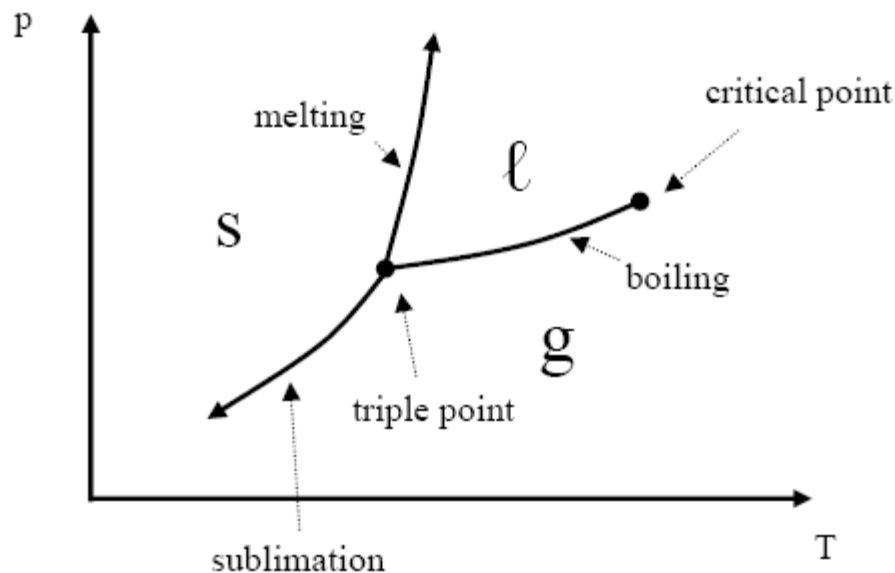


Key Concepts for Exam 3

Material covered: Lectures 18 – 28, phase changes, phase equilibria, statistical mechanics.

One Component Phase Equilibrium

- Understand what a first order phase transition is (As one changes T holding p constant or changes p holding T constant, there is a discontinuity in the properties of the system. *e.g.* density, heat capacity, molar entropy, molar enthalpy, etc.)
- Understand how chemical potential determines phase equilibrium. (Generally, a substance will be in the phase that has the lower chemical potential, if $\mu_\ell < \mu_s$ then the system will be in the liquid state. If the chemical potentials of the two phases are equal $\mu_\ell = \mu_s$, then phase equilibrium will occur.)
- Look through the lecture notes (lecture 18) and refresh on how we made the μ vs. T plot at constant pressure, and how plotting this for many different pressures enabled us to construct the standard T vs. p phase diagram.



- For the solid liquid line, understand how the slope is determined by the relative density of the solid and liquid.
- Refresh on the derivation of the Clapeyron equation, $\left(\frac{dp}{dT}\right)_{coexist} = \frac{\Delta\bar{S}}{\Delta\bar{V}} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$ (note that no approximations are made in this derivation), and understand how this determines the slope of solid-gas and liquid-gas phase lines.

- Know the Clausius- Clapeyron equation: $\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}$, where ΔH is the enthalpy of sublimation or vaporization. Follow the derivation and understand the approximations/assumptions used to get from the Clapeyron to the Clausius- Clapeyron equation (ΔV_{sub} or $\Delta V_{vap} = V_{gas}$ and the gas is ideal).
- Using the assumption that ΔH is independent of temperature, know how to get to the integrated form of the Clausius- Clapeyron equation:

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
- Understand the effects of adding an inert gas over a liquid, and how entropy of mixing increases the vapor pressure. Understand why the partial pressure of a liquid compound increases as we add inert gas at constant volume.

Two Component Phase Equilibrium

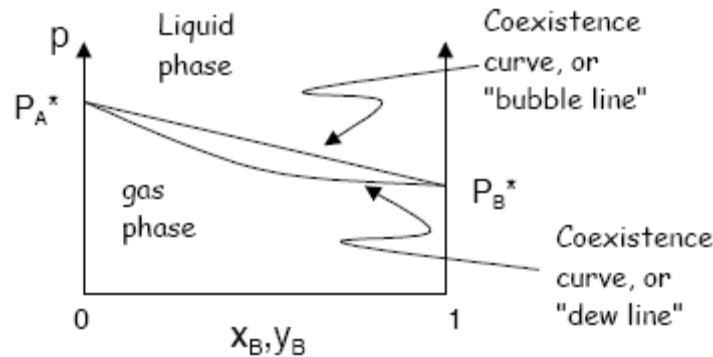
- Review the derivation of Gibb's phase rule: $F = C - P + 2$, with F the number of degrees of freedom or independent variables, C the number of components, and P the number of phases. Be able to modify the phase rule for situations where there are extra degrees of freedom (like the ferroelectric phases and the presence of an electric field) or where extra constraints are applied (like the chemical equilibrium in solution).
- Understand the definition of an "ideal" solution (that energetically speaking, interactions between like molecules is identical to interactions between different molecules) and how this implies that entropy is the driving force behind mixing.
- Know the laws we used to derive the behavior of "ideal" solutions
 - Dalton's Law: $p_A = py_A$, $p_B = py_B$
 (with p_A the partial pressure of component A in the gas, p_B the partial pressure of B, p the total pressure, and y_A and y_B the mole fractions in the gas of components A and B respectively.)
 - Raoult's Law: $p_A = p_A^*x_A$, $p_B = p_B^*x_B$
 (with p_A and p_B the partial pressures of A and B, p_A^* and p_B^* the vapor pressure of pure A and B respectively, and x_A and x_B the mole fractions in the liquid of A and B.)
 - Definition of mole fractions: $x_A + x_B = 1$, $y_A + y_B = 1$
- Understand how these laws were used to come up with expressions for the dew line and the bubble line. If we start entirely in the gas phase and increase the pressure of a two-component system, the dew line corresponds to the pressure (for a particular mole fraction) at which the first drops of liquid form. If we start

entirely in the liquid phase, the bubble line corresponds the pressure at which the first bubbles of gas form as we decrease the pressure.

$$\text{Dew line: } p = \frac{P_A^* P_B^*}{P_B^* + (P_A^* - P_B^*) y_B}$$

$$\text{Bubble line: } p = (P_B^* - P_A^*) x_B + P_A^*$$

- Be comfortable with the plot (remembering there are actually two plots here with different x -axes):



and be able to figure out the mole fractions of A and B in the liquid and gas phase for any pressure, given initial mole fractions. Know what happens if you start completely in the gas or liquid phase and increase or decrease the pressure, respectively.

- Know how a non-ideal solution differs from an ideal solution, and be able to apply Henry's Law in the dilute solution limit, $p_B = K_B x_B$, with K_B the Henry's Law constant, an experimentally determined value that is dependent on solute/solvent concentration and temperature.
- Know the colligative properties (again applicable in the dilute solute limit) on page 1 of lecture 23. Be comfortable using the concentration expressed as molality (moles solute/kg solvent) and the molar mass given in kilograms.

Statistical Mechanics

- Be comfortable with Boltzmann factors and what they tell us about the relative probabilities of a molecule being in two states: $\frac{P(\epsilon_i)}{P(\epsilon_j)} = \frac{e^{-\epsilon_i/kT}}{e^{-\epsilon_j/kT}}$, and how we can use the (obvious) fact that the particle has a probability of 1 of being in *some* state to write: $P(\epsilon_i) = \frac{e^{-\epsilon_i/kT}}{\sum_j e^{-\epsilon_j/kT}}$.

- Know that the denominator of the expression above is defined as the molecular partition function, $q = \sum_j e^{-\epsilon_j/kT}$ where \sum_j indicates a sum over all states. Be comfortable with re-writing this as $q = \sum_i g_i e^{-\epsilon_i/kT}$ where now the \sum_i indicates a sum over energy levels and g_i is the degeneracy of each energy level. Understand how q is a measure of the total number of occupied states when we define the energy of the ground state to be zero.

- Know how to get from the molecular partition function to the system partition function:

$Q = q^N$ when the particles are distinguishable from each other

$Q = \frac{q^N}{N!}$ when the particles are indistinguishable (this usually applies to translational motion, and should not be applied to rotation or vibrational motion as well.)

- Know how to get from the partition functions to macroscopic thermodynamic properties starting from the internal energy and using the fundamental equations and the definition of thermodynamic properties to get everything else:

$$\blacksquare U = \langle E \rangle = N \langle \epsilon \rangle = N \sum_i \epsilon_i P_i = \frac{N}{q} \sum_i \epsilon_i g_i e^{-\epsilon_i/kT} = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$\blacksquare A = -kT \ln Q$$

$$\blacksquare S = \frac{U - A}{T} = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = -k \sum_j P_j \ln P_j$$

$$\blacksquare p = - \left(\frac{\partial A}{\partial V} \right)_{T,N} = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}$$

$$\blacksquare \mu = - \left(\frac{\partial A}{\partial N} \right)_{T,V} = kT \left(\frac{\partial \ln Q}{\partial N} \right)_{T,V}$$

$$\blacksquare C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

- Know Ludwig Boltzmann's famous equation $S = k \ln \Omega$, where Ω is generally referred to as the number of microstates, or the degeneracy of the most probable energy level, and understand what this approximation means. Be able to use the binomial distribution to calculate Ω for simple systems.
- Be comfortable applying the above the concepts as has been done in problem sets to finite and infinite ladders of states, and develop intuition for U , C_V , A , S , etc in these different cases.