SPRING 2019
ECH 4123 Phase Equilibria

Book

Essential Thermodynamics
A. Panagiotopoulis

This book is very simple and direct and it introduces all the important ideas in an orderly way.

The problems are many times difficult but mostly instructive.

I will add to it:

1. Equilibrium in a force field
2. Equilibrium across curved surfaces
3. Extensions to vapor-liquid, liquid-liquid and vapor-liquid-liquid phase equilibria

Aim

Aside from deriving phase equilibrium conditions and putting them to use via fugacities and activities, our main aim is to make certain we understand the value of the phase rule and the direction it provides us in our planning to make phase equilibrium estimates.

Class

2 lectures and 1 problem session per week

Tests

I would like to give a 1-problem, 1-hour test each week, but that might be more than I can fit in.

Plan

Proceed through the book in the order

Chapters 2, 3, 5, 6, 7, 8, 9, 10

Main Ideas

Chapter 2. 1^{st} law, open and closed systems, tank filling problems

Irreversible expansion of a van der Waals gas: Does T go up or down? Why?

Chapter 3. 2nd Law, Closed and open systems. Reversible work as a bound. Problem 3.8: an example of making heat go from cold to hot.

Chapter 5. U and S are functions of their natural variables, viz., S, V, and N and U, V, N.

Deriving new functions H, A and G and identifying their natural variables.

Euler's theorem

Chapter 6. Equilibrium and stability conditions.

S greatest at constant U, V, N

U least at constant S, V, N
A least at constant T, V, N
G least at constant T, P, N

Common tangent construction: A vs V at constant T
P vs T diagram
Clapeyron Equation
Phase Rule
Van der Waals spinodal

Chapter 7. Pure Component Equilibrium

Definition of fugacity
Calculations of fugacity using a pressure explicit equation of state. Eq. 7.41
Vapor-liquid two phase coexistence for a van der Waals fluid

Chapter 8. Many Component Equilibrium

Mixing functions, heats of solution
Partial Molar functions
Gibbs-Duhem equation
Graphical estimates of chemical potentials
Common tangent construction

Ideal gases and ideal solutions:

ΔS and ΔG of mixing

The ideal solution formula

Fugacity

Activity, Activity Coefficients
Excess Functions
Models for Excess Functions
Models for Activity Coefficients

Chapter 9: Phase Equilibrium

Liquid-Liquid
Liquid-Liquid bubble point i.e., Liquid-Liquid-Vapor
Vapor-Liquid
Azeotropes
Predictions using the one constant Margules equation and the 2 constant Margules equation at C = 2 and the 3 constant Margules equation at C = 3. Running a C = 2 and C = 3 Rayleigh still. A C = 3 total reflux calculation
Osmotic pressure
Boiling point rise

Chapter 10.

Independent reactions
The reaction-molecule matrix. The molecule-atom matrix. The ir product
Extent of Reaction
Reaction equilibrium conditions
The equilibrium constant: K(T)
Effect of T and P on equilibrium extent of reaction.

Websites

Solutions to several problems in each chapter

Sites.google.com/site

Solutions to test problems

Sites.google.com/site

Office Hours

Tuesday and Thursday afternoons
I will MOL answer your questions

Chapter	Examples	Problems
2	1, 5,6,8	5, 6,9,11, 12, 15, 16
3	8	1, 2, 4, 5, 8, 15
5	1, 5	1, 2, 3, 7, 11, 13
6	3	5, 6, 7, 8, 9, 10
7	1, 2	2, 5, 6, 8, 9, 11
8	1, 2, 3, 4, 5	1,2, 3,8,9,22
9	1, 2, 3, 6	7, 8, 10, 11, 12, 21, 22, 24
10	1, 2, 3, 4	1, 2, 5, 8, 11, 13, 14