A Thermodynamic Relation in the Theory of Homogeneous Nucleation of Supercooled Droplets

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Thermodynamic analysis (Mason, 1957; Fletcher, 1962) of the process of homogeneous nucleation of supercooled water yields the familiar relation

$$\Delta G^* = (16\pi\sigma^3)/3(\rho_i \Delta g_b)^2 \qquad (1)$$

for the critical increase in total (not specific) Gibbs free energy accompanying formation of a single critical embryo. In (1), σ is the specific surface free energy of the water-ice interface, ρ_i is the ice density, and Δg_b is the bulk specific Gibbs free energy increase accompanying the phase change. As is well known, the quantity ΔG^* plays an important role in the nucleation-rate equation for supercooled water, as was first made clear by Mason (1952).

The present writer has given (McDonald, 1953) a derivation for Δg_b which he reduced to the expression $-L_f \ln(T_0/T)$, where L_f was interpreted as the irreversible latent heat of fusion of supercooled water freezing at temperature T, T_0 being the triple point. Earlier, Mason (1952) had given for Δg_b the expression $-L_{f0}(T_0-T)/T_0$, where L_{f0} is the reversible latent heat of fusion at the triple point, namely 79.7 cal g^{-1}. Neither of these expressions is correct. The writer's version has unfortunately been carried into several parts of the literature, and Mason's version has also been used by others (Fletcher, 1962, p. 204). Clearly this has been a troublesome point. The following corrects the matter.

By considering any of several possible reversible paths by which unit mass of water substance can be made to pass from a supercooled liquid state at T to ice at T (an isothermal distillation process being simplest), one can readily obtain the form

$$\Delta g_b = -R'T \ln(e_w/e_i), \qquad (2)$$

where R' is the gas constant per gram of water vapor and e_w and e_i are the saturation vapor pressures over supercooled water and ice, respectively, at T. What is desired, in order to correct the previously used expressions for Δg_b, is an equivalent to (2) in which the vapor pressures are replaced by temperatures; this will bring out explicitly the dependence of Δg_b on the degree of supercooling T_0-T, the natural measure of degree of metastability for supercooled water. This can be achieved by integrating the Clausius-Clapeyron equation from T up to T_0 first along the vapor pressure curve for supercooled water and secondly along the vapor pressure curve for ice, obtaining thereby,

$$\ln(e_t/e_w) = \bar{L}_v(T_0-T)/(R'TT_0), \qquad (3)$$

and

$$\ln(e_t/e_i) = \bar{L}_s(T_0-T)/(R'TT_0), \qquad (4)$$

where e_t denotes the saturation vapor pressure over water or ice at the triple point T_0, and L_v and L_s denote, respectively, the latent heats of vaporization and sublimation. The bars over those latent heats indicate that we momentarily assume that we have found, by some independent means, that particular value of each latent heat which renders the integration exact.

Eliminating e_i between (3) and (4) we get

$$\ln(e_w/e_i)=(\bar{L}_s-\bar{L}_v)(T_0-T)/(R'TT_0). \tag{5}$$

Putting (5) into (2) gives

$$\Delta g_b=-(\bar{L}_s-\bar{L}_v)(T_0-T)/T_0. \tag{6}$$

Equation (6) provides what we sought, namely an expression for Δg_b in which explicit dependence on the degree of supercooling appears. It is to be emphasized that it comes from (2) by a step that is no more than a transformation of variables made with the aid of the Clausius-Clapeyron equation.

We can simplify (6) somewhat by considering the prefactor involving the latent heats. First we observe that exactly at the triple point (and only there) we have

$$L_f=L_s-L_v, \tag{7}$$

where all three latent heats are the reversible latent heats. But for supercooled water freezing irreversibly at $T<T_0$ the heat released in the freezing process is not a well-defined quantity, its magnitude depending somewhat on the thermodynamic path along which that freezing happens to occur. However, one can show that for isothermal irreversible freezing, the heat released per unit mass of ice frozen from supercooled water at T is given to very high accuracy by the difference L_s-L_v, evaluated at T, those latter two latent heats being the familiar reversible heats. The proof hinges upon the fact that if one writes expressions for L_s and L_v from the first law of thermodynamics, then the pressure-volume work terms in each expression are the same to within the limits of accuracy of the ideal-gas approximation (which holds to a fraction of a per cent here). In fact, the two work terms are each equal to $R'T$, and hence cancel on taking the difference L_s-L_v. On the other hand, the pressure-volume work term in the first-law expression for the irreversible latent heat of fusion at T, though not quite zero, is extremely small, being of order 10^{-6} times the internal energy term. From these circumstances, it can be shown that (7) gives, to quite high accuracy, the latent heat of isothermal irreversible freezing of supercooled water when the reversible values of L_s and L_v are inserted on the right side of (7).

Return now to (6) and recall that the barred values of the latent heats are those which rendered (3) and (4) numerically exact, the existence of such values being assured by the mean value theorem. If numerical precision were the prime goal here it would be easy to tabulate mean values for various T that would give accuracy as high as one pleased. In fact, all we seek is a formalistic expression, so it suffices to note that if one does no better than to take as the barred values the values of L_s and L_v at a temperature halfway between T and T_0, the right members of (3) and (4) are rendered very nearly exact. When the difference is taken between such "mean" L's in (5) and (6), the error is found to be only of order one per cent even for that rather crude definition of the means. Using such a definition, or any more exact definition we may choose, we define

$$\bar{L}_f\equiv\bar{L}_s-\bar{L}_v$$

combining both the concept of the irreversible latent heat of fusion and the above-suggested averaging process, and use it in writing, finally

$$\Delta g_b\doteq-\bar{L}_f(T_0-T)/T_0 \tag{8}$$

as our desired expression to replace that previously given by the writer (McDonald, 1953). Mason (1960) has given an alternative expression, but does not discuss how one is to view the irreversible latent heat of fusion in such an expression.

It deserves emphasis that the primary reason for seeking an expression for Δg_b involving temperatures rather than vapor pressures is a formalistic reason. If one seeks numerical values of Δg_b for use in (1), then he should realize that *exact* values are given by (2), and should be computed from that relation. Fortunately, it can be shown that the numerical errors made (e.g., in back-calculations of σ from experimental nucleation data) through use of the writer's incorrect formulation (McDonald, 1953) for Δg_b have not been serious.

REFERENCES

Fletcher, N. H., 1962: *The physics of rainclouds.* Cambridge, Cambridge University Press, 386 pp.

Mason, B. J., 1952: The spontaneous crystallization of supercooled water. *Quart. J. R. meteor. Soc.*, **78**, 22–27.

——, 1960: Nucleation of water aerosols. *Physical chemistry of aerosols*, Discussions of the Faraday Soc., No. 30, 20–38.

McDonald, J. E., 1953: Homogeneous nucleation of supercooled water drops. *J. Meteor.*, **10**, 416–533.