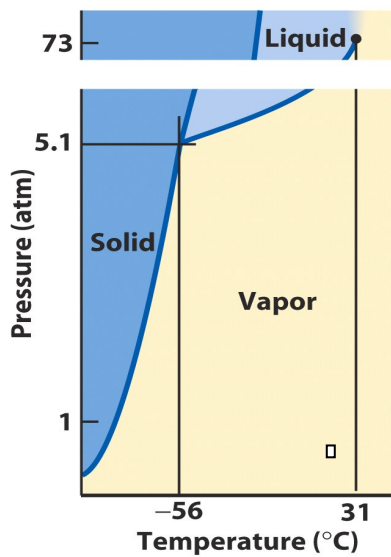


Note that in the heating of a solid until it becomes a vapor there are five distinct points at which you can calculate an amount of heat change.

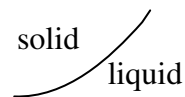
- and finally, the Pressure-Temperature Phase Diagram



As described below, the PT diagram is used to determine the phase of a substance at any combination of pressures and temperatures. In addition, the lines that separate the phases define equilibrium transition pressures and temperatures.

Things to notice on any PT diagram:

- (1) If you assign a P and a T, then you can read the actual phase (s,l,g) at that PT point.
- (2) In general, and sensibly,
  - as T  $\uparrow$  gas forms
  - as T  $\downarrow$  solid forms
  - as P  $\uparrow$  solid forms
  - as P  $\downarrow$  gas forms
- (3) The solid lines on a PT diagram represent equilibrium phase transitions (the six shown on the triangle above.) So for example, at the line separating solid from liquid, both liquid and solid

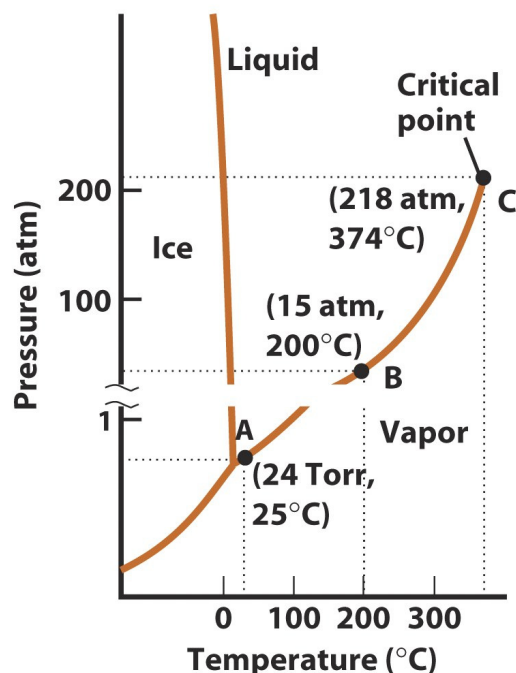


exist simultaneously and define the melting or freezing point for the compound. For example, on a water PT diagram, at 1 atm pressure you would expect to see crossing points at 0°C and 100 °C.

- (4) When you are on a line, you are at equilibrium. In other words, if you see both phases present simultaneously,  $\Delta G=0$ . We will use this fact to do a calculation shortly.
- (5) There are two special regions on a PT diagram.
  - The **triple point** where all 3 phases exist at equilibrium simultaneously. (For water this occurs just below 0 deg. C at 4.6 torr) Were you to create this environment you would see ice, water, and steam all present at the same time—kind of gives you chills just thinking about it.
  - **Supercritical region.** An odd thing happens if you crank up the pressure and temperature. You reach a place at the end of the gas-liquid line where a new fluid, termed a **supercritical fluid**, is formed. It has different properties than either the liquid or vapor of a substance. (For example, this is the region where supercritical carbon dioxide solubilizes caffeine in coffee--there was a commercial a few years ago for decaf coffee that referred to “the natural effervescence found in nature” as a way to describe using supercritical CO<sub>2</sub> rather than a dry cleaning solvent to extract the caffeine from coffee beans.) What is interesting to note about the supercritical region is above the critical temperature it is not possible to turn vapor into a liquid by increasing the pressure. For water the critical temperature is 374 °C at a pressure of 218 atm. For CO<sub>2</sub> it is 31°C at 73 atm.

## Water is Weird and its PT Diagram Proves It.

The PT diagram proves it. Compare the slope of the water diagram's ice-liquid transition to that of a typical substance's. The water diagram has a negative slope, while most others have a positive slope.



PT Diagram for water: spend some time staring at this diagram and looking at the numbers, especially around phase transitions. Your familiarity with the quantitative aspects of water's phase changes will help you appreciate the kind of information realized from this kind of graph.

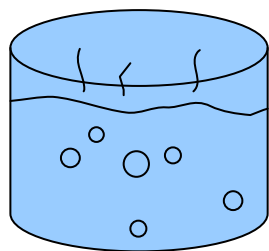
The unique feature of the graph is the negative slope of the ice-liquid transition. (Every other phase diagram shows a positive slope for the solid-liquid interface. Why is this negative slope for H<sub>2</sub>O so interesting? It means that

- Ice is less dense than water--it is why ice floats on water but in all other substances the solid form sinks. It is also why when you put a glass of water in the freezer, the frozen ice increases in size and can break the glass.
- The PT diagram also suggests that for water, as the pressure goes up, ice melts. Think about it this way: when you bite an ice cube it liquefies. When you bite any other solid, it stays a solid!!

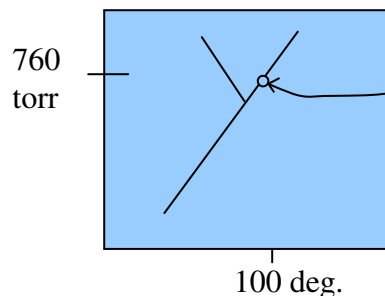
By the way, the reason for this peculiar behavior of water is the enormous H-bonding capacity of H<sub>2</sub>O that more tightly packs it in liquid form/

**Calculating phase change temperatures.** Finally, an exciting feature of PT diagrams we can combine with thermodynamics to calculate phase changes (like boiling points of H<sub>2</sub>O) from Appendix K data. Wow, you'll never need a thermometer again!!

Calculating a phase transition temperature from thermodynamic data.



<----- notice the boiling water and think about where it is located on a PT diagram



at this point on a phase diagram there is an equilibrium established between two phases.

As we have learned in Ch 7, at equilibrium the free energy of a system is 0.  $\Delta G = 0$  at equilibrium. So  $\Delta G = \Delta H - T \Delta S = 0$  at a phase transition

Rearranging  
a phase transition temperature like boiling point

$$T = \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}}$$

} two thermo values you can get from Hess' Law and App K data

Example: Calculate the boiling point of H<sub>2</sub>O



from App K

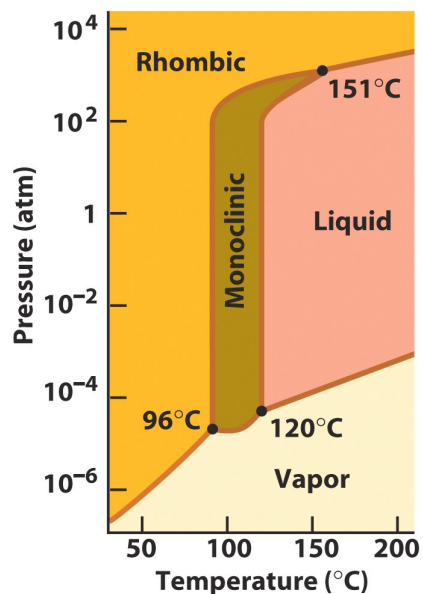
	$\Delta H_f$	$\Delta S_f$
H <sub>2</sub> O <sub>g</sub>	- 241 kJ	.188 kJ
H <sub>2</sub> O <sub>l</sub>	- 285 kJ	.069 kJ

$$\left. \begin{aligned} \Delta H_{\text{rxn}} &= -241 - (-285) \\ &= 44 \text{ kJ} \\ \Delta S_{\text{rxn}} &= .188 - .069 \\ &= 0.119 \text{ kJ} \end{aligned} \right\}$$

$$T = \frac{\Delta H}{\Delta S} = \frac{44}{.119} = 97 \text{ deg (close enough to } 100^\circ\text{C)}$$

### Phase diagrams can get more complicated:

The simple phase diagram that suggests a single liquid, solid and gas phase for a compound doesn't always hold. In fact, it is a simplification. At different temperatures and pressures, solids can assume different crystalline forms. For example, in the PT diagram for sulfur below



there are two different solid phases. A rhombic form that exists at lower temperature and a monoclinic form that exists at higher temperature.

Note that when there are more phases, there is an increase in the number of triple points—in this case with sulfur there are three different triple points where three phases exist simultaneously.