

Explain the latent heat and specific heat of water, ammonia, and methanol with degrees of freedom



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Abstract

The internal energies of 0°C water and ice are considered from the perspective of degree of freedom and latent heat of fusion of water is calculated, which is in good agreement with the published value. With the same consideration, the latent heats of fusion of ammonia and methanol are calculated and the results are in reasonable agreement with the published values. This simple strategy can give specific heats of water, liquid ammonia, and methanol, which are in good agreement with known data.

Keywords: Degree of freedom, latent heat, specific heat, water, ice.

Resumen

Se calculan las energías internas del agua y del hielo a 0°C consideradas desde la perspectiva de los grados de libertad y el calor latente de fusión del agua, las cuales están en buena concordancia con los valores publicados. Con la misma consideración, se calculan los calores latentes de fusión del amoníaco y del metanol y los resultados están en acuerdo razonable con los valores publicados. Esta sencilla estrategia puede dar los calores específicos del agua, del amoníaco líquido, y del metanol, los cuales se encuentran en buena concordancia con los datos conocidos.

Palabras clave: Grados de libertad, calor latente, calor específico, agua, hielo.

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I. INTRODUCTION

There are 15 known crystalline solid phases of water and all of them are called ice. But here the ice in our context is the one when water is cooled down to 0°C at 1 atmosphere. It is well known that at 0°C and 1 atmosphere, the density of water is 0.9998 g/cm³ and the density of ice is 0.9162 g/cm³ [1]. There is a question: For 0°C water and ice, which has a higher internal energy? Because they have same temperature, their molecules should have same kinetic energies. Therefore it seems that we need to compare their potential energies among molecules. There might be 2 answers: 1) Water has higher internal energy. This is because the latent heat of fusion of water is $L_f = 33.5 \times 10^4$ J/kg [2], which means that 1 kg of ice at 0°C needs 33.5×10^4 J of heat to change to 0°C water (we can ignore the work done by the expansion of volume which is about 9 J). 2) Ice has higher internal energy. This is because ice's density is lower so the distance between molecules is larger, resulting in larger potential energy. Of course the latter argument doesn't agree to our common sense. But how do we explain this paradox?

We believe that the main difference of internal energy between 0 °C water and ice comes from the alteration of degree of freedom of molecules. Let us estimate the latent heat energy of water according to equipartition theorem. For an ice molecule, it can only vibrate so it has only 3 degrees of freedom; while for a water molecule, it can also move in

space (translational motion) and rotate so it has 6 more degrees of freedom. Therefore, 1 mole of 0°C water should have $3RT$ of more energy than 0°C ice. For 1 kg of water, then, this energy difference is:

$$\frac{1}{18 \times 10^{-3}} (3 \times 8.31 \times 273) = 37.8 \times 10^4 \text{ J/kg.}$$

Which is in good agreement with the published latent heat $L_f = 33.5 \times 10^4$ J/kg. The difference: 4.3×10^4 J/kg, can be attributed to the potential energy change among molecules.

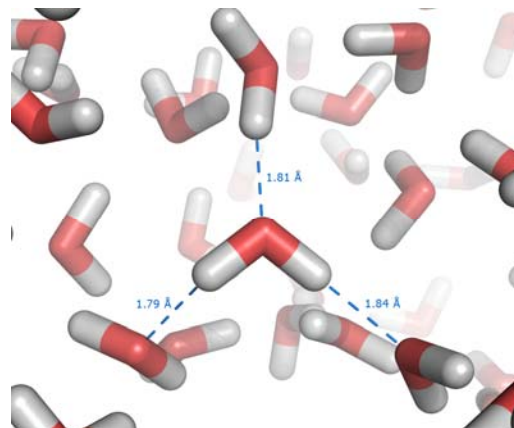


FIGURE 1. Schematic view of water molecules. The dashed blue lines from the molecule in the center of the picture represent hydrogen bonds.

Actually, when water is frozen to ice, the hydrogen bonds are formed among water molecules, which line up water molecules less efficiently – larger spaces among molecules. The water molecules and their hydrogen bonds are shown in Fig. 1. In this sense, we may say that interaction among water molecules has changed from random electrostatic intermolecular attraction to a much stronger fixed dipole – dipole van der Waals interaction.

Based on this assumption, the water's specific heat should be $9R$ which is composed of $3R$ from vibration of atoms in a water molecule; $3R$ from vibration of water molecules; and $3R$ from rotation and translation. That is, $9R = 74.79 \text{ J/(mol K)}$, which is close to the published data of 75.35 J/(mol K) [2].

We can apply the same strategy to Ammonia and Methanol that have similar molecular structure as water. For Ammonia, its published latent heat of fusion $L_f = 5.643 \text{ kJ/mol}$, and the freezing point is 195 K [3]. So its latent heat of fusion is $3RT = 3 \times 8.31 \times 195 = 4.87 \text{ kJ/mol}$. The error is about 15% compared to its published value.

If we apply $9R$ to calculate ammonia's liquid specific heat that is, again, 74.79 J/(mol K) which is in good agreement with the published data of 76.84 kJ/(mol K) .

For Methanol, its published latent heat of fusion is $L_f = 3.215 \text{ kJ/mol}$ at 176 K . And so its latent heat of fusion is $3RT = 4.388 \text{ kJ/mol}$. Compared to its published data, the error is about 31%.

Comparing $9R$ with liquid Methanol's published specific heat of 81.08 J/(mol K) [4], 74.79 J/(mol K) is in good agreement with it.

In summary, we believe that the degree of freedom change plays an important role in the phase change and the majority of the heat needed for the fusion goes to the excitation of more degrees of freedom.

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