The Thermodynamic Web

Chapter-5

Types of Thermodynamic Properties

- Measured Properties
  - ✓ *P, v, T, Composition*
- Fundamental Properties
  - ✓ *u, s which are the basis for the 1st and 2nd laws of thermodynamics*
- Derived Thermodynamic Properties
  - ✓ *A combination of the above two types of properties,*
    - ➢ *H=u+Pv*
    - ➢ *a=u-Ts (Helmholz energy)*
    - ➢ *g=h-Ts (Gibbs energy)*

Thermodynamic Property Relationships

- Objective: To develop mathematical expressions through which we can relate the properties of a system to one another and to forms in which data are reported.
- State Postulate:

Knowing two independent intensive properties (*x*,*y*) constrains the state of a system of constant composition. Then, change in any intensive property such as *z* is:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \quad u=u(T,v)$$

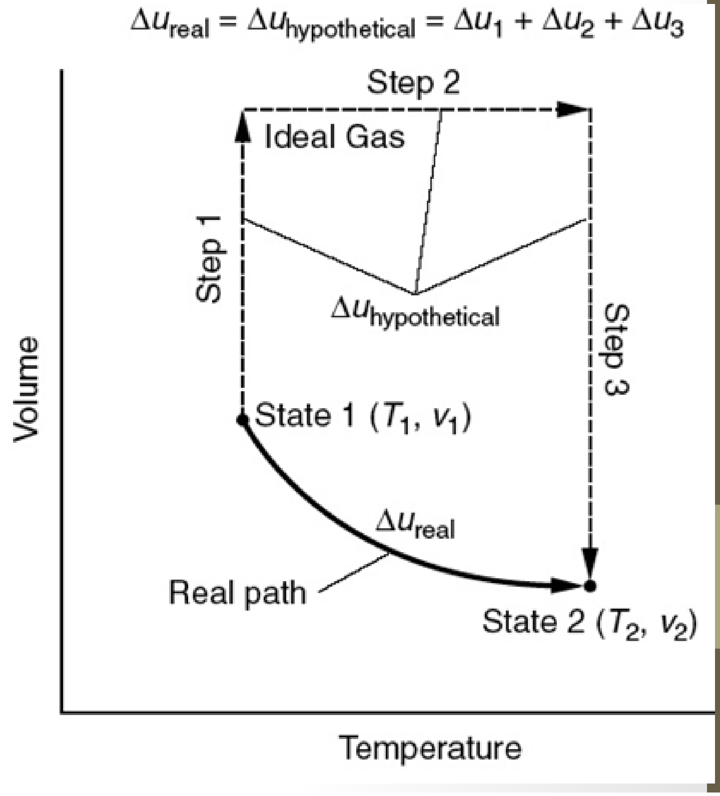
change in the dependent variable ***z*** with respect to the independent variable ***x*** over a path where independent ***y*** is constant

Thermodynamic Property Relationships

Question: Why should we derive the following equation? useful?

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

- We want to calculate Δu for a nonideal gas.
  - u is a state function, path-independent.
  - We can choose hypothetical paths.
  - We only have C_p, C_v data for ideal gases.



Fundamental Property Relations

- Fundamental Property Relations:

$$du = \delta q_{\text{rev}} + \boxed{\delta w_{\text{rev}}} = \underbrace{T\,ds \boxed{- P\,dv}}$$

$$dh = du + d(Pv) = T\,ds + v\,dP$$

$$da = du - d(Ts) = -s\,dT - P\,dv$$

$$dg = dh - d(Ts) = -s\,dT + v\,dP$$

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv \longrightarrow \left(\frac{\partial u}{\partial s}\right)_v = T \text{ and } \left(\frac{\partial u}{\partial v}\right)_s = -P$$

Maxwell Relations

The second derivative of the fundamental property relationships are referred to as the Maxwell Relationships.

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

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

Measured Properties

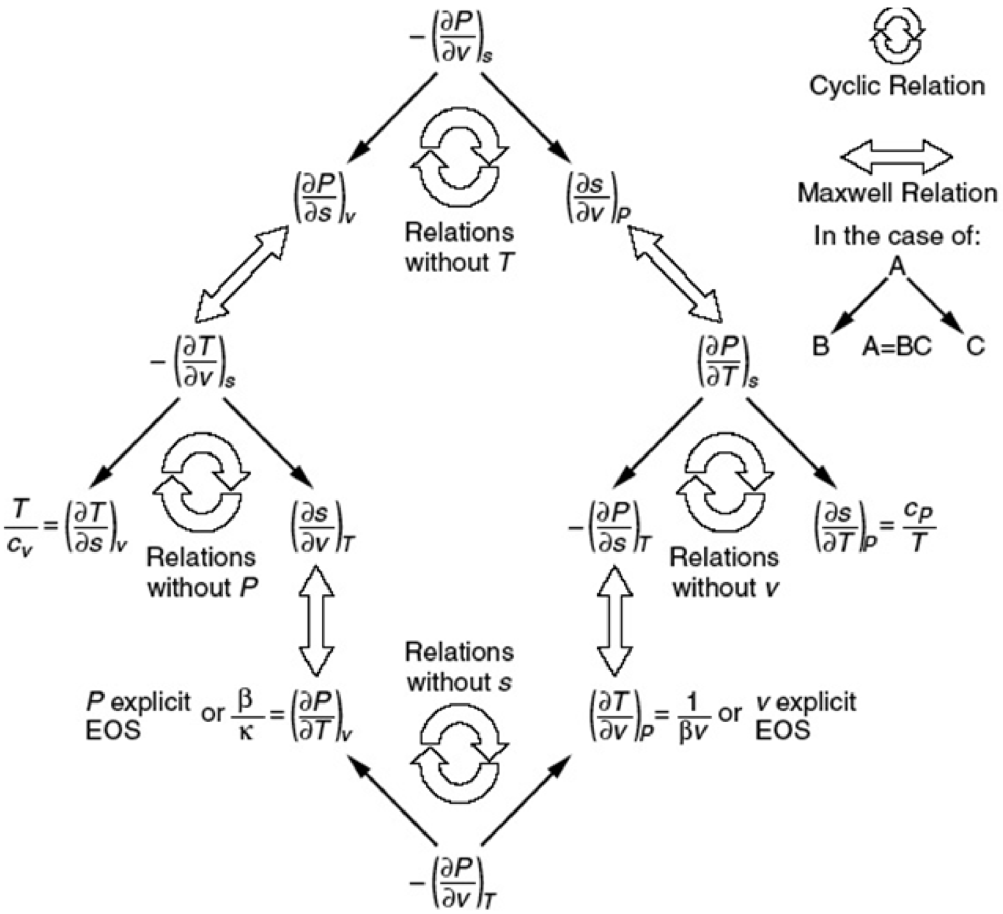
Thermodynamic Web

Problem solving in thermodynamics ⟶ Hypothetical Paths ⟶ to find the change in a property between two states ⟶ Partial derivative of a property with respect to another.

Objective: Use thermodynamic web to translate partial derivatives as C_v, C_p, β, and κ.

$$\begin{tikzcd}
-\left(\frac{\partial P}{\partial V}\right)_s = \left(\frac{\partial P}{\partial S}\right)_V \arrow[d] & \times\left(\frac{\partial S}{\partial V}\right)_P \arrow[d] \\
-\left(\frac{\partial T}{\partial V}\right)_s \arrow[d] & \left(\frac{\partial P}{\partial T}\right)_s \arrow[d] \\
\frac{T}{C_v}\times\left(\frac{\partial S}{\partial V}\right)_T \arrow[d] & -\left(\frac{\partial P}{\partial S}\right)_T \times \frac{C_p}{T} \arrow[d] \\
\frac{\beta}{k} & \frac{1}{\beta v}
\end{tikzcd}$$

$$\underbrace{\frac{\beta}{k} \qquad \frac{1}{\beta v}}_{\boxed{-\left(\frac{C_P}{vkC_v}\right)}}$$



S in terms of measured properties, *v* and *T*:

- Mathematics:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

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

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

$$\left(\frac{\partial P}{\partial T}\right)_v dv$$

Maxwell Relation

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

u in terms of measured properties, *v* and *T*:

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

$$\left(\frac{\partial u}{\partial v}\right)_T = \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]$$

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

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

$$\boxed{du(T, v) = c_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv}$$

dh in terms of T and P

$$\mathrm{d}h = \left(\frac{\partial h}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial h}{\partial P}\right)_T \mathrm{d}P$$

and

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

Maxwell

$h=Tds+vdP$ →

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

→

$$\mathrm{d}h = c_P \mathrm{d}T + \left[-T\left(\frac{\partial v}{\partial T}\right)_P + v\right]\mathrm{d}P$$

Example 5.2

One mole of propane gas is to be expanded from 0.001 m³ to 0.040 m³ while in contact with a heating bath at 100°C. The expansion is not reversible. The heat extracted from the bath is 600 J. Using the van der Waals equation of state, determine the work for the expansion.

$$\Delta u = q + w$$

600 J

Thermo. Web

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

$$\Delta u = \int \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \longrightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$$

$$\boxed{\Delta u = \int \left[\frac{a}{v^2}\right] dv}$$

READ EXAMPLE 5.3

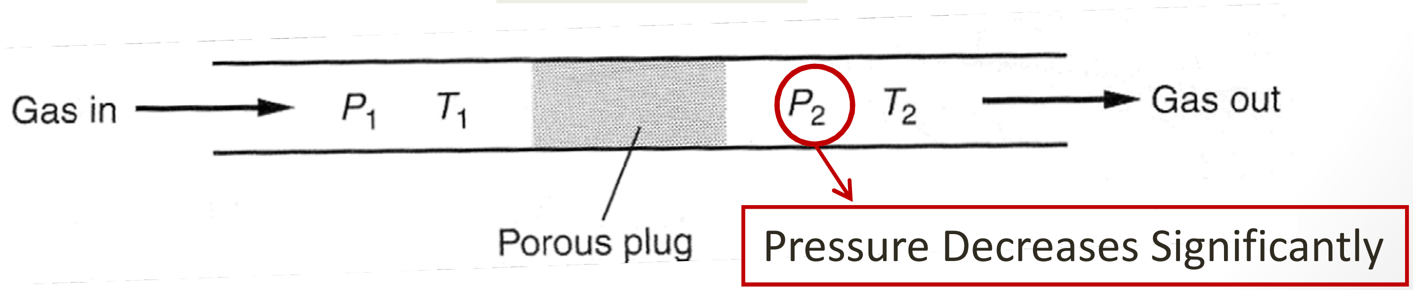
Joule-Thomson Expansion

- Unrestrained, free expansion of real gases.
- Analysis:
  - Gas spends little time in the plug, thus no heat transfer i.e. adiabatic.
  - Shaft work=*0*
- *First Law at steady state:*

$H_2 - h_1 = \Delta H = 0$ isenthalpic

We can determine the change in temperature as the pressure decreases in an isenthalpic process if we know the Joule-Thomson coefficient:

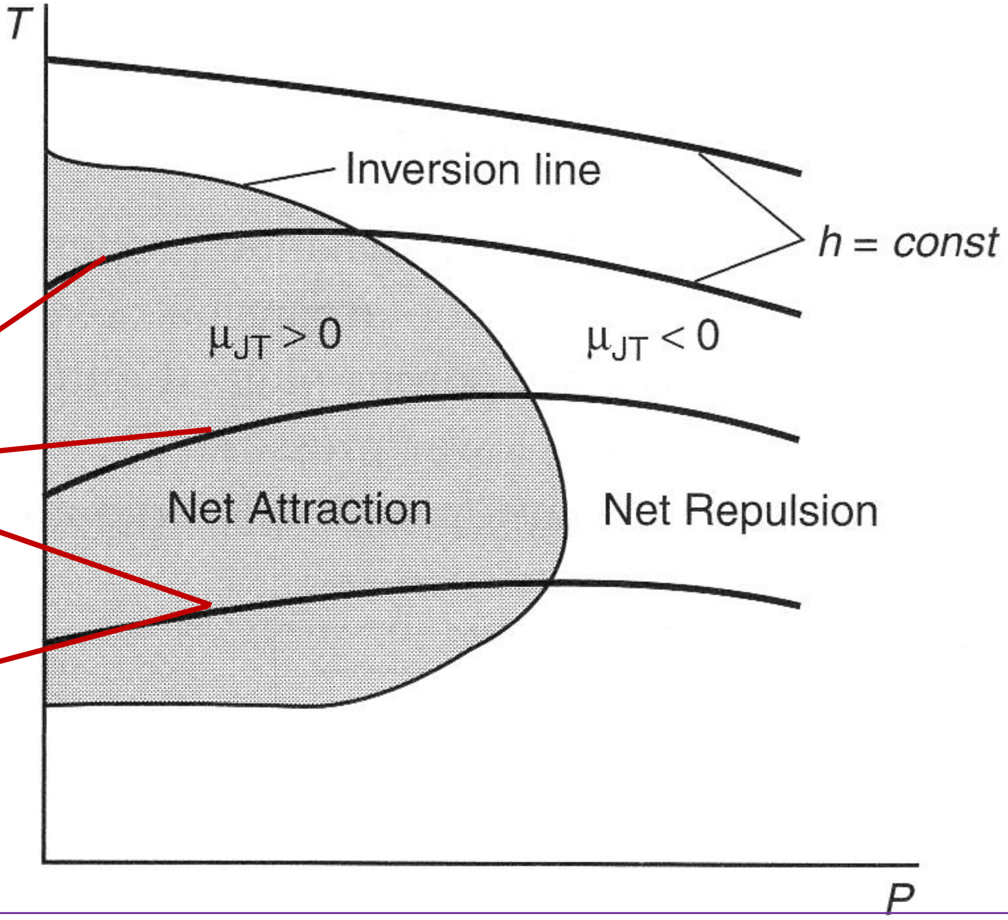
$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P} \right)_h$$



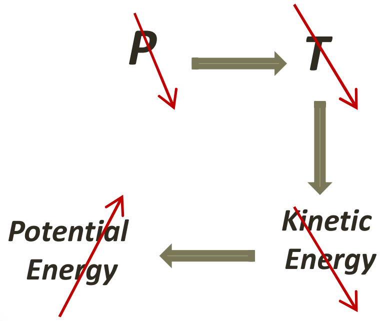
Pressure Decreases Significantly

Joule-Thomson Expansion

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_h$$



Local Slope >0


P → T

Kinetic Energy → Potential Energy

Boyle Temperature: **For a given pressure, the temperature at which attractive and repulsive interactions balance.**

Expression for μ_{JT}

$$\mathrm{d}h = c_P \mathrm{d}T + \left[-T \left(\frac{\partial v}{\partial T} \right)_P + v \right] \mathrm{d}P$$

$$c_P^{\text{real}} = c_P(T\;\,P) = c_P^{\text{ideal gas}} - \int_{P_{\text{ideal gas}}}^{P_{\text{real}}} \left[T \left(\frac{\partial^2 v}{\partial T^2} \right)_P \right] \mathrm{d}P$$

since interactions are important

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial P} \right)_h = \frac{\left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right]}{c_P} = \frac{\left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right]}{c_P^{\text{ideal gas}} - \displaystyle\int_{P_{\text{ideal gas}}}^{P_{\text{real}}} \left[T \left(\frac{\partial^2 v}{\partial T^2} \right)_P \right] \mathrm{d}P}$$

If we have an equation of state and the heat capacity of a fluid, we can evaluate μ_{JT}.

Example 5.7

Develop an expression for the Joule–Thomson coefficient using the pressure-based expansion of the virial equation truncated at the second virial coefficient. Use the corresponding state relationships presented in Chapter 4 for the temperature dependence of B to develop a generalized correlation for μ_{JT}.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = \frac{\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]}{c_P} = \frac{\left[T\overset{?}{\left(\frac{\partial v}{\partial T}\right)_P} - v\right]}{c_P^{\text{ideal gas}} - \int_{P_{\text{ideal gas}}}^{P_{\text{real}}} \left[T\overset{?}{\left(\frac{\partial^2 v}{\partial T^2}\right)_P}\right] \mathrm{d}P}$$

Virial Eq.:

$$v = \frac{RT}{P}(1 + B'P) = \frac{RT}{P} + B'RT \Rightarrow \left[\begin{aligned} \left(\frac{\partial v}{\partial T}\right)_P &= \frac{R}{P} + RB' + RT\left(\frac{\mathrm{d}B'}{\mathrm{d}T}\right) \\ \left(\frac{\partial^2 v}{\partial T^2}\right)_P &= R\left(\frac{\mathrm{d}B'}{\mathrm{d}T}\right) + RT\left(\frac{\mathrm{d}^2B'}{\mathrm{d}T^2}\right) \end{aligned}\right.$$

$$\boxed{\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = \frac{RT^2\overset{?}{\left(\frac{\mathrm{d}B'}{\mathrm{d}T}\right)}}{c_P^{\text{ideal gas}} - \int_{P_{\text{ideal gas}}}^{P_{\text{real}}} \left\{T\left[R\left(\frac{\mathrm{d}B'}{\mathrm{d}T}\right) + RT\overset{?}{\left(\frac{\mathrm{d}^2B'}{\mathrm{d}T^2}\right)}\right]\right\} \mathrm{d}P}}$$

Corresponding State Relationship:

$$B_r = \frac{BP_c}{RT_c} = B^{(0)} + \omega B^{(1)} \qquad \begin{cases} B^{(0)} = 0.083 - \dfrac{0.422}{T_r^{\,1.6}} \\ B^{(1)} = 0.139 - \dfrac{0.172}{T_r^{\,4.2}} \end{cases}$$

$$B' = \frac{B}{RT} = \frac{B_r T_c}{P_c T} = \frac{B_r}{P_c T_r} = \frac{B^{(0)} + \omega B^{(1)}}{P_c T_r} \Rightarrow B' = \frac{1}{P_c}\left[\left(\frac{0.083}{T_r} - \frac{0.422}{T_r^{2.6}}\right) + \omega\left(\frac{0.139}{T_r} - \frac{0.172}{T_r^{5.2}}\right)\right]$$

$$\begin{cases} \left(\dfrac{\mathrm{d}B'}{\mathrm{d}T}\right) = \dfrac{1}{P_c}\left[\left(-\dfrac{0.083}{TT_r} + \dfrac{1.097}{TT_r^{2.6}}\right) + \omega\left(-\dfrac{0.139}{TT_r} + \dfrac{0.894}{TT_r^{5.2}}\right)\right] \\ \\ \left(\dfrac{\mathrm{d}^2B'}{\mathrm{d}T^2}\right) = \dfrac{1}{P_c}\left[\left(\dfrac{0.166}{T^2T_r} - \dfrac{3.950}{T^2T_r^{2.6}}\right) + \omega\left(\dfrac{0.278}{T^2T_r} - \dfrac{5.545}{T^2T_r^{5.2}}\right)\right] \end{cases}$$

$$\boxed{\mu_{\mathrm{JT}} = \frac{-\dfrac{T_c}{P_c}\left[\left(-0.083 + \dfrac{1.097}{T_r^{1.6}}\right) + \omega\left(-0.139 + \dfrac{0.994}{T_r^{4.2}}\right)\right]}{\dfrac{c_P^{\text{ideal gas}}}{R} - P_r\left[\left(\dfrac{0.083}{T_r} - \dfrac{2.853}{T_r^{2.6}}\right) + \omega\left(\dfrac{0.139}{T_r} - \dfrac{4.651}{T_r^{5.2}}\right)\right]}}$$

If the critical properties and acentric factor are known, the JT coefficient can be calculated at *T* and *P*.