CHAPTER V

EQUILIBRIUM WITH SMALL DROPLETS AND CRYSTALS

In this chapter we shall deal with a particular type of heterogeneous system, which is important in cloud physics. The reader who is not interested in that field can omit the chapter without loss of continuity.

We shall consider the equilibria associated with changes of phase in systems with one or two components and two phases, as those considered in the previous chapter, but with the difference that one of the phases is in such a state of subdivision that the effects of interfacial tensions cannot be ignored. We shall be interested, in particular, in obtaining expressions for the vapor pressure of small droplets and crystals, and for the temperature at which small crystals are in equilibrium with the liquid phase.

The general difference with the systems studied so far lies in that the work δA performed by external forces on the system consists not only of the work of expansion $-p\,\mathrm{d}V$ but also of another term giving the work necessary to increase the area of the interface separating the condensed from the gaseous phase. By definition of interfacial tension, this term must be written $\sigma\,\mathrm{d}\mathscr{S}$ where σ is the interfacial tension and $\mathscr{S}$ the area of the interface. The differential of the Gibbs function in a reversible process becomes in this case

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sigma\,\mathrm{d}\mathscr{S} \tag{1}$$

5.1. Vapor Pressure of Small Droplets of a Pure Substance

In Chapter IV, Section 6, the vapor pressure of a liquid was defined as that pressure at which the vapor is in equilibrium with the liquid phase. It was implicitly understood in that definition that the separation surface between the phases should be plane. If the surface has a pronounced curvature, the vapor pressure depends on it; the pressure will be higher for convex surfaces, and smaller for concave surfaces, than for a plane one. The reason for this, as we shall see, is that the evaporation from a convex surface decreases its area, which contributes negatively to the variation of Gibbs function, while the opposite occurs with a concave surface. The curvature of an element of surface is described, in general, by means of two radii of curvature; however, we shall restrict consideration to the case when both radii are equal, i.e., to spherical surfaces. We shall be particularly interested in the case of small droplets suspended in gaseous phase and in these conditions the drops adopt a spherical shape*.

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* When the drops are bigger, the falling velocity becomes appreciable and the drop may become deformed. But when this occurs the effect of curvature on vapor pressure is already negligible.

Let us now consider a spherical drop of radius R, in equilibrium with the vapor, which will be at the pressure p_R. We shall also consider a plane liquid surface, in equilibrium with its vapor at the pressure p_s (where the subscript s indicates saturation with respect to the liquid with a plane surface).

Let us assume now that we transfer dn moles of liquid from the mass with a plane surface to the drop. We can imagine two paths (A and B) to perform this operation:

(A) (a) Evaporation of dn moles from the mass with a plane surface, at constant pressure p_s and temperature T;
  (b) Isothermal compression of the vapor from p_s to p_R;
  (c) Condensation of the dn moles on the drop at constant pressure $\mathrm{p_R}$ and temperature T;
(B) (a) dn moles are separated mechanically from the mass with plane surface;
  (b) the dn moles are incorporated into the drop.

We must calculate the variation of Gibbs function of the total system (drop and mass with plane surface) for the considered modification (transference of the dn moles) by the two described paths.

We observe that in the first path the steps (a) and (c) do not contribute to the change in Gibbs function, because they occur reversibly at constant pressure and temperature. For step (b) we assume ideal behaviour for the vapor, and calculate*:

$$\mathrm{d}G_A = \mathrm{d}n \int_{p_s}^{p_R} V\,\mathrm{d}p = \mathrm{d}nR^*T \ln \frac{p_R}{p_s} \tag{2}$$

where V represents the molar volume.

In order to calculate the variation $\mathrm{d}G_B$ corresponding to the second path, we consider first the variation of surface and volume when a drop of radius R increases by dn moles. Let n be the total number of moles in the drop, M the molecular weight of the liquid, ϱ its density and $\mathscr{V}$ the volume of the drop. We shall have:

$$\mathscr{V} = \frac{nM}{\varrho} = \tfrac{4}{3}\pi R^3, \qquad \mathscr{S} = 4\pi R^2$$

where $\mathscr{S}$ is the surface of the drop. We obtain by differentiating:

$$\mathrm{d}\mathscr{V} = \frac{M}{\varrho}\mathrm{d}n = 4\pi R^2\,\mathrm{d}R, \qquad \mathrm{d}\mathscr{S} = 8\pi R\,\mathrm{d}R$$

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* Notice that the term with surface tension, which does not act as an external force, does not contribute to dG. During the condensation on the drop, which is the step in which its surface increases, we can imagine both the drop and the surrounding vapor subject, as a whole, to a pressure p_R as the sole external force acting on the system.

and, comparing both expressions,

$$\mathrm{d}\mathscr{S} = \frac{2M}{\varrho R}\,\mathrm{d}n \tag{3}$$

The mass with a plane surface can be considered as a part of a drop of infinite radius. $\mathrm{d}\mathscr{S}$ is in that case a second-order infinitesmal; for the small drop, formula (3) will be valid with its corresponding value of R. The only work performed on the system in the step (B.a) is the work necessary to separate the $\mathrm{d}n$ moles (thereby creating an interface) from the mass with a plane surface. This work must be compensated in step (B.b) (where that interface disappears again); but in this last step the system must also receive the necessary work to increase the surface by $\mathrm{d}\mathscr{S}$. According to (1), this work appears as the only term in the variation of Gibbs function because the process occurs at constant pressure and temperature. Therefore:

$$\mathrm{d}G_{\mathrm{B}} = \sigma\,\mathrm{d}\mathscr{S} = \frac{2M\sigma}{\varrho R}\,\mathrm{d}\mathscr{S}. \tag{4}$$

Equation (4) expresses the fact that the only difference between the values of Gibbs function for the initial and the final system (which only differ from the first in having $\mathrm{d}n$ fewer moles in the mass with a plane surface and $\mathrm{d}n$ more moles in the drop) is that corresponding to the difference in the drop surface area. As the variation in Gibbs function must be equal for both paths, we equate Equations (2) and (4) and obtain:

$$\ln\frac{p_{\mathrm{R}}}{p_{\mathrm{s}}} = \frac{2M\sigma}{\varrho R^{*}TR} = \frac{P}{R} \tag{5}$$

where $P = 2M\sigma/\varrho R^{*}T$; i.e.,

$$p_{\mathrm{R}} = p_{\mathrm{s}}\,\mathrm{e}^{\mathrm{P/R}} \tag{6}$$

If R is not very small, Equation (6) can be approximated by developing the exponential to the first-order term:

$$p_{\mathrm{R}} \cong p_{\mathrm{s}}\left(1 + \frac{P}{R}\right) \tag{7}$$

For water at 0 °C we have:

$\sigma = 0.0757\ \mathrm{N\ m^{-1}}$
$\varrho = 1000\ \mathrm{kg\ m^{-3}}$
$M = 0.01802\ \mathrm{kg\ mol^{-1}}$
$P = 1.20 \times 10^{-9}\ \mathrm{m} = 1.20 \times 10^{-3}\ \mu\mathrm{m}$

with which are calculated the values of Table V-1 for the ratio $p_{\mathrm{R}}/p_{\mathrm{s}}$.

We may remark that the range of R values corresponding to water droplets in clouds goes from 1 to 100 μm.

The theory assumes that the surface tension is not affected by the curvature. This hypothesis becomes doubtful for radii much smaller than 0.01 μm.

TABLE V-1
Vapor pressure of small water drops

R (μm)	p_R/p_s
100	1.000012
10	1.00012
1	1.0012
0.1	1.012
0.01	1.128
0.001	3.32

As a consequence of the variation in vapor pressure with the size of drops, a system consisting of vapor and drops of various sizes cannot be in equilibrium; the bigger drops must grow at the expense of the smaller ones. In other words, the liquid distills from the smaller to the bigger drops until the former disappear.

This theory is still valid in the presence of an inert gas (e.g., air in a system of water drops and water vapor) and is therefore applicable to clouds. We must only take into account, in that case, that the pressures considered are the partial pressures of water vapor.

We shall call *saturation ratio* r, the ratio of water vapor pressure to the saturation vapor pressure $r = p/p_s$, and *supersaturation*

$$\frac{p}{p_s} - 1 = r - 1.$$

When air is present, r becomes equal to the relative humidity U_w. For instance, we can see in Table V-1 that, for an atmosphere saturated with respect to water droplets to have a supersaturation of 1%, the droplets must not be larger than approximately 0.1 μm radius.

In Figure V-2, the upper curve represents the values of the equilibrium saturation ratio $r_R = p_R/p_s$, as a function of the radius R, for pure water.

5.2. Vapor Pressure of Solution Droplets

We shall consider now the case of small drops of solutions of a non-volatile solute in a solvent. This is the case, for instance, of a salt dissolved in water and therefore it finds application in the study of cloud physics, because the droplets of the cloud form by condensation of vapor on nuclei of hygroscopic substances suspended in the air.

We assume now that we have a mass of pure solvent with a plane surface and a spherical drop of solution. We shall call p'_R the vapor pressure of the drop and σ' its surface tension (primed symbols will be used for the solution and unprimed symbols for the pure solvent). We shall imagine, as before, that we transfer $\mathrm{d}n_1$ moles of solvent from the mass with plane surface to the drop; $\mathrm{d}n_1$ is infinitesimal and it therefore does not alter the composition of the drop. With the subscript 1 we characterize the solvent, while subscript 2 will be used for the solute.

The first term will be, as before, the isothermal evaporation at pressure p_s, the isothermal compression (or expansion) to p'_R and the isothermal condensation over the drop at pressure p'_R. The variation in Gibbs function (assuming ideal behaviour) will have the value

$$dG_A = dn_1 R^* T \ln \frac{p'_R}{p_s}. \tag{8}$$

Path B will consist now of the following steps:

(a) dn_1 moles of pure solvent are separated from the mass with a plane surface. To do this it is necessary to create a new interface with an increase of the Gibbs function. But, as in the previous section, this will be compensated by the disappearance of that interface in step (c).

(b) The pressure over the drop is modified isothermally from p'_R to $p_s + \Pi$, where Π is the osmotic pressure of the drop solution*.

(c) The dn_1 moles are introduced reversibly into the drop through a semi-permeable membrane that only permits the pure solvent to pass through. In this step, the interface created in (a) disappears, and the surface area of the drop increases. Schematically, we can represent the process as in Figure V-1.

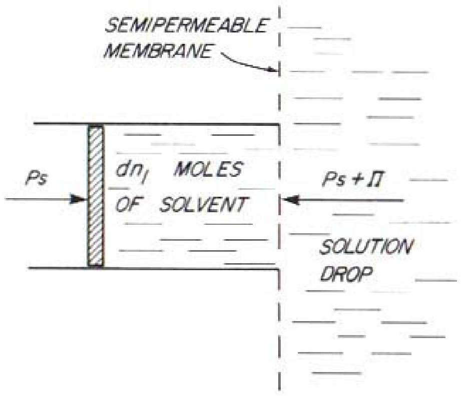

Fig. V-1. Reversible introduction of solvent into solution drop.

(d) The pressure over the drop is brought again, isothermally, to the value p'_R.

Let us calculate now the variation in Gibbs function by this path. The variation in step (a) is compensated by that in step (c). In step (b) we have

$$dG_{Bb} = \int_{p'_R}^{p_s+\Pi} V' \, dp$$

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* By definition, Π is the difference between the pressure acting at both sides of a semi-permeable membrane which only permits the passage of pure solvent and that separates the solution from the pure solvent (i.e., the pressure over the solution less the pressure over the solvent), in equilibrium conditions.

where V' is the volume of the drop. In step (c), which occurs at constant pressure and temperature*, the drop surface increases, so that according to Equation (1):

$$\mathrm{d}G_{\mathrm{Bc}} = \sigma' \,\mathrm{d}\mathscr{S}.$$

Finally, in step (d) we have

$$\mathrm{d}G_{\mathrm{Bd}} = \int_{p_s+\Pi}^{p'_R} (V' + \mathrm{d}n_1 \bar{V}_1)\,\mathrm{d}p$$

where $\bar{V}_1$ is the partial molar volume of the solvent in the solution (see Chapter IV, Section1).

The sum of the three differentials gives

$$\mathrm{d}G_{\mathrm{B}} = \mathrm{d}n_1 \int_{p_s+\Pi}^{p'_R} \bar{V}_1\,\mathrm{d}p + \sigma'\,\mathrm{d}\mathscr{S}. \tag{9}$$

As a first approximation, we can take $\bar{V}_1$ as independent of the pressure and equal to the molar volume of the pure solvent V_1; the first term then becomes

$$\mathrm{d}n_1 \int_{p_s+\Pi}^{p'_R} \bar{V}_1\,\mathrm{d}p \cong \mathrm{d}n_1 V_1(p'_R - p_s - \Pi) \cong -V_1 \Pi\,\mathrm{d}n_1$$

where, in the last expression, we have considered that the difference $(p'_R - p_s)$ is negligible against Π. As to the second term, we consider that

$$V' = n_1\bar{V}_1 + n_2\bar{V}_2 = \tfrac{4}{3}\pi R^3$$

where $\bar{V}_2$ is the molar partial volume of the solute in the solution, and n_1 and n_2 the number of moles of solvent and solute in the drop (cf. Equation (8) of Chapter IV). As the solvent increases, the volume of the drop will increase by:

$$\mathrm{d}V' = V_1\,\mathrm{d}n_1 = 4\pi R^2\,\mathrm{d}R.$$

Then:

$$\mathrm{d}\mathscr{S} = 8\pi R\,\mathrm{d}R = \frac{2\bar{V}_1\,\mathrm{d}n_1}{R} \cong \frac{2V_1\,\mathrm{d}n_1}{R}$$

and

$$\sigma'\,\mathrm{d}\mathscr{S} = \frac{2V_1\sigma'\,\mathrm{d}n_1}{R}. \tag{10}$$

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* We remark that the process can be assumed reversible, even though the pressures and the chemical potentials of the solute are different on both sides of the membrane, because the latter is neither deformable nor permeable to the solute.

Now we can equate the total variation of Gibbs function for the two paths considered (Equations (8) and (9)). It will be

$$\mathrm{d}n_1 R^*T \ln \frac{p'_R}{p_s} = \frac{2V_1\sigma'\,\mathrm{d}n_1}{R} - \Pi V_1\,\mathrm{d}n_1$$

or

$$R^*T \ln \frac{p'_R}{p_s} = \frac{2V_1\sigma'}{R} - \Pi V_1 \tag{11}$$

We must substitute here an expression for Π. In order to derive it, it is sufficient to consider Equation (11) for the particular case when the solution is, like the solvent, in a large mass without appreciable curvature at its surface: $R = \infty$, $p'_R = p'_s$, and

$$\Pi V_1 = -R^*T \ln \frac{p'_s}{p_s}. \tag{12}$$

According to Raoult's law, assuming that the solute is non-volatile,

$$\frac{p'_s}{p_s} = N_1 \tag{13}$$

where N_1 is the molar fraction of the solvent in the solution.

Therefore:

$$\Pi V_1 = -R^*T \ln N_1 \tag{14}$$

which is the thermodynamic expression usually derived for the osmotic pressure Π*. Substituting in Equation (11), we obtain:

$$\ln \frac{p'_R}{p_s} = \frac{2\sigma' V_1}{R^*TR} + \ln N_1. \tag{15}$$

And writing $V_1 = M/\varrho$, the equation becomes

$$\ln \frac{p'_R}{p_s} = \frac{2\sigma' M}{R^*T\varrho R} + \ln N_1$$

or else

$$\frac{p'_R}{p_s} = r_R = N_1 \exp(2\sigma' M/R^*T\varrho R). \tag{16}$$

In this formula, we must take into account that, if the solute is an electrolyte, its concentration must be corrected by multiplying the number of moles n_2 by the van 't Hoff factor i. Therefore, if N_2 is the molar fraction of the solute:

$$N_2 = \frac{in_2}{n_1 + in_2}; \quad N_1 = \frac{n_1}{n_1 + in_2}.$$

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* Other current expressions are derived from this one for dilute solutions, in which $n_2 \ll n_1$ and $\ln N_1 = \ln(1 - N_2) \simeq -N_2$.

For dilute solutions of strong electrolytes, i is equal to the number of ions into which each molecule dissociates. Thus, for NaCl, dissociated into Cl^- and Na^+, $i = 2$. For concentrated solutions, i can vary appreciably from this value.

We can replace N_1 in Equation (16):

$$N_1 = 1 - N_2 = 1 - \frac{in_2}{n_1 + in_2}$$

and for dilute solutions, $in_2 \ll n_1$,

$$N_1 \cong 1 - \frac{in_2}{n_1} = 1 - \frac{im_2 M}{M_2(4/3)\pi R^3 \varrho} = 1 - \frac{Q}{R^3} \tag{17}$$

where m_2 is the mass of solute, M_2 its molecular weight, and

$$Q = \frac{3im_2 M}{4\pi\varrho M_2}.$$

If the drop is not very small, the exponent in Equation (16) is small and we can write:

$$\exp(2\sigma' M/R^* T\varrho R) \cong 1 + \frac{2\sigma' M}{R^* T\varrho R} = 1 + \frac{P}{R}$$

where

$$P = \frac{2\sigma' M}{R^* T\varrho}.$$

Thus, for not very small drops of not very concentrated solution,

$$r_R = \frac{p'_R}{p_s} \cong \left(1 + \frac{P}{R}\right)\left(1 - \frac{Q}{R^3}\right) \cong 1 + \frac{P}{R} - \frac{Q}{R^3} \tag{18}$$

where we have assumed that the terms P/R and Q/R^3 are both small.

The coefficient P depends on temperature and (through σ') on the nature and concentration of the solution. Q is almost independent of temperature (ϱ is only slightly dependent), but depends on the nature and mass of the solute; therefore, Q will be constant for any droplet formed on a hygroscopic nucleus of a specified mass, which is the important case for the physics of clouds.

If the concentration does not exceed about 1‰, we can assume $\sigma' \cong \sigma$, and P has the value given in Section 1. As for Q, it becomes, writing $i = 2$ (mono-monovalent, strong electrolyte):

$$Q = 8.6 \frac{m_2}{M_2} \text{ cm}^3.$$

If the solute is sodium chloride:

$$M_2 = 58.45 \text{ g mol}^{-1}$$

$$Q = 0.147\, m_2 \text{ cm}^3$$

where m_2 is expressed in grams.

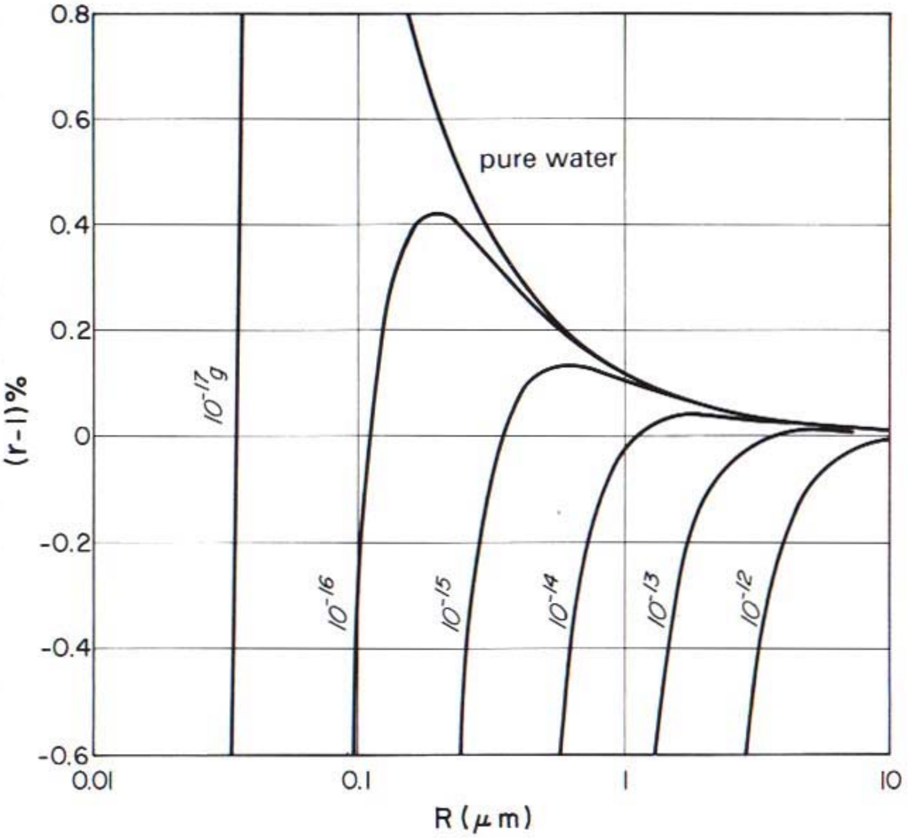

Fig. V-2. Vapor pressure of NaCl solution drops, as a function of drop radius R. $(r-1)$: supersaturation. Numbers on curves indicate mass of NaCl.

Figure V-2 represents the saturation vapor pressure as a function of the radius R for NaCl and $T = 273$ K; the different curves correspond to different values of the mass m_2. The upper, right-hand curve corresponds to pure water.

We can see in the figure that the curves pass through a maximum (except for pure water). Let us consider a drop of large radius R containing a certain mass of solute m_2. Its vapor pressure will be very close to p_s ($r \cong 1$). If we now assume that the water gradually evaporates, R will decrease (we shift towards the left in the graph); the effect of curvature will become noticeable and, with it, the term P/R in Equation (18): p'_R will increase approximately following the pure water curve, because the term Q/R^3 is still very small. However, as R decreases, this last term increases as R^{-3}, while P/R increases only as R^{-1}. A stage will be reached, therefore, where the term Q/R^3 becomes first noticeable, then grows rapidly and soon becomes more important than P/R: the curve diverges from that of pure water, passes through a maximum and then decreases rapidly. The curve will finish at that value of the saturation ratio r corresponding to the vapor pressure of the saturated solution of NaCl ($r = 0.78$); in this last part (left branch of the curve) the approximation (18) ceases to be valid because the solution is too concentrated.

If the solution drop is in an atmosphere kept at a value of r lower than the maximum of the curve, it will become stable with the corresponding value of the radius R, as given by the curve. If r is higher than the maximum, the drop will start growing indefinitely, while its vapor pressure p'_R decreases along the right side of the curve. In this sense, the values corresponding to the maximum, r_c and R_c, are critical values for the activation of hygroscopic nuclei in the atmosphere, leading to the formation of cloud drops.

In order to obtain the critical values, we should differentiate Equation (16) with respect to R and equate to 0. But it is easy to verify that the maximum is already in a region in which the solution is dilute enough to apply the approximate Equation (18). Differentiating the latter and equating to 0, we obtain:

$$R_c = \sqrt{\frac{3Q}{P}} \tag{19}$$

which, substituted into Equation (18), gives:

$$r_c = 1 + \frac{2\sqrt{P^3}}{3\sqrt{3Q}} \tag{20}$$

Table V-2 gives the critical values for several sizes of sodium chloride nuclei. For instance, a nucleus of 10^{-15} g will become activated with a supersaturation of 0.13%, in a drop of radius 0.62 μm.

TABLE V-2
Critical activation values (drop radius and supersaturation) for sodium chloride nuclei

m_2 (g)	R_c (μm)	$r_c - 1$
10^{-16}	0.19	4.2×10^{-3}
10^{-15}	0.62	1.3×10^{-3}
10^{-14}	1.9	4.2×10^{-4}
10^{-13}	6.2	1.3×10^{-4}
10^{-12}	19.0	4.2×10^{-5}

5.3. Sublimation and Freezing of Small Crystals

We can make, step by step, the same derivation that we made for condensation in Section 1, for the phenomenon of sublimation. Therefore we can write:

$$\ln \frac{p_R}{p_s} = \frac{2\sigma_{sv} M}{\varrho_s R^* T R} \tag{21}$$

where p_R and p_s are now referred to the solid, σ_{sv} is the surface tension of the solid in the presence of its vapor, and ϱ_s is the density of the solid. This equation implies the approximation of considering the small crystal as if it had spherical shape, because it has been assumed that

$$\mathrm{d}\mathscr{S} = \frac{2}{R}\,\mathrm{d}V.$$

If the relation between $\mathrm{d}\mathscr{S}$ and $\mathrm{d}V$ is different from $2/R$, we should substitute this factor in the formula by another factor which will depend on the shape of the crystal.

For the melting equilibrium (small crystals in equilibrium with the liquid) a similar derivation which will not be included here shows that the equilibrium temperature T is lower than that corresponding to a macroscopic plane surface of the crystal (T_0), and the difference is given by the formula

$$T_0 - T = \frac{2\sigma_{\mathrm{sl}} T_0}{l_{\mathrm{f}} \varrho_{\mathrm{s}} R} \tag{22}$$

where σ_{sl} is the interfacial tension solid-liquid, l_{f} is the latent heat of fusion, and the shape of the crystal has been again approximated by a sphere of radius R. The difference $(T_0 - T)$ is very small, except for extremely small values of R; for example, for ice, it reaches 1 K when R becomes equal to 0.036 μm (accepting a value $\sigma_{\mathrm{sl}} = 20$ dyn cm^{-1} for the interfacial tension).

PROBLEMS

1. Calculate the radii of water droplets in equilibrium with an atmosphere whose supersaturation is (a) 1‰; (b) 0.1‰; (c) 0.05‰. Assume a temperature of 0 °C.
2. Consider a nucleus of NaCl of mass 3×10^{14} g. Derive:
   (a) The radius of a droplet containing this nucleus in solution, for which the vapor pressure e_{r}' is exactly equal to that of pure water with a plane surface e_{s}.
   (b) The critical radius, over which the nucleus becomes activated. The two results will be in the order of magnitude of micrometers. You can use this fact to simplify the calculations. The temperature is 0 °C. The van't Hoff factor is $i = 2$.
3. A water droplet containing 3×10^{-16} grams of sodium chloride has a radius of 0.3 μm.
   (a) Calculate its vapor pressure.
   (b) If the droplet is in equilibrium with the environment, what is the supersaturation (expressed in percentage) of this environment?
   (Note: In computing molar ratios, each formula weight ('molecular weight' M_{NaCl}) of NaCl must be considered as 2 moles, because of the total dissociation in solution; i.e. the van't Hoff factor is $i = 2$). The temperature is 25 °C. At that temperature, the saturation vapor pressure is $e_{\mathrm{s}} = 31.67$ mb.