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The Thermodynamics of Cluster Formation in Nucleation Theory

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We have derived a precise thermodynamic definition of the standard free energy to form a cluster which is used in nucleation theory. The results [Eq. (9)] have a form differing slightly from the form usually used in nucleation theory and show that the Lothe–Pound correction factor is based on a misconception concerning the standard states involved.

KEY WORDS: Nucleation; condensation; thermodynamics; clusters; surface tension; droplets.

In nucleation theory as applied to condensation, one considers the mechanism of growth of a liquid drop by the addition and loss of molecules.$^{(1)}$ The work to form a drop of n monomer units (an n-mer) is considered to be the sum of a surface free energy and a bulk free energy. For the condensation of a liquid (or solid) from a supersaturated vapor, this model leads to values of the work to form a drop which increase with an increase of n up to a maximum at the critical size, and then decrease at larger n. The work (or standard Gibbs free energy ΔG) to form a drop of n monomers has never been clearly defined and

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controversy has arisen concerning its meaning and calculation.(2,3) In this note, we well give a precise thermodynamic definition of this quantity and show that much of the controversy has been based on a misconception arising from the imprecision of the definition of ΔG.

Let us consider the partial pressure of an n-mer, p_n, in terms of chemical potentials,

$$p_n/p^\circ = \exp[(\mu_n - \mu_n{}^\circ)/RT] \tag{1}$$

or

$$\mu_n = \mu_n{}^\circ + RT\, ln(p_n/p^\circ)$$

where μ_n is the chemical potential of n-mer and $\mu_n{}^\circ$ is the standard chemical potential of n-mer at unit pressure p°. (In the usual thermodynamic notation, the unit pressure p° is conventionally taken as 1 atm and the symbol is omitted. In this paper, we will write it explicity for clarity.)

The pressure equilibrium constant K_n is conventionally defined as

$$K_n \equiv (p_n/p^\circ)/(p_1/p^\circ)^n = (p_{ne}/p^\circ)/(p_{1e}/p^\circ)^n \tag{2}$$

where p_1 is the partial pressure of monomer, where the subscript e denotes partial pressures in equilibrium with pure liquid and where the second equality is valid for ideal gas mixtures. By rearrangement,

$$p_n/p^\circ = (p_{ne}/p^\circ)(p_1/p_{1e})^n = \exp[(\mu_n - \mu_n{}^\circ)/RT] \tag{3}$$

Since the liquid is in equilibrium with the vapor at pressure p_{ne}, the chemical potential of the pure liquid, μ_l, is given by

$$n\mu_l = \mu_{ne} = \mu_n{}^0 + RT\, ln(p_{ne}/p^\circ) \tag{4}$$

Thus, combining Eqs. (3) and (4), one obtains

$$\begin{aligned} -RT\, ln(p_n/p^\circ) = -(\mu_n - \mu_n{}^\circ) &= -nRT\, ln(p_1/p_{1e}) + (\mu_n{}^\circ - n\mu_l) \\ &= -nRT\, ln\, S + (\mu_n{}^\circ - n\mu_l) \end{aligned} \tag{5}$$

where S is the supersaturation ratio. The right-hand side of Eq. (5) is the form used in classical nucleation theory.(1,4) The last term is the negative of the free-energy change for taking n liquid molecules and forming one molecule of gaseous n-mer at unit pressure and has been conventionally identified as the surface free energy.(1,4)

However, in nucleation theory, what has always been used is not p_n/p°, but p_n/p_1 (or p_n/p_T where the total pressure of the component studied, p_T, is close to p_1), i.e., the equation one usually sees is

$$N_n = N_1 \exp(-\Delta G/RT) \tag{6}$$

where N_n and N_1 are the number densities of n-mer and monomer, respectively. Since one always assumes the vapor to be an ideal gas mixture, this is the same as

$$p_n/p_1 = N_n/N_1 = \exp(-\Delta G/RT) \tag{7}$$

The problem is to *properly* define ΔG. To do this, we write an equation for p_1 similar to Eq. (5)

$$-(\mu_1 - \mu_1^\circ) = -RT\, ln\, S + (\mu_1^\circ - \mu_l) = -RT\, ln(p_1/p^\circ) \tag{8}$$

Consequently, by combining Eqs. (5), (7), and (8), one obtains

$$\Delta G = -(n-1)\, RT\, ln\, S + [\mu_n^\circ - \mu_1^\circ - (n-1)\, \mu_l] \tag{9}$$

where the last term on the right-hand side is the standard chemical potential change for one mole of monomer vapor $+(n-1)$ moles of liquid to form one mole of n-mer.

We see, then, that the ΔG which should be used in nucleation theory is the one defined in Eq. (9) and not the one given in Eq. (5). Note that the coefficient of $ln\ S$ is $(n-1)$, not n, and it is $\mu_n^\circ - \mu_1^\circ - (n-1)\ \mu_l$ which in classical nucleation theory should be identified as the surface free energy $4\pi r^2\sigma$, not $\mu_n^\circ - n\mu_l$.

Using only thermodynamics, one cannot know $\mu_n^\circ - \mu_1^\circ - (n-1)\ \mu_l$ in terms of measurable variables. However, the main point made here is that whatever one assumes it to be *must* be consistent with this expression. Thus, if one insists on including a translational contribution, because the expression is $\mu_n^\circ - \mu_1^\circ + \ldots$, it can *only* enter as the difference between the translational contribution of an n-mer and a monomer.

Lothe and Pound$^{(2)}$ in a series of articles have argued that ΔG must also include the free-energy change due to the conversion of six vibrational to three translational and three rotational degrees of freedom, i.e.,

$$\begin{aligned} G_{\text{tr}} + G_{\text{rot}} - G_{\text{vib}} = &-RT \ln(2\pi mkT/h^2)^{3/2}(kT/p_n) \\ &-RT \ln(8\pi^2 kT/h^2)^{3/2}(\pi I^3)^{1/2} + 5RT \end{aligned} \tag{10}$$

They calculated these rotational and translational terms by using the ideal gas formula for rigid spherical molecules and used various methods to approximate the vibrational term. For a water n-mer containing 100 molecules, they found $G_{\text{tr}} \simeq -24RT$, $G_{\text{rot}} \simeq -21RT$, $G_{\text{vib}} \simeq -5RT$. However, as was explained above, the translational degrees of freedom are not only significant for the n-mer, but also for the monomer. Consequently, the translational contribution to be added is not the first term on the right-hand side of (10), but rather

$$G_n(\text{tr}) - G_1(\text{tr}) = -RT \ln n^{3/2} \tag{11}$$

which is considerably smaller than proposed by Lothe and Pound. For example, when $n = 100$, the contribution is $-6.9RT$ per mole independent of the molecular weight of n-mer, rather than $-21.5RT$ per mole ($-24RT$ translational $+$ $2.5RT$ vibrational) and a function of molecular weight as they state.(2)

An equally acceptable point of view is to adopt Eq. (5) as a proper definition of the free energy of formation of n-mer. If one does so, one *can* interpret $\mu_n{}^\circ - n\mu_l$ to include a Lothe–Pound translational contribution. However, to then obtain N_n, one needs to eliminate p° by dividing by Eq. (8), and thus returns to the same result. In other words, one can say, *yes*, Lothe and Pound were consistent with thermodynamics when they included a translational free energy, but the preexponential factor used in nucleation theory is wrong, or one can say, *no*, Lothe and Pound were wrong since most of the translational contribution they wanted to include is already present in the preexponential factor in nucleation theory as it is conventionally used.

While the lines of argument adopted here do not exclude Lothe and Pound's assumption that three rotational degrees of freedom replace three other degrees of freedom of the liquid, for the following reasons, even if one wishes to accept such an assumption, the effect, if any, must be smaller than their estimates. The entropy contribution from these degrees of freedom is hard to estimate exactly, but an upper limit can be guessed by examining the standard entropy of vaporization of a liquid of polyatomic molecules. The excess of such an entropy over that expected for monatomic fluids might be attributed to rotational degrees of freedom. Such calculations have been carried out for polyatomic molecules by Yosim and Owens,(5) who showed that for nonassociating vapors, there is generally a small difference of entropy ($<R$) between the entropy of vaporization of a hard-sphere fluid with no rotational entropy and that for polyatomic fluids. The n-mers discussed here are much larger than the molecules discussed by Yosim and Owens. However, they indicate that even for nonlabile polyatomic molecules, only a small entropy increase related to the rotational entropy is possible in vaporization. For labile molecules (e.g., the n-mer) where there is more communal entropy in the liquid, the change should be even smaller than for nonlabile molecules.

Another indication of the smallness of the supposed rotational contribution can be seen if one considers a polyatomic monomer molecule. For such a case, $\mu_1{}^0$ contains a contribution from three rotational degrees of freedom and if the molecules can be considered rigid bodies, one can write

$$G_n(\text{rot}) - G_1(\text{rot}) = -RT \ln[\sigma_1 I_n^{2/3}/(I_A I_B I_C)^{1/2}\sigma_n] \qquad (12)$$

where the σ's are symmetry numbers, I_n is the moment of inertia of the

n-mer and I_A, I_B, and I_C are the moments of inertia of the monomer molecule. This quantity can be estimated for particular monomers and the rotational contribution computed will always be smaller than that calculated by Lothe and Pound. For example, if the monomer and n-mer behave, even approximately, as spheres of uniform density, then the ratio of the moments of inertia is $(I_n/I_1) = n^{5/3}$ and for $n = 100$,

$$G_n(\text{rot}) - G_1(\text{rot}) \simeq -11.5RT + RT \ln(\sigma_n/2)$$

The symmetry number of n-mer, σ_n, should be significantly larger than α and the last term is positive. For molecules (such as water) where the moments of inertia are smaller than for a uniform sphere, this contribution is more negative, but always less so than the Lothe–Pound correction.

Of course, by a self-consistent statistical mechanical argument, one can obtain a clearer picture of what the term $\mu_n{}^\circ - \mu_1{}^\circ$ actually represents. Reiss(6) and Kikuchi(7) have shown that it is not self-consistent to identify the term $\mu_n{}^\circ - \mu_1{}^\circ$ as containing a translational and rotational contribution. What we have shown is that even if one were to insist on including a rotational and translational contribution, it would have to be much smaller than that suggested by Lothe and Pound.

The conclusions we reach are: (1) the basis for the Lothe–Pound "correction factor" is inconsistent with thermodynamics when the work to form a drop of n molecules is defined precisely; and (2) the coefficient of the $\ln S$ term is $n - 1$, which differs slightly from what is usually used in nucleation theory.

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