PHASES OF WATER - PLOTS OF GIBBS ENERGY

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 5.30 - 5.31.

We can apply a similar analysis to that for graphite and diamond to the three phases of water.

Using the data in Schroeder's book, we can get some insight into the stability of these three forms by considering the Gibbs free energy. The thermodynamic potential for the Gibbs free energy is

$$dG = -S\ dT + V\ dP + \mu\ dN \qquad (1)$$

If P and N are constant, we have

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \qquad (2)$$

If T and N are constant, we have

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \qquad (3)$$

We can use these derivatives to sketch qualitative graphs for G as a function of P and T for water. First, we look at 2. Since the slope of the G versus T curve is the negative entropy, and the entropy of steam is higher than liquid water which is in turn higher than ice, we'd expect the curves for ice, water and steam to have increasingly negative slopes. To arrange them in the correct relative position, we can look at a phase diagram for water, such as Schroeder's Figure 5.11. At a pressure of $P = 1$ bar, ice and liquid water are equally stable at $T = 0°$ C, so we'd expect the G curves for water and ice to intersect at that temperature. Below $0°$ C, ice is the stable form. At $T = 100°$ C, water and steam are equally stable, so we'd expect the G curves for water and ice to intersect at that temperature, with steam being the stable form above $T = 100°$ C. Thus the plot should look something like this (in all these plots, the values on the G axis are not numerically correct; they merely serve to show whether G is higher or lower when comparing curves):

P = 1 bar

200

100

- 100   0   100   200
                                         T (C)

- 100

- 200

G

- 300

- 400

- 500
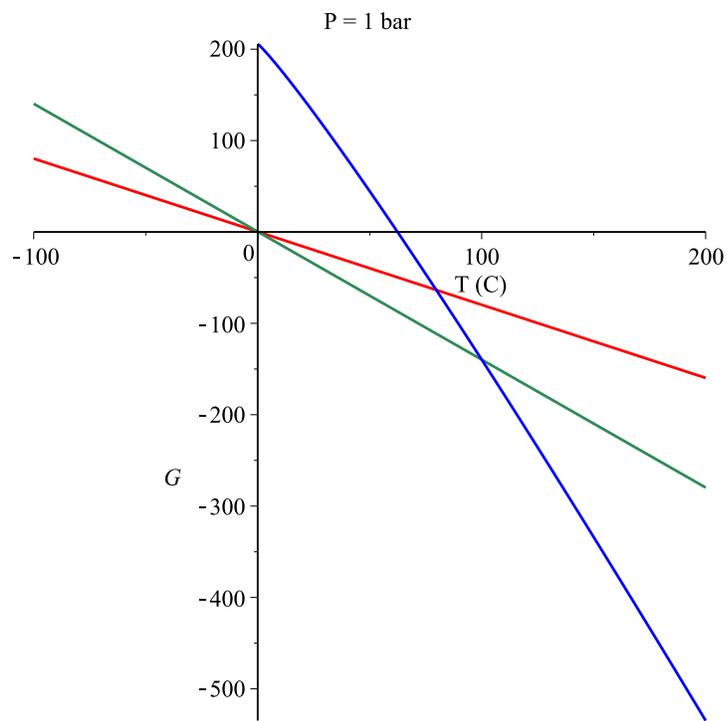
Here, red is ice, green is liquid water and blue is steam.

For a much smaller pressure such as $P = 0.001$ bar, the phase diagram shows that ice sublimes directly to steam at a temperature less than 0° C so the graph would look something like this:

P = 0.001 bar
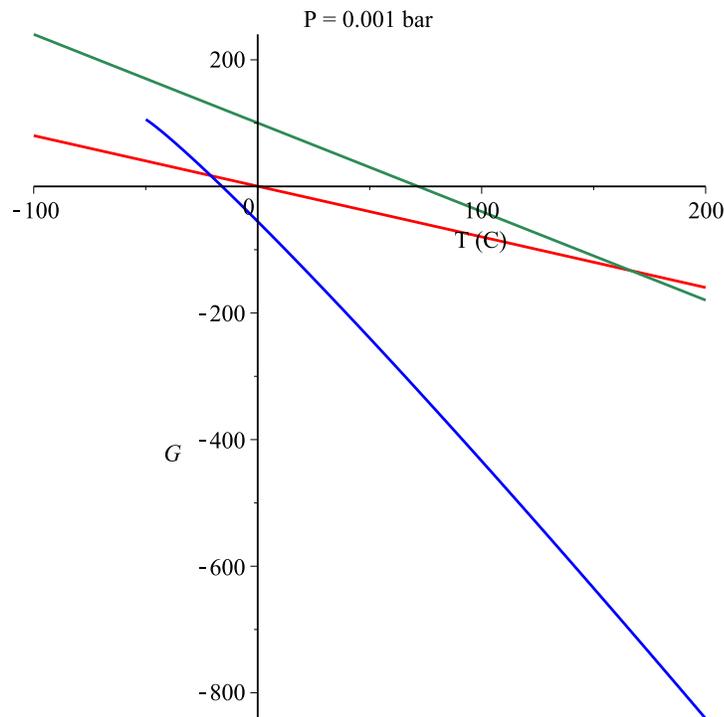
At this pressure, water is never found in liquid form.

Turning now to 3, we see that at constant temperature, the slope of the G versus P plot gives the volume. Consider first $T = 0°$ C. At low pressure, we have only steam which has a large molar volume, so we'd expect the slope to be large and positive (tending to $+\infty$ as $P \to 0$). From the phase diagram, we see that as we increase the pressure, the steam first condenses to ice, then at $P = 1$ bar (roughly), ice and water are equally stable. Increasing the pressure further actually causes the ice to melt into liquid water (a peculiarity of water, since its liquid phase is denser than the solid; with most substances, increasing the pressure converts a liquid into a solid). Thus we'd expect a plot something like this:

T = 0 ° C
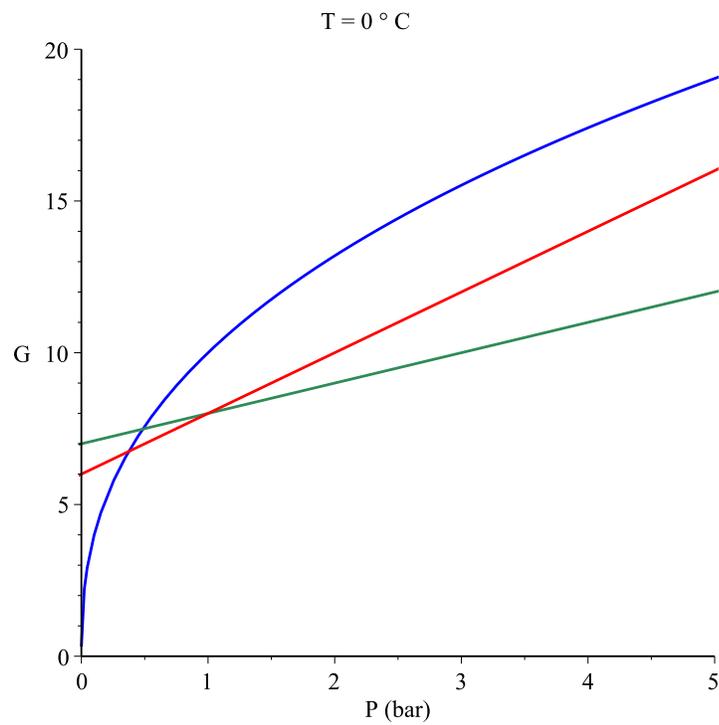
There's a small interval where the solid phase (red) is the most stable.

If we increase the temperature a few degrees, then we still have steam at low pressures but this condenses directly to liquid as we increase the pressure, so there is no point where the solid is the stable form. The graph looks like this:

T = 10 ° C
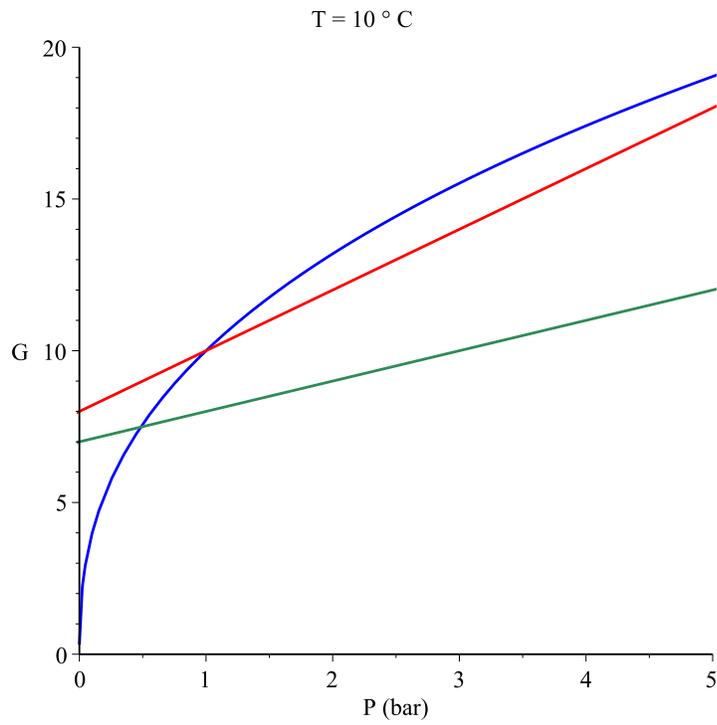
We see that the solid (red line) is never the lowest energy, so is never stable.

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