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# Phase Equilibria

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# I. 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.
- Freezing point  $VP_{\text{liq}} = VP_{\text{solid}}$   
 $\Delta G = 0$  for liq  $\hat{U}$  solid
  - Boiling pt  $VP_{\text{liq}} = \text{applied pressure}$   
 $\Delta G = 0$  for liq  $\hat{U}$  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**

**$G' = G + VDP$  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!**

## **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<sub>2</sub>. Thus the G for the solid is always less than the G for the liq in going from pt. x to pt. Y.**

## **C. Carbon**

**This phase diagram is not complete but does show the transitions between diamond and graphite which are T&P dependent.**

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## II. Nonelectrolyte solutions

### A. Concentration units

- **Molarity = moles of solute / liter of solution**
- **Molality = moles of solute / kg of solvent**
- **Mole fraction = moles of solute or solvent / total moles of solution**

### B. Partial molar quantities - the contribution per mole that a substance makes to a property of a system

#### 1. Partial molar volume

$$V = n_A V_A + n_B V_B$$

$V_A$  and  $V_B$  are partial molar volumes.

The partial molar volume depends on the environment of the substance. For pure water the partial molar volume is 18 ml/mole, but in ethanol it is only 14 ml/mole.