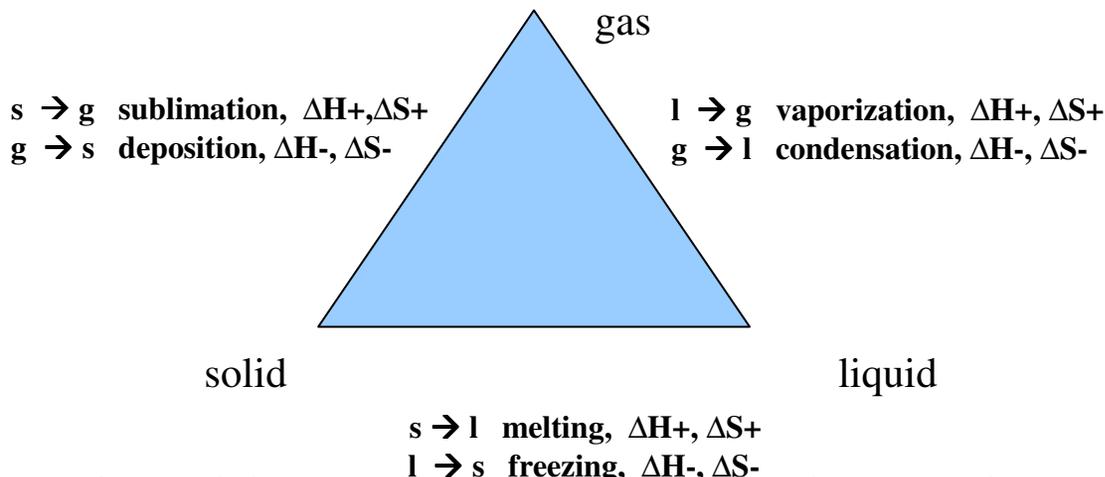


## Lecture 2: Phase Diagrams

It is particularly instructive to assemble graphs and diagrams that contrast the properties of a compound's phases. For example, the phase diagram that is most famous is a plot of pressure vs. temperature in which the various states of matter are identified. We will be examining this kind of plot, along with two others, in this section of the notes.

Presented below are three ways we can draw a phase diagram:

- Certainly the simplest is a triangle with the 3 phases at the vertices and the names of the phase changes along the sides of the triangle. Although simple, if you can actually draw this from scratch and assign the phase and associated thermodynamic sign changes that you learned from first semester thermodynamics, then you know quite a bit:

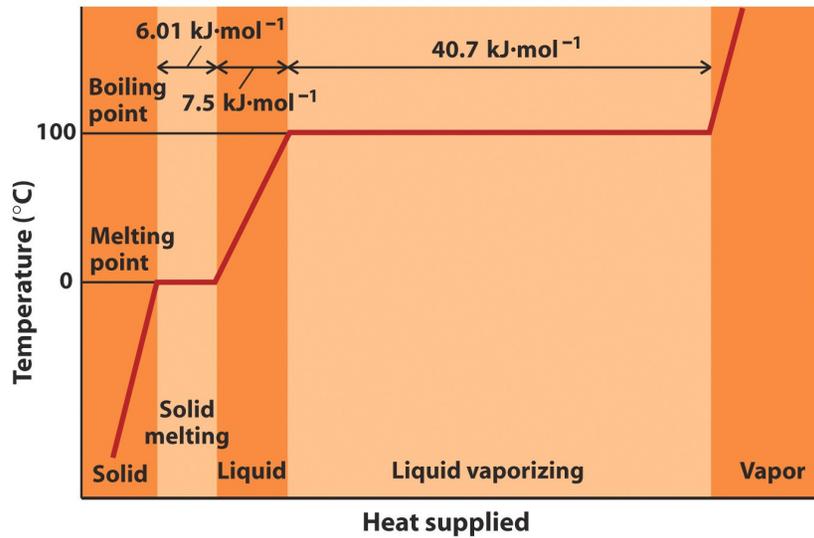


- A second phase transition tracks the temperature change over time energy is added or removed from the system.

From thermo you learned to calculate  $\Delta H$  at phase transitions and over temperature intervals in which you use  $C\Delta T$  to find  $\Delta H$ . Note that there are five different constants for five different possible calculations within specific temperature regions.

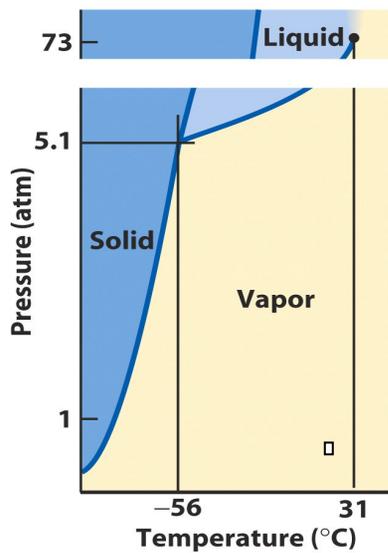
The total energy change is simply determined by adding up the individual energy changes over the temperature range.

$C_{\text{solid}}$	which is used in a $\Delta H = mC\Delta T$
$\Delta H_{\text{fus}}$	which is a molar quantity that needs to be scaled to the amount of material to find the heat change
$C_{\text{liquid}}$	which is used in a $\Delta H = mC\Delta T$
$\Delta H_{\text{vap}}$	which is a molar quantity that needs to be scaled to the amount of material to find the heat change
$C_{\text{gas}}$	which is used in a $\Delta H = mC\Delta T$



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.

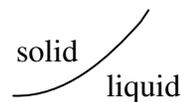
- A third, and most informative phase diagram: the Pressure-Temperature (PT) Phase Diagram



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 are given 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

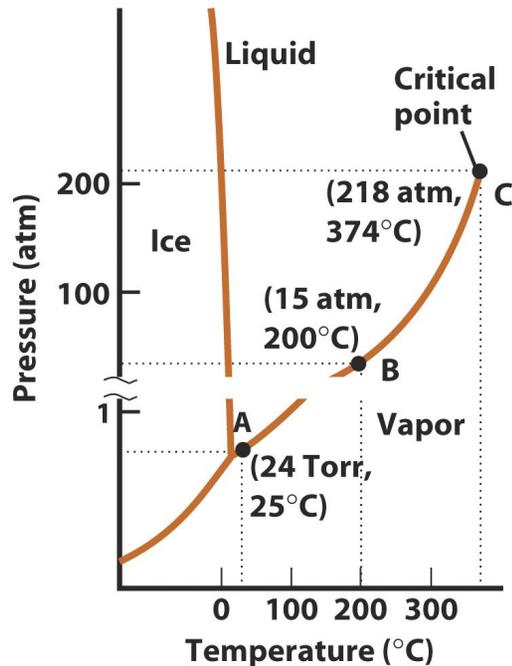


exist simultaneously and define the melting or freezing point for the compound. For example, on a water PT diagram, at 1 atm pressure you would expect to see crossing points at 0°C and 100 °C.

- (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 the excitement of it all.
  - **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. The slope of the line at the solid/liquid phase diagram is like no other common material--it is negative!!



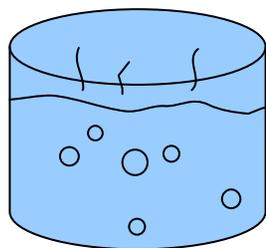
PT Diagram for water: spend some time staring at this diagram and looking at the numbers, especially around phase transitions. Your familiarity with the quantitative aspects of water's phase changes will help you appreciate the kind of information realized from this kind of graph.

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

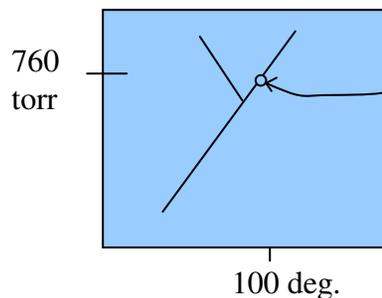
- Ice is less dense than water--it is why ice floats on water but in all other substances the solid form sinks. It is also why when you put a glass of water in the freezer, the frozen ice increases in size and can break the glass.
- The PT diagram also suggests that for water, as the pressure goes up, 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 tables of thermodynamics 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 thermo, 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 thermo data

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



from thermo tables

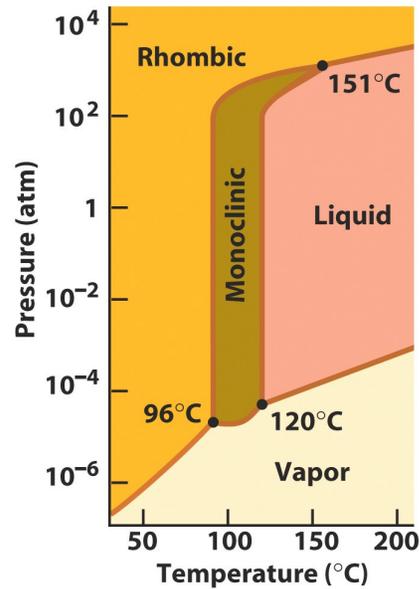
	$\Delta H_f$	$S_f$
H <sub>2</sub> O <sub>g</sub>	- 241 kJ	.188 kJ
H <sub>2</sub> O <sub>l</sub>	- 285 kJ	.069 kJ

}  $\Delta H_{\text{rxn}} = -241 - (-285) = 44 \text{ kJ}$   
 $\Delta S_{\text{rxn}} = .188 - .069 = 0.119 \text{ kJ}$

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

### 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.