School of Physics and Astronomy

Junior Honours **Thermodynamics**   GJA 2019-2020
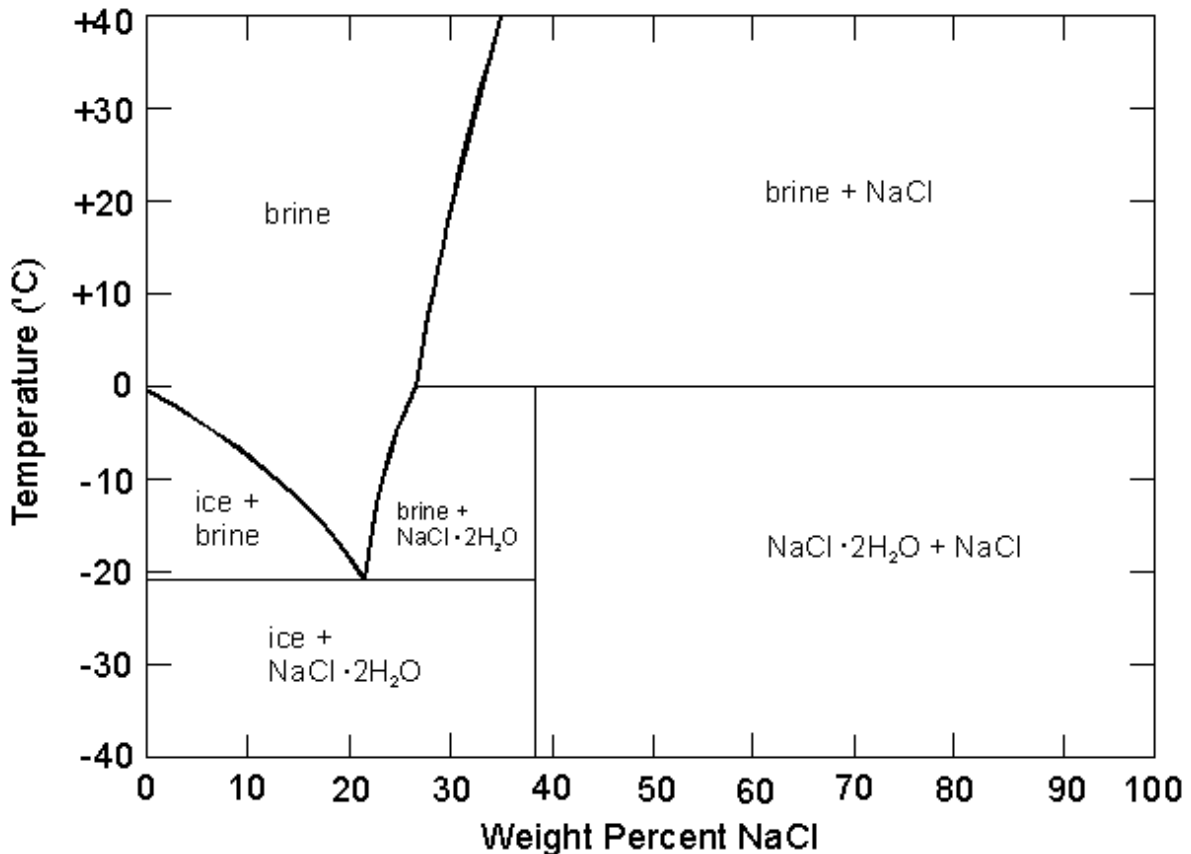
Demonstration Lecture

Brinicles and ice cream makers - Adding salt to ice water

Consider mixing salt into a system containing water and ice initially at its melting point (0^oC) together. What final temperature will one get?

To answer this consider the equilibrium situation of a two-component solution of ice in contact with a salt solution. Salt can dissolve in water, but not in ice. So the chemical potential of liquid water with a fraction X of salt is the gibbs free energy of the pure water, plus the enthalpy of solution, comprising the increased chemical attraction between water and salt H_{sol}.

$$\mu_L(T,P,X) = \mu_L(T,P,0) + XH_{sol} + RT\ln(1-X)$$

Note the chemical potential of the water depends on the concentration of the salt.

Ice and liquid are in contact, so the chemical potential of H_2O in the ice, μ_I, and in the salt solution, μ_L, must be equal at equilibrium.

Assuming that there is no change in pressure[1] ($dP = 0$), we can Taylor expand $\mu_L(p,T,X)$ about $X = 0$, where X is the molar fraction of ions, $Na^+ + Cl^-$ in the solution [2].

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[1]This will be true if the system is in contact with the atmosphere, and can quickly expand of contract. We also assume that no heat is lost to the atmosphere, since the heat conduction of air is low.

[2]the molar fraction of both ions are identical since we are only adding NaCl) with $X = 2N_{Na^+}/(2N_{Na^+} + N_L)$

$$d\mu_L = \left(\frac{\partial \mu_L}{\partial T}\right)_{P,X} dT + \left(\frac{\partial \mu_L}{\partial X}\right)_{P,T} dX = -s_L dT + \left(\frac{\partial \mu_L}{\partial X}\right)_{P,T} dX$$

Where in the last equality we used $s = -(\partial \mu/\partial T)_P$ from TOPIC 17. For the ice

$$d\mu_I = \left(\frac{\partial \mu_I}{\partial T}\right)_P dT = -s_I dT$$

Provided we always have ice in equilibrium with salt water[3], the system moves along the coexistence line in the $\{X,T\}$ plane as ice melts. So we must have a Clausius-Clapeyron type relation $(d\mu_L)_{\text{saltwater-ice}} = (d\mu_I)_{\text{saltwater-ice}}, \Rightarrow$

$$\left(\frac{dT}{dX}\right)_{\text{saltwater-ice}} = \left(\frac{\partial \mu_L}{\partial X}\right)_T \left(\frac{1}{s_L - s_I}\right) = \frac{T}{L}\left(\frac{\partial \mu_L}{\partial X}\right)_T$$

with L the latent heat of melting of pure ice into pure water evaluated at the point $X = 0$.

To simplify matters further, we assume that the salt solution is ideal ($H_{sol} = 0$).

$$\mu_L(T,P,X) = \mu_L(T,P,0) + RT \ln(1 - X)$$

$$\Rightarrow \left(\frac{\partial \mu_L}{\partial X}\right)_T = \frac{-RT}{1 - X} = -RT \qquad \text{(assume much more water than salt, } X << 1)$$

So finally,

$$\boxed{\left(\frac{dT}{dX}\right)_{\text{saltwater-ice, X=0}} = -\frac{RT^2}{L}}$$

Remarkably, the final temperature of the mixture is lower than the initial temperature of either component. Essentially the final state is obtained if the salt was added as a hot solution of brine, provided only that there was enough ice initially that it didn't all melt.

This result is independent of the properties of salt (other than that it forms an ideal solution).

Given the concentration of salt added we can estimate the drop in temperature. From the Clausius-Clapeyron slope on the phase diagram $L = 6010\,\text{Jmol}^{-1}$, T = 273.15 K. The maximum solubility of salt in water is $X = 0.16$ at the lowest temperature achievable[4]. Therefore within the above approximations (eg no heat transfer, L is independent of X and $H_{sol} = 0$) we estimate an achievable drop in temperature of 16.5 K.

The lowest freezing point of salt solution is actually -21.1°C indicating that the dominant effect in cooling is entropic. If we relax the approximations of constant L and $H_{sol} = 0$ we find

$$\left(\frac{dT}{dX}\right)_{\text{saltwater-ice, X=0}} = \frac{-RT^2 + (1 - X)H_{sol}T}{(1 - X)L(X)}$$

Separating this expression into T and X integrals is fiddly, but the outcome is that the cooling effect is even bigger. At -21.1^{o}C one has pure water ice and pure hydrated salt with no salt solution. This cooling effect can be used in ice-cream makers.

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[3]This is an assumption, but once the derivation is completed we could use the first law to check that all the water didn't freeze

[4]This is molar fraction, in the phase diagram the axis in weight percentage