

Lecture 13

1. From the first law of thermodynamics, and various definitions

$$du = Tds - Pdv$$

$$dh = d(u + Pv) = du + Pdv + vdP$$

$$\rightarrow dh = Tds + vdP$$

$$da = d(u - Ts) = du - Tds - sdT$$

$$\rightarrow da = -sdT - Pdv$$

$$dg = d(u + Pv - Ts) = du + Pdv + vdP - Tds - sdT$$

$$\rightarrow dg = -sdT + vdP$$

- This yields the “natural dependencies”:

$$u = u(s, v), h = h(s, P), a = a(T, v), g = g(T, P)$$

- **Relationships of properties** $\{s, P, v, T\}$ to partial derivatives of energies

$$\text{a) } \begin{aligned} du &= Tds - Pdv \\ du &= (\partial u / \partial s)_v ds + (\partial u / \partial v)_s dv \end{aligned} \rightarrow \begin{aligned} T &= (\partial u / \partial s)_v \\ P &= -(\partial u / \partial v)_s \end{aligned}$$

$$\text{b) } \begin{aligned} dh &= Tds + vdP \\ dh &= (\partial h / \partial s)_P ds + (\partial h / \partial P)_s dP \end{aligned} \rightarrow \begin{aligned} T &= (\partial h / \partial s)_P \\ v &= (\partial h / \partial P)_s \end{aligned}$$

$$\text{c) } \begin{aligned} da &= -sdT - Pdv \\ da &= (\partial a / \partial T)_v dT + (\partial a / \partial v)_T dv \end{aligned} \rightarrow \begin{aligned} s &= -(\partial a / \partial T)_v \\ P &= -(\partial a / \partial v)_T \end{aligned}$$

$$\text{d) } \begin{aligned} dg &= -sdT + vdP \\ dg &= (\partial g / \partial T)_P dT + (\partial g / \partial P)_T dP \end{aligned} \rightarrow \begin{aligned} s &= -(\partial g / \partial T)_P \\ v &= (\partial g / \partial P)_T \end{aligned}$$

2. Maxwell Relations (relationship among partial derivatives based on $\{s, P, v, T\}$)

- After using the symmetry of second order partial derivatives

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

3. Cyclic Relationships among : $\{s, P, v\}$, $\{s, P, T\}$, $\{s, v, T\}$, $\{P, v, T\}$

$$\left(\frac{\partial s}{\partial P}\right)_v \left(\frac{\partial P}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_P = -1$$

$$\left(\frac{\partial s}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_s \left(\frac{\partial T}{\partial s}\right)_P = -1$$

$$\left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_s \left(\frac{\partial T}{\partial s}\right)_v = -1$$

$$\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v = -1$$

4. Auxiliary Relations to Available Data

$$c_P = \left(\frac{\partial h}{\partial T}\right)_P \quad \text{heat capacity at constant pressure}$$

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \quad \text{heat capacity at constant volume}$$

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P \quad \text{isobaric thermal expansion coefficient}$$

$$\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T \quad \text{isothermal compressibility}$$

a) For $(\partial s/\partial T)_v$: use chain rule with u

$$\rightarrow \left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial s}{\partial u}\right)_v \left(\frac{\partial u}{\partial T}\right)_v = \frac{1}{T} c_v$$

b) For $(\partial s/\partial T)_P$: use chain rule with h

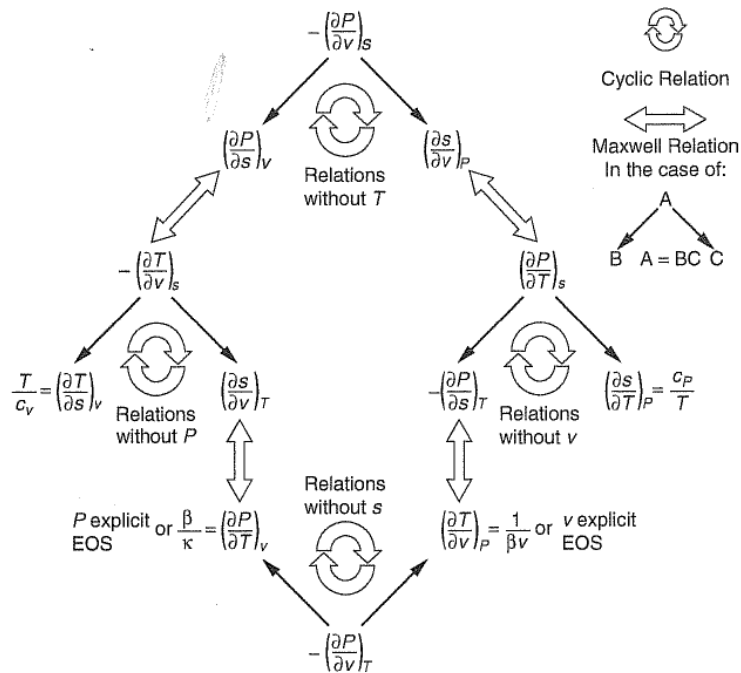
$$\rightarrow \left(\frac{\partial s}{\partial T}\right)_P = \left(\frac{\partial s}{\partial h}\right)_P \left(\frac{\partial h}{\partial T}\right)_P = \frac{1}{T} c_P$$

c) For $(\partial P/\partial T)_v$: use cyclic relations among P, v, T

$$\rightarrow \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial v}{\partial P}\right)_T = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_v = -\frac{\left(\frac{\partial v}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial P}\right)_T} = \frac{\beta}{\kappa}$$

5. Combining results on the partial derivatives among $\{s, P, v, T\}$



(Figure taken from M. Koretsky, Engineering and Chemical Thermodynamics, 2nd Ed, J.Wiley, 2013)

6. Fundamental Properties and Derived Properties Using Equations of State and other Measured Quantities:

- Properties: $\{s, u, h, a, g\}$
- EOS, e.g. Van der Waals, Peng-Robinson, Virial Equation, etc.
- Available measured quantities: c_p, c_v, β and κ

a) Entropy

i) $s = s(T, v)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv = \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$\Delta s = \int_{T_1}^{T_2} \frac{c_v}{T} dT + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T}\right)_v dv$$

ii) $s = s(T, P)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$\Delta s = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T}\right)_P dP$$

b) Internal Energy

i) $u = u(T, v)$

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv = c_v dT + \left(\frac{T\partial s - P\partial v}{\partial v}\right)_T dv$$

$$= c_v dT + \left(T \left(\frac{\partial s}{\partial v}\right)_T - P\right) dv = c_v dT + \left(T \left(\frac{\partial P}{\partial T}\right)_v - P\right) dv$$

$$\Delta u = \int_{T_1}^{T_2} c_v dT + \int_{v_1}^{v_2} \left(T \left(\frac{\partial P}{\partial T}\right)_v - P\right) dv$$

ii) $u = u(T, P)$

$$du = \left(\frac{\partial u}{\partial T}\right)_P dT + \left(\frac{\partial u}{\partial P}\right)_T dP$$

$$= \left(\frac{T\partial s - P\partial v}{\partial T}\right)_P dT + \left(\frac{T\partial s - P\partial v}{\partial P}\right)_T dP$$

$$= \left(T \left(\frac{\partial s}{\partial T}\right)_P - P \left(\frac{\partial v}{\partial T}\right)_P\right) dT + \left(T \left(\frac{\partial s}{\partial P}\right)_T - P \left(\frac{\partial v}{\partial P}\right)_T\right) dP$$

$$= \left(c_p - P \left(\frac{\partial v}{\partial T}\right)_P\right) dT - \left(T \left(\frac{\partial v}{\partial T}\right)_P + P \left(\frac{\partial v}{\partial P}\right)_T\right) dP$$

$$\Delta u = \int_{T_1}^{T_2} \left(c_p - P \left(\frac{\partial v}{\partial T}\right)_P\right) dT - \int_{P_1}^{P_2} \left(T \left(\frac{\partial v}{\partial T}\right)_P + P \left(\frac{\partial v}{\partial P}\right)_T\right) dP$$

c) Enthalpy

i) $h = h(T, v)$

$$\begin{aligned}dh &= \left(\frac{\partial h}{\partial T}\right)_v dT + \left(\frac{\partial h}{\partial v}\right)_T dv \\&= \left(\frac{T\partial s + v\partial P}{\partial T}\right)_v dT + \left(\frac{T\partial s + v\partial P}{\partial v}\right)_T dv \\&= \left(T\left(\frac{\partial s}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial T}\right)_v\right) dT + \left(T\left(\frac{\partial s}{\partial v}\right)_T + v\left(\frac{\partial P}{\partial v}\right)_T\right) dv \\&= \left(c_v + v\left(\frac{\partial P}{\partial T}\right)_v\right) dT + \left(T\left(\frac{\partial P}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial v}\right)_T\right) dv \\ \Delta h &= \int_{T_1}^{T_2} \left(c_v + v\left(\frac{\partial P}{\partial T}\right)_v\right) dT + \int_{v_1}^{v_2} \left(T\left(\frac{\partial P}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial v}\right)_T\right) dv\end{aligned}$$

ii) $h = h(T, P)$

$$\begin{aligned}dh &= \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP = c_P dT + \left(\frac{T\partial s + v\partial P}{\partial P}\right)_T dP \\&= c_P dT + \left(T\left(\frac{\partial s}{\partial P}\right)_T + v\right) dP = c_P dT + \left(-T\left(\frac{\partial v}{\partial T}\right)_P + v\right) dP \\ \Delta h &= \int_{T_1}^{T_2} c_P dT + \int_{P_1}^{P_2} \left(-T\left(\frac{\partial v}{\partial T}\right)_P + v\right) dP\end{aligned}$$