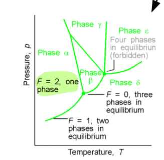
59-240 Lecture 18 The Phase Rule

Phase diagrams

- pictorial way of understanding properties of a system
- important in the development of a wide variety of materials
- all based on the **Phase Rule**, developed by Gibbs

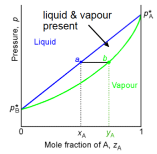
Definitions

- Phase
  - form of matter that is uniform throughout
  - number of phases, *P*
  - ideal mixtures vs. slurries vs. dispersions
  - not always obvious
- Constituent
  - chemical species that is present in a system
- Component
  - smallest number of independently variable constituents needed to express the composition of each phase
  - OR: the total number of constituents *N* minus the total number of chemical constraints on the complete system and within each phase *R*, *C* = *N*-*R*
  - number of constituents, *C*
  - simple examples of 1, 2 and 3 component systems
- Variance
  - degrees of freedom
  - number of intensive variables in a system that can be changed independently without disturbing the number of phases in equilibrium
  - variance, *F*
    - bivariant, 2
    - univariant, 1
    - no degrees of freedom, 0
    - negative degrees of freedom: can't exist!

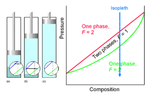


- Phase Rule
  - $F = C - P + 2$
  - one component system: *F* = 3 - *P*
  - two component system: *F* = 4 - *P*
  - two component system, with either pressure or temperature fixed: *F'* = 3 - *P*

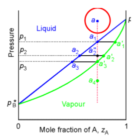
Interpretations of phase diagrams



- Total composition z_A, liquid phase has composition x_A, and gas phase has composition y_A



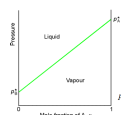
- Lowering pressure example; along **isopleth** (constant composition)



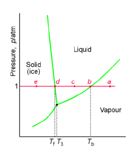
- Learn this interpretation
- Lever Rule
  - **Tie lines**
  - $$n_\alpha l_\alpha = n_\beta l_\beta$$
  - tie lines: identify relative amounts of contributing phases, as well as the compositions of these phases
  - **BRING RULER TO FINAL EXAM!**

Two-component systems

- Pressure-composition phase diagrams
- *F'* = 3 - *P*
- Ideal mixture
  - $$p_A = x_A p_A^* \qquad p_B = x_B p_B^*$$

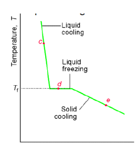


  - Compositions in vapour and liquid phases could be different
    - $$y_A = \frac{p_A}{p} \qquad y_B = \frac{p_B}{p}$$ Gas phase mole fractions
    - $$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A}$$
    - $$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*)y_A}$$



Cooling curves

- Slopes for cooling; gases cool faster than liquids which cool faster than solids
- halts for phase transitions



- cooling curves are used to construct phase diagrams