Solidification in Heat Packs: I. Nucleation Rate

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The solidification of sodium acetate trihydrate in a commercial heat pack is investigated in a series of three articles. In the first work, the classic nucleation theory is used to predict the range of temperatures and pressures for which a subcooled solution of sodium acetate solidifies spontaneously. The nucleation temperature was determined experimentally and it was shown that it is insensitive to concentration, at atmospheric pressure. Using the theoretical results for high pressure and the experimental measurements at atmospheric pressure, an equation for the nucleation temperature was derived as a function of pressure. This relation takes into account heterogeneous nucleation on ever-present impurities suspended in the solution.

Introduction

The ability of an aqueous sodium acetate solution to remain liquid at temperatures well below its liquidus temperature has been known for at least one hundred years and was originally proposed as a means of storing solar energy in the form of latent heat (Ulman and Valentin, 1983). Nowadays, the most common use for this method of heat storage is in portable heat packs, used for warming drinks, soothing muscle aches, and as a treatment for hypothermia in remote locations.

A heat pack consists of a sealed, flexible PVC envelope (typically 20×10 cm^2) containing a subcooled aqueous solution of sodium acetate. A metallic trigger located within the container initiates the solidification of the liquid to release latent heat (Kapralis et al., 1990). Figure 1 shows a sequence of photographs illustrating the crystallization process in a heat pack. By flexing the metal disc in the top left corner of the pack, the subcooled solution is made to crystallize and release latent heat. The crystals grow from the trigger site in all directions where liquid is available. A network of solid is very rapidly formed throughout the pack. This phase-change releases a large quantity of heat that is transferred to the surroundings of the pack at a smaller rate than it is generated; as a result, the temperature of the solid−liquid mixture rises to a maximum of 54°C, the liquidus temperature of the solution. However, some liquid remains in the interstices of the network of the solid. This liquid solidifies gradually at a rate controlled by the heat transfer to the surroundings. Eventually, the temperature of the heat pack decreases gradually to the temperature of the surroundings. The latent heat of solidification of the heat-pack solution is 125 kJ/kg (Araki et al., 1995), yielding 41 kJ in total for a typical pack of 300 mL. Before being used again, the pack is regenerated. *Regeneration* is accomplished by simply melting the crystals and allowing them to cool. The simplest and safest method is by boiling the pack in water until all the crystals are melted. When the solution is completely liquid, it is allowed to cool below its freezing temperature. It is then ready to be activated again. This process of melting and activating can be repeated hundreds of times, as long as the pack remains sealed.

The operation of a heat pack is not, however, as reliable as would be desired. Small vibrations during transport can trigger the crystallization process, making the pack unavailable when it is needed. In order to be able to improve the operation of heat packs, we need to understand the fundamentals of the solidification of sodium acetate trihydrate. In this series of three articles, we investigate the mechanism by which solidification is induced in a sodium acetate heat pack with a metallic trigger.

Figure 2 shows the phase diagram for sodium acetate in water. As a solid, sodium acetate exists in two forms, the anhydrite ($NaCH_3COO$) and the trihydrate-($NaCH_3COO.3H_2O$). The trihydrate is the thermodynamically more stable form and is produced when a heat pack solidifies. It is the production of this form that is considered in this work. Sodium acetate solution at high concentration will precipitate anhydrite until the concentration of the remaining solution is reduced to the solid line shown in the phase diagram. This precipitation of anhydrite limits the possible maximum

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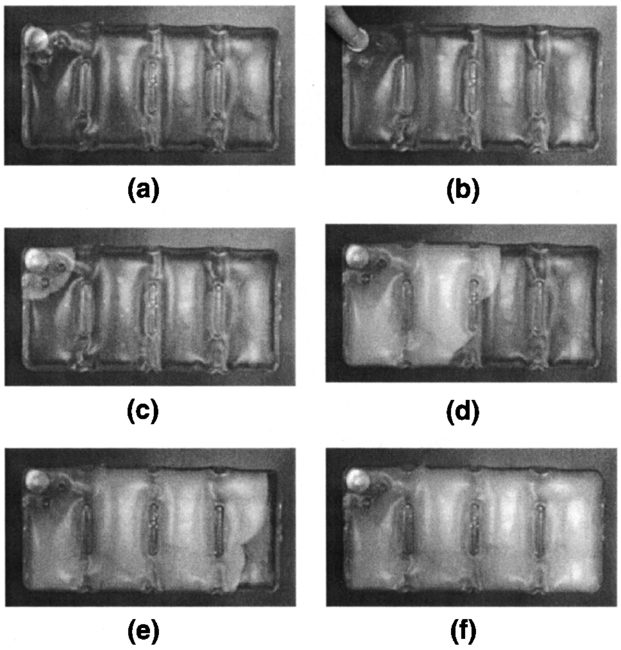


Figure 1. Sequence of the onset and development of crystallization in a heat pack.

(a) Subcooled solution and metal trigger; (b) metallic trigger flexed; solidification front at times (c) 3 s, (d) 5 s, and (e) 6 s after triggering; and (f) solution completely solidified 7 s after triggering.

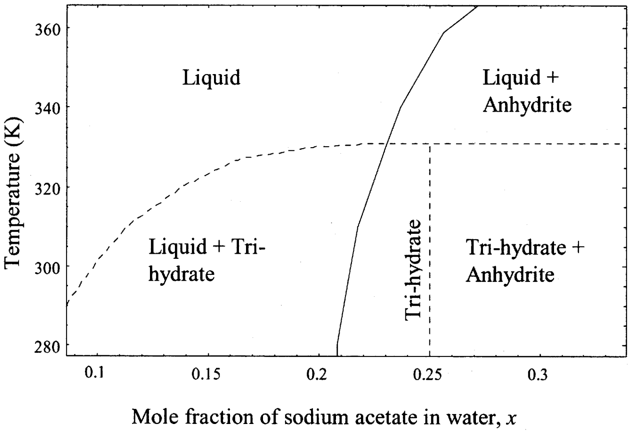


Figure 2. Phase-diagram sodium acetate in water [Data from Araki et al. (1995)].

concentration of the solution used in heat packs. Figure 2 shows that at 20°C, the maximum molar fraction of sodium acetate in solution is approximately $x = 0.21$. To prevent precipitate forming in the packs, a concentration of $x = 0.206$ (corresponding to trihydrate with 10% by mass of additional water) is typically used in heat packs, and hereafter is referred to as the *standard* concentration. The dashed lines in the phase diagram in Figure 2 represent the trihydrate–liquid and trihydrate–anhydrite coexistence lines. These lines are dashed because, in the absence of a seed crystal, the metastable liquid phase exists well into these regions.

The Gibbs phase rule limits the number of ways a sodium acetate solution can be made to solidify. Either the temperature, pressure, or concentration must be altered or a catalyst, such as a seed crystal, added. In this article, the classic theory of nucleation is used to quantify the effects of temperature, concentration, and pressure on the nucleation process. We also determine the limits of the metastable state.

We begin with a description of a set of carefully controlled laboratory experiments to determine the nucleation temperature of a heat-pack sodium acetate solution, at atmospheric pressure. We then develop a mathematical model to predict the rate of nucleation in a sodium acetate solution. The experimental data are used to test and extend the accuracy of the mathematical model. Much work involving the classic theory of nucleation exists in the literature, but a complete account as applied to the sodium acetate solution is given here for two reasons. First, other works on nucleation do not adequately address sodium acetate, being either too broad in their scope or limited to highly specific systems that are not applicable. Second, no adequate single reference could be adapted to describe the thermodynamics of the solidification of a sodium acetate solution of standard concentration. Such knowledge is required to understand the mechanism of solidification in heat packs, described in Parts 2 and 3 of this series of articles.

Experimental Procedure and Results

Experiments were carried out to determine the temperature at which a sodium acetate solution crystallizes, at atmospheric pressure. The effect of concentration of the solution on the nucleation temperature was assessed. The experiments are described below.

Sodium acetate solution

The sodium acetate solution was prepared from sodium acetate trihydrate crystals (Rectapur 98% pure) and distilled water. The concentration of the solution was varied between $x = 0.100$ and $x = 0.206$ mole fraction of sodium acetate trihydrate in water.

Cooling in a test tube

A sample of solution of approximately 10 mL was placed in a glass test tube. The test tube was immersed in a slurry of acetone and dry ice, which has a temperature of approximately 195 K. The temperature of the sample was measured with a thermocouple. When nucleation occurred, a rise in temperature was noted. The temperature of the sample just before the onset of solidification was taken as the nucleation temperature.

Differential scanning calorimetry

The experiments were carried out using a differential scanning calorimeter (DSC) Pyris 1 (Perkin-Elmer instruments),

Table 1. Experimental Results for the Nucleation Temperature of Sodium Acetate Aqueous Solutions, T_n (K), at Atmospheric Pressure

Method	$x = 0.100$	$x = 0.150$	$x = 0.206$
DSC	262 ± 3	261 ± 3	255 ± 4
Test tube	250 ± 1	263 ± 2	248 ± 2

Note: x is the mole fraction of sodium acetate in solution.

fitted with a mechanical refrigeration unit Pyris intracooler 1P, capable of cooling to a temperature of 243 K.

Two drops of aqueous sodium acetate solution were placed in an aluminum pan. The pan was subsequently crimped but not hermetically sealed. The sample was subjected to linearly programmed cooling, at a rate of 0.4 K/min, between 293 K and 243 K. The nucleation temperature was obtained from the sample temperature curve at the time corresponding to the onset of an exothermal peak.

A few experiments were repeated with a stainless-steel pan; no difference in results was observed.

Results

Table 1 summarizes the experimental measurements of the nucleation temperature of a sodium acetate solution at atmospheric pressure. The average temperature of four identical runs and the root-mean-square deviation are shown.

The results in Table 1 suggest that the nucleation temperature does not vary with concentration, in the concentration range studied. The results obtained with the DSC indicate a nucleation temperature of approximately 259 K. The results using the test tube suggest a nucleation temperature of approximately 250 K. This discrepancy between the results on the DSC and the test-tube methods has also been observed by other authors (Wada and Yamamoto, 1982), but is not understood.

Solidification Mechanism

Consider the process of solidification at the molecular level. Molecules in the liquid collide and stick together to form solid-like clusters. These clusters then may grow by further molecular attachment or by collision and attachment to other clusters. The clusters can also shrink by molecular detachment or by breaking up into smaller clusters. For nucleation, the size of the cluster is of major importance (see, e.g., Gunton, 1999, and Oxtoby, 1992). Below a critical size, the cluster may persist suspended in solution, but will not grow rapidly to solidify the entire body of liquid, whereas as soon as a cluster of critical size is formed, continuous growth occurs very rapidly. A cluster of critical size is called an *incipient nucleus*.

$$\begin{tikzcd}
\cdots \arrow[r, shift left, "f_{n-2}"] & A_{n-1} \arrow[l, shift left, "b_{n-1}"] \arrow[r, shift left, "f_{n-1}"] & A_n \arrow[l, shift left, "b_n"] \arrow[r, shift left, "f_n"] & A_{n+1} \cdots \arrow[l, shift left, "b_{n+1}"]
\end{tikzcd}$$

Figure 3. Growth and shrinkage of a cluster.

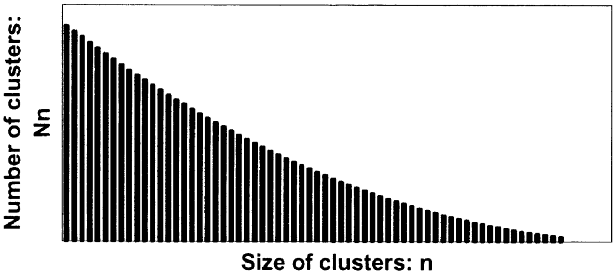


Figure 4. Distribution of cluster sizes in a subcooled solution.

N_n is the number of clusters that consists of n molecules.

The formation of solid sodium acetate trihydrate requires three parts water and one part sodium acetate, but for simplicity these four parts together may be thought of as a "molecule." For example, cluster A containing $n-1$ molecules (A_{n-1}) can change to A_n, A_{n+1}, …, as shown in Figure 3. The molecular attachment rate, f, and the molecular detachment rate, b, vary with the size of the cluster (Farkas, 1927). Changes in size by more than one molecule at a time are not shown but can be represented in the same way.

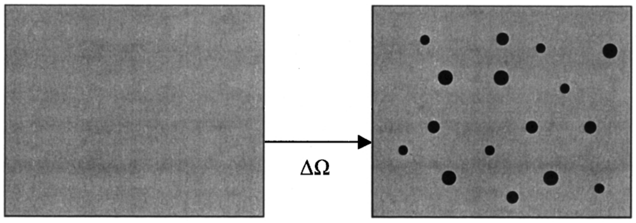
The equilibrium state of subcooled sodium acetate solution is complete solidification. However, such an equilibrium state is not achieved because, although f and b are fast, the expected number of incipient nuclei is so low that effectively a nucleus is never formed, that is, there is an energy barrier (Zettlemoyer, 1969). Instead of equilibrium, a metastable state exists that consists of a distribution of cluster sizes in solution (Volmer and Weber, 1926).

We can calculate the metastable distribution of clusters by considering how the free energy of the system changes with the number of clusters and their size in solution (Gibbs, 1876, 1878; Becker and Döring, 1935). A diagram of this size distribution is shown in Figure 4. The cluster of largest size in the metastable state occurs with the lowest frequency. This cluster defines the critical size. The frequency of clusters each side of this critical size increases monotonically with increasing and decreasing n (Kaschiev, 2000). However, in a stable subcooled solution, the expected number of incipient nuclei is very small and clusters must grow by passing through each size, so no clusters greater than the critical size can form. The minimum in the size distribution, at the critical size, arises because the critical size is the cluster with the largest free energy of formation (Kurz and Fisher, 1986).

Nucleation occurs when the physical conditions change such that the expected number of incipient nuclei becomes appreciable. The expected nucleation rate is the product of the expected number of incipient nuclei and the expected rate of attachment to such an incipient nucleus. In this work, we will estimate the expected number of incipient nuclei as well as the rates of molecular attachment.

Size and Number of Incipient Nuclei

In this section, we calculate the metastable distribution of clusters for a subcooled solution of sodium acetate trihydrate



(*a*) (*b*)

Figure 5. Free-energy change $\Delta\Omega$ associated with transforming (a) a solution containing only molecules into (b) a solution containing N_1 molecules and N_n clusters of n molecules ($n = 2, 3, 4, \ldots$), at constant temperature and pressure.

in water. Our theoretical development builds upon the works by Kashchiev (2000), Carey (1992), Kurz and Fisher (1986), and Zettlemoyer (1969).

Consider the free-energy change associated with the formation of clusters of molecules in a solution. The two states between which the free-energy change, $\Delta\Omega$, is taken are shown in Figure 5. This free-energy change can be expressed as the sum of the free-energy changes due to forming each cluster and the free-energy change of mixing the clusters into solution:

$$\Delta\Omega = \Delta\Omega_{\text{formation}} + \Delta\Omega_{\text{mixing}} \tag{1}$$

$$\Delta\Omega_{\text{formation}} = \sum_n N_n \Delta\Omega_n, \tag{2}$$

where N_n is the number of clusters that consist of n molecules, and $\Delta\Omega_n$ is the free-energy change in forming one cluster of n molecules. Also

$$\Delta\Omega_{\text{mixing}} = kT \sum_n N_n \ln x_n, \tag{3}$$

where $x_n = (N_n / \sum_n N_n)$, and k is Boltzmann's constant, assuming ideal mixing between the clusters and molecules (Sandler, 1998). T denotes temperature.

The function $\Delta\Omega$ displays a minimum with n. This minimum occurs because the free energy of formation of subcritical-sized clusters is always positive, but the free energy of mixing is always negative. Taking the derivative of $\Delta\Omega$ with respect to the number of incipient nuclei, N_{n^*}, and setting it to zero, gives

$$\frac{\partial(\Delta\Omega)}{\partial N_{n^*}} \approx \Delta\Omega_{n^*} + kT \ln \frac{N_{n^*}}{\sum_n N_n} = 0 \tag{4}$$

and

$$N_{n^*} = N_1 \exp\left(\frac{-\Delta\Omega_{n^*}}{kT} \right) \tag{5}$$

We have assumed in Eq. 5 that the quantity of solution is much greater than the number of clusters, that is, $N_1 \approx \sum_n N_n$. The consequence of this assumption is that the number of incipient nuclei will not be dependent on the concentration of the sodium acetate solution.

The expression for the number of incipient nuclei in Eq. 5 requires the calculation of the free energy of forming one incipient nucleus, $\Delta\Omega_{n^*}$. We can represent the energy of forming a cluster of n molecules, $\Delta\Omega_n$, as a sum of three contributions, from volume effects ΔG_v (melting), surface effects ΔG_s (wetting), and mixing effects ΔG_m. A detailed derivation of the expressions for each of these contributions for sodium acetate trihydrate is presented in the Appendix.

It is important to note here that the contribution from surface effects, ΔG_s, depends critically on the surface energy between solid and liquid sodium acetate trihydrate, σ. Following Kashchiev (2000), in our calculations in the Appendix, we have assumed that σ is independent of cluster size and does not vary with temperature, pressure, and concentration. A more exact dependence of ΔG_s on these parameters is not well established in the literature and few data are available, even for common substances (Kashchiev, 2000). Therefore, to estimate a reasonable σ for sodium acetate trihydrate, use is made of the available data for water and for several ionic salts; σ between water and ice has been well documented at $0.033\ \text{J}\cdot\text{m}^{-2}$ (Ketcham and Hobbs, 1969); and σ for several sulphate salts are in the range $0.1\text{–}0.2\ \text{J}\cdot\text{m}^{-2}$ (Walton, 1969). We have therefore assumed that $\sigma \sim 0.07\ \text{J}\cdot\text{m}^{-2}$ for sodium acetate trihydrate. This is an important approximation, which significantly affects the predictions of our theory. However, we shall see later that this value of σ is compatible with our experimental determination of the nucleation temperature at atmospheric pressure.

The contribution from mixing effects, ΔG_m, was found to become appreciable only when the volume of fluid is very small, of the order of 1 nm^3, so we will neglect ΔG_m in this work. We then have (see the Appendix):

$$\Delta\Omega_r = \Delta G_s + \Delta G_v = 4/3\pi r^3 \Delta g_v(T, p) + 4\pi r^2 \sigma, \tag{6}$$

where

$$\Delta g_v(T,p) = \frac{(331+5p-T)\left\{152.5\left[(331+5p)^2 - 331^2\right] + 1.09\times10^6(5p) + 3.77\times10^8\right\}}{331+5p}$$
$$-152.5(331+5p-T)^2 + 1.09\times10^6\left(T \ln\frac{331+5p}{T} - (331+5p-T)\right), \tag{7}$$

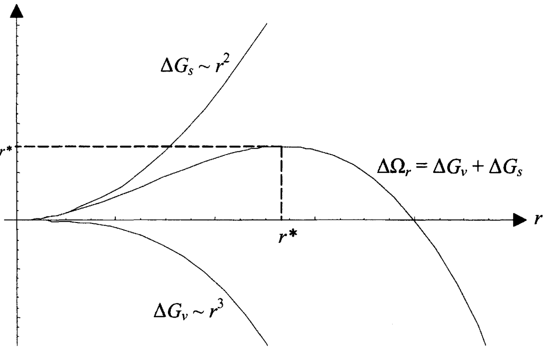


Figure 6. Free energy of cluster formation of radius r, $\Delta\Omega_r$, and its components ΔG_v and ΔG_s.

where p is pressure in kbar. In the preceding equations, we have considered a continuous distribution of sizes of clusters; each cluster is denoted by its radius, r, rather than the number of molecules it contains, n. Similarly, the size of an incipient nucleus will now be denoted by r^* instead of n^*. This *continuous* approach simplifies the mathematics.

A typical variation of $\Delta\Omega_r$ with increasing radius of a nucleus is shown in Figure 6. As expected, the positive r^2 dependency of the ΔG_s term dominates at low r, whereas the negative r^3 dependency of the ΔG_v term dominates at high r, so that the total free-energy change passes through a maximum $\Delta\Omega_{r^*}$ at the critical radius r^*.

In order to calculate the size of the incipient nucleus (the critical radius), r^*, at a particular temperature and pressure, the expression for $\Delta\Omega_r$ (Eq. 6) is differentiated with respect to r and set to zero, giving

$$r^* = \frac{-2\sigma}{\Delta g_v} \tag{8}$$

Equation 8 shows that the critical sizes of sodium acetate trihydrate nuclei are typically of the order of nanometers, for example, at $T = 294$ K and $p = 1$ bar, $r^* = 3.5$ nm. The number of molecules contained within a nucleus is predicted to vary from thousands in a stable subcooled solution to less than one molecule for a solution close to nucleation. The physical basis for the classic theory, of course, breaks down in this latter case.

Substituting Eq. 8 in Eq. 6, we obtain the free-energy change in forming a critical-sized cluster as

$$\Delta\Omega_{r^*} = \frac{16\pi}{3}\frac{\sigma^3}{\Delta g_v^2}. \tag{9}$$

The number of incipient nuclei per unit volume of solution is then given from Eq. 5 by

$$N_{r^*} = 2.5\times10^{28}\exp\left(-\frac{16\pi}{3kT}\frac{\sigma^3}{\Delta g_v^2}\right) \quad (\text{nuclei/m}^3), \tag{10}$$

where we have substituted the number of molecules per unit volume of solution $N_1 = 42{,}650 \times 6 \times 10^{23} = 2.5 \times 10^{28}$ molecules/m^3 (see the Appendix). The number of incipient nuclei is very sensitive to temperature and pressure, and can vary from 10^{-17} nuclei/m^3 close to the onset of nucleation to 10^{-500} nuclei/m^3 in the stable subcooled state. The number of incipient nuclei at any one time must be a whole number. For predicted numbers well below unity, such as for the stable subcooled states in this work, there will almost always be zero incipient nuclei present, very occasionally one, and effectively never more than one. Neglecting any probability of finding more than one incipient nucleus means the value of N_{r^*} just given is equivalent to the expected or mean number of incipient nuclei present over a period of time.

Nucleation Rate J

If we assume that all collisions of molecules with an incipient nuclei result in attachment, then the rate of molecular attachment is equal to the flux of molecules toward the surface of the nucleus. Kashchiev (2000) sets down the results for the rate of diffusion through a spherical boundary, and shows that after an insignificant lead time of $r^{*2}/D \sim 10^{-9}$ s, the flux of molecules toward the surface of the spherical nucleus reduces to

$$f_{r^*} = 4\pi r^* D C_o. \tag{11}$$

The concentration of a standard sodium acetate solution, C_o, was calculated to be 42,650 mol·m^{-3} (see the Appendix) and assumed to vary negligibly with temperature and pressure. The diffusion coefficient, D, will be taken as the average of that tabulated for sodium ions, acetate ions, and water in dilute aqueous solutions (Lide, 1996). D is assumed not to vary with pressure, and the variation with temperature is taken as that recommended by Lide (1996), so that

$$D = 1.86\times10^{9}\times1.025^{T-298}. \tag{12}$$

Substituting Eqs. 8 and 12 into Eq. 11 gives

$$f_{r^*} = \frac{-3.8\times10^{20}\sigma\pi1.025^{T-298}}{\Delta g_v}. \tag{13}$$

The nucleation rate, J, is given by the product of the number of incipient nuclei and the rate of molecular attachment

$$J = N_{r^*}\times f_{r^*}. \tag{14}$$

Substituting from Eqs. 10 and 13, gives

$$J = \frac{-9.5\times10^{47}\sigma\pi1.025^{T-298}}{\Delta g_v}\exp\left(\frac{-16\pi}{3kT}\frac{\sigma^3}{\Delta g_v^2}\right). \tag{15}$$

The rate of nucleation is therefore a strong function of the temperature and pressure, and depends only weakly on the concentration of the solution. For a given volume of solution, J is proportional to the concentration; this effect arises from the control of diffusion on the attachment rate.

In this work, we consider that nucleation is *instantaneous* if the expected rate of nucleation is greater than three nuclei forming per heating pack (300 mL) per second. This corre-

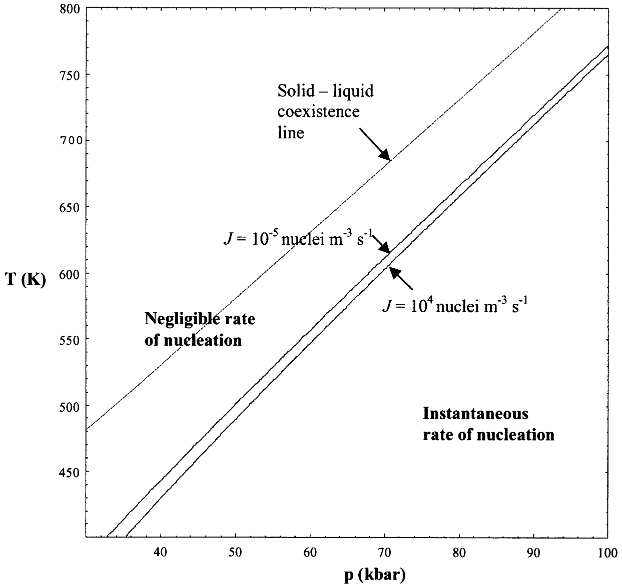


Figure 7. Pressure–temperature diagram indicating the regions of negligible ($J = 10^{-5}$ nuclei $m^{-3} \cdot s^{-1}$) and instantaneous ($J = 10^{4}$ nuclei $m^{-3} \cdot s^{-1}$) nucleation for a standard sodium acetate solution.

sponds to a nucleation rate, J, of 10^4 nuclei $m^{-3} \cdot s^{-1}$. Similarly, nucleation is considered effectively *negligible* if the expected rate of nucleation is less than one nucleus forming per pack per 600 days, which corresponds to $J = 10^{-5}$ nuclei $m^{-3} \cdot s^{-1}$. These negligible and instantaneous nucleation rates define the temperature and pressure conditions under which nucleation is likely to occur. The boundaries corresponding to a negligible nucleation rate and an instantaneous nucleation rate, predicted by Eq. 15, are shown in Figure 7. Also shown is the liquid–solid coexistence line ($\Delta g_v = 0$).

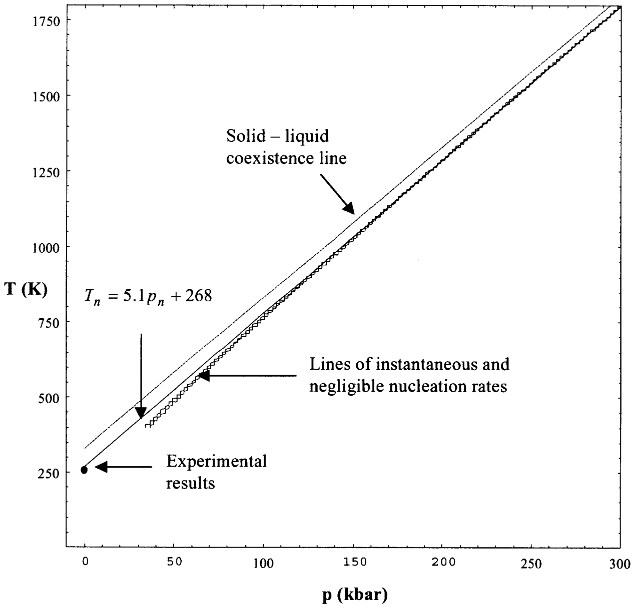


Figure 8. Prediction of the nucleation temperature as a function of pressure for a standard sodium acetate solution (Eq. 16).

The boundaries of negligible and instantaneous nucleation are quite close together, indicating a narrow range of temperatures and pressures beyond which nucleation is predicted to occur, in accordance with our experimental observations. These boundaries are so close together that it makes sense to speak of a nucleation temperature, T_n, and nucleation pressure, p_n, defined by a line running between those boundaries. As expected, the nucleation temperature increases with pressure.

Our experimental measurements of the nucleation temperature at atmospheric pressure are shown in Figure 8. We also plot the lines of instantaneous and negligible nucleation. The relationship between T_n and p_n is linear at high temperatures and pressures. At lower temperatures and pressures, our predictions using Eq. 15, are less accurate due to the extrapolation of the physical data for sodium acetate trihydrate beyond its range of applicability (see the Appendix).

If we extrapolate the nucleation theory predictions to the low-pressure range, the result is consistent with our experimental measurements; this extrapolation is shown by the solid line in Figure 8. The equation for this line is

$$T_n = 5.1 p_n + 268. \qquad (16)$$

Equation 16 predicts a nucleation pressure of 5 kbar at 20°C and a nucleation temperature of 268 K at 1 bar. The latter value is in acceptable agreement with our experimental measurements, of 259 K using the DSC and 250 K using the test-tube method (see Experimental Results).

We should note that the relationship between nucleation pressure and temperature just developed is likely to take into account heterogeneous nucleation on ever-present impurities suspended in the solution. This effect is included in the theory in the magnitude of the surface energy, which was chosen from a range of values for ionic salts and to suit our experimental measurement of the nucleation temperature at low pressure (see the Appendix).

Conclusions

In this article, we used classic nucleation theory to predict the range of temperatures and pressures for which a subcooled solution of sodium acetate of standard concentration solidifies spontaneously. We showed that the range of temperatures and pressures over which nucleation rates increase from negligible to instantaneous values is very narrow. We can therefore speak of a nucleation temperature for a given pressure, or a nucleation pressure for a given temperature. Using our theoretical results for high pressure and our experimental measurements at atmospheric pressure, we derived an equation for the nucleation temperature as a function of pressure (Eq. 16). This relation takes into account heterogeneous nucleation on ever-present impurities suspended in the solution.

The relationship between nucleation pressure and temperature developed here is necessary to investigate the mechanism by which solidification is triggered in heat packs. This is the subject of the work in Parts 2 and 3 of this series of articles.

Acknowledgment

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Appendix: Free Energy of Formation of a Solid Cluster

In this Appendix, we develop an expression for the free-energy change during the formation of a solid cluster. In the equations below, we shall consider a continuous distribution of sizes of clusters; each cluster will be denoted by its radius, r, rather than the number of molecules it contains, n. This *continuous* approach simplifies the mathematics.

Process of cluster formation

The process of growth of a single cluster is considered in Figure A1. The initial state of the system is shown as State I, and the system after a cluster of arbitrary radius, r, has formed is shown in State II. It is assumed that the cluster is spherical.

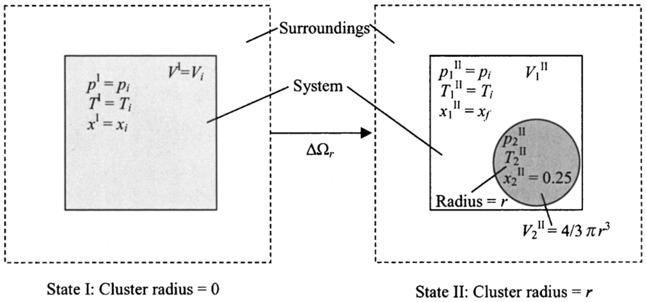

Figure A1. Growth of a cluster from solution.

State I comprises a volume V_i of sodium acetate solution at pressure, p_i, temperature, T_i, and mole fraction of sodium acetate in water, $x = x_i$. State II is the same system after a solid cluster of pure sodium acetate trihydrate ($x = 0.25$) of radius, r, has formed. The surroundings are chosen such that the temperature and pressure of the solution remain constant at T_i and p_i. In State II, the concentration of the solution, x_1^{II}, decreases with increasing r because $x_i < 0.25$ and is calculated by performing a mass balance over the system.

The remaining variables to completely define State II are the temperature and pressure of the cluster, T_2^{II} and p_2^{II}, respectively. These are determined by assuming that thermal and mechanical equilibrium between the cluster and the surrounding solution holds throughout its growth. This assumption is valid if the rate processes to reach mechanical and thermal equilibrium are sufficiently fast for such equilibrium to be achieved as the crystal grows, and faster than the rate processes to achieve chemical potential equilibrium, which is not met except when the cluster reaches the critical size. It is not important, however, which two of these three conditions of thermal, chemical, and mechanical are met while the cluster grows, because the thermodynamic state at the critical size will be the same. It is only the free-energy barrier at the critical size that is of relevance in calculating the rate of nucleation. Hence the assumption used to calculate T_2^{II} and p_2^{II} will not affect our results.

Thermal equilibrium between cluster and solution requires that $T_2^{II} = T^I$. The condition for mechanical equilibrium is given by the Laplace equation, $p_2^{II} = p^I + 2\sigma/r$, where σ is the surface energy of the interface between cluster and solution. Laplace's equation shows that the equilibrium pressure of the cluster is higher than that in the surrounding solution (Kashchiev, 2000). The system under consideration is completely prescribed by fixing the parameters just identified.

The volume of solution in State II, V_1^{II}, can in principle be determined from an equation of state in terms of T_1^{II}, p_1^{II}, and x_1^{II}. However, for ease of calculation and because the error introduced will be small, this volume is assumed to remain constant such that $V_1^{II} = V_i - 4\pi r^3/3$.

Derivation of $\Delta\Omega_r$ in terms of Gibbs free energy

The free energy of a system, Ω, is defined as the quantity that decreases during a spontaneous change. The change in free energy of a system, $d\Omega$, is given by the fundamental equation of thermodynamics $d\Omega = dU + pdV - TdS$, where U is the internal energy, V is the volume, and S is the entropy of the entire system, while p and T are the pressure and temperature at the system boundary, respectively. In terms of the free energies of systems I and II in Figure A1, $\Omega^{\mathrm{I}} = \Omega^{\mathrm{II}} = U + p_i V - T_i S$, because the temperature, T_i, and pressure, p_i, of the system boundary are constant.

Furthermore, State I is a single phase, and so $\Omega^{\mathrm{I}} = G^{\mathrm{I}}$, where G^{I} is the Gibbs free energy of State I. The cluster is at a higher pressure, so $\Omega^{\mathrm{II}} = G_1^{\mathrm{II}} + [G_2^{\mathrm{II}} - V_2^{\mathrm{II}}(p_2^{\mathrm{II}} - p_1^{\mathrm{II}})]$, where G_1^{II} and G_2^{II} are the Gibbs free energy of phases 1 and 2 in State II. Assuming that the cluster is incompressible, the free-energy change for the compression of the nucleus from p_1^{II} to p_2^{II} is $\Delta G_{\mathrm{compression}} = \int_{P_1^{II}}^{P_2^{II}} V_2^{\mathrm{II}} dp = V_2^{\mathrm{II}}(p_2^{\mathrm{II}} - p_1^{\mathrm{II}})$. Hence, $\Omega^{\mathrm{II}} = G_1^{\mathrm{II}} + G_2^{\mathrm{II}}(p_1^{\mathrm{II}})$, where $G_2^{\mathrm{II}}(p_1^{\mathrm{II}})$ is the free energy of the cluster as if it were at the same pressure as the surrounding solution, p_1^{II}.

We then conclude that $\Delta\Omega_r$ is equivalent to $\Delta G'_r$, the Gibbs free-energy change between states I and II when the free energy of the cluster is evaluated at the system boundary pressure and not at its actual pressure. Therefore calculating $\Delta G'_r$ gives a method for obtaining $\Delta\Omega_r$.

For simplicity, the process of cluster formation is analyzed by dividing it into three subprocesses. These subprocesses are chosen to partition the total free-energy change into contributions from mixing effects, ΔG_m, volume effects, ΔG_v (melting), and surface effects, ΔG_s (wetting). Figure A2 shows a sequence of stages in the process representing the free-energy differences, ΔG_m, ΔG_v, and ΔG_s. The free-energy change during each of these subprocesses can be calculated with reference to accepted theory and experimentally determined parameters. In the following subsections, we derive expressions for ΔG_m, ΔG_v, and ΔG_s in terms of T_i, p_i, x_i, r, and V_i.

Expression for ΔG_v. The expression for ΔG_v is given by the product of the volume of the cluster and the difference in free energy between a solid and liquid cluster of unit volume:

$$\Delta G_v = 4/3\pi r^3 \alpha \left(g_{\mathrm{solid}} - \frac{\hat{V}_{\mathrm{liquid}}}{\hat{V}_{\mathrm{solid}}} g_{\mathrm{liquid}} \right). \tag{A1}$$

Here, α is included to account for nonspherical clusters, g is the Gibbs free energy per unit volume, and $\hat{V}$ denotes the volume per unit mass. We shall assume that $\alpha = 1$ and that $\hat{V}_{\mathrm{liquid}}/\hat{V}_{\mathrm{solid}} = 1$. Even though the macroscopic crystal shape of sodium acetate trihydrate is monoclinic, the shape of the nanometer-sized cluster is unknown. Assuming that the cluster is spherical does introduce a factor of uncertainty into the prediction of $\Delta\Omega_{r^*}$. However, we shall see later that no measurement of the surface tension between the solid surface and the liquid, σ, is available, and hence all our uncertainties and approximations will be reflected in this parameter. The ratio of the specific volume of liquid to solid is not expected to vary significantly from 1 with pressure and temperature. Therefore

$$\Delta G_v = 4/3\pi r^3 \Delta g_v, \tag{A2}$$

where $\Delta g_v = g_{\mathrm{solid}} - g_{\mathrm{liquid}}$; Δg_v is a function of temperature and pressure, and is calculated using the definition of the Gibbs free energy: $\Delta g_v = \Delta h_v - T\Delta s_v$, where Δh_v and Δs_v are the differences in enthalpy and entropy between liquid and solid sodium acetate trihydrate, respectively, and are also both functions of temperature and pressure.

For sodium acetate trihydrate, Δh_v and Δs_v are not available over a sufficiently wide range of temperatures and pressures. However, Thompson and Spaepen (1979) showed that if, at each particular pressure, the difference in heat capacity, ΔC_p, between solid and liquid sodium acetate trihydrate varies linearly with temperature, that is, $\Delta C_p = AT + B$, then Δg_v can be written as

$$\Delta g_v = \frac{\Delta h_f^{T_m}(T_m - T)}{T_m} - 1/2 A (T_m - T)^2 + B\left[T \ln \frac{T_m}{T} - (T_m - T) \right], \tag{A3}$$

where T is the temperature, T_m is the melting temperature of sodium acetate trihydrate, and $\Delta h_f^{T_m}$ is the enthalpy of

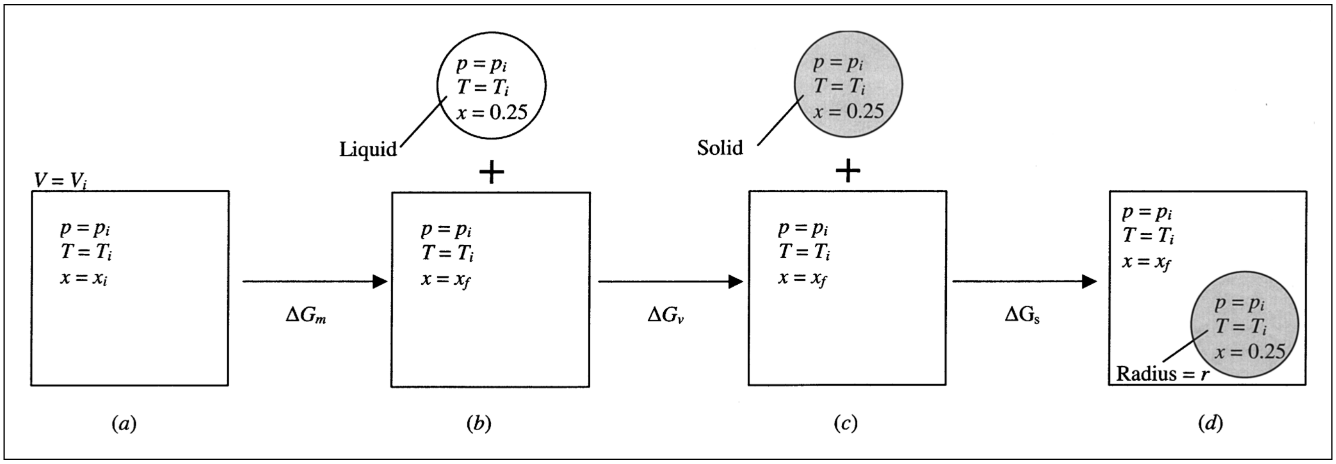

Figure A2. Hypothetical stages in the formation of a cluster.

(a) Solution of sodium acetate. (b) Liquid cluster of pure sodium acetate trihydrate formed and separated from solution. (c) Cluster has solidified to form crystal. (d) Cluster immersed in solution.

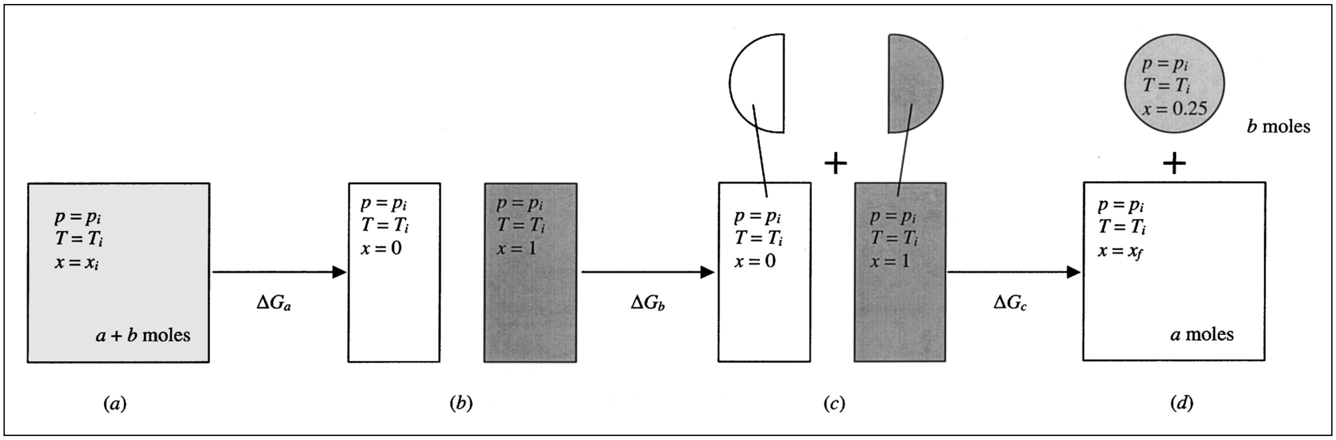

Figure A3. Hypothetical stages in the liquid cluster formation of pure sodium acetate trihydrate from solution.

fusion at the melting temperature. Araki et al. (1995) measured the heat capacity of solid and liquid sodium acetate at atmospheric pressure and did find a linear relationship between ΔC_p and T in the temperature range 303 to 328 K (i.e., $3 < T_m - T < 28$ K). They found $A = 2.1\times10^{-4}$ kJ·kg^{-1} and $B = 0.75$ kJ·kg^{-1}·K^{-1} (or $A = 305$ J·m^{-3} and $B = 1.09\times10^{6}$ J·m^{-3}·K^{-1}, assuming the density of liquid and solid sodium acetate trihydrate is that of the solid at standard conditions, 1,450 kg·m^{-3}).

To extend the validity of Eq. A3 to pressures greater than atmospheric, expressions for $\Delta h_f^{T_m}$ and T_m as a function of pressure must be determined. Given that $\Delta C_p = AT + B$, it follows that

$$\Delta h_f^{T_m} = 1/2\,A\left(T_m^2 - T_e^2\right) + B\left(T_m - T_e\right) + \Delta h_f^{T_e}. \qquad \text{(A4)}$$

Here, T_e is a reference temperature at which the enthalpy of fusion $\Delta h_f^{T_e}$ has been measured. $\Delta h_f^{T_m}$ is 260 kJ·kg^{-1} or 3.77×10^{8} J·m^{-3} at atmospheric pressure, at which $T_m = 331$ K (Araki et al., 1995). Substituting these values in Eq. A4, gives

$$\Delta h_f^{T_m} = 152.5\left(T_m^2 - 331^2\right) + 1.09\times10^{6}\left(T_m - 331\right) + 3.77\times10^{8} \quad \left(\mathrm{J/m^3}\right). \qquad \text{(A5)}$$

No data are available for the melting temperature of sodium acetate trihydrate at high pressure. We shall therefore assume that T_m increases with p at the same rate as that of water above 200 bar. Then, $T_m = 331 + 5p$, where p is pressure in kbar (Kennedy, 1998). Combining Eqs. A2, A3, and A5 gives the relationship for ΔG_v with temperature and pressure as

$$\Delta G_v = 4/3\pi r^2\left[\frac{(331+5p-T)\left\{152.5\left[(331+5p)^2 - 331^2\right] + 1.09\times10^{6}(5p) + 3.77\times10^{8}\right\}}{331+5p}\right] - 4/3\pi r^3\left\{152.5(331+5p-T)^2 + 1.09\times10^{6}\left[T\ln\frac{331+5p}{T} - (331+5p-T)\right]\right\}. \qquad \text{(A6)}$$

This equation shows that:

(1) ΔG_v is proportional to r^3.

(2) ΔG_v approaches 0 as T approaches T_m.

(3) ΔG_v is always negative for $T < T_m$, that is, when the solution is subcooled.

(4) ΔG_v decreases monotonically with pressure.

(5) ΔG_v decreases monotonically as the temperature is lowered below the melting point. This implies that the solid phase becomes more thermodynamically stable with respect to the liquid, as expected.

The variation of ΔG_v in aspect 5 is reversed at temperatures significantly below the melting temperature. This effect is thought to be due to the extrapolation of the linear relationship for ΔC_p beyond its range of applicability of $3 < T_m - T < 28$ K. Estimation of ΔG_v at temperatures below the melting temperature of more than 28 K, at any pressure, should be treated with caution.

Expression for ΔG_s. The expression for ΔG_s is given by the product of the surface area of the nucleus and the surface energy between solid and liquid sodium acetate trihydrate, σ:

$$\Delta G_s = 4\pi r^2\sigma, \qquad \text{(A7)}$$

where ΔG_s accounts for the disruption to the solid and liquid phases due to the presence of the interface between them. This is required because ΔG_v is calculated assuming that the cluster is part of a much larger body of the same phase.

Following Kashchiev (2000), it is assumed that σ is independent of r and it does not vary with T, p, and x. A more exact dependence of ΔG_s on these parameters is not well established in the literature and little data are available, even for common substances (Kashchiev, 2000). Therefore, to estimate a reasonable σ for sodium acetate trihydrate, use is made of the available data for water and for several ionic salts. Between water and ice, σ has been well documented at $0.033\ \mathrm{J \cdot m^{-2}}$ (Ketcham and Hobbs, 1969), and σ for several sulphate salts is in the range $0.1–0.2\ \mathrm{J \cdot m^{-2}}$ (Walton, 1969). We shall therefore assume that $\sigma \sim 0.07\ \mathrm{J \cdot m^{-2}}$ for sodium acetate trihydrate. We shall see later that this value is compatible with our experimental determination of the nucleation temperature at atmospheric pressure.

Then, from Eq. A7, we have

$$\Delta G_s = 0.28 \pi r^2. \tag{A8}$$

As expected, ΔG_s is proportional to the surface area of the nucleus and is always positive.

Expression for ΔG_m. The expression for ΔG_m is given by the product of the total number of moles of sodium acetate and water in the system, η, and the free energy change on mixing per mole Δg_m

$$\Delta G_m = \eta \Delta g_m, \tag{A9}$$

where Δg_m is given by the equation for mixing

$$\Delta g_m = RT \sum_i x_i \ln \gamma_i x_i, \tag{A10}$$

where $R = 8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ is the gas constant, and γ_i is the activity coefficient for species i (Sandler, 1998). Activity coefficients for sodium acetate in water are only available at very large dilutions, and not at the concentrations considered in this work. In the absence of these data, it was assumed that sodium acetate and water form an ideal mixture and $\gamma_i = 1$ for both species.

As illustrated in Figure A3, ΔG_m may be calculated by considering a sequence of separation and mixing stages. State (a) shows the solution at the initial concentration, x_i. State (b) is this solution separated into pure water and pure sodium acetate. State (c) is the water and sodium acetate from state (b) further divided into portions that when mixed will give a cluster of liquid sodium acetate trihydrate and also the resulting solution of final concentration x_f. In state (d) mixing has been accomplished. We then have

$$\Delta G_m = \Delta G_a + \Delta G_b + \Delta G_c, \tag{A11}$$

where ΔG_b is the free energy change of dividing portions of fluid of the same concentration and so is equal to zero; and ΔG_a and ΔG_c correspond to mixing processes and are determined by Eq. A10. Hence,

$$\Delta G_a = -RT(a+b)\left[x_i \ln x_i + (1-x_i)\ln(1-x_i)\right] \tag{A12}$$

and

$$\Delta G_c = RTa\left[x_f \ln x_f + (1-x_f)\ln(1-x_f)\right] + RTb(0.25 \ln 0.25 + 0.75 \ln 0.75), \tag{A13}$$

where

$$x_f = \frac{x_i(a+b) - 0.25b}{a}.$$

To express ΔG_a and ΔG_c, and hence ΔG_m, in terms of r, V_i, and x_i, it is necessary to substitute:

$$a = \frac{4}{3}\pi r^3 \frac{\rho_{0.25}}{M_{0.25}} \tag{A14}$$

$$b = \frac{V_i \rho_{x_i}}{M_{x_i}} - \frac{4}{3}\pi r^3 \frac{\rho_{0.25}}{M_{0.25}}, \tag{A15}$$

where ρ_x and M_x are the average density and molar mass, respectively, of sodium acetate solution of mole fraction x. We have

$$M_x = 0.082x + 0.018(1-x) = 0.064x + 0.018 \tag{A16}$$

$$\rho_x = 42{,}650 \times M_x, \tag{A17}$$

where it is assumed that the molar volume of the solution is constant with temperature and pressure at $42{,}650\ \mathrm{mol \cdot m^{-3}}$; this corresponds to the density of solid sodium acetate trihydrate at standard temperature and pressure, $1{,}450\ \mathrm{kg \cdot m^{-3}}$.

By combining Eqs. A11–A13, an expression for ΔG_m is obtained in terms of V_i, r, x_i, and T. However, it is more helpful to rewrite this expression in terms of the variables V_i, ϵ, x_i, and T, where ϵ is the ratio between the volume of solution remaining after cluster formation and the initial volume of solution,

$$\epsilon = 1 - \frac{\frac{4}{3}\pi r^3}{V_i} = \frac{a}{a+b}. \tag{A18}$$

We then have

$$\begin{aligned} \Delta G_m = 42{,}650 \times RTV_i\{1 - &\left[x_i \ln x_i + (1-x_i)\ln(1-x_i)\right] \\ &+ \epsilon\left[x_f \ln x_f + (1-x_f)\ln(1-x_f)\right] \\ &+ (1-\epsilon)(0.25 \ln 0.25 + 0.75 \ln 0.75)\}, \end{aligned} \tag{A19}$$

where

$$x_f = \frac{x_i - 0.25(1-\epsilon)}{\epsilon}.$$

Equation A19 shows that

(1) ΔG_m is always positive.

(2) ΔG_m approaches zero as x_i approaches x_f, which is the case for nucleation of a solid from its melt.

(3) ΔG_m decreases monotonically with x_i when x_i is less than x_f.

(4) ΔG_m increases proportionally with temperature.

(5) If ϵ is constant, ΔG_m increases proportionally with the volume of the cluster r^3.

(6) For a constant initial volume, V_i and ΔG_m increase monotonically with r.

The total free energy change of the system is the sum of the three components: $\Delta\Omega_r = \Delta G_m + \Delta G_v + \Delta G_s$. However, the effect of ΔG_m was found to become appreciable only when the volume of fluid is very small, of the order of 1 nm^3. The effect of ΔG_m is therefore negligible in this work. We then have the final expression for the free energy of formation of an incipient nucleus:

$$\Delta\Omega_r = \Delta G_s + \Delta G_v = \frac{4}{3}\pi r^3 \Delta g_v(T,p) + 4\pi r^2 \sigma, \quad \text{(A20)}$$

where

$$\Delta g_v(T,p) = \frac{(331+5p-T)\left\{152.5\left[(331+5p)^2 - 331^2\right] + 1.09\times10^6(5p) + 3.77\times10^8\right\}}{331+5p} - 152.5(331+5p-T)^2 + 1.09\times10^6\left[T\ln\frac{331+5p}{T} - (331+5p-T)\right]. \quad (21)$$

The maximum of the free energy, $\Delta\Omega_r$, as a function of cluster size r is the free energy required to create a single incipient nucleus, $\Delta\Omega_{r^*}$.

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