Note

Thermophysical Interpretation of the Latent Heat of Vaporization of Water

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A simple model is introduced to interpret the heat of vaporization of water, which assumes the gaseous state as an ideal gas and the condensed state as an ideal "solid." Making the approximations $\hbar\omega_j \gg kT$ and $\hbar\omega_i \ll kT$ simultaneously for the vibrational energies of the molecules in the gaseous and condensed phases, respectively, in the temperature region near room temperature, the temperature dependence of the molar heat of vaporization of water is theoretically $dL/dT = -5R$. This is in excellent agreement with the experimental value $dL/dT = -5.12R$ in the temperature range $273 < T < 373$ K.

KEY WORDS: latent heat; thermodynamics; vaporization; water.

1. INTRODUCTION

In order to interpret the heat of vaporization of water a simple model, in which the gaseous state is considered an ideal gas with some internal freedom and the condensed state an ideal "solid," is introduced.

2. THE THEORY

For the gaseous phase, supposing that the number of molecules in a volume, $V_g = L^3$, is N_g and making use of the classical distribution function, one has

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$$N_g = \int_0^\infty \left(\frac{1}{2} \pi n^2 \, dn \right) \frac{1}{8\pi^3 \hbar^3} \iiiint\!\!\!\int e^{-(p_A^2/2I_A + p_B^2/2I_B + p_C^2/2I_C)/kT}$$

$$\cdot \sin\theta \, d\varphi \, d\theta \, d\psi \, dp_A \, dp_B \, dp_C$$

$$\cdot \exp\left\{ \left[\mu_g - \frac{\hbar^2}{2m} \left(\frac{\pi n}{L} \right)^2 \right] \Big/ kT \right\}$$

$$\cdot \sum_{n_j} \exp - \left[\left(n_j \hbar \omega_j + \frac{1}{2} \hbar \omega_j \right) \Big/ kT \right], \qquad j = 1, 2, 3$$

where n is the translational quantum number, I_A, I_B, and I_C are the principal moments of inertia, P_A, P_B, and P_C are the corresponding angular momenta, θ, φ, and ψ are the coordinates, n_j and ω_j are the vibrational quantum number and the angular frequency of the vibration mode j, $\hbar$ is Planck's constant divided by 2π, k is Boltzmann's constant, T is the absolute temperature, μ_g is the chemical potential of a molecule, and m is the mass of a water molecule.

Performing the integrations and summations, one has

$$N_g = \frac{V_g \exp \mu_g}{(2\pi\hbar^2/mkT)^{3/2}} \frac{\sqrt{\pi}(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{8\pi\hbar^3} \prod_{j=1}^{3} \frac{\exp(-\omega_j \hbar/2kT)}{1 - \exp(\omega_j \hbar/kT)}$$

$$\equiv a V_g e^{\mu_g} (kT)^3 \prod_{j=1}^{3} \frac{\exp(-\omega_j \hbar/2kT)}{1 - \exp(\omega_j \hbar/kT)} \tag{1}$$

As for the molecules in the "solid" state, a stricter restriction assuming that the molecules are all restricted to the lattice site and bounded to the "solid" by nine vibrational modes, is made. Taking the energy of a free molecule as zero, one can write the distribution function as follows:

$$Z_s = \sum_{n_i=1}^{\infty} \exp[(\varepsilon_0 - n_i \omega_i \hbar)/kT] = \frac{\exp(\varepsilon_0/kT)}{\prod_{i=1}^{9} [1 - \exp(-\omega_i \hbar/kT)]}$$

where $-\varepsilon_0$ is the energy of the molecule when all the modes are in the ground state and ω_i is the angular frequency of mode i. Then the free energy and the chemical potential per molecule are

$$F_s = -kT \log Z_s$$

and

$$G_s = F_s + pv_s = \mu_s$$

respectively, where p and v_s are the pressure and specific volume of the solid phase.

When the "solid" and gaseous phases are in equilibrium, the pressure of the two phases are the same, but the specific volume of the solid phase is much smaller than that of the gaseous phase, and the second term in G_s can be omitted, so that

$$G_s \cong F_s$$

The absolute activity of a molecule in the solid phase is

$$\lambda_s \equiv \exp(\mu_s/kT) \cong \exp(F_s/kT)$$

$$= \exp(-\varepsilon_0/kT) \cdot \prod_{i=1}^{9} [1 - \exp(-\omega_i \hbar/kT)]$$

Similarly, from Eq. (1) one has

$$\lambda_g = \frac{N_g}{V_g a} (kT)^{-3} \prod_{j=1}^{3} \exp(\omega_j \hbar/2kT)[1 - \exp(-\omega_j \hbar/kT)]$$

Letting $\lambda_s = \lambda_g$ and making use of the relationship $N_g/V_g = P/kT$ for the gaseous phase, one has

$$P = a(kT)^4 \exp\left[-\left(\varepsilon_0 + \sum_{j=1}^{3} \frac{1}{2}\omega_j \hbar \right)\bigg/ kT \right]$$

$$\cdot \frac{\prod_{i=1}^{9}[1 - \exp(-\omega_i \hbar/kT)]}{\prod_{j=1}^{3}[1 - \exp(-\omega_j \hbar/kT)]} \tag{2}$$

In the temperature region near room temperature, water can be easily evaporated, but the chemical bond in the water molecule in the gaseous state cannot be broken by thermal motion. So we can make the approximations $\omega_i \hbar \ll kT$, $i = 1, 2,..., 9$, and $\omega_j \hbar \gg kT$, $j = 1, 2, 3$, simultaneously, then Eq. (2) becomes

$$P = a(kT)^{-5} \exp\left[-\left(\sum_{j=1}^{3} \frac{1}{2}\omega_j \hbar + \varepsilon_0 \right)\bigg/ kT \right] \hbar^9 \prod_{i=1}^{9} \omega_i$$

$$\frac{dP}{dT} = -5\frac{P}{T} + \left(\sum_{j=1}^{3} \frac{1}{2}\omega_j \hbar + \varepsilon_0 \right)\frac{P}{T^2}$$

$$= \left[-5kT + \left(\sum_{j=1}^{3} \frac{1}{2}\omega_j \hbar + \varepsilon_0 \right) k \right]\frac{1}{Tv_g} \tag{3}$$

Inserting Eq. (3) into Clausius–Clapeyron's equation, $dP/dT = l/T \, \Delta v$, and

making the approximation $\Delta v = v_g - v_s \cong v_g$, one can simply obtain the latent heat of vaporization of one water molecule,

$$l = -5kT + \sum_{j=1}^{3} \frac{1}{2} \omega_j \hbar k + \varepsilon_0 k$$

The latent heat of vaporization of a mole of water is

$$L = -5RT + \sum_{j=1}^{3} \frac{1}{2} \omega_j R\hbar + \varepsilon_0 R$$

or

$$\frac{dL}{dT} = -5R$$

where R is the gas constant.

3. COMPARISON WITH EXPERIMENT

The experimental data in the temperature range from 273.15 to 373.15 K are taken from Ref. 1 at a temperature interval of 5 K as shown in Fig. 1. A linear least-squares fitting to a straight line yields

$$\frac{dL}{dT} = -5.12R$$

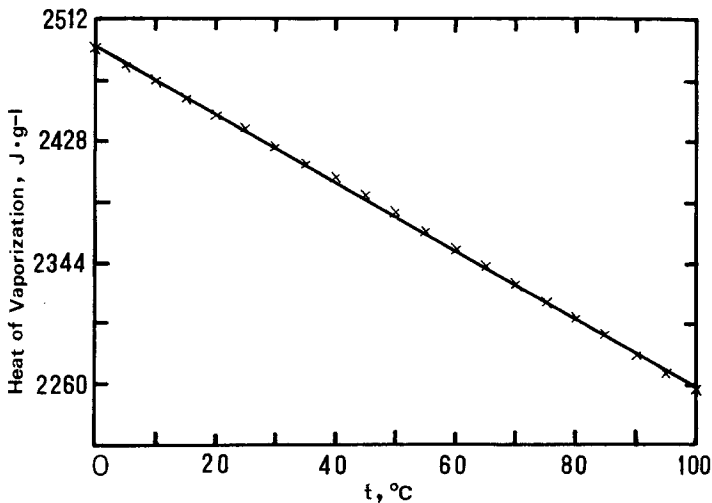with the correlation coefficient $r = 0.9996$.

Fig. 1. The latent heat of vaporization of water as a function of temperature. Data taken from Ref. 1.

4. DISCUSSION

The author has no available data related to the sublimation of ice, and it should not be expected that this model would apply to the sublimation of ice accurately, because in that temperature region the approximation $\omega_i \hbar \ll kT$ may not be a good one.

In the high-temperature region, for instance, $T > 373$ K, the ideal solid approximation may not be as good as for the case near room temperature, and the agreement between theory and experiment may not be as good as expected. In fact the experimental value for dL/dT increases slightly with temperature even in the temperature range from 273 to 373 K.

However, the excellent agreement between theory and experiment in the temperature region near room temperature and the clear physical picture it suggests make the model an interesting one.

REFERENCE

1. D. Charles et al., eds., *Handbook of Chemistry and Physics*, 44th ed. (Chemical Rubber, Cleveland, Ohio, 1962–1963), pp. 2544–2554.