Physical Chemistry

Lecture 2

Virial Expansion and Corresponding States

Equations of state for gases

- Ideal-gas law
  - Good at modest conditions
- Empirical laws
  - Van der Waals gas law
  - Redlich-Kwong gas law
  - Bertholet gas law
  - Beattie-Bridgman gas law
  - Peng-Ronbinson gas law

Empirical gas laws

- Van der Waals
- Redlich-Kwong
- Beattie-Bridgman
- Dieterici
- Peng-Robinson

- Try to “correct” the ideal-gas law to release assumptions
- Empirical, “fitting” experimental data

Expansion of a function

- Any function, f(x), of a variable (x) may be expanded as an infinite series in the variable
  - Maclaurin series
    - Expanded about the point x = 0

$$f(x) = f_0 + f_1 x + f_2 x^2 + \cdots$$

  - Taylor series
    - Expanded about an arbitrary point

$$f(x) = f(x_0) + f_{01}(x-x_0) + f_{02}(x-x_0)^2 + \cdots$$

Expansion of a function

- For a function, f(x,y) of two variables, the series expansion applies
- The “coefficients” in such a series are functions of the second variable

$$f(x,y) = f_0(y) + f_1(y)x + f_2(y)x^2 + \cdots$$

- One can generalize this procedure to multiple variables, if necessary

Compressibility of a gas

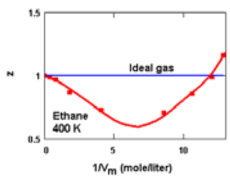
- Definition

$$z = \frac{PV_m}{RT}$$

- Function of state parameters only
- Describes the state of a gas
- Knowing the dependence of the compressibility on any two of the parameters T, V_m, and P is knowing the gas law

Compressibility of ethane

- $z(T, 1/V_m)$ not a simple function
- z_{ideal} = 1 at all conditions
- All gases approach ideal behavior at large molar volumes or low pressures, typically P < 10 MPa



Virial expansion

- The compressibility may be expanded as a function of its independent variables
  - Usually choose the molar density and temperature

$$z(V_m,T) = 1 + B(T)\left(\frac{1}{V_m}\right) + C(T)\left(\frac{1}{V_m}\right)^2 + \cdots$$

  - May also expand as a function of pressure and temperature

$$z(P,T) = 1 + \beta(T)P + \gamma(T)P^2 + \cdots$$

  - Absolutely correct, but requires an infinite number of parameters to define the functional form exactly

Virial expansion

- Truncation of the series
  - If most of the deviation from ideal behavior is in one or a few terms in the virial expansion, a finite series may explain experimental data sufficiently
- Example: Truncated one-term expansion in pressure

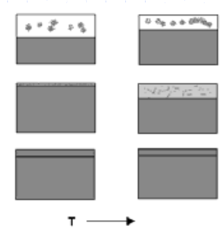
$$z(P,T) \cong 1 + \beta(T)P$$

- Allows one to perform mathematical operations that may not be possible with infinite series
- A perturbation-expansion technique

$$V_m(T,P) \cong \frac{RT}{P} + \beta RT = V_{m,ideal} + V_{m,corr}$$

Critical condition

- Condition at which gas and liquid are identical
- Characterized by a specific set of parameters (T_c, P_c, $V_{m,c}$)
- Determined by balance of attractive and repulsive forces between molecules

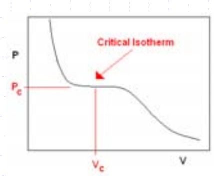


Critical parameters

- Critical parameters and gas-law parameters measure the same thing in different ways
- Can relate them by equations for the isotherm properties
- Example: van der Waals parameters
  - $a = 27R^2T_c^2/64P_c$
  - $b = RT_c/8P_c$
  - $z_c = 3/8$
- Only as good as the data or the gas law is

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$



Reduced parameters

- Define temperature, pressure and volume relative to the critical point through the reduced parameters
- Expressing the relationships in terms of reduced parameters "normalizes" the scales for these parameters based on the strengths of interactions between molecules

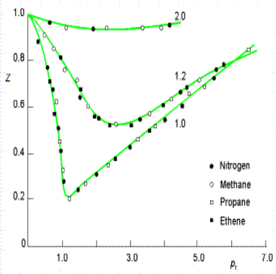
$$T_r = \frac{T}{T_c}$$

$$P_r = \frac{P}{P_c}$$

$$V_r = \frac{V_m}{V_{m,c}}$$

Law of corresponding states

- Observation: All gases behave the same way in some sense
- Critical behavior is the key to the explanation
- Plots of data as a function of reduced variables, T_r, P_r, V_r, shows remarkable similarities of gas behavior
- Every gas has a common equation of state in terms of reduced variables
- Estimate any gas parameter at any condition graphically
  - Can find Newton graphs in Handbook for use in estimation of gas parameters



From P. Atkins, *Physical Chemistry*

Virial expansion summary

- Virial expansion quite accurate in predicting the behavior of gases
- Approximation by truncation is very useful, if done carefully
  - Requires that most of the deviation from ideality be included in a few terms
- Can relate virial coefficients to parameters of empirical gas laws
  - Makes a connection to predict one set if the other set is known
  - Must be done with care

Corresponding states summary

- Gas behaviors are similar, if expressed in terms of reduced parameters
- Critical condition plays a central role in describing a gas's behavior
- May use general graphs to estimate accurately any one of P, V_m, T, when the others are known