

Introduction

CHEM 323 Physical Chemistry I

"It is supposed to be hard. If it wasn't hard, everyone would do it.
It's the hard that makes it great."

-Tom Hanks

"In science there is only physics, all the rest is stamp collecting."

-Rutherford

Preliminaries

- Housekeeping
 - Syllabus
 - Course calendar
- Keys to Success
 - Don't panic
 - Read the book and do the problems
 - Ask questions
 - Don't be afraid of the math
 - Remember the system
 - Don't get behind

"I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of Science, whatever the matter may be."

Sir William Thomson
Lord Kelvin

Basics of Physical Chemistry

- Use Mathematical Approach with accurate, precise Measurements of Physical Phenomena to describe Chemistry
- Mathematical Approach
 - Analyze patterns
 - Describe mathematically
 - Solve equations
 - Apply to real world

Basics of Physical Chemistry

- Chemical Systems described in terms of macroscopically observable Physical Properties
 - Size of system (V)
 - Amount of material (n, m)
 - Height of Hg column in open tube (p)
 - Height of Hg column in closed capillary (T, q)
 - Movement of a physical barrier (w)
- Mechanical Equilibrium of Gases
- Zeroth Law of Thermodynamics

Basics of Physical Chemistry

- State Variables: p, V, n, T
 - Completely define physical state
 - If know three, fourth is completely determined
 - Standard states (usually p and T)
- Equation of State
 - Mathematical expression in the state variables describing physical state of chemical system
 - Not generally easy to find, or need be found
 - Inherently multivariate function

Ideal Gas Law

$$p = \frac{n \cdot R \cdot T}{V}$$

- Empirically-Derived Equation of State
 - Boyle ($p = \frac{\text{constant}}{V}$)
 - Charles/Gay-Lussac ($V = \text{constant} \times T$)
 - Avogadro ($V = \text{constant} \times n$)
- Only simple Equation of State
- Limiting Behavior of Gases
 - High temperature
 - Low pressure

Mathematics with Equations of State and State Functions

- Generally can't write
 - Empirical approximation
 - Derivatives (other measurable quantities)
- Define State Function in Terms of Changes in State Variables
 - Partial derivatives
 - Role of integrals
- Example: $p = f(n, T, V) = \frac{n \cdot R \cdot T}{V}$

On to Mixtures

- Physical Chemistry's Model Hierarchy
 - Ideal pure substances
 - Ideal mixtures
 - Real pure substances
 - Real mixtures

- Dalton's Law for Gas Mixtures $p = \sum p_i$

$$p_i = \frac{n_i \cdot R \cdot T}{V}$$

Ideal Gases

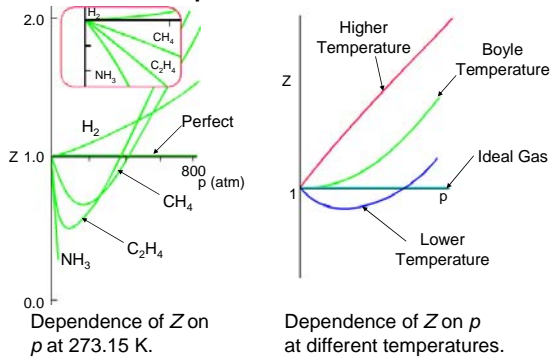
$$p_i = \chi_i \cdot p \quad \chi_i = \frac{n_i}{\sum n_j}$$

Real Gases

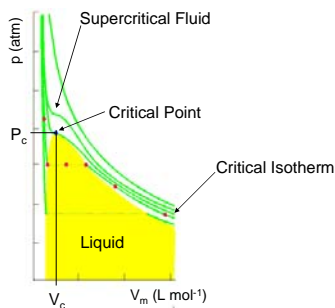
Real Gases

- Definition of an Ideal System
- Real Gases do not behave ideally at low Temperature and/or high Pressure
 - Intermolecular interactions
 - Definite volume of gas particles
- Manifestations
 - Compression factor, $Z = \frac{V_m}{V_m^o}$
 - Condensation
 - Supercritical fluid behavior

Compression Factor



Condensation and Supercritical Fluid Formation



Modeling Real Gases

- General Procedure in Physical Chemistry
 - Start with the ideal case
 - Make empirical corrections to model so it fits data, and/or
 - Derive corrections from new, or corrected, model
- Examples for Gases
 - Power expansion in p , virial equation of state
 - Corrected model, van der Waals equation

Virial Equation

$$p \cdot V_m = R \cdot T (1 + B' \cdot p + C' \cdot p^2 + \dots)$$

$$p \cdot V_m = R \cdot T \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$

- Advantages
 - Reproduces behavior of Z
 - Small number of empirical parameters
- Disadvantages
 - Virial coefficients are temperature-dependent
 - Not readily relatable to chemistry

van der Waals Equation

$$p = \frac{n \cdot R \cdot T}{V - n \cdot b} - a \left(\frac{n}{V} \right)^2$$

- Advantages
 - van der Waals coefficients unique to a gas and temperature independent
 - Physical meaning of a and b
 - Predicts condensation
- Disadvantages
 - van der Waals loops, Maxwell construction

Selection of Models

- Other Equations of States for Gases exist
 - More complex, but better agreement with data
- But, when do you use a particular Model?
- Depends on
 - Precision
 - Accuracy
 - What you are attempting to model

Selection of Models

- Example:
 - 1 mole of gas in 1 L at 273.15 K
- | Gas | p_{ideal} (atm) | $p_{\text{van der Waals}}$ (atm) | % Difference |
|-----------------|--------------------------|----------------------------------|--------------|
| He | 22.414 | 22.926 | 2.2 |
| CO ₂ | 22.414 | 19.801 | 13.2 |

- 1 mole of gas in 1000 L at 273.15 K
- | Gas | p_{ideal} (atm) | $p_{\text{van der Waals}}$ (atm) | % Difference |
|-----------------|--------------------------|----------------------------------|--------------|
| He | 0.022414 | 0.022414 | 0.002 |
| CO ₂ | 0.022414 | 0.022411 | 0.01 |
