Phase Equilibria - Single substances

A. Since a process is spontaneous if $\Delta G < 0$, this means that a substance will undergo a phase transition if it can go to a lower free energy. This is the thermodynamically stable phase.

B. The phase diagram shows what phase is thermodynamically stable under various T & P conditions.

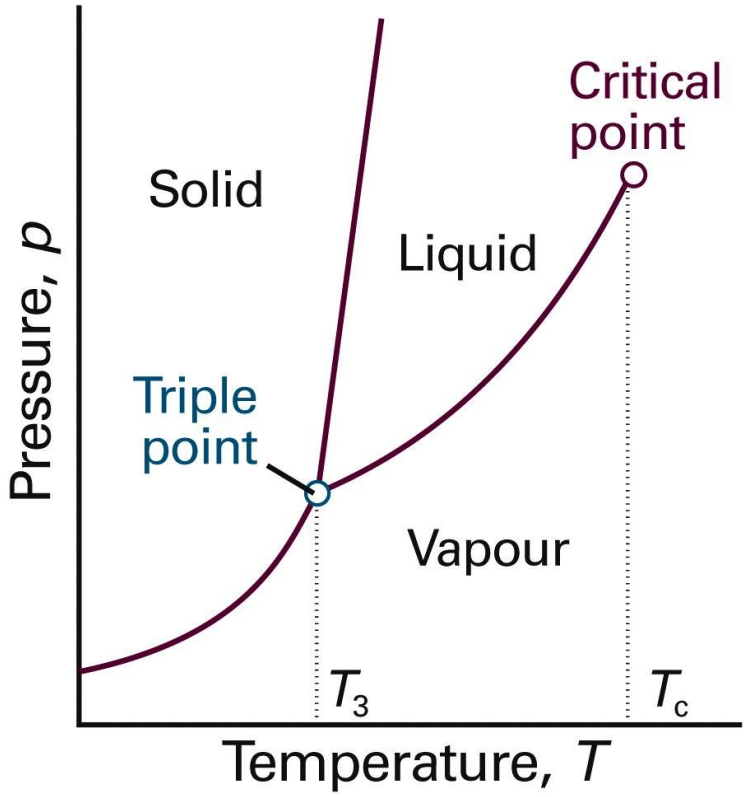

Figure 4-1
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- **Freezing point $VP_{liq} = VP_{solid}$**
  $\Delta G_m = 0$ for liq Û solid
- **Boiling pt VP_{liq} = applied pressure**
- **$\Delta G_m = 0$ for liq Û gas Critical pt T&P above which the liquid phase does not exist**

The critical temp is a measure of the strength of the interparticle forces. T_c increases as the interparticle forces increase.

The triple point (T_3) is the point at which all three phases coexist with each other.

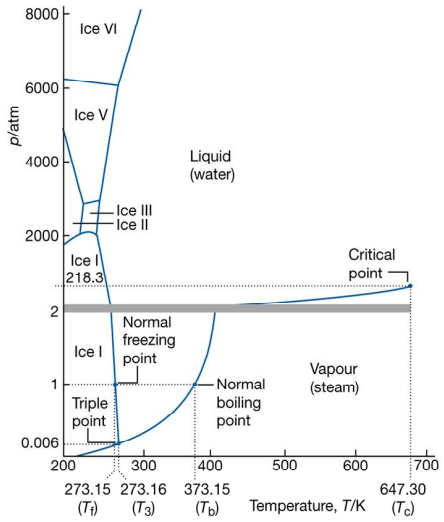
C. The Water Phase Diagram

T_c = 647 K, T_3 = 273.16 K at a pressure of 0.006 bar

The slope of the solid liquid equil. line shows that the freezing point decreases as P increases - very unusual. The thermo argument involves the use of expression

$G_m` = G_m + V_m DP$ under isothermal conditions.

Since V is greater for solid water (ice) than for liquid water, the free energy increases faster for the solid than for the liq under an increase in P.



In going from pt. X to pt Y we see that there will be a pressure at which the solid has a higher G than the liquid and the liquid becomes the thermodynamically stable phase.

There are other phases for ice other than the phase that we normally see. Ice VII even melts at 100°C but at a pressure of 25,000 bar!

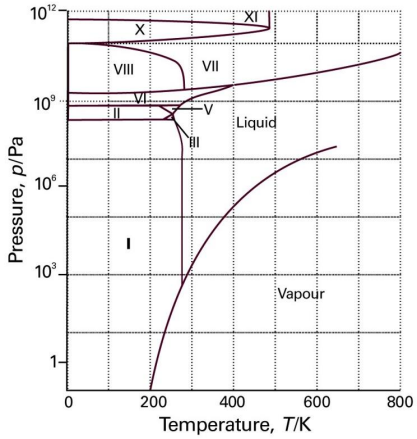


Figure 4-5
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B. Carbon dioxide phase diagram

The slope of the solid/liq equil line shows that the freezing point increases as P increases. This is a result of the greater V for the liquid versus solid CO_2. Thus the G for the solid is always less than the G for the liq in going from pt. X to pt. Y.

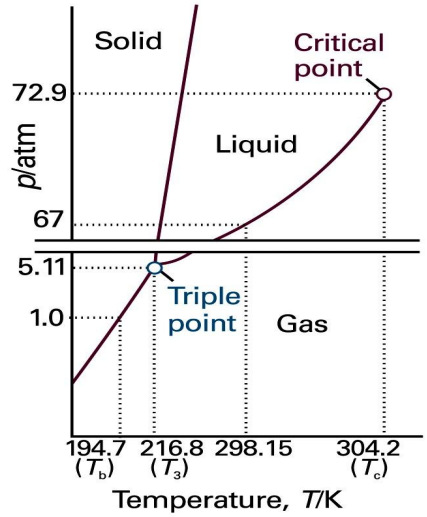

Figure 4-4
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