Statistical Molecular Thermodynamics

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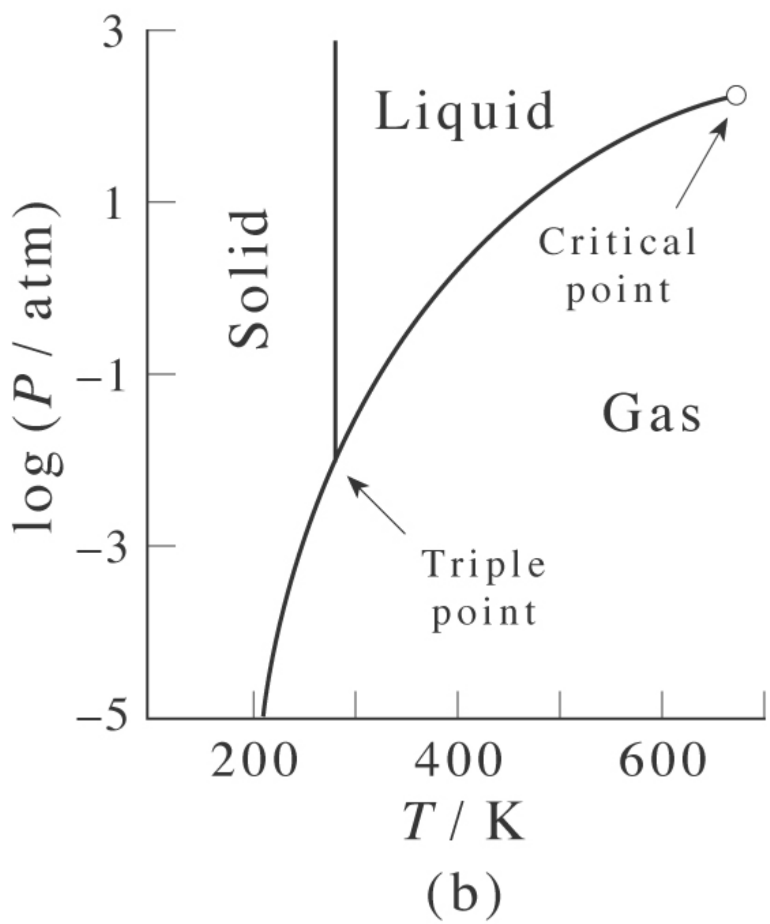
Video 9.2

Phase Diagram for Water

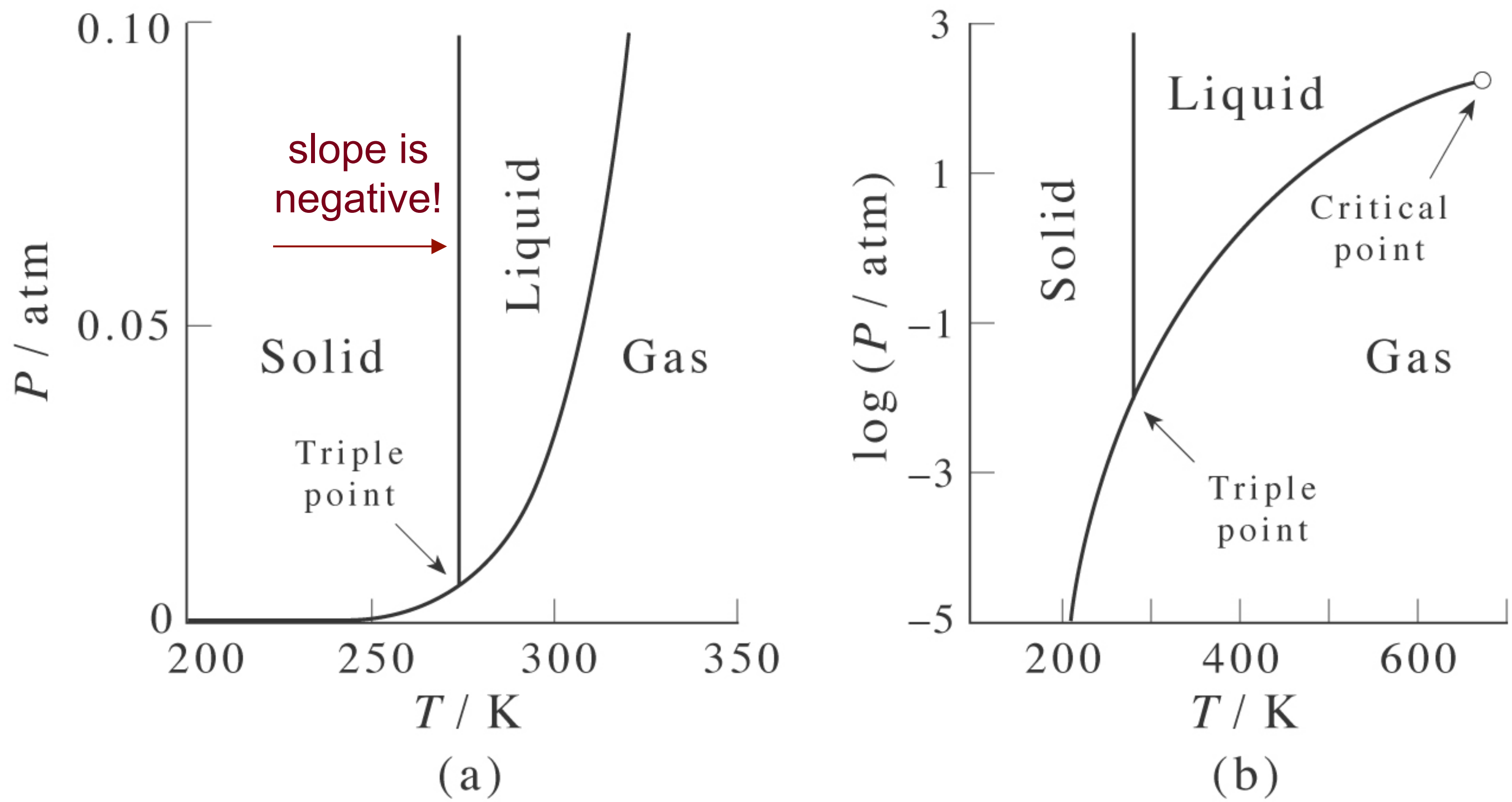
Phase Diagram of Water



Water exhibits properties that are remarkable in some respects, including one that is critical for life on Earth

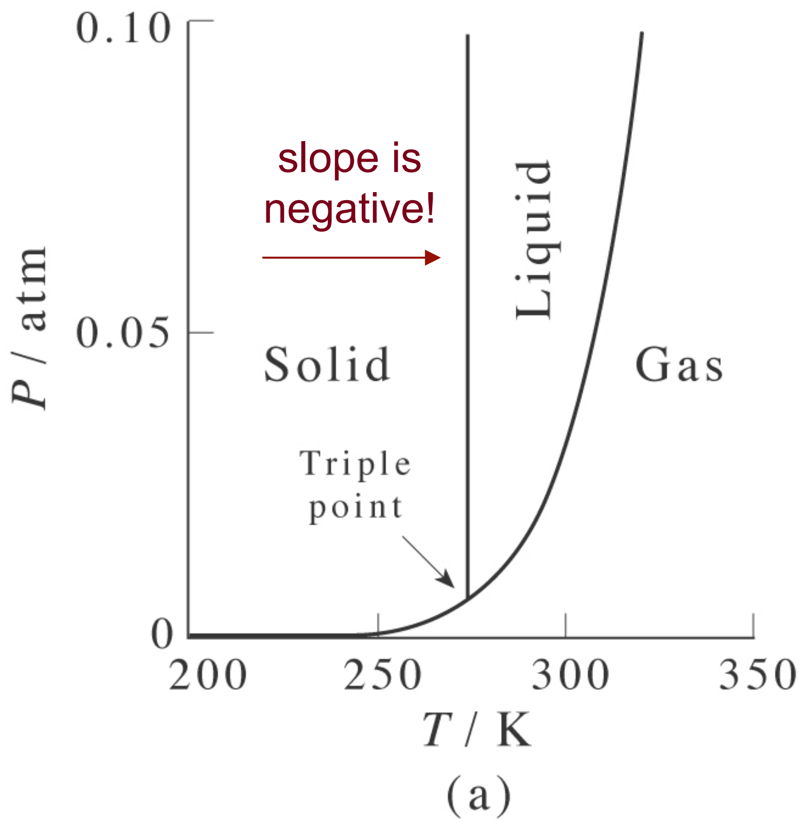
Note the ~273 K melting point and, at 1 atm, ~373 K boiling point (and a triple point with very low vapor pressure and a critical point at quite high temperature)

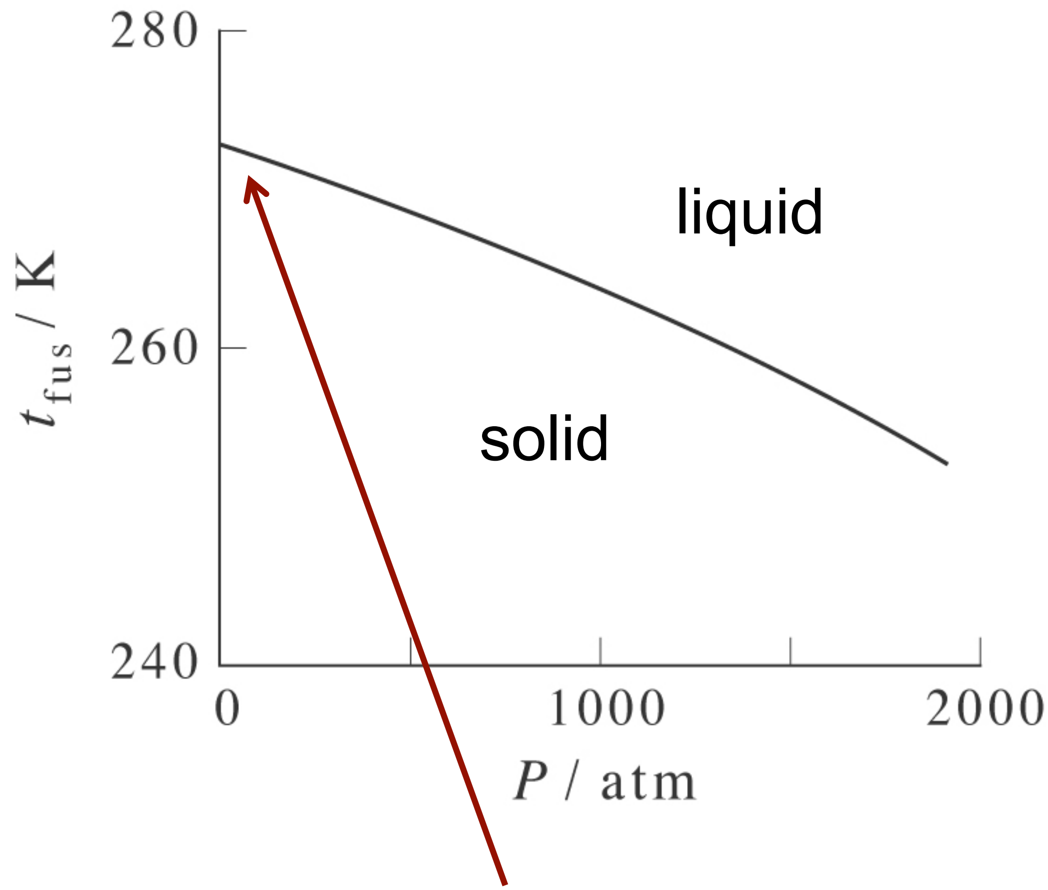
H_2O Solid-Liquid Coexistence Curve



Fascinatingly, if you increase the pressure on ice(I) at constant temperature, it melts — a very unusual behavior

Ice(I) Melting Point vs. Pressure





The slope of this curve near P = 1 atm is –7.7 x 10 $^{-3}$ °C•atm^{-1}

Self-assessment

One ice skate blade is typically 0.5 cm wide and 30 cm long.

What temperature would an ice rink have to be keeping its ice at for the weight of a 160 pound skater to change the ice from solid to liquid because of the pressure exerted by the skates? (To spare you some of the physics, 160 pounds is about 750 N of force...)

Recall from the last slide that the melting point of ice decreases by 7.7×10^{-3} °C per atmosphere of pressure.

Self-assessment Explained

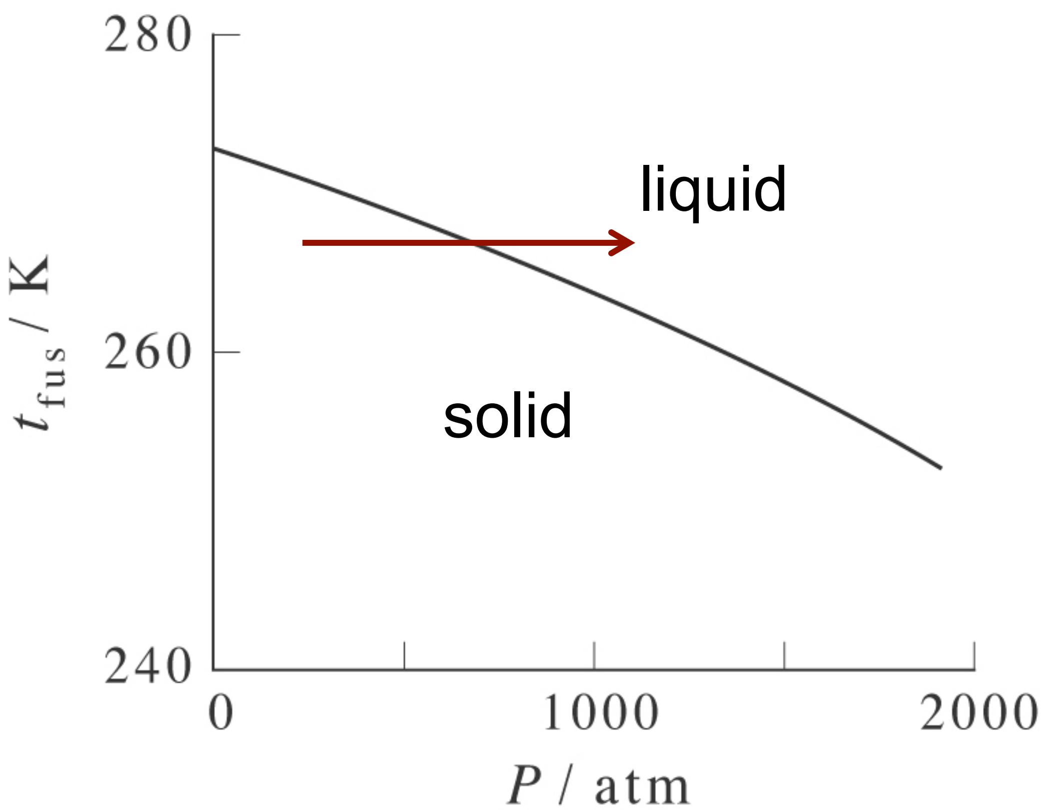
The total surface area of the two ice skate blades is
$2 \times 0.005\ m \times 0.30\ m = 0.003\ m^2$

The pressure (force per area) is thus $750\ N / 0.003\ m^2$ or 250,000 Pa. That's roughly 2.5 atm pressure, which would correspond to a melting point change for water of barely 0.02 °C.

So, that would have to be one soupy ice rink (within less than 0.02 °C of the normal melting point) for the pressure under the skates to create a water layer.

Thus perishes ignominiously another urban legend...

Why Does Ice Melt Under Pressure?



Recall that: $\left(\frac{\partial G}{\partial P}\right)_T = V$

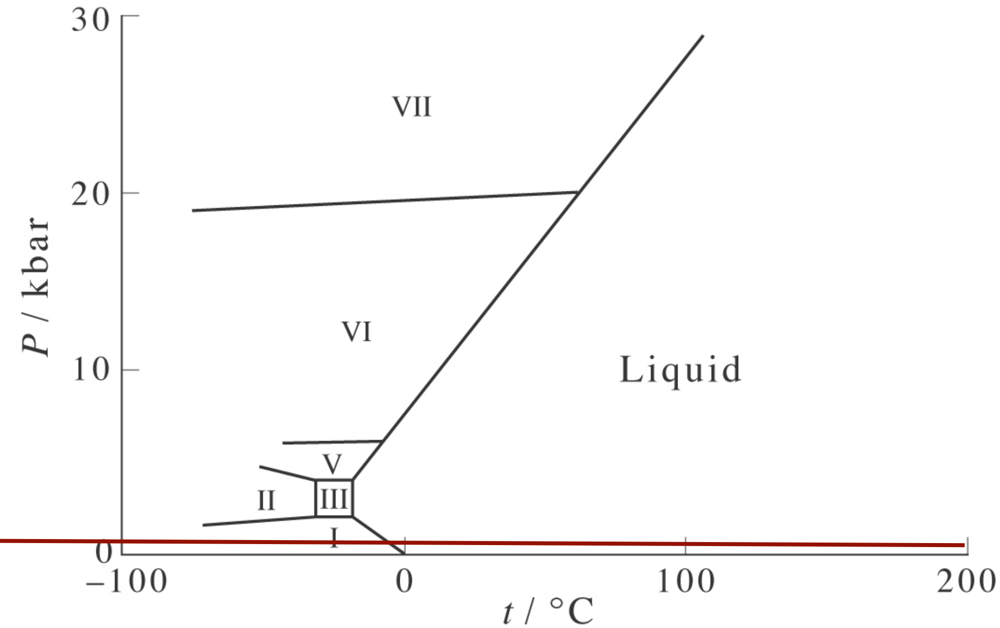
Spontaneous (*negative* ΔG) melting with *positive* ΔP at constant temperature (brown arrow at left) implies ΔV must be *negative*, i.e., volume of liquid is *smaller* than volume of solid.

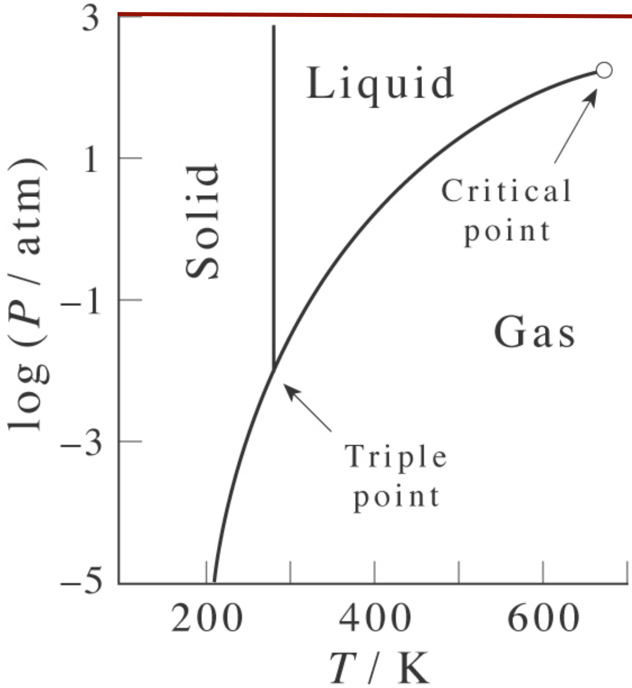
Liquid water is denser than ice(I)

Ice(I) floats

Many Ices Aren't Cold!

Isn't *everything* a solid at ultra-high pressure?

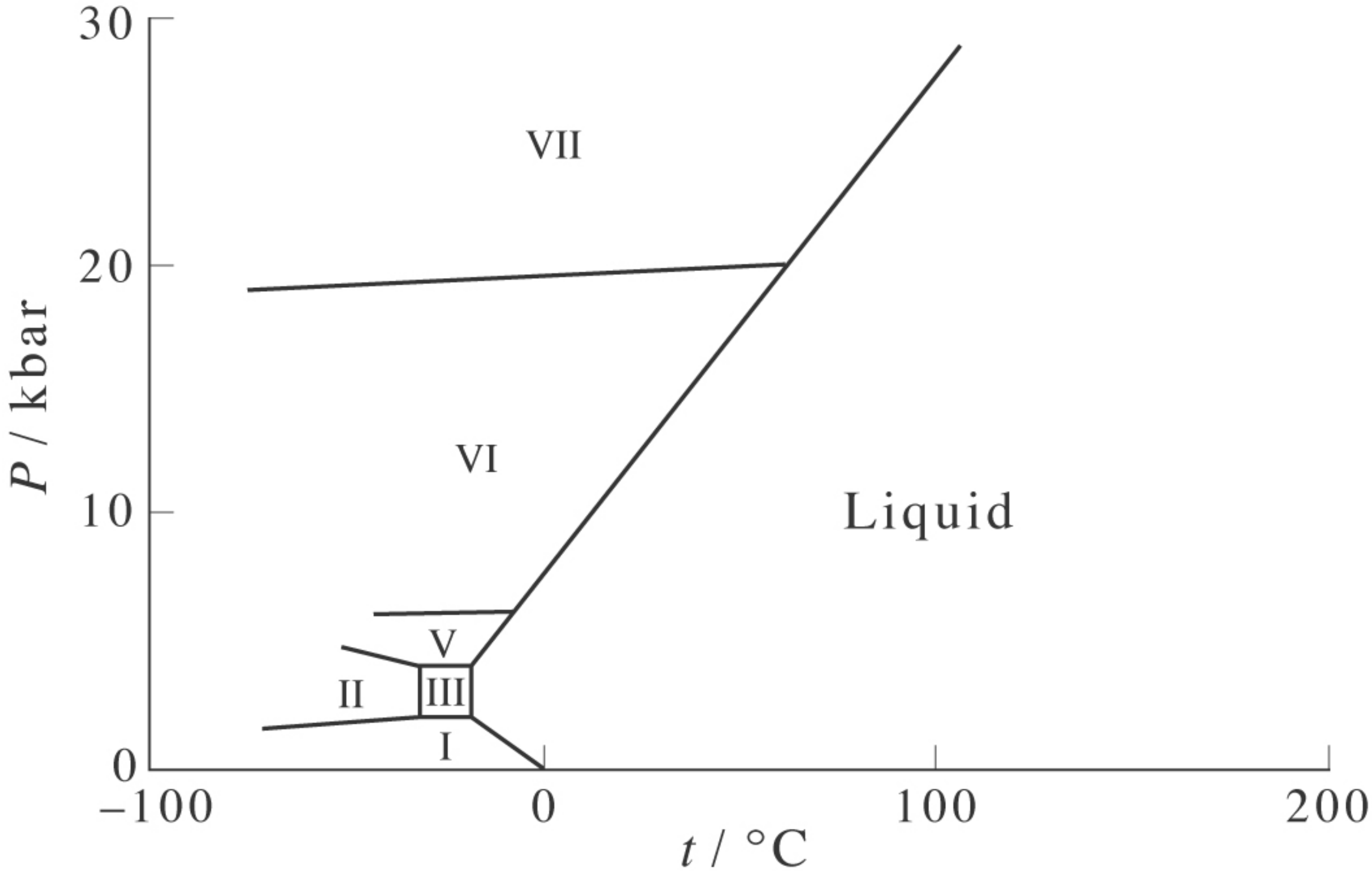




(b)

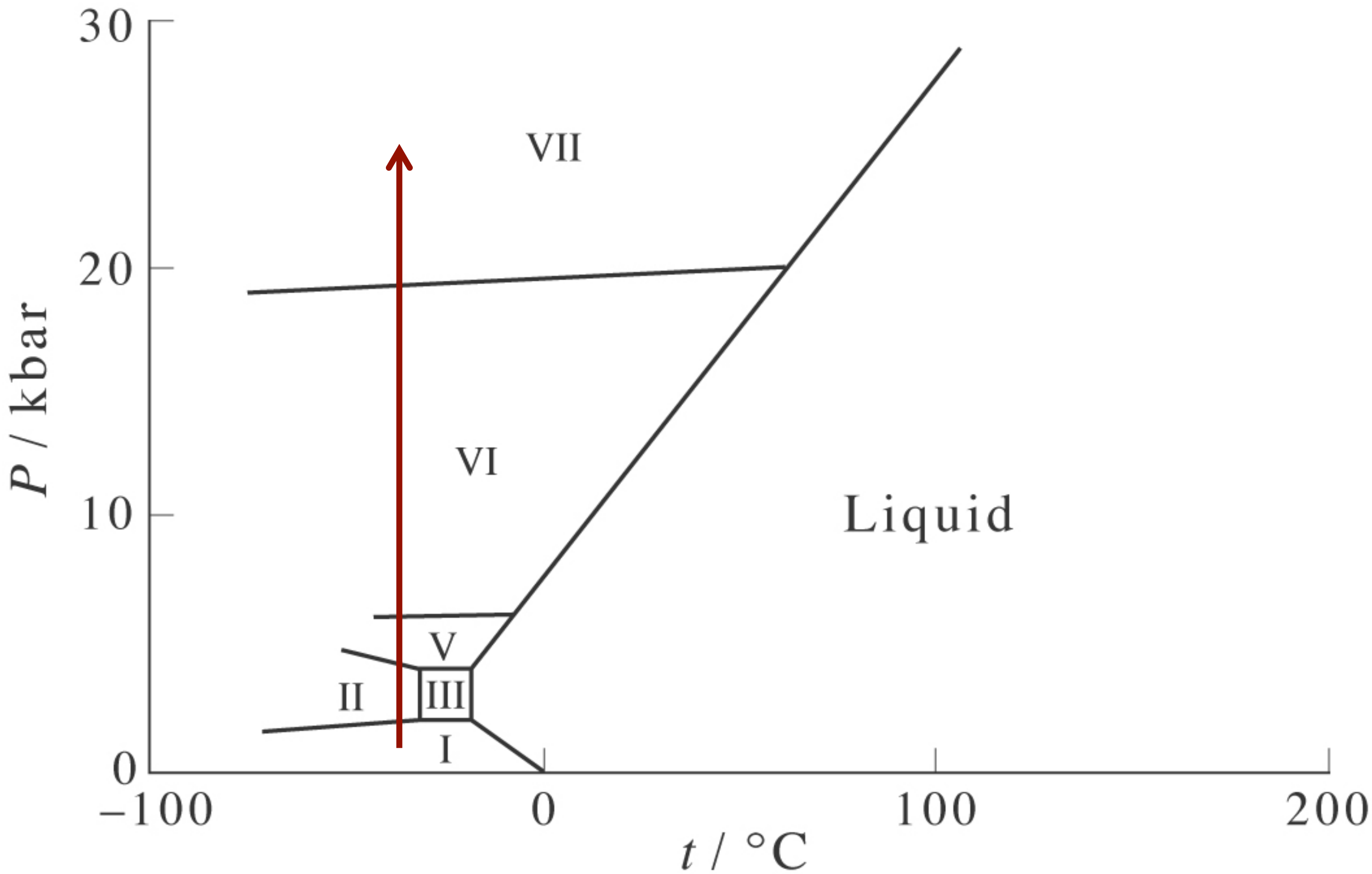
There are many crystalline solid forms of water that are the most stable phases at very high pressures. Some are found at T > 100 °C!

Self-assessment



Order the densities of ices I, II, V, VI, and VII at –30 °C

Self-assessment Explained



Ices I, II, V, VI, and VII become the most stable phases (i.e., have lower free energies than the preceding phase) with increasing pressure at –30 °C, hence their volumes must be *decreasing*, hence their densities must be *increasing*.

Next: Supercritical Behavior