

CLAUSIUS-CLAPEYRON RELATION; CHANGING THE FREEZING POINT OF WATER

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.32.

At a phase transition point, two (or more) phases of a single pure substance are in equilibrium, so the Gibbs free energies of the two phases is equal at all points along the phase transition line. From the thermodynamic potential for the Gibbs free energy

$$(0.1) \quad dG = -S dT + V dP + \mu dN$$

we have (assuming that the total molecule number N is fixed, so that $dN = 0$), for phases 1 and 2:

$$(0.2) \quad dG_1 = dG_2$$

$$(0.3) \quad -S_1 dT + V_1 dP = -S_2 dT + V_2 dP$$

This allows us to get an equation for the slope of the boundary curve on a graph of P versus T :

$$(0.4) \quad \frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1}$$

Since a phase transition involves the transfer of heat into or out of the substance (usually at constant pressure), the entropy difference between the two phases can be written in terms of the latent heat L , which is the amount of heat required to effect the phase change, plus any additional energy required for the change in volume. That is, L is actually a form of enthalpy, since it is the sum of the change in internal energy U and the work done $P\Delta V$ when the substance changes its volume due to the phase change. A phase change occurs at a constant temperature T , so the entropy change can be written as

$$(0.5) \quad S_2 - S_1 = \frac{L}{T}$$

Note that L can be positive or negative, depending on whether heat is absorbed or released during the phase change. Melting ice absorbs heat, so $L > 0$, while freezing liquid water releases heat, so $L < 0$.

We can therefore write 0.4 as

$$(0.6) \quad \frac{dP}{dT} = \frac{L}{T\Delta V}$$

This is known as the Clausius-Clapeyron equation.

As an example, we'll return to the case of water and consider the transition from ice to liquid. Water is a curious case, as the volume *decreases* when ice melts, although the entropy increases. Therefore, from 0.4, the slope $\frac{dP}{dT} < 0$. However, the relative volume change is quite small, so the slope is actually very large and negative. As a result, quite a large change in pressure is needed to affect the freezing point of water significantly.

For example, suppose we try to increase the pressure to a point where the freezing point becomes -1°C . To find this, we need a bit of data. The density of ice is 917 kg m^{-3} so the volume of 1 kg of ice is $\frac{1}{917} = 1.0905 \times 10^{-3}\text{ m}^3$. Liquid water has a density of 10^3 kg m^{-3} so 1 kg of water has a volume of 10^{-3} m^3 . The latent heat of fusion is $L = 3.3355 \times 10^5\text{ J kg}^{-1}$. The freezing point of water at a pressure of 1 bar is 273.15 K, and we want to lower this by $\Delta T = -1\text{ K}$. The change in pressure is therefore

$$(0.7) \quad \Delta P = \frac{L\Delta T}{T\Delta V}$$

$$(0.8) \quad = \frac{(3.3355 \times 10^5)(-1)}{(273.15)(-0.0905 \times 10^{-3})}$$

$$(0.9) \quad = 1.349 \times 10^7\text{ Pa}$$

$$(0.10) \quad = 134.9\text{ bars}$$

Since we started at a pressure of 1 bar, we'd need to increase the pressure to 135.9 bars to lower the freezing temperature by 1 K. This is actually a tremendous increase in pressure and is not likely to be found naturally on Earth. For example, how thick would a glacier have to be to produce this pressure from the weight of the ice alone?

The pressure is the force exerted by a column of ice 1 m^3 in cross-sectional area and depth d is (where $\rho = 917\text{ kg m}^{-3}$ is the density of ice and $g = 9.8\text{ m s}^{-2}$ is the acceleration of gravity)

$$(0.11) \quad P = \rho dg = 1.359 \times 10^7$$

$$(0.12) \quad d = \frac{1.359 \times 10^7}{917 \times 9.8}$$

$$(0.13) \quad = 1.51 \times 10^3 \text{ m}$$

Thus the glacier would need to be 1.5 km thick to reduce the freezing point by only 1 degree. Some Antarctic glaciers are believed to be up 4.7 km thick, so the pressure does reach these levels in some places. However, given that the Antarctic temperatures are many tens of degrees below 0° C, it's unlikely that even at these depths, the pressure is enough to melt the ice.

Finally, what about the notion that an ice skater can glide across ice because the pressure exerted by the skate blade is enough to melt the ice, so the skater is actually gliding along on a thin film of water? As I'm not a skater, I'll have to guesstimate the dimensions of a skate blade, but let's say it's 5 mm wide and 20 cm long, so that if the skater's entire weight is on one skate, the contact area is $A = 0.005 \times 0.2 = 10^{-3} \text{ m}^2$. Assuming a large skater of mass 100 kg, the pressure exerted by skate blade is

$$(0.14) \quad P = \frac{100g}{10^{-3}} \approx 10^6 \text{ Pa} = 10 \text{ bars}$$

From 0.6, this pressure lowers the freezing point by

$$(0.15) \quad \Delta T = \frac{T \Delta V \Delta P}{L}$$

$$(0.16) \quad = \frac{(273.15) (-0.0905 \times 10^{-3}) (10^6)}{3.3355 \times 10^5}$$

$$(0.17) \quad = -0.074 \text{ K}$$

Thus the skater is unlikely to cause any melting of the ice rink.

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