

Reproducing Black's experiments: freezing point depression and supercooling of water

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Abstract

We carried out two historical experiments referred to by Joseph Black, one on freezing mixtures of salted water with ice and another on freezing supercooled pure water by a small disturbance. The results confirm thermodynamical predictions for the depression of the freezing point of salted water and for the latent heat of freezing of supercooled water respectively, which came after Black. The depression of the freezing point can hardly be fitted in the framework of the caloric theory of heat, which was taken for granted by Black, and the instantaneous freezing of supercooled water also poses some difficulties for that theory.

1. Introduction

We discuss here two calorimetric experiments described and performed by Joseph Black. We believe that historical experiments like those reported in this paper provide an interesting pedagogical approach to thermodynamics.

The Scottish scientist Joseph Black (1728–1799) was born in Bordeaux (France) into a family of wine merchants. He studied in Ulster and Scotland and became Professor of Medicine and Chemistry in Glasgow in 1756, and in Edinburgh in 1766. His main interests were, nevertheless, physics and chemistry. He was the first to distinguish between temperature and heat, to use correctly the concept of specific heat (coined by the Portuguese João Jacinto Magalhães) and to introduce the notion of latent heat [1]³. Black's lectures and demonstrations were very popular and attracted lots of students.

³ Black did not publish his discoveries himself. The book *Lectures on the Elements of Chemistry ... by the late J Black* (1803) was edited by his student J Robinson. The expression 'specific heat' had already appeared in the memoir *Essay sur la nouvelle théorie du feu élémentaire et de la chaleur des corps ...*, London (1780), by the Portuguese scientist João Jacinto Magalhães. Magalhães, in an exchange of letters in 1780 with James Watt (a close friend of Black), tried to ascertain the contribution of Black to the concept of specific heat.

In the years after starting his professorship in Glasgow, Black became interested in heat phenomena, being intrigued in particular by the freezing of water. He introduced the term *sensible heat* to describe temperature variations of a body upon heating and, with this concept, was able to interpret various experiments within the caloric theory of heat, which was prevalent at the time [2]. Caloric was seen as a fluid which could penetrate all substances and would flow from hot to cold bodies. The conservation of caloric (a term coined by the French Laurent de Lavoisier) was a cornerstone of that theory. On the other hand, Black also introduced the term *latent heat* to denote the energy which seemed to hide ('conceal') in melting, reappearing in freezing, and also to hide in evaporation, reappearing in condensation. In changes of state, temperature does not change, so that latent heat was quite distinct from sensible heat although the two were interchangeable. In an atomistic picture, latent caloric was seen as resulting from a 'reaction' of sensible caloric with the constituent atoms.

The first experiment discussed in this paper was invoked by Black to discard old ideas about phase transitions, namely that they occurred quickly at a given temperature with a small heat exchange. This experiment refers to melting ice (units are converted from the original degrees Fahrenheit) [3]:

'I put a lump of ice into an equal quantity of water heated to the temperature 80 °C and the result was that the fluid was no hotter than water just ready to freeze. Nay, if a little sea salt be added to the water and it be heated only to 74 or 76 °C, we shall produce a fluid sensibly colder than the ice was in the beginning, which has appeared a curious and puzzling thing to those unacquainted with the general fact'.

Black described another experiment which was used to counteract the old idea that water reaching the normal freezing point freezes by 'loss of a little more heat'. It was actually carried out by his contemporary the German Gabriel Daniel Fahrenheit [3] (again, degrees are converted from Fahrenheit to Celsius):

'He [Fahrenheit] exposed globes of water in frosty weather so long that he had reason to be satisfied that they freeze down to the degree of the air, which was 2° or 3° below the freezing point. That water, however, still remained fluid, so long as the glasses were left undisturbed, but, on being taken up and shaken a little, a sudden freezing of a part of the water was instantly seen (. . .). But the most remarkable fact is that, while this happens, the mixture of ice and water suddenly becomes warmer, and makes a thermometer, immersed in it, rise to the freezing point'.

In the physics undergraduate curriculum, experiments on thermodynamics are given limited attention [4]. Experiments on mixtures of salted water with ice and on freezing of pure water, in spite of being feasible in introductory thermodynamics courses, are not common.

We have performed the two above-mentioned calorimetric experiments with modern equipment. First, we mixed, as Black did, a certain amount of hot salted water with ice at 0 °C. The mixture attained a temperature well below the freezing point. In the second experiment, we prepared water following Fahrenheit's trial. It is nowadays called supercooled water. A small perturbation of the supercooled system led to a sudden solidification with an abrupt increase of the temperature up to 0 °C. This spectacular experiment is a nice classroom demonstration of metastable thermal equilibrium.

The two experiments reported here were made with physics majors in an introductory lecture course on thermodynamics. The second experiment used the freezing mixture prepared in the first one. The feedback from the students was very positive since both experiments have an element of surprise, which propitiates learning. In fact Black himself pointed out that the outcome of the first experiment 'has appeared a curious and puzzling thing'. He did not notice, however, the obvious difficulty in interpreting it in the framework of caloric theory since the final temperature is below the two initial temperatures of the bodies in contact (which are isolated from their surroundings). On the other hand, the result of the second experiment is also unexpected ('remarkable', in the words of Black) but is not in obvious conflict with caloric theory. However, taking the atomistic point of view, one cannot but wonder how the

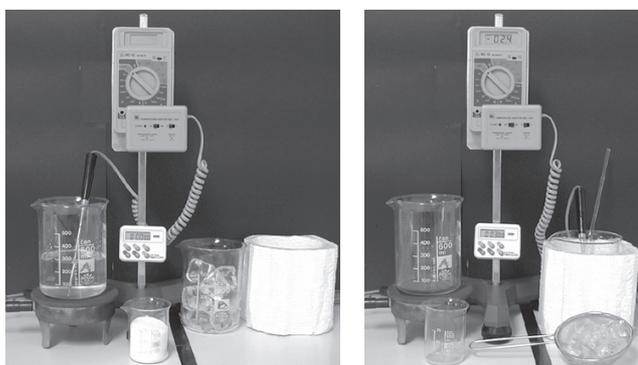


Figure 1. Hot salted water and ice. A vessel with hot salted water is poured in a calorimeter with ice at 0°C (on the left). The equilibrium temperature is below 0°C (on the right).

'reaction' to produce latent caloric can take place so quickly. Students are surprised by the sudden freezing of water with the corresponding temperature jump in the thermometer, since they are expecting phase transitions to be slow.

We think that the performance of these simple experiments could reinforce some thermodynamical concepts, such as latent heat (variation of enthalpy in a phase transition) and chemical potential. In fact, the depression of the freezing point may only be explained with the help of chemical potential, a concept which was unknown in Black's time and which came about only in the late nineteenth century with the American Josiah Willard Gibbs. And the fact that the latent heat of supercooled water is not the same as the normal latent heat is best examined under the light of Hess's additivity law for enthalpy.

In section 2 we describe our experiment with salted water and ice and use Gibbs' theory on heterogeneous substances to explain it [5, 6]. In section 3 we present the experiment with supercooled water which, although more spectacular, is easier to explain. Section 4 contains some concluding remarks, in particular regarding the challenges these experiments represent to the caloric theory of heat.

2. Mixtures of salted water and ice

To perform the first experiment (see figure 1), we placed some ice at 0°C in a calorimeter, a glass vessel with adiabatic wrapping (styrofoam). In another glass vessel we dissolved sea salt (with mass $m_S \approx 15\text{--}60\text{ g}$) in water (mass $m_W \approx 180\text{ g}$) and heated up the mixture to a few degrees above the desired initial temperature, $t_i \approx 65\text{--}95^{\circ}\text{C}$. Then, we let the salted water cool down until t_i was reached and quickly poured the water into the calorimeter. We stirred vigorously with a glass stirring rod until the temperature stabilized. Surprisingly enough (to Black and also, today, to many students!) the final temperature, t_f , was below the normal freezing point. The process took 2–3 min for final temperatures between -1 and -3°C and 6–7 min for final temperatures in the range -7 to -8°C . It is essential to stir continuously while the temperature decreases. We extracted the melted ice which remained floating and weighted it in order to measure the mass of melted ice (this turned out to be $m_1 \approx 160\text{--}260\text{ g}$).

Table 1 shows the measured values for all masses and the initial and final temperatures. We note that Black did not provide data for his experiment of mixing salted water with ice.

The analysis of this experiment requires concepts such as the enthalpy (all processes evolve at constant pressure), and also the chemical potential, which was introduced by Gibbs in his studies of equilibrium of heterogeneous substances [5].

From the first law, the infinitesimal enthalpy change is $dH = \delta Q + v dP$ [7], with δQ an infinitesimal heat, v the specific volume and P the pressure. At constant pressure, the enthalpy

Table 1. Data from our experiment on mixing salted water with ice. m_W , m_I and m_S are the masses of water, ice and salt, respectively, while t_i and t_f are the initial and final temperatures.

Exp	m_W (g)	m_I (g)	m_S (g)	t_i (°C)	t_f (°C)
1	179.5 ± 0.2	201.0 ± 0.2	55.2 ± 0.2	65.0 ± 0.1	-8.5 ± 0.1
2	179.6 ± 0.2	187.1 ± 0.2	39.1 ± 0.2	65.0 ± 0.1	-6.6 ± 0.1
3	180.1 ± 0.2	176.2 ± 0.2	23.6 ± 0.2	65.0 ± 0.1	-4.2 ± 0.1
4	180.2 ± 0.2	165.1 ± 0.2	17.0 ± 0.2	65.0 ± 0.1	-3.2 ± 0.1
5	180.7 ± 0.2	223.3 ± 0.2	55.1 ± 0.2	75.0 ± 0.1	-8.3 ± 0.1
6	178.6 ± 0.2	246.5 ± 0.2	54.9 ± 0.2	85.0 ± 0.1	-7.4 ± 0.1
7	178.8 ± 0.2	260.1 ± 0.2	53.7 ± 0.2	95.0 ± 0.1	-6.7 ± 0.1

is conserved since the calorimeter is an adiabatic system. For a substance undergoing a phase transition $\Delta H = n\Delta h + nc\Delta t$, with n the number of moles, Δh the variation of the molar enthalpy in the phase transition (latent heat) and c the (molar) specific heat at constant pressure, which is assumed to be independent of the temperature.

In the situation under consideration, the sum of all enthalpy variations vanishes:

$$\Delta H_W + \Delta H_S + \Delta H_I + Q_C = 0 \quad (1)$$

where the successive terms refer to the enthalpy variations of liquid water, salt and ice respectively and the last term to the heat transferred to/from the calorimeter. More specifically, equation (1) can be written as

$$n_W c_W (t_f - t_i) + n_S c_S (t_f - t_i) + n_I c_W (t_f - 0) + n_I \Delta h_F + n_C c_W (t_f - 0) = 0 \quad (2)$$

where $c_W = 75.24 \text{ J mol}^{-1} \text{ K}^{-1}$ and $c_S = 49.95 \text{ J mol}^{-1} \text{ K}^{-1}$ are the molar specific heats of water and salt, and $n_W = m_W/18$, $n_S = m_S/58.5$ and $n_I = m_I/18$ are the numbers of moles of water, salt and melted ice respectively. For the latent heat of fusion of ice we take its value at 0°C , $\Delta h_F = 333.8 \text{ J g}^{-1}$. The last term accounts for the water equivalent of the calorimeter, i.e. the amount of water that would provide/receive the same energy as the calorimeter when the mixing takes place. One has $n_C = m_C/18$, where m_C is the mass of the water equivalent of the calorimeter.

To determine the water equivalent of the calorimeter we used the mixtures method [8]: different known masses of hot and cold water at known temperatures were mixed in the calorimeter and the final temperature of the mixture was measured. The water equivalent has to be determined in conditions similar to those of our water–ice mixtures. We took therefore similar amounts (170 g) of hot water (at 92.7°C) and cold water (at 2.7°C). The final temperature, after 4 min, was 41.9°C . From an equation similar to (1), $\Delta H_{HW} + \Delta H_{CW} + Q_C = 0$, where ‘HW’ and ‘CW’ stand for hot and cold water respectively [8], the water equivalent of the calorimeter was found to be $m_C \approx 57 \pm 4 \text{ g}$.

Another condition to be fulfilled by the final equilibrium state is the equality of the chemical potentials of liquid and solid water [9]. From this condition one obtains the following depression of the freezing point (see appendix A)

$$\Delta t = t_f \approx -K\chi \quad (3)$$

where χ is the molar fraction of the dissolved salt and $K = 103.2 \text{ K}$ is the so-called cryoscopic constant of water [6, 10]. The molar fraction of the dissolved salt is given by

$$\chi = \frac{fn_S}{n_W + n_I + fn_S} \quad (4)$$

where $f = 2$ for NaCl (number of ions generated by the molecule) [6].

Using equations (3) and (4) the final temperature is

$$t_f = -\frac{Kfn_S}{n_W + n_I + fn_S}. \quad (5)$$

Table 2. Comparison of theoretical and experimental (Exp) final temperatures, t_f , and numbers of moles of ice, n_I , on the basis of table 1. The third column is the same as the last column of table 1.

Exp	t_f ($^{\circ}\text{C}$)		n_I (mol)	
	Equation (5)	t_f^{Exp} ($^{\circ}\text{C}$)	Equation (7)	n_I^{Exp} (mol)
1	-8.5 ± 0.3	-8.5 ± 0.1	11.3 ± 0.5	11.18 ± 0.01
2	-6.4 ± 0.3	-6.6 ± 0.1	10.4 ± 0.5	10.37 ± 0.01
3	-4.0 ± 0.3	-4.2 ± 0.1	9.5 ± 0.5	9.76 ± 0.01
4	-3.0 ± 0.3	-3.2 ± 0.1	9.1 ± 0.5	9.19 ± 0.01
5	-8.0 ± 0.4	-8.3 ± 0.1	12.7 ± 0.6	12.37 ± 0.01
6	-7.6 ± 0.4	-7.4 ± 0.1	13.8 ± 0.6	13.68 ± 0.01
7	-7.2 ± 0.4	-6.9 ± 0.1	15.1 ± 0.6	14.42 ± 0.01

We have checked this result experimentally. In table 2, the predicted of the final temperature is compared with the experimental value.

Inserting t_f given by equation (5) in (2), one obtains a quadratic equation for the number of moles of melted ice

$$an_I^2 + bn_I + c = 0 \quad (6)$$

where

$$a = \Delta h_F$$

$$b = (n_W + fn_S)\Delta h_F - (n_Wc_W + n_Sc_S)t_i - c_WKfn_S$$

$$c = -(n_Wc_W + n_Sc_S)(n_W + fn_S)t_i - [c_W(n_W + n_C) + n_Sc_S]Kfn_S.$$

The positive root is

$$n_I = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad (7)$$

(the other root has no physical meaning).

In table 2 the *predictions* for the number of moles of melted ice (equation (7)) are compared with the *measured* quantities. Theory agrees well with experiment.

The most important sources of uncertainty are: (i) some liquid water is removed with the unmelted ice and is also weighed; (ii) the measurements of the final temperatures are somewhat uncertain when equilibrium takes a long time to attain, especially when the initial temperature or the salt concentration are high.

3. Supercooled water

Supercooling is the phenomenon discovered by Fahrenheit and described by Black with water remaining fluid well below the freezing point [11].

The experiment with salted water and ice described in the previous section shows that such mixtures can be used to obtain temperatures below 0°C . In fact, using mixtures of saturated salted water and ice we reached temperatures of -12°C after vigorous stirring for 10 min. To prepare supercooled water we poured approximately $m_W = 50$ g of doubly distilled water into a test tube with diameter of 2.5 cm and height 10 cm (in tubes with a larger diameter water did not become supercooled). Water, initially at room temperature (20°C), may, in 10 min, reach $t_i = -10^{\circ}\text{C}$ when immersed in a receptacle containing a mixture of saturated salted water and ice below the freezing point. If one slightly disturbs this unstable equilibrium (for instance, with the thermometer), some water freezes spontaneously, while the temperature rises to $t_f \approx 0^{\circ}\text{C}$. Figure 2 shows the test tube before and after the formation of ice.

Let us analyse the experiment. The mass of formed ice, m_I , may be estimated from the energy balance equation (the reasoning is the same as for equation (2))

$$(m_W - m_I + m_{\text{tube}})c_W(t_f - t_i) + m_Ic_I(t_f - t_i) + m_I\Delta h_{\text{SC}}^{(t=t_i)} = 0. \quad (8)$$



Figure 2. Supercooled water. A test tube with bidistilled water was introduced into a receptacle containing a mixture of saturated salted water and ice below the freezing point (on the left). When crystallization occurs, the temperature increases to 0 °C (on the right).

The c 's and Δh here and hereafter are related to mass rather than molarity as in section 2. We assume that the specific heats of supercooled water and stable water are equal.

The water equivalent of the test tube, m_{tube} , is determined in a separate experiment as for the calorimeter in the previous section. Moreover, $\Delta h_{\text{SC}}^{(t=t_i)}$ is the latent heat of freezing of supercooled water, which can be obtained from Hess's law [12, 13] (see appendix B):

$$\Delta h_{\text{SC}}^{(t=t_i)} = \Delta h_{\text{SC}}^{(t=0)} - (c_{\text{W}} - c_{\text{I}})(t_i - 0) \quad (9)$$

with $\Delta h_{\text{SC}}^{(t=0)} = -333.8 \text{ J g}^{-1}$ (specific latent heat of freezing at 0 °C), $c_{\text{W}} = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and $c_{\text{I}} = 2.09 \text{ J g}^{-1} \text{ K}^{-1}$. From equations (8) and (9) the prediction for the mass of ice formed is

$$m_{\text{I}} = -\frac{(m_{\text{W}} + m_{\text{tube}}) c_{\text{W}}(t_f - t_i)}{\Delta h_{\text{SC}}^{(t=0)} + (c_{\text{I}} - c_{\text{W}}) t_f}. \quad (10)$$

In order to measure this quantity, we placed in a metallic calorimeter a certain mass of water, m_{W}^{C} , at room temperature, t_i^{C} . When the temperature of supercooled water attained $t_f \approx 0 \text{ °C}$, the mixture of ice and water (with mass $m_{\text{W+I}} = m_{\text{W}}$) was thrown in the calorimeter. Equilibrium was reached in about 1 min and the final temperature in the calorimeter, t_f^{C} , was then measured. The enthalpy balance, similar to equation (2), may be written

$$(m_{\text{W}}^{\text{C}} + m_{\text{C}}) c_{\text{W}}(t_f^{\text{C}} - t_i^{\text{C}}) + m_{\text{W+I}} c_{\text{W}}(t_f^{\text{C}} - t_f) + m_{\text{I}}^{\text{Exp}} \Delta h_{\text{F}} = 0 \quad (11)$$

where $\Delta h_{\text{F}} = -\Delta h_{\text{SC}}^{(t=0)}$ and m_{C} is the water equivalent of the calorimeter. The mass of ice formed in the experiment is

$$m_{\text{I}}^{\text{Exp}} = -\frac{c_{\text{W}}}{\Delta h_{\text{F}}} [(m_{\text{W}}^{\text{C}} + m_{\text{C}})(t_f^{\text{C}} - t_i^{\text{C}}) + m_{\text{W+I}}(t_f^{\text{C}} - t_f)]. \quad (12)$$

Table 3 presents data obtained in five runs of our experiment on supercooled water. In an independent set of experiments, the water equivalents of the test tube and of the metallic calorimeter were estimated to be $m_{\text{tube}} = 5 \pm 1 \text{ g}$ and $m_{\text{C}} = 20 \pm 5 \text{ g}$, respectively.

Table 4 shows the results obtained from equations (10) and (12). Again, good agreement is found between theory and experiment.

4. Conclusions

We have reproduced two experiments mentioned by Joseph Black. We have explained the results of the two experiments using concepts that were unavailable at the time of Black (they

Table 3. Data obtained in our experiment on supercooled water. The mixture of ice and water, with mass m_{W+I} —initially supercooled water at t_i —is poured, at temperature t_f , into a calorimeter containing a mass m_W^C of water at t_i^C . The final calorimeter temperature is t_f^C .

Exp	m_{W+I} (g)	t_i (°C)	t_f (°C)	m_W^C (g)	t_i^C (°C)	t_f^C (°C)
1	52.3 ± 0.2	-8.6 ± 0.1	-0.2 ± 0.1	52.1 ± 0.2	20.8 ± 0.1	8.1 ± 0.1
2	47.7 ± 0.2	-9.6 ± 0.1	-0.2 ± 0.1	50.3 ± 0.2	20.8 ± 0.1	8.1 ± 0.1
3	51.3 ± 0.2	-8.9 ± 0.1	-0.2 ± 0.1	52.2 ± 0.2	21.1 ± 0.1	8.3 ± 0.1
4	47.1 ± 0.2	-10.0 ± 0.1	-0.3 ± 0.1	30.4 ± 0.2	21.0 ± 0.1	5.6 ± 0.1
5	50.8 ± 0.2	-9.2 ± 0.1	-0.2 ± 0.1	31.5 ± 0.2	21.0 ± 0.1	5.6 ± 0.1

Table 4. Theoretical, m_I , and experimental, m_I^{Exp} , masses of ice obtained in experiments on supercooled water, using equations (10) and (12) respectively and the data of table 3.

Exp	m_I (g) Equation (10)	m_I^{Exp} (g) Equation (12)
1	6.0 ± 0.3	6.0 ± 1.1
2	6.2 ± 0.3	6.2 ± 1.1
3	6.1 ± 0.3	6.1 ± 1.1
4	6.3 ± 0.3	6.2 ± 1.2
5	6.3 ± 0.3	6.2 ± 1.2

were put forward only after the two main laws of thermodynamics were formulated): in the first experiment, the depression of the freezing point and, in the second, Hess's law. Both were nicely confirmed.

The discussion of heterogeneous substances and metastable states may be part of a first course on thermodynamics [7]. It is a final topic since it requires advanced concepts. In fact, the depression of the freezing point can only be understood after chemical potential has been taught.

The two experiments described here may be done in modest laboratories, one after the other. They can teach students not only about the history of physics, which is often neglected, but also the centrality of the laboratory in thermodynamics. Since our students, motivated by the historical context, were strongly engaged by these experimental activities, we hope that the same may happen with others.

Finally, we stress the relation of both experiments to the caloric theory of heat. The first experiment defies that theory, which dominated the thermodynamical thinking from 1750 to 1850 and which is still remnant in students' thinking [14]. It can therefore be used to eliminate wrong ideas about heat besides more traditional approaches such as the friction experiments of Count Rumford.

The second experiment, although in principle compatible with the idea of caloric, poses some difficulties if one starts to think microscopically. The latent caloric being seen as a 'chemical' combination of sensible caloric with atoms, one may ask how such a transformation could go so quickly, in perfect contrast with the previous experiment.

Appendix A. Freezing point depression

Ice and liquid water, under normal pressure, $P_0 = 101.3$ kPa, are in equilibrium at $T_F = 273.15$ K. However, if salt is added to water, a new equilibrium is reached at a lower temperature. The new equilibrium condition is expressed by the equality of the chemical potentials

$$\mu_{\text{SW}}(T_F + \Delta T, P_0, \chi) = \mu_I(T_F + \Delta T, P_0) \quad (13)$$

where χ is the molar fraction of the salt in the solution, and the indices ‘SW’ and ‘I’ stand for salted water and ice respectively. Following [9], we expand both sides of the equation around the normal fusion point of pure water:

$$\mu_{\text{SW}}(T_{\text{F}}, P_0, 0) + \left. \frac{\partial \mu_{\text{SW}}}{\partial T} \right|_{T=T_{\text{F}}, \chi=0} \Delta T + \left. \frac{\partial \mu_{\text{SW}}}{\partial \chi} \right|_{T=T_{\text{F}}, \chi=0} \chi = \mu_{\text{I}}(T_{\text{F}}, P_0) + \left. \frac{\partial \mu_{\text{I}}}{\partial T} \right|_{T=T_{\text{F}}} \Delta T. \quad (14)$$

The first term on the left-hand side equals the first term on the right-hand side (see equation (13)). On the other hand, since the infinitesimal change of the Gibbs function is $dg = -s dT + v dP$ and $\mu \equiv g$ for a pure substance, one may relate the temperature derivative of the chemical potential to the entropy

$$\left(\frac{\partial \mu}{\partial T} \right)_P = -s. \quad (15)$$

Therefore, equation (14) becomes

$$-s_{\text{SW}} \Delta T + \left. \frac{\partial \mu_{\text{SW}}}{\partial \chi} \right|_{T=T_{\text{F}}, \chi=0} \chi = -s_{\text{I}} \Delta T \quad (16)$$

or

$$\Delta T = \frac{1}{s_{\text{SW}} - s_{\text{I}}} \left. \frac{\partial \mu_{\text{SW}}}{\partial \chi} \right|_{T=T_{\text{F}}, \chi=0} \chi. \quad (17)$$

But, at phase equilibrium, the variation in entropy is related to the latent heat by

$$\Delta s = s_{\text{SW}} - s_{\text{I}} = \frac{\Delta h_{\text{F}}}{T_{\text{F}}}. \quad (18)$$

If one assumes that the salted solution is ideal, i.e. that its chemical potential is given by [7]

$$\mu_{\text{SW}} = \mu_0 + RT \ln(1 - \chi) \quad (19)$$

where μ_0 is the molar Gibbs function of the solvent in the pure state, then

$$\left. \frac{\partial \mu_{\text{SW}}}{\partial \chi} \right|_{T=T_{\text{F}}, \chi=0} = -RT_{\text{F}} \quad (20)$$

and, finally, equation (17) becomes

$$\Delta T = -\frac{RT_{\text{F}}^2}{\Delta h_{\text{F}}} \chi = -K \chi. \quad (21)$$

If we use $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, $T_{\text{F}} = 273.15 \text{ K}$ and $\Delta h_{\text{F}} = 6010 \text{ J mol}^{-1}$ the molar latent heat of fusion, the cryoscopic constant is $K = 103.2 \text{ K}$.

Appendix B. Hess’s law

Let us denote by Δh_1 the enthalpy variation of a liquid (L)–solid (S) phase transition at atmospheric pressure and temperature T_1 , and by Δh_2 the enthalpy variation of the same phase transition at the same pressure but at temperature T_2 (for example freezing of stable water or freezing of supercooled water). Since enthalpy is a function of state, we may evaluate the enthalpy variation Δh_2 considering the path defined by: (i) the isobaric process undergone by the liquid from T_1 to T_2 ; (ii) the liquid–solid phase transition at this temperature; (iii) the isobaric process now undergone by the solid from T_2 to temperature T_1 . Altogether one may write (Hess’s law or the additivity rule of the enthalpy) [13]

$$\Delta h_1 = \int_{T_1}^{T_2} c_{\text{L}} dT + \Delta h_2 + \int_{T_2}^{T_1} c_{\text{S}} dT. \quad (22)$$

Assuming constant specific heats, one obtains

$$\Delta h_2 = \Delta h_1 - (c_{\text{L}} - c_{\text{S}})(T_2 - T_1). \quad (23)$$

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