CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)

04 - THE MOLAR GIBBS ENERGY & FUGACITY OF A PURE COMPONENT

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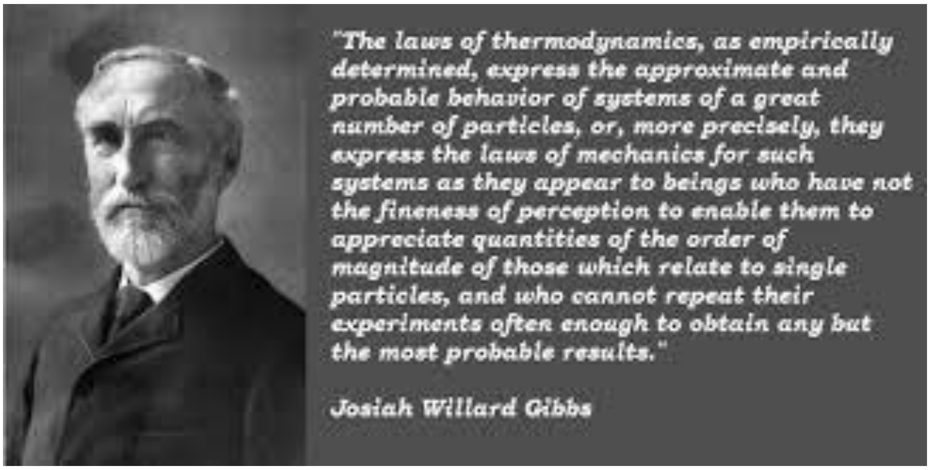
Outline

- Fugacity & Fugacity Coefficient
- Properties of Fugacity and its Coefficient
- Equilibrium Criterion Using Fugacity
- Fugacity and Phase Equilibria
- Effect of T and P on the Fugacity
- Fugacity of a Pure gaseous Species
- Fugacity of a Pure Liquid
- Poynting Correction
- Fugacity of a Pure Solid (Phase)
- Vapor Pressure from EOS



"The laws of thermodynamics, as empirically determined, express the approximate and probable behavior of systems of a great number of particles, or, more precisely, they express the laws of mechanics for such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probable results."

Josiah Willard Gibbs

Josiah Willard Gibbs (February 11, 1839 – April 28, 1903) was an American scientist. Together with James Clerk Maxwell and Ludwig Boltzmann, he created statistical mechanics (a term that he coined), explaining the laws of thermodynamics as consequences of the statistical properties of ensembles of the possible states of a physical system composed of many particles.

Fugacity & Fugacity Coefficient

- The product of pressure times exponential of the residual Gibbs energy divided by *RT* is termed the "**FUGACITY**"

$$f = P\exp\left[\frac{g(T,P) - g^{IG}(T,P)}{RT}\right] = P\exp\left[\frac{1}{RT}\int_0^P\left(v - \frac{RT}{P}\right)dP\right]$$

- The fugacity divided by pressure is the "**FUGACITY COEFFICIENT**"

$$\phi = \frac{f}{P} = \exp\left[\frac{g(T,P) - g^{IG}(T,P)}{RT}\right] = \exp\left[\frac{1}{RT}\int_0^P\left(v - \frac{RT}{P}\right)dP\right]$$

Properties of Fugacity and its Coefficient

- Fugacity has units of pressure.

$$\lim_{P\to 0} f = P$$

- Fugacity coefficient is dimensionless

$$\lim_{P\to 0}\phi = \lim_{P\to 0}\frac{f}{P} = 1$$

- Fugacity is very useful in phase equilibria calculations.

Equilibrium Criterion Using Fugacity: Derivation

- Derive an expression for the equilibrium criterion based on fugacity.
  - Start with the three equilibrium conditions. Note that T and P are fixed and the Gibbs free energy must be equal for the coexisting phases

$$g^{I}(T,P) = g^{II}(T,P)$$

$$g^{IG}(T,P) + RT\ln\frac{f^{I}(T,P)}{P} = g^{IG}(T,P) + RT\ln\frac{f^{II}(T,P)}{P}$$

Equilibrium Criterion Using Fugacity: Final Form

- The ideal gas molar Gibbs free energy has the same value at the same *T* and *P*

$$\ln\frac{f^{I}(T,P)}{P}=\ln\frac{f^{II}(T,P)}{P}$$

$$f^{I}(T,P)=f^{II}(T,P)$$

- At equilibrium:
  - **the fugacity must be equal in the coexisting phases.**

Fugacity and Phase Equilibria

- Since fugacity is related to EOS. It provides an approach to solving phase equilibria problems
- The problem with using the definition of fugacity directly is that the integration requires the EOS to be in the form $v = f(T,P)$.
- The EOS so far use $P = f(T, v)$. With the nonlinear forms of EOS it is difficult to transform them to the form required by fugacity

Transformation of Integration Variable

- Convert the integration from volume explicit to pressure explicit using the following transformation

$$dP = \frac{1}{v}d(Pv) - \frac{P}{v}dv = \frac{P}{Z}dZ - \frac{P}{v}dv$$

- Using this transformation the expression for the fugacity coefficient becomes

$$\boxed{\ln\phi = \ln\frac{f(T,P)}{P} = \frac{1}{RT}\left[\int_{v=\infty}^{v}\left(\frac{RT}{v} - P\right)dv\right] - \ln Z + (Z-1)}$$

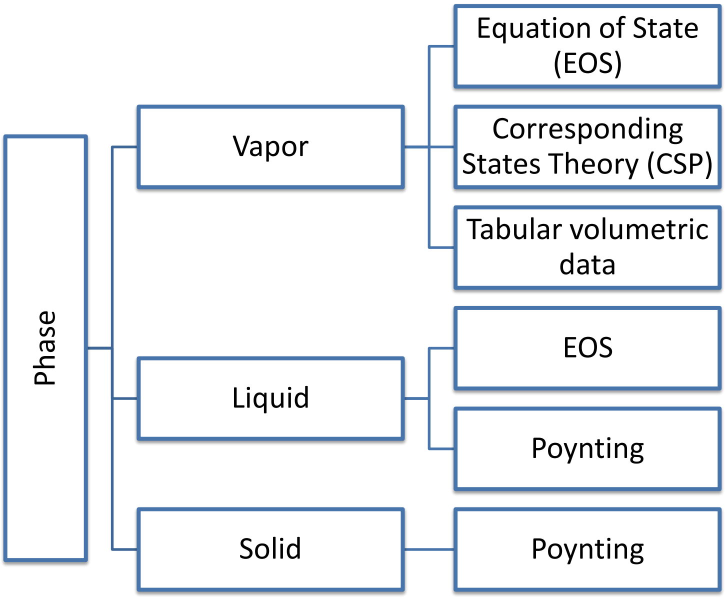
Effect of *T* and *P* on the Fugacity

- The effect of temperature and pressure upon the fugacity can be derived and are given by:

$$RT\left(\frac{\partial \ln f(T,P)}{\partial P}\right)_T = v = \left(\frac{\partial g}{\partial P}\right)_T$$

$$\left(\frac{\partial\left[\ln f(T,P)/P\right]}{\partial T}\right)_P = -\frac{h(T,P) - h^{IG}(T,P)}{RT^2}$$

Fugacity in Various Phases: Road Map



- Phase
  - Vapor
    - Equation of State (EOS)
    - Corresponding States Theory (CSP)
    - Tabular volumetric data
  - Liquid
    - EOS
    - Poynting
  - Solid
    - Poynting

Fugacity of a Pure gaseous Species

- For gases, use an EOS combined with the definition of the fugacity.
  - The EOS is used to provide the dependence of pressure on volume.
  - Frequently, you may need to numerically integrate certain numerical data instead of using an EOS

The Virial EOS

- The virial EOS is a series expansion around the ideal gas limit.
- The coefficients in the series are called the "virial coefficients".
- It can be derived rigorously from statistical thermodynamics and the virial coefficients are related to molecular forces.
- Usually truncated to the second term.

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$$

Effect of T on Virial Coefficients

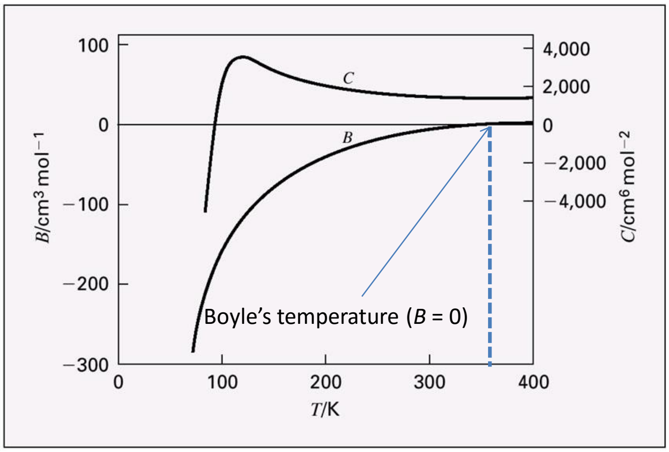


Figure 3.10: Virial coefficients *B* and *C* for nitrogen.

For –ve B: $Z < 1$ (Attractive forces)
For +ve B: $Z > 1$ (Repulsive forces)
For Boyle's temperature $B = 0$: $Z = 1$ (Attractive = repulsive forces)

Pure Component Fugacity from the Virial EOS

- Fugacity coefficient using truncated virial EOS to the second term

$$\ln\phi = \frac{BP}{RT} \Rightarrow f = P\exp\left[\frac{BP}{RT}\right]$$

- The second virial coefficient (*B*) can be estimated using Pitzer's correlation

$$B_r = \frac{BP_c}{RT_c} = \left(0.083 - 0.422/T_r^{1.6}\right) + \omega\left(0.139 - 0.172/T_r^{4.2}\right)$$

Representative EOS

Soave-Redlich-Kwong (SRK)

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}$$

$$a(T) = 0.42748\frac{(RT_c)^2}{P_c}\alpha(T)$$

$$\sqrt{\alpha(T)} = 1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)$$

$$\kappa = 0.480 + 1.57\omega - 0.176\omega^2$$

$$b = 0.08664\frac{RT_c}{P_c}$$

Peng-Robinson (PR)

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$

$$a(T) = 0.45724\frac{(RT_c)^2}{P_c}\alpha(T)$$

$$\sqrt{\alpha(T)} = 1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)$$

$$\kappa = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

$$b = 0.07779\frac{RT_c}{P_c}$$

Cubic EOS Coefficients

$$Z^3+\alpha Z^2+\beta Z+\gamma=0$$

	vdW	SRK	PR
α	$-1-B$	-1	$-1+B$
β	A	$A-B-B^2$	$A-2B-3B^2$
γ	$-AB$	$-AB$	$-AB+B^2+B^3$
Z_c	0.3750	0.3333	0.3074

$$A=\frac{aP}{(RT)^2}\qquad B=\frac{bP}{RT}$$

Initial Guess for solution

Vapor (Vapor like): ideal gas ($Z=1$).

Liquid: Reduced covolume ($Z=B$).

Solution Methodology for PR EOS

1. Obtain (T_c;P_c;ω).
2. Find b in PR EOS.
3. Find a in PR EOS
    1. Determine κ.
    2. Determine α.
    3. Determine $a(T)$.
4. Determine reduced parameters A and B.
5. Evaluate the cubic constants in the Z expression.
6. Solve the cubic for the roots and determine if they fall in the subcooled liquid, superheated vapor or the two phase coexistence region.

$$b=0.07779\frac{RT_c}{P_c}$$

$$\kappa=0.37464+1.5422\omega-0.26992\omega^2$$

$$\sqrt{\alpha(T)}=1+\kappa\left(1-\sqrt{\frac{T}{T_c}}\right)$$

$$a(T)=0.45724\frac{(RT_c)^2}{P_c}\alpha(T)$$

$$A=\frac{aP}{(RT)^2}$$

$$B=\frac{bP}{RT}$$

$$Z^3+(-1+B)Z^2+(A-2B-3B^2)Z$$
$$+(-AB+B^2+B^3)=0$$

Fugacity of a Gas Using the PR EOS

$$\ln \phi = \ln \frac{f^{V}(T,P)}{P} = \left[\frac{1}{RT} \int_{v=\infty}^{v=Z^{V}RT/P} \left(\frac{RT}{v} - P \right) dv - \ln Z^{V} + (Z^{V} - 1) \right]$$

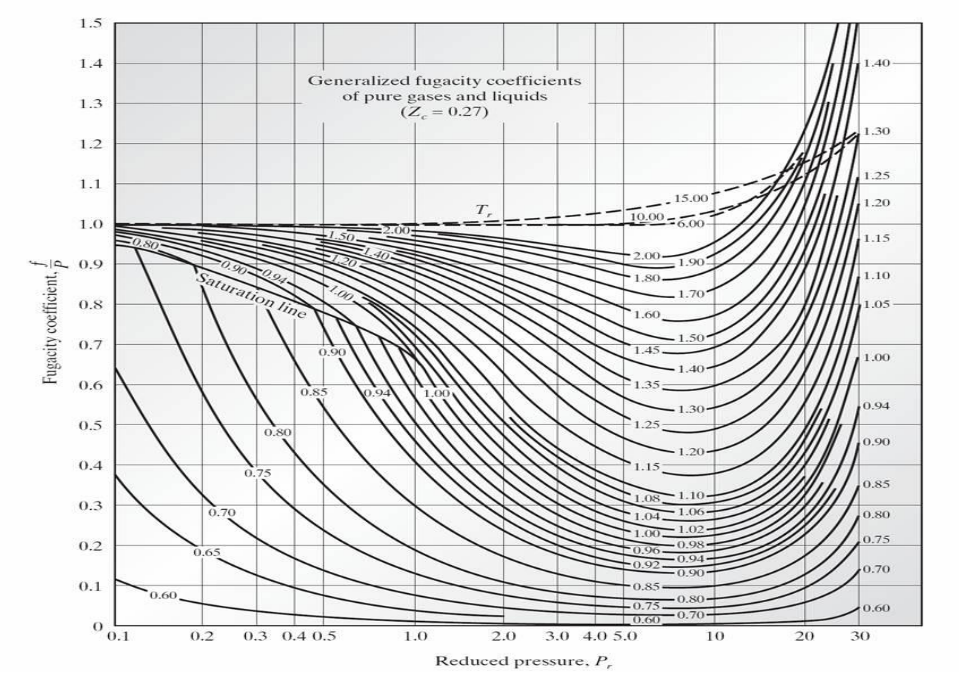
$$\ln \frac{f^{V}}{P} = (Z^{V} - 1) - \ln\left(Z^{V} - B\right) - \frac{A}{2\sqrt{2}B} \ln\left[\frac{Z^{V} + (1+\sqrt{2})B}{Z^{V} + (1-\sqrt{2})B} \right]$$

$$A = \frac{aP}{(RT)^{2}}$$

$$B = \frac{bP}{RT}$$

Fugacity Using Corresponding States Principle (CSP)

- The principle of corresponding states may be used to obtain the fugacity utilizing the reduced temperature and pressure as parameters.
  - A third factor may be used to enhance the accuracy. This third factor may be Pitzer’s acentric factor, or the critical compressibility.



- Compute the fugacity of superheated steam at 300°C and 8 MPa.

Fugacity of a Pure Liquid

- You can use an EOS to get the fugacity of a liquid in a manner similar to that for a gas e.g., Peng-Robinson EOS yields

$$\ln\frac{f^L}{P} = (Z^L - 1) - \ln\left(Z^L - B\right) - \frac{A}{2\sqrt{2}B}\ln\left[\frac{Z^L + (1+\sqrt{2})B}{Z^L + (1-\sqrt{2})B}\right]$$

- Alternatively, one can derive an expression for fugacity from the equilibrium condition of the equality of fugacity to obtain

$$f^L(T,P) = P^{vap}\phi^{sat}(T,P^{vap})\exp\left[\frac{1}{RT}\int_{P^{vap}}^{P} v\,dP\right]$$

Poynting Correction

- P^{vap} is the vapor pressure at the specified T, and the $(f/P)_{\text{sat}}$ is the fugacity coefficient of the fluid (liquid = vapor) at saturation.
- The exponential term is referred to as the **Poynting** pressure correction. It is important
  - At high pressures
  - At low temperatures (cryogenic systems)
- Assuming that liquids are incompressible

$$f^L(T,P) = P^{vap}\phi^{sat}(T,P^{vap})\exp\left[\frac{v^{L,sat}\left(P - P^{vap}\right)}{RT}\right]$$

Fugacity of a Pure Solid (Phase)

- Solids may undergo several phase transitions.
- Usually dealing with solids that undergo sublimation; which is what the superscript ^{sat} refers to in this case.

$$f^{S}(T,P) = P^{sub}(T)\phi^{sat}(T,P^{sub})\exp\left[\frac{1}{RT}\sum_{J=1}\int_{P^{J}}^{P^{J+1}} v^{J}\,dP\right]$$

- Similar to the derivation of liquids assuming that
  - Solids' sublimation pressures are usually very small (ϕ~1).
  - Solids are incompressible

$$f^{S}(T,P) = P^{sub}(T)\phi^{sat}(T,P^{sub})\exp\left[\frac{v^{S}\left(P-P^{sub}(T)\right)}{RT}\right]$$

Vapor Pressure from EOS

- We know that f^L and f^V can be obtained via an EOS using the liquid and vapor compressibility respectively. For the PR EOS

$$\ln\frac{f^{V}}{P} = (Z^{V}-1)-\ln\left(Z^{V}-B\right)-\frac{A}{2\sqrt{2}B}\ln\left[\frac{Z^{V}+(1+\sqrt{2})B}{Z^{V}+(1-\sqrt{2})B}\right]$$

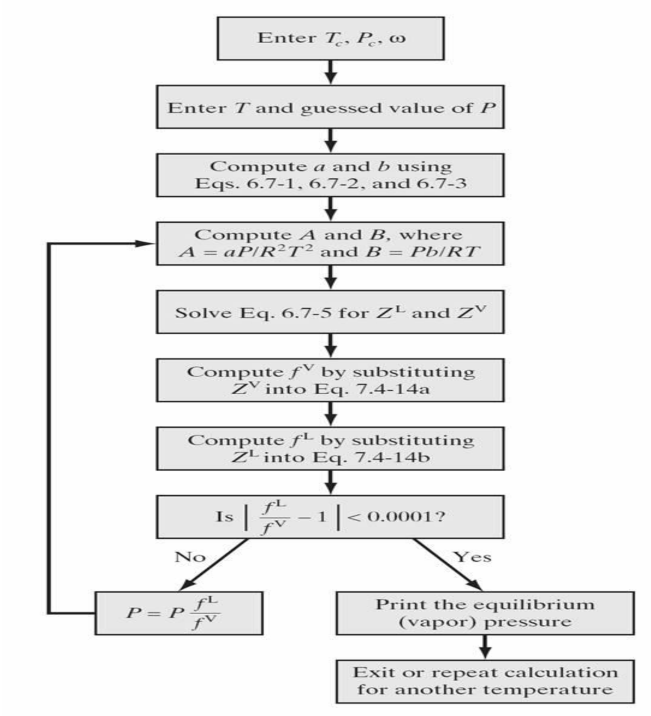
$$\ln\frac{f^{L}}{P} = (Z^{L}-1)-\ln\left(Z^{L}-B\right)-\frac{A}{2\sqrt{2}B}\ln\left[\frac{Z^{L}+(1+\sqrt{2})B}{Z^{L}+(1-\sqrt{2})B}\right]$$

- At equilibrium

$$\boxed{f^{L}(T,P^{vap}) = f^{V}(T,P^{vap})}$$

Algorithm for vapor Pressure Using EOS

- Consequently, solve for the vapor pressure using any EOS.
- This solution is iterative in nature:
  - Assume a pressure
  - Solve the cubic for Z^L and Z^V
  - Evaluate f^L and f^V
  - If the two fugacities are equal to within a certain convergence criteria then the pressure assumed is the vapor pressure
- Always check for trivial solutions (too low or too high pressures leading to single phase).



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