 shows the stepwise enthalpy changes for the clustering of four different ligands (L=H₂O, CH₃OH, NH₃, and C₅H₅N) about H⁺L_{*n-1*} ions. The symbols are the experimental values from various measurements. The dashed lines

are the predictions based on CKT equation⁸ and the solid lines represent the calculations based on the MKT equation. The rectangle bar on the right of each panel indicates the enthalpy of vaporization for the specie at the given temperature (data from *Handbook of Chemistry and Physics*²⁶). It is clear that the measured $\Delta H_{n-1,n}^0$ at $n=2$ are consistently about 15 kcal/mol more negative than those predicted by CKT equation. The difference between measured results and CKT predictions decreases as n increases and is around 3–6 kcal mol⁻¹ at $n=5$. MKT gives very good agreement with observed values for small ions ($n \leq 5$) of all four species. For relative large clusters ($n \geq 6$), MKT values appear to be consistent with observed ones for CH₃OH. The MKT predicted value at $n=6$ for NH₃ is a few kcal/mol more negative than the observed ones but there is no data available at $n > 6$ for comparison with the predictions.

The measurements at larger n are available for H₂O and Fig. 3(a) shows that $-\Delta H_{n-1,n}^0$ for H₂O has a minimum at $n=9$. MKT predicts a smooth and continuous change of $\Delta H_{n-1,n}^0$ as n increase but the observed values have a discontinuous transition at $n=6$ for NH₃ and $n=7–13$ for H₂O. Such a discontinuous transition is probably associated with the formation of inner shell.^{8,16} The liquid droplet approximation is not able to account for the formation of a stable and compact inner shell which forces the additional ligand molecule into an outer position and causes the discontinuous transition. It is interesting to note that the observed $-\Delta H_{n-1,n}^0$ for H₂O increases with n at $n > 9$ and approaches the MKT predicted values at $n > 13$. The observed $-\Delta H_{n-1,n}^0$ decreases again at $n=25$ which is probably associated with another shell formation. The effect of ions diminishes significantly as n increase, and Fig. 3 shows that both CKT and MKT values converge to bulk heat of vaporization at larger cluster sizes for all four species.

Figure 4 shows the stepwise entropy changes corresponding to the species shown in Fig. 3. Compared to the measured enthalpy values, the observed entropy values are

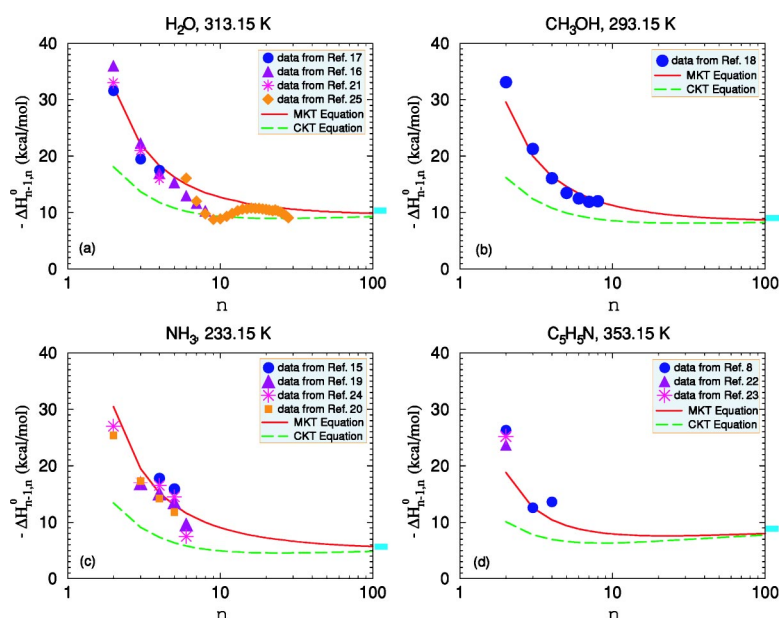


FIG. 3. Standard stepwise enthalpy changes for the clustering of four different ligands about H⁺L_{*n-1*} ions: (a) H₂O, (b) CH₃OH, (c) NH₃, and (d) C₅H₅N. The symbols are the experimental values from various measurements. The dashed lines are the predictions based on classical Kelvin–Thomson (CKT) equation (Ref. 8) and the solid lines represent the calculations based on the modified Kelvin–Thomson (MKT) equation presented in this paper. The rectangle bar on the right of each panel indicates the enthalpy of vaporization for the specie at the given temperature.

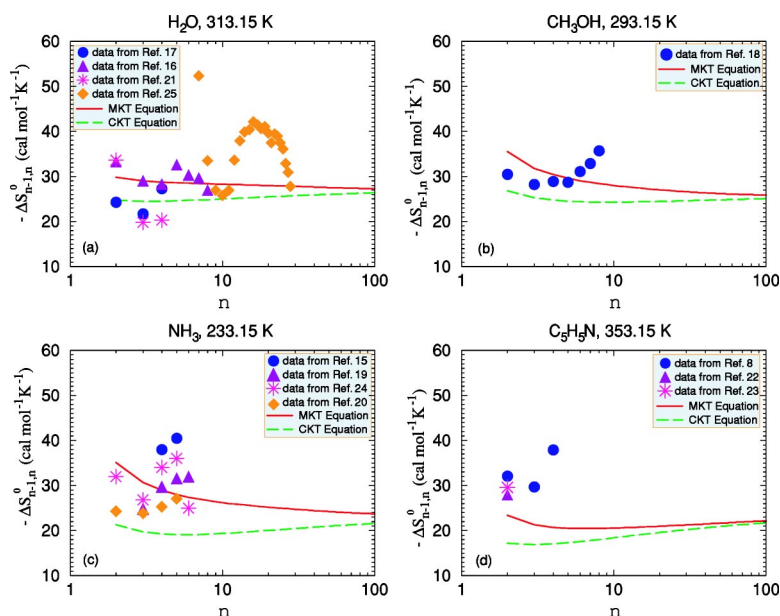


FIG. 4. Standard stepwise entropy changes corresponding to the species shown in Fig. 3.

widely scattered and do not follow a simple trend as n increases. There are two possible reasons for this.

(1) Observed entropy values are subject to a combined experimental error as they are obtained from the difference of two large terms ($\Delta G_{n-1,n}^0$ and $\Delta H_{n-1,n}^0$) (Ref. 16).

(2) The structure of small clusters changes significantly upon addition of a ligand.⁸

Nevertheless, it is obvious from Fig. 4 that CKT systematically underestimates the entropy changes (up to ~ 15 cal mol⁻¹ K⁻¹). Holland and Castleman⁸ have contributed the difference to a more ordered structure (orientation of ligand molecules about the ion) than can be accounted for by the CKT equation. Figure 4 indicates that MKT predictions are in a better agreement with experimental data than the CKT predictions, though MKT equation still cannot reproduce the upward trend of $-\Delta S_{n-1,n}^0$ values at certain values of n . The fluctuation in entropy values is probably associated with the internal structure change of the clusters or the difference in the bonding configuration of the ligands. Inclusion of dipole-ion interaction effect increases the entropy changes by 5–15 cal mol⁻¹ K⁻¹ for small ion clusters, which suggests that the ordered structure in the cluster can somewhat be accounted for by including the dipole-ion interaction term. It is physically sound that the force of ion on dipole molecules will lead to more order structure of ligands around ions.

IV. SUMMARY

The classical Kelvin–Thomson equation, which was derived by Thomson about a century ago, has been the fundamental of classical ion-induced nucleation theory. In CKT equation, the effect of charge on Gibbs free energy change for the formation of the cluster (or equilibrium vapor pressure over an ion cluster) is taken into account by considering the electrostatic potential energy of the cluster. However, CKT theory assumes that the condensing ligands have the same property in the vicinity of ions as the ligands far away from the ions. In other words, CKT theory does not consider

the interaction of condensing ligands with the ions, which is a good approximation when the ligands are nonpolar molecules. It has been shown recently^{11,12} that ion-dipole interaction is important in reproducing the observed dependence of reduced critical supersaturation on temperature and in explaining the systematic discrepancy between Kelvin–Thomson diameters and the corresponding mobility equivalent diameters of small ions. In this paper, we derive the modified Kelvin–Thomson equation, which takes into account the effect of dipole-ion interaction, in an approach that is different from our earlier derivation.¹¹ We consider the effect of dipole-ion interaction by taking into account the kinetic energy change of condensing polar ligands as they approach the ions, while in the earlier derivation the effect is included by considering the forcing acting on the gaseous dielectric in the vicinity of the charge and the enhancement in the number concentration of polar molecules in the vicinity of the charged clusters.

The stepwise enthalpy and entropy changes for small ion-clustering reactions are calculated using the MKT equation and are compared with the experimental results. In this study, we focus on the protonated clusters H^+L_n with $L = H_2O$, NH_3 , CH_3OH , and C_5H_5N . Earlier studies⁸ have shown that the experimental enthalpy values are up to 20 kcal mol⁻¹ more negative than those predicted by CKT equation and the experimental entropy values are systematically 5–20 cal mol⁻¹ K⁻¹ more negative than the predicted ones. Our calculations indicate that MKT equation gives very good agreement in enthalpy changes with experimental results for small ions ($n \leq 5$) of all four species. For relative large clusters ($n \geq 6$), the enthalpy values predicted by MKT equation appear to be consistent with observed ones for CH_3OH . For H_2O , MKT equation predicts a smooth and continuous change of $-\Delta H_{n-1,n}^0$ as n increase but the observed values for H_2O have a minimum at $n=9$. The MKT-predicted $\Delta H_{n-1,n}^0$ values for H_2O are consistent with the observed ones for $n=14-25$. The discontinuous transition in enthalpy changes at $n=6$ for NH_3 and $n=7-13$ for H_2O is

probably associated with the formation of inner shell. Overall, the enthalpy values predicted by MKT equation are in better agreement with observed ones than those predicted by CKT equation. MKT predictions of stepwise entropy changes are also in a better agreement with experimental results than the CKT predictions. Inclusion of dipole-interaction effect increases the entropy changes by $5\text{--}15\text{ cal mol}^{-1}\text{ K}^{-1}$ for small ion clusters, which suggests that the ordered structure in the cluster can somewhat be accounted for by including the dipole-ion interaction term. Both CKT and MKT equations cannot reproduce discontinuous change of $\Delta H_{n-1,n}^0$ and $\Delta S_{n-1,n}^0$ at certain values of n which is probably associated with the internal structure change of the clusters or the difference in the bonding configuration of the ligands.

ACKNOWLEDGMENT

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