

1 Surface tension and the latent heat of evaporation

In order that a liquid be evaporated, some heat is needed. One has to heat the water in order to make it boil. Even when the water vaporizes but not boiled, some heat is needed. That is why we feel cool when our sweat vaporizes. The heat needed for evaporation comes from our body.

Why is that heat needed, although the temperature doesn't change? To answer this question, let's examine the difference between a liquid and a gas. The main difference is that in a gas, molecules are far from each other, so that the interaction between them is negligible. In liquids that is not the case. The molecules are near each other and there is a considerable interaction between them. This interaction could be described through a potential energy. In a liquid, there is a potential energy ($-u$) between two neighboring molecules. Actually this potential energy is not the same for all pairs, but one can use an average value. u itself is positive, and the potential energy corresponding to two molecules far from each other is essentially zero. So, to take two close molecules away from each other, an energy of u is needed. This is the root of the latent heat of evaporation. To estimate the total energy needed to vaporize a certain amount of liquid, consider N molecules of the liquid, and assume that each molecule has f nearby molecules. Then, the energy needed for each molecule would be (fu) . But in this calculation, the energy corresponding to each pair has been calculated twice. The correct value for the total needed energy is then $(Nfu/2)$. So, the latent heat of evaporation would be of the order $(fu/2)$ per molecule, or $(N_A fu/2)$ per mole, where N_A is the Avogadro's constant. u is called the binding energy, and $(N_A u)$ is similarly called the molar binding energy. This calculation relates a macroscopic quantity (the latent heat) to a microscopic one (the binding energy). But actually it doesn't give a way to measure the binding energy directly, using macroscopic measurements. Knowing the molar latent heat, one can only determine the molar binding energy.

There is another macroscopic quantity which is related to the binding energy. Again consider a volume of liquid, with some free surface, where the liquid ends. For the molecules on the free surface, the number of neighboring molecules is smaller, compared to those in the bulk. For molecules exactly on the boundary, the number of neighboring molecules could be half that of the bulk molecules. For the molecules near the boundary, the number of the neighboring molecules could be between that of the bulk molecules and half of it. So the number of neighboring molecules gradually changes from f for the bulk molecules to $(f/2)$ for the surface molecules. This means the whole volume has less negative energy compared to a similar value but without a free surface. As the interaction between the molecules is short-ranged (the range being of the order of molecular sizes), the molecules which have less neighbors are those which are very near to the surface. So there is a thin boundary layer of the thickness ℓ , for which the energy per molecule is $(-f'u/2)$, where f' is some average number of neighbors in this layer, and is less than f . The result is that the total energy of this liquid

minus the total energy of a similar liquid without boundary layer is $[\mathcal{N}(f - f')u/2]$, where \mathcal{N} is the number of molecules in the boundary layer. The number is equal to the volume of the layer times the number density. The number density is the number of molecules per volume. That is, the number density is (N/V) , where N is the number of molecules and V is the volume of the liquid. The volume of the boundary layer is (ℓS) , where S is the surface area of the boundary layer. The overall result is that corresponding to a free surface, the liquid has an additional energy, equal to $[(N/V)(\ell S)(f - f')u/2]$, which can be reorganized as (τS) , where τ is called the surface tension. A liquid with a free surface has an extra energy, relative to a similar liquid without that free surface. This extra surface energy is proportional to the surface area, and the proportionality constant is the surface tension.

Now consider the two macroscopic quantities, the latent heat L and the surface tension τ :

$$L = \frac{N f u}{2}. \quad (1)$$

$$\tau = \frac{N (f - f') \ell u}{2 V}. \quad (2)$$

It is seen that

$$\frac{\tau}{(L/V)} = \frac{f - f'}{f} \ell. \quad (3)$$

(L/V) is the latent heat per volume. The fraction on the right-hand side is of the order of one: it is smaller, but not very much smaller than one. Approximating it by one, the following is resulted.

$$\ell \sim \frac{\tau}{(L/V)}. \quad (4)$$

In this last equation, the right-hand side is a macroscopic quantity. But the left-hand side is a microscopic one. Using this, one can estimate the thickness of the boundary layer, or the range of the molecular interactions, or the size of molecules, using just macroscopic measurements, without directly measuring anything about the molecules.

Find the latent heat per volume and the surface tension, say for water, and estimate ℓ .