CM 3230 Thermodynamics, Fall 2014

Lecture 12

Compressiblity Charts (continued) p. 245-246

- Mixing rules for n components

$$\text{Kay's Rules:} \quad T_{pc} = \sum_{i=1}^{n} y_i T_{c,i} \quad ; \quad P_{pc} = \sum_{i=1}^{n} y_i P_{c,i} \quad ; \; \omega_{pc} = \sum_{i=1}^{n} y_i \omega_i$$

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1. Three types of properties

i. Measured Properties: P, v, T
ii. Fundamental Properties: u, s
iii. Derived (Combined) Properties

$$\begin{aligned} \text{Enthalpy}: &\quad h = u + Pv \\ \text{Helmholz Energy}: &\quad a = u - Ts \\ \text{Gibbs Energy}: &\quad g = h - Ts \; (= u + Pv - Ts) \end{aligned}$$

Note: all these properties do not depend on the path

- Natural dependencies:

$$\begin{aligned} \text{Internal Energy}: &\quad u = u(s, v) \\ \text{Enthalpy}: &\quad h = h(s, p) \\ \text{Helmholz Energy}: &\quad a = a(T, v) \\ \text{Gibbs Energy}: &\quad g = g(T, P) \end{aligned}$$

2. Some Mathematical Preliminaries

- *Two types of functions*:
    a) Implicit form: $\phi(x, y, z) = 0$
        Example: $\sqrt{x^2 + y^2 + z^2} = 5$
    b) Explicit form: $z = f(x, y)$
        Example: $z = \sqrt{25 - (x^2 + y^2)}$

Remarks: not all implicit forms can be rearranged into explicit forms

- *Main Rule for Differentials of Multivariable Functions*

$$d[\phi(x, y, z)] = \left(\frac{\partial \phi}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \phi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \phi}{\partial z}\right)_{x,y} dz$$

Example: $\phi(x, y, z) = 5$ where $\phi(x, y, z) = \sqrt{x^2 + y^2 + z^2}$,

$$d\phi = \left(\frac{2x}{2\sqrt{x^2 + y^2 + z^2}}\right) dx + \left(\frac{2y}{2\sqrt{x^2 + y^2 + z^2}}\right) dy + \left(\frac{2z}{2\sqrt{x^2 + y^2 + z^2}}\right) dz$$

$$= \frac{1}{\sqrt{x^2 + y^2 + z^2}}\left(xdx + ydy + zdz\right) = 0$$

Equivalently, using an explicit form, $z = \sqrt{25 - (x^2 + y^2)}$

$$dz = \frac{1}{2\sqrt{25 - (x^2 + y^2)}}(-2xdx - 2ydy)$$

$$= \frac{1}{z}(-xdx - ydy)$$

Or

$$xdx + ydy + zdz = 0$$

Example: Obtain the differential of $u(s, v)$ and $h(s, P)$

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

$$dh = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP$$

- ***From Differentials to Derivatives:***

  - treat the coefficient of the differentials as just functions
  - divide the whole equation by the specific differential of interest
  - change symbols to reflect partial derivatives and note other variables that are kept constant, replacing the differentials of constants by zero

Example: Let $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$ and $\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$, find β/κ using Redlich-Kwong EOS.

Solution:

- *Chain Rule*

$$\phi(x,y,z) = 0 \quad \rightarrow \quad d\phi = \left(\frac{\partial \phi}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \phi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \phi}{\partial z}\right)_{x,y} dz$$

$$\psi(x,y,z) = 0 \quad \rightarrow \quad d\psi = \left(\frac{\partial \psi}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \psi}{\partial z}\right)_{x,y} dz$$

$$\left(\frac{\partial \phi}{\partial \psi}\right)_{y,z} = \left[\frac{\left(\frac{\partial \phi}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \phi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \phi}{\partial z}\right)_{x,y} dz}{\left(\frac{\partial \psi}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \psi}{\partial z}\right)_{x,y} dz}\right]_{y,z}$$

$$\left(\frac{\partial \phi}{\partial \psi}\right)_{y,z} = \frac{\left(\frac{\partial \phi}{\partial x}\right)_{y,z}}{\left(\frac{\partial \psi}{\partial x}\right)_{y,z}} \qquad \text{or} \qquad \left(\frac{\partial \phi}{\partial x}\right)_{y,z} = \left(\frac{\partial \phi}{\partial \psi}\right)_{y,z} \left(\frac{\partial \psi}{\partial x}\right)_{y,z}$$

- *Reciprocal of partial derivatives*

Using the chain rule, let $\phi = x$,

$$\left(\frac{\partial \phi}{\partial x}\right)_{y,z} = \left(\frac{\partial \phi}{\partial \psi}\right)_{y,z} \left(\frac{\partial \psi}{\partial x}\right)_{y,z} \quad \rightarrow \quad 1 = \left(\frac{\partial x}{\partial \psi}\right)_{y,z} \left(\frac{\partial \psi}{\partial x}\right)_{y,z}$$

$$\text{or} \qquad \left(\frac{\partial x}{\partial \psi}\right)_{y,z} = \frac{1}{\left(\frac{\partial \psi}{\partial x}\right)_{y,z}}$$

Example: $\psi(x,y,z) = 5x^3 - \ln(x - yz)$

$$d\psi = \left(15x^2 - \frac{1}{x - yz}\right) dx + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} dy + + \left(\frac{\partial \psi}{\partial z}\right)_{x,y} dz$$

$$\left(\frac{\partial \psi}{\partial x}\right)_{y,z} = 15x^2 - \frac{1}{x - yz} \qquad \text{while} \qquad \left(\frac{\partial x}{\partial \psi}\right)_{y,z} = \left(15x^2 - \frac{1}{x - yz}\right)^{-1}$$

- *Symmetry of Second Order Partial Derivatives*

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial \phi}{\partial x}\right)_{y,\ldots}\right]_{x,\ldots} = \left[\frac{\partial}{\partial x}\left(\frac{\partial \phi}{\partial y}\right)_{x,\ldots}\right]_{y,\ldots}$$

Example: $\psi(x,y,z) = 2x^2y - \exp(x - yz)$

$$\left(\frac{\partial \psi}{\partial x}\right)_{y,z} = 4xy - \exp(x-yz) \quad ; \quad \left(\frac{\partial \psi}{\partial y}\right)_{x,z} = 2x^2 + z\exp(x-yz)$$

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial \psi}{\partial x}\right)_{y,z}\right]_{x,z} = 4x + z\exp(x-yz) = \left[\frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial y}\right)_{x,z}\right]_{y,z} = 4x + z\exp(x-yz)$$

- *Cyclic Relationships of Partial Derivatives (for 3 variables)*

Let $\phi(x,y,z) = 0$

$$\left(\frac{\partial \phi}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \phi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \phi}{\partial z}\right)_{x,y} dz = 0$$

Divide by dx and while keeping z constant, then repeat but keep y constant:

$$\left(\frac{\partial \phi}{\partial x}\right)_{y,z} + \left(\frac{\partial \phi}{\partial y}\right)_{x,z}\left(\frac{\partial y}{\partial x}\right)_{z} = 0$$

$$\left(\frac{\partial \phi}{\partial x}\right)_{y,z} + \left(\frac{\partial \phi}{\partial z}\right)_{x,y}\left(\frac{\partial z}{\partial x}\right)_{y} = 0$$

Combining,

$$\left(\frac{\partial y}{\partial x}\right)_{z}\left(\frac{\partial x}{\partial z}\right)_{y} = \frac{\left(\frac{\partial \phi}{\partial z}\right)_{x,y}}{\left(\frac{\partial \phi}{\partial y}\right)_{x,z}}$$

Back to $d\phi$, divide by z but keep x constant,

$$\left(\frac{\partial \phi}{\partial y}\right)_{x,z}\left(\frac{\partial y}{\partial z}\right)_{x} + \left(\frac{\partial \phi}{\partial z}\right)_{x,y} = 0 \quad \rightarrow \quad \frac{\left(\frac{\partial \phi}{\partial z}\right)_{x,y}}{\left(\frac{\partial \phi}{\partial y}\right)_{x,z}} = -\left(\frac{\partial y}{\partial z}\right)_{x}$$

Thus,

$$\left(\frac{\partial y}{\partial x}\right)_{z}\left(\frac{\partial x}{\partial z}\right)_{y}\left(\frac{\partial z}{\partial y}\right)_{x} = -1$$

Alternatively, $$\left(\frac{\partial x}{\partial y}\right)_{z}\left(\frac{\partial y}{\partial z}\right)_{x}\left(\frac{\partial z}{\partial x}\right)_{y} = -1$$

Example: Verify the cyclic equation for the Van der Waals EOS: $(x, y, z) = (P, v, T)$

Solution:

Example: Show that $\beta/\kappa = (\partial P/\partial T)_v$

Solution: