

Crystallization and Freezing of Acrecus Cordersation Ntclets.

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Crystallization and Freezing of Aqueous

Condensation Nucleus

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I. Introduction

Condensation nuclei active in the atmosphere are considered to be the minute particles of the aqueous solution of hygroscopic substances. In this paper the author intend to treat some problems concerning the processes which occur in such nuclei. As for hygroscopic substances we consider only crystallizable ones, for instance, NaCl and MgCl₂, which are most common in the atmosphere.

There are three important processes which occur in such a nucleus by the change of meteorological conditions of the surrounding air. First, it increases its diameter with humidity and forms a cloud or fog particle when the humidity rises over a critical value. Secondary, at a sufficiently low humidity the hygroscopic substance begins to crystallize. Lastly, the aqueous nucleus becomes frozen at a temperature which is lower than that of bulk water.

Maximum water vapour pressure on such a nucleus increases with the diminution of its size and decreases with the increase of the concentration of the dissolved hygroscopic substances. Thus the size and the concentration of nucleus are the dominating factors on the growth of the nucleus and also on the formation of the cloud particle. Above relations, which are very important on the physics of cloud and rain, have been investigated by many investigators.

On the contrary, however, strict treat-

ment of other two processes, *i.e.* the crystallization and freezing of the nucleus, have not been done.

Crystallization of the dissolved substance begins around a crystallization nucleus contained in the condensation nucleus. The crystallization nucleus is sometimes an aggregate of molecules of the dissolved substance and at other times it may be consisted of foreign substances.

The humidity of the air in equilibrium with the aqueous nucleus depends not only on the size but also on the concentration of the nucleus. Therefore the critical humidity at which the hygroscopic substance in the nucleus begins to crystallize will depend on the nature and the size of the crystallization nucleus. In addition, it depends on the nature and the size of the condensation nucleus. The author treated this problem thermodynamically and calculated the humidity at which NaCl and MgCl₂ in the condensation nucleus start to crystallize.

Similarly as crystallization, freezing of water in the aqueous condensation nucleus begins around a freezing nucleus. Freezing point of such a nucleus is lower than that of bulk water (0°C). It depends not only on the size and the concentration of the condensation nucleus but also on the size and the nature of the freezing nucleus, which is quite similar as the temperature of crystallization. This problem was also studied thermodynamically and the freezing point was calculated for NaCl and MgCl₂ nucleus.

II. Crystallization of Nucleus

As stated above, crystallizable solvent dissolved in the condensation nucleus begins to crystallize at low humidity. Let us consider the state in which such solvent is crystallizing in the nucleus. In this case the system is composed of two chemical components, *i.e.* H₂O and the solvent, the former of which being in gaseous and liquid phases and the latter in liquid and solid ones. To obtain the humidity at which the solvent begins to crystallize, it is necessary to get an equilibrium condition for the system. We shall denote the number of molecules and Gibbs free energy of each component and phase by n and g as follows.

Component \ Phase	Gas	Liquid	Solid
H ₂ O	n'_1, g'_1	n''_1, g''_1	n'''_1, g'''_1
Solvent	n'_2, g'_2	n''_2, g''_2	n'''_2, g'''_2

In the above table suffices 1 and 2 denote H₂O and the solvent, ', '', ''' indicate gaseous, liquid, and solid phase respectively. In the case we consider, $n'_2 = 0$, $n'''_1 = 0$, thus the molecular concentration of each phase is given by

$$\theta' = \frac{n'_2}{n'_1 + n'_2} = 0, \quad \theta'' = \frac{n''_2}{n''_1 + n''_2}, \quad (1)$$

$$\theta''' = \frac{n'''_2}{n'''_1 + n'''_2} = 1.$$

Total free energy G' of the gas is given by

$$G' = n'_1 g'_1. \quad (2)$$

As the liquid is the mixture of two compounds and has a spherical form its total free energy G'' will be represented by

$$G'' = n'_1 g'_1 + n'_2 g'_2 + kT \{ n'_1 \log \theta'' + n'_2 \log(1 - \theta'') \} + 4\pi\sigma r^2 + G''_1, \quad (3)$$

where k : Boltzmann const., T , σ , r : absolute temperature, surface tension and radius of the nucleus respectively, G''_1 : increment of free energy due to the attractive force between molecules of water and dissolved solvent. Similarly, total free energy G''' of the solid is given by

$$G''' = n'''_1 g'''_1 + 4\pi\sigma' r_c^2, \quad (4)$$

where σ' is the surface tension of the crystallized solvent in contact with liquid solution, and r_c is the radius of the crystallized solvent assuming as a sphere.

For equilibrium, we must find the change of total free energy G of the system when the numbers of molecules of each component change, and set this change equal to zero. Using (2), (3), and (4) we have

$$\begin{aligned} \delta G &= \delta G' + \delta G'' + \delta G''' \\ &= g'_1 \delta n'_1 + g''_1 \delta n''_1 + g''_2 \delta n''_2 + kT \{ \log \theta'' \delta n''_1 \\ &\quad + \log(1 - \theta'') \delta n''_2 \} + 4\pi\sigma \delta(r^2) + \delta G''_1 \\ &\quad + g'''_1 \delta n'''_1 + 4\pi\sigma' \delta(r_c^2) = 0. \end{aligned} \quad (5)$$

As stated above, $n'_1 + n''_1 = \text{const.}$, $n'_2 + n''_2 = \text{const.}$, from which we have

$$\delta n'_1 + \delta n''_1 = 0, \quad \text{and} \quad \delta n''_2 + \delta n'''_2 = 0. \quad (6)$$

Putting these relations into (5) we get

$$\begin{aligned} \delta G &= \left\{ g'_1 - g''_1 - kT \log \theta'' - \frac{\partial G''_1}{\partial n''_1} - A_1 \right\} \delta n'_1 \\ &\quad + \left\{ g''_2 - g'''_2 + kT \log(1 - \theta'') + \frac{\partial G''_1}{\partial n''_2} \right. \\ &\quad \left. + A_2 - A_3 - A_4 \right\} \delta n''_2 = 0, \end{aligned} \quad (7)$$

where A_1 , A_2 , A_3 and A_4 are given by

$$\begin{aligned} 4\pi\sigma \delta(r^2) &= 4\pi\sigma \left\{ \frac{\partial(r^2)}{\partial n''_1} \delta n''_1 + \frac{\partial(r^2)}{\partial n''_2} \delta n''_2 \right. \\ &\quad \left. + \frac{\partial(r^2)}{\partial n'''_2} \delta n'''_2 \right\} \equiv A_1 \delta n''_1 + A_2 \delta n''_2 + A_3 \delta n'''_2, \end{aligned} \quad (8)$$

$$4\pi\sigma' \delta(r_c^2) = 4\pi\sigma' \frac{\partial(r_c^2)}{\partial n'''_1} \delta n'''_1 \equiv A_4 \delta n'''_1. \quad (9)$$

From (7) we have two relations, *i.e.*,

$$g'_1 = g''_1 + kT \log \theta'' + \frac{\partial G''_1}{\partial n''_1} + A_1, \quad (10)$$

and

$$\begin{aligned} g''_2 = g'''_2 - kT \log(1 - \theta'') - \frac{\partial G''_1}{\partial n''_2} \\ - A_2 + A_3 + A_4. \end{aligned} \quad (11)$$

As we are concerned only with the state in which the solvent is crystallizing, the aqueous solution of the nucleus must be saturated with the dissolved solvent. Therefore if

we denote the maximum water vapour pressure on the plane water at T by p_x and that on the nucleus by p_r' , then we have

$$\log \frac{p_r'}{p_x} = \frac{1}{kT} (g_1' - g_1'') = \log \theta'' + \frac{1}{kT} \frac{\partial G_1''}{\partial n_1''} + \frac{A_1}{kT}. \quad (12)$$

Two terms of the beginning on the right-hand side of the above formula express the effect of the dissolved solvent on the maximum water vapour pressure on the nucleus, and the last one depends on the size of the nucleus.

Calculating A_1 from (8) we have

$$A_1 = \frac{2\sigma}{Nr} M_1 \frac{1+2rC}{(1+rC)^2}, \quad (13)$$

where N : Loschmidt number, M_1 : molecular weight of water, C : mass concentration of the solvent = $\frac{n_2'' M_2}{n_1'' M_1 + n_2'' M_2}$, M_2 : molecular weight of the solvent. For aqueous solutions treated by us the density ρ'' increases nearly in proportion to the mass concentration C , therefore we can put $\rho'' = 1 + \gamma C$, in which γ depends only on the nature of the solvent.

On the bulk solution, *i.e.* $r = \infty$, with the same concentration and temperature as the nucleus, the maximum water vapour pressure p_x' will be given by

$$\log \frac{p_x'}{p_x} = \log \theta'' + \frac{1}{kT} \frac{\partial G_1''}{\partial n_1''}. \quad (14)$$

With the exception of the nature of the solvent the value of the left-hand side of the above equation depends only on the temperature. Furthermore, the concentration of saturated solution is uniquely determined by the temperature, therefore it is clear that the value of the right-hand side of (14) depends only on the concentration θ'' .

From (12) and (14) we have the maximum water vapour pressure on the nucleus in relation to that on the bulk solution with the same concentration and temperature,

$$\log \frac{p_r'}{p_x'} = \frac{A_1}{kT}. \quad (15)$$

For the next step we shall consider the second equation (11) which was derived from the equilibrium condition.

The temperature T at which the solvent dissolved in the bulk solution starts to crystallize will be related with the concentration θ'' of the solution by

$$g_2''(T) = g_2'''(T) - Tf(\theta''), \quad (16)$$

where

$$f(\theta'') = k \log(1 - \theta'') + \frac{1}{T} \left(\frac{\partial G_1''}{\partial n_1''} \right). \quad (17)$$

In the presence of embryonic crystal with a radius r_c this starting temperature of the condensation nucleus must be lower than T . Or the concentration of the nucleus at which crystallization starts at T must exceed θ'' , the difference from which is denoted by $\Delta\theta''$. Then we have

$$g_2''(T) = g_2'''(T) - Tf(\theta'' + \Delta\theta'') - A_2 + A_3 + A_4. \quad (18)$$

In conjunction (16) with (18) we get

$$-T \frac{df}{d\theta''} \Delta\theta'' = A_2 - A_3 - A_4. \quad (19)$$

Near the crystallization temperature,

$$\frac{\partial}{\partial T} (g_2'' - g_2''') = -\frac{q_2}{T}, \quad (20)$$

where q_2 is the heat of dissolution referred to one molecule of the crystallized solvent. Differentiation of (16) leads also to

$$\frac{\partial}{\partial T} (g_2'' - g_2''') = -f(\theta''). \quad (21)$$

Using (19), (20) and (21) we can express the increment of the concentration as

$$\Delta\theta'' = \frac{T}{q_2} \frac{d\theta''}{dT} (A_2 - A_3 - A_4),$$

$$\text{or } \Delta C = \frac{T}{q_2} \frac{dC}{dT} (A_2 - A_3 - A_4). \quad (22)$$

Calculating A_2 , A_3 and A_4 from (8) and (9) we have

$$A_2 = \frac{2\sigma}{Nr} M_2 \frac{1 - \gamma + 2rC}{(1 + \gamma C)^2},$$

$$A_3 = \frac{2\sigma}{Nr} \frac{M_2}{\rho_c}, \quad A_4 = \frac{2\sigma'}{Nr_c} \frac{M_2}{\rho_c},$$

where ρ_c is the density of the crystallized solvent. Putting these expressions into (22) we can get the final expression for ΔC as

$$\Delta C = \frac{2TM_2\sigma}{Nq_2} \left[\frac{1}{r} \left\{ \frac{1-\gamma+2\gamma C}{(1+\gamma C)^2} - \frac{1}{\rho_c} \right\} - \frac{\sigma'}{\sigma} \frac{1}{r_c\rho_c} \right] \frac{dC}{dT}. \quad (23)$$

The difference of the saturated concentration of the condensation nucleus which contains a crystallization nucleus with a radius r_c from that of the bulk solution both at T will be calculated from (23).

So far we have treated the crystallization nucleus as if it were the same substance as dissolved one. However as stated afore it may be a foreign substance and in this case the numerical value of σ' must be different from that of the crystallized solvent. The numerical value of the surface tension of solid is unknown, but it is considered in general to be about one-tenth of that in liquid state. Because of the uncertainty of the numerical value of σ' we shall consider the crystallization nucleus as an aggregate of molecules of the solvent.

Next, in general the form of the crystallization nucleus is not spherical but is polyhedral. As the surface area of a sphere is smaller than that of a polyhedron with the same mean radius, σ' in (23) should be multiplied by a numerical factor which is larger than 1 and depends on the form of the crystallization nucleus. For convenience and because of the uncertainty of the numerical value of both σ' and the factor stated above, we shall adopt in place of σ' the surface tension of melted solvent multiplied by 0.2.

In (23) M_2 , q_2 , γ , ρ_c and σ' depend only on the nature of the solvent, whereas C , T and $\frac{dC}{dT}$ depend both on the nature and the temperature, thus concentration increment ΔC will be determined by the temperature, the nature and the radius of the crystallized solvent

which is acting as a crystallization nucleus.

The increment of the concentration of the solution is accompanied by the fall of the humidity of the surrounding air. The relation connecting them will be obtained by differentiating (15), namely

$$\Delta p_r' = \Delta p_\infty' + \Delta \exp\left(\frac{A_1}{kT}\right).$$

As is obvious from the result of calculation the value of the second term on the right-hand side of the above equation is far smaller than that of the first term. Consequently we can

put $\Delta p_r' = \frac{dp_\infty'}{dC} \Delta C$, from which the approximate expression for the change of the relative humidity ΔH by % will be given by

$$\Delta H = \frac{\Delta p_r'}{p_\infty} \times 100 = \frac{p_\infty'}{p_\infty} \frac{1}{p_\infty'} \left(\frac{dp_\infty'}{dC} \right)_T \Delta C \times 100. \quad (24)$$

Using (23) and (24) we can calculate the humidity at which the condensation nucleus begins to crystallize. Some examples are shown below.

(1) NaCl nucleus

Numerical constants which appear in (23) are as follows. $Nq_2 = -4.6 \times 10^{10}$ ergs, $\sigma = 76$, $\rho_c = 2.2$, $\gamma = 0.77$, $\sigma' = 0.2 \times 110 = 22$, $M_2 = 58.5$ (for $>0.1^\circ\text{C}$). At 10°C , $C = 26.34 \times 10^{-2}$,

$$\left(\frac{dC}{dT} \right)_{p_\infty'} = 7.5 \times 10^{-5}, \quad \frac{p_\infty'}{p_\infty} = 0.75,$$

$$\frac{1}{p_\infty'} \left(\frac{dp_\infty'}{dC} \right)_T \times 100 = -1.2 \times 10^3,$$

thus we have $\Delta H = -3.6 \times 10^{-3} \left(\frac{1}{r} + \frac{14}{r_c} \right) \%$.

As the size of the condensation nucleus is larger than that of the crystallization nucleus, the above result shows that the effect of the size of the former on the humidity is negligibly small. The change of the humidity by % for the various sizes of the crystallization nucleus is tabulated below.

r_c	10^{-7}	10^{-6}	10^{-5}	10^{-4}	cm
ΔH	-0.50	-0.050	-0.005	-0.0005	%

As aqueous solution of NaCl with plane surface begins to crystallize at humidity between 75 and 78 %, above result leads to the conclusion that the small drop of NaCl solution which contains a crystallization nucleus with a radius of, for instance, 10^{-7} cm starts to crystallize at the humidity between 74.5 and 77.5 %.

Below 0.1°C sodium chloride changes from anhydrate to hydrate, in which case the problem is so complicated that we are obliged to give up the calculation. However, below 0.1°C the numerical value of $\frac{dC}{dT}$ is far larger than that at normal temperature, therefore it is presumed that at low temperature the fall of the humidity is exceedingly large in comparison with that at normal temperature.

(2) MgCl_2 nucleus

Normal state of magnesium chloride is that of a hydrate combined with six molecules of water, *i.e.* $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Numerical constants are as follows,

$$Nq_2 = +1.26 \times 10^{11}, \quad \sigma = 76, \quad \rho_0 = 1.56, \quad \gamma = 0.90, \\ \sigma' = 0.2 \times 100 = 20, \quad M_2 = 203.3.$$

$$\text{At } 10^\circ\text{C}, \quad C = 34.9 \times 10^{-3}, \quad \left(\frac{dC}{dT}\right)_{p'_x} = 2.7 \times 10^{-4},$$

$$\frac{p'_x}{p_x} = 0.4, \quad \frac{1}{p_x} \left(\frac{dp'_x}{dC}\right)_T \times 100 = -3.2 \times 10^2,$$

$$\text{thus we have } \Delta H = 5.2 \times 10^{-7} \left(\frac{1}{r} + \frac{0.82}{r_c}\right) \%$$

As seen from the above result the relative humidity at which crystallization starts is higher for MgCl_2 nucleus than for bulk solution. The numerical values of ΔH for various sizes of the crystallization nucleus are tabulated below.

r_c	10^{-7}	10^{-6}	10^{-5}	10^{-4}	cm
ΔH	4.3	0.43	0.043	0.004	%

At low temperatures $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ turns to $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ or $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ and as in these circumstances numerical constants which appear in (23) are not well known no calculations were made for these cases.

In general it is considered that aqueous solution of NaCl starts to crystallize at the humidity between 75 and 78%. WOODCOCK⁽³⁾, however, observed that sea-salt drops did not crystallize for humidity as low as 30 % and DESSENS⁽⁴⁾ also found that the drop of the aqueous solution of NaCl remained in equilibrium with the atmosphere at humidities between 100 and 40 %. From the results obtained by us, however, it is not easy to explain such an excessive discrepancy. Perhaps droplets observed by them would contained no adequate crystallization nucleus and the solvent would crystallized barely around a very minute nucleus or a mass of the dissolved solvent. Further investigations on the behaviour of these droplets at low humidity are requested to be done.

III. Freezing of Nucleus

Let us consider the state in which water in a small drop of aqueous solution is freezing at low temperature. Similarly as in the case of crystallization we shall assume the freezing nucleus as an aggregate of water molecules, *i.e.* a minute ice crystal. Now, as the solvent is only in liquid state or $n_2^* = 0$, $n_2^{**} = 0$, the molecular concentration of both gaseous and solid phases are equal to 0. Quite similarly as afore the maximum water vapour pressure on the condensation nucleus is given by

$$\log \frac{p'_r}{p'_x} = \frac{A_1}{kT}. \quad (15)$$

The second relation derived from the equilibrium condition and corresponds to (11) is expressed by

$$g_1'' = g_1''' - kT \log \theta'' - \frac{\partial G_1''}{\partial n_1''} - A_1 + A_5 + A_6, \quad (25)$$

where $A_5 = 4\pi\sigma \frac{\partial(r^3)}{\partial n_1''}$, $A_6 = 4\pi\sigma' \frac{\partial(r_i^3)}{\partial n_1'''}$, r_i is the radius of the freezing nucleus assumed as a sphere. If we denote the freezing point of pure water and that of the aqueous solution

both with plane surface by T ($=273$) and $T + \Delta T_1$ respectively, then we have

$$g_1''(T) = g_1'''(T), \tag{26}$$

$$\text{and } g_1''(T + \Delta T_1) = g_1'''(T + \Delta T_1) - (T + \Delta T_1)f(\theta''). \tag{27}$$

From two equations above we get

$$\frac{\partial}{\partial T} (g_1'' - g_1''') \Delta T_1 = -Tf(\theta''). \tag{28}$$

Latent heat of freezing of water q_1 is given by

$$-\frac{\partial}{\partial T} (g_1'' - g_1''') = -\frac{q_1}{T}. \tag{29}$$

Combining (27) with (28) the difference of freezing point can be expressed by

$$\Delta T_1 = \frac{T^2}{q_1} f(\theta''). \tag{30}$$

Numerical values of ΔT_1 referred to θ'' are found in any chemical table. Again, denoting the freezing point of the condensation nucleus by $T + \Delta T_1 + \Delta T_2$ and putting it in (25) we get

$$g_1''(T + \Delta T_1 + \Delta T_2) = g_1'''(T + \Delta T_1 + \Delta T_2)f(\theta'') - A_1 + A_5 + A_6.$$

Using (27), (29) and (30) we have

$$\Delta T_2 = (-A_1 + A_5 + A_6) / \left(-\frac{q_1}{T + \Delta T_1} + \frac{q_1}{T^2} \Delta T_1 \right) = \frac{T}{q_1} (A_1 - A_5 - A_6). \tag{31}$$

As A_5 and A_6 in (25) are expressed by

$$A_5 = \frac{2\sigma}{Nr} \frac{M_1}{\rho_i}, \quad A_6 = \frac{2\sigma' M_1}{Nr_i \rho_i},$$

where ρ_i is the density of the freezing nucleus and σ' means its surface tension, we can obtain the final expression for the depression of freezing point as

$$\Delta T_2 = \frac{2\sigma M_1}{Nq_1} T \left\{ \frac{1}{r} \left(\frac{1 + 2rC}{(1 + rC)^2} - \frac{1}{\rho_i} \right) - \frac{\sigma'}{\sigma r_i \rho_i} \right\}. \tag{32}$$

The depression of the freezing point of the NaCl solution with plane surface referred

to the concentration, which is expressed by (30), is tabulated below.

$C \times 10^2$	0	5	10	15	20	22.4
ΔT_1	0	-4.8	-9.5	-14.3	-19.0	-21.2

We shall, then, obtain the numerical values of ΔT_2 for the condensation nucleus of the aqueous solution of NaCl. Numerical constants involved in (32) are as follows. $\sigma = 75$, $M_1 = 18$, $Nq_1 = 18 \times 80 \times 4.2 \times 10^7 = 6.1 \times 10^{10}$, $\rho_i = 0.9$, $\sigma'/\sigma = 0.2$. Thus at -10°C , we have

$$\Delta T_2 = 1.4 \times 10^{-6} \left(\frac{1}{r} - \frac{1.8}{r_i} \right).$$

From the above result the effect of the size of the condensation nucleus will be found to be negligibly small as in the case of crystallization. The numerical values of the depression of freezing point ΔT_2 referred to the radius of the crystallization nucleus are tabulated below.

r_i	10^{-7}	10^{-6}	10^{-5}	10^{-4}	cm
ΔT_2	-25	-2.5	-0.25	-0.025	

Even at other temperatures the values of ΔT_2 are nearly equal to those shown above. Furthermore as the depression of the freezing point is influenced only slightly by the size of the condensation nucleus these values also hold for droplets of aqueous solution of other solvents.

As will be seen from two tables above, the condensation nucleus which contains a freezing nucleus of a radius, for instance, of 10^{-6} cm starts to freeze for various concentrations at temperatures tabulated below.

$C \times 10^{-2}$	0	5	10	15	20	22.4
$\Delta T_1 + \Delta T_2$	-2.5	-7.3	-12.0	-16.8	-21.5	-23.7

It may be concluded that the freezing point of the condensation nucleus is influenced considerably not only by the concentration of the solution or the humidity of the surrounding air but also by the size of the freezing nucleus contained in it.

Such a condensation nucleus floating in the air will become frozen at a relatively low temperature when the humidity is low and also when the freezing nucleus contained is small.

Recently HOLLSTEIN⁽²⁾ observed that the small drop of NaCl solution could be supercooled as low as -35.5°C . From the result obtained by us it is presumed that the smallest size of the freezing nuclei contained in the drops prepared by her is as small as 1.8×10^{-7} cm.

IV. Acknowledgment

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