Thermodynamic Property Relations
General Relations, Part 2
Objectives

• Understand how thermodynamicists find properties that can’t be directly measured
  – What can be measured?
    • Temperature, pressure, volume, mass
  – Other properties?
    • Entropy, Joule Thompson coefficient, . . .

• General relations for property changes

• Ideal Gases
Entropy Change via $h$

- Find Entropy change in terms of things we can measure
- We’ll start with $h$ and get to $s$. From Calculus

\[ h = h(T, P) \rightarrow dh = \left( \frac{\partial h}{\partial T} \right)_P dT + \left( \frac{\partial h}{\partial P} \right)_T dP \]

- Using the definition of $C_p$

\[ dh = C_p dT + \left( \frac{\partial h}{\partial P} \right)_T dP \]
Entropy Change

• Hold that thought, we’ll be back

• From Calculus

\[ s = s(T, P) \rightarrow ds = \left( \frac{\partial s}{\partial T} \right)_P dT + \left( \frac{\partial s}{\partial P} \right)_T dP \]

• Put the above in 1st Law: \( dh = Tds + vdP \)

\[ dh = T \left( \left( \frac{\partial s}{\partial T} \right)_P dT + \left( \frac{\partial s}{\partial P} \right)_T dP \right) + vdP \]
Entropy Change

- Group like terms

\[ dh = T \left( \left( \frac{\partial s}{\partial T} \right)_p \right) dT + \left( T \left( \frac{\partial s}{\partial P} \right)_T \right) + v\right) dP \]

- Recall: \( dh = C_p dT + \left( \frac{\partial h}{\partial P} \right)_T dP \)

\[ C_p = T \left( \frac{\partial s}{\partial T} \right)_p \rightarrow \left( \frac{\partial s}{\partial T} \right)_p = \frac{C_p}{T} \]
Entropy Change

• Focusing on the change in $s$ with respect to $P$, from one of the Maxwell equations (12)

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

• So the total derivative is

$$ds = \frac{C_p}{T} dT - \left( \frac{\partial v}{\partial T} \right)_P dP \quad \text{Eq. 1}$$
Entropy Change

\[ ds = \frac{C_p}{T} \ dT - \left( \frac{\partial V}{\partial T} \right)_p \ dP \]

- This can be integrated to find an entropy change

\[ \int_{s_1}^{s_2} ds = \int_{T_1}^{T_2} \frac{C_p}{T} \ dT - \int_{T_1}^{T_2} \left( \frac{\partial V}{\partial T} \right)_p \ dP \]

\[ s_2 - s_1 = \int_{T_1}^{T_2} \frac{C_p}{T} \ dT - \int_{T_1}^{T_2} \left( \frac{\partial V}{\partial T} \right)_p \ dP \]
Entropy Change — Ideal Gas

\[ S_2 - S_1 = \int_1^2 \frac{C_p}{T} \, dT - \int_1^2 \left( \frac{\partial V}{\partial T} \right)_P \, dP \]

- What if \( P v = RT \)?

\[ \left( \frac{\partial V}{\partial T} \right)_P = \frac{R}{P} \]

\[ \int_1^2 \left( \frac{\partial V}{\partial T} \right)_P \, dP = \int_1^2 \frac{R}{P} \, dP = R \ln \left( \frac{P_2}{P_1} \right) \]

\[ S_2 - S_1 = \int_1^2 \frac{C_p}{T} \, dT - R \ln \left( \frac{P_2}{P_1} \right) \]
Entropy Change – Ideal Gas

\[ s_2 - s_1 = \int_1^2 \frac{C_p}{T} \, dT - R \ln \left( \frac{P_2}{P_1} \right) \]

- If \( C_p \) is a (strong) function of Temperature, we can’t pull it out of the integrand

\[ \int_1^2 \frac{C_p}{T} \, dT \equiv s_2^0 - s_1^0 \]

\[ s_2 - s_1 = s_2^0 - s_1^0 - R \ln \left( \frac{P_2}{P_1} \right) \]
Entropy Change – Ideal Gas

\[ s_2 - s_1 = \int_1^2 \frac{C_p}{T} \, dT - R \ln \left( \frac{P_2}{P_1} \right) \]

- If \( C_p \) isn’t a strong function of Temperature, or \( \Delta T \) is small, we can pull it out of the integrand

\[ \int_1^2 \frac{C_p}{T} \, dT = C_{p,\text{avg}} \int_1^2 \frac{dT}{T} = C_{p,\text{avg}} \ln \left( \frac{T_2}{T_1} \right) \]

\[ s_2 - s_1 = C_{p,\text{avg}} \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{P_2}{P_1} \right) \]
Entropy Change via $u$

- Find Entropy change in terms of things we can measure
- We’ll start with $u$ and get to $s$. From Calculus

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

- Using the definition of $C_v$

$$du = C_v \, dT + \left( \frac{\partial u}{\partial v} \right)_T \, dv$$
Entropy Change

• Hold that thought, we’ll be back

• From Calculus

\[ s = s(T, v) \rightarrow ds = \left( \frac{\partial s}{\partial T} \right)_v dT + \left( \frac{\partial s}{\partial v} \right)_T dv \]

• Put the above in 1\textsuperscript{st} Law: \( du = T ds - P dv \)

\[ du = T \left( \left( \frac{\partial s}{\partial T} \right)_v dT + \left( \frac{\partial s}{\partial v} \right)_T dv \right) - P dv \]
Entropy Change

• Group like terms

\[ du = T \left( \frac{\partial s}{\partial T} \right)_P \ dT + \left( T \left( \frac{\partial s}{\partial v} \right)_T - P \right) dv \]

• Recall:

\[ du = C_v \ dT + \left( \frac{\partial u}{\partial v} \right)_T \ dv \]

\[ C_v = T \left( \frac{\partial s}{\partial T} \right)_P \rightarrow \left( \frac{\partial s}{\partial T} \right)_P = \frac{C_v}{T} \]
Entropy Change

• Focusing on the change in $s$ with respect to $P$, from one of the Maxwell equations (11)

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

• So the total derivative is

$$ds = \frac{C_v}{T} dT + \left( \frac{\partial P}{\partial T} \right)_v dv$$
Entropy Change

\[ ds = \frac{C_v}{T} \, dT + \left( \frac{\partial P}{\partial T} \right)_v \, dP \]

- This can be integrated to find an entropy change

\[ \int_1^2 ds = \int_1^2 \frac{C_v}{T} \, dT + \int_1^2 \left( \frac{\partial P}{\partial T} \right)_v \, dv \]

\[ s_2 - s_1 = \int_1^2 \frac{C_v}{T} \, dT + \int_1^2 \left( \frac{\partial P}{\partial T} \right)_v \, dv \]
Entropy Change – Ideal Gas

\[ s_2 - s_1 = \int_1^2 \frac{C_v}{T} \, dT + \int_1^2 \left( \frac{\partial P}{\partial T} \right)_v \, dv \]

• What if \( P v = RT \)?

\[ \left( \frac{\partial P}{\partial T} \right)_v = \frac{R}{v} \]

\[ \int_1^2 \left( \frac{\partial P}{\partial T} \right)_v \, dv = \int_1^2 \frac{R}{v} \, dv = R \ln \left( \frac{v_2}{v_1} \right) \]

\[ s_2 - s_1 = \int_1^2 \frac{C_v}{T} \, dT + R \ln \left( \frac{v_2}{v_1} \right) \]
Entropy Change – Ideal Gas

\[ s_2 - s_1 = \int_1^2 \frac{C_v}{T} \,dT + R \ln \left( \frac{V_2}{V_1} \right) \]

- If \( C_v \) isn’t a strong function of Temperature, or \( \Delta T \) is small, we can pull it out of the integrand

\[ \int_1^2 \frac{C_v}{T} \,dT = C_{v, \text{avg}} \int_1^2 \frac{dT}{T} = C_{v, \text{avg}} \ln \left( \frac{T_2}{T_1} \right) \]

\[ s_2 - s_1 = C_{v, \text{avg}} \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2}{V_1} \right) \]
Enthalpy Change – Ideal Gas

• We proved a while ago that for an Ideal gas, the enthalpy change is

\[ h_2 - h_1 = \int_1^2 C_p \, dT \]

\[ h_2 - h_1 = C_{p, \text{avg}} \left( T_2 - T_1 \right) \]

• We’d really like to be able to conclude that enthalpy is not a function of pressure for an Ideal Gas, but what if \( C_p \) depends on pressure?
Specific Heat

• Earlier (Eq. 1) we found that

\[ ds = \frac{C_p}{T} \, dT - \left( \frac{\partial v}{\partial T} \right)_p \, dP \]

\[ \left( \frac{\partial s}{\partial T} \right)_p = \frac{C_p}{T} \]

\[ \left( \frac{\partial s}{\partial P} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_p \]
Specific Heat

• Cross differentiating the partial derivatives

\[
\frac{\partial}{\partial P} \left[ \left( \frac{\partial s}{\partial T} \right)_P \right]_T = \frac{\partial}{\partial T} \left[ \left( \frac{\partial s}{\partial P} \right)_T \right]_P
\]

\[
\frac{\partial}{\partial P} \left[ \frac{C_P}{T} \right]_T = -\frac{\partial}{\partial T} \left[ \left( \frac{\partial v}{\partial T} \right)_P \right]_P
\]

\[
\frac{\partial C_P}{\partial P} = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P
\]
Specific Heat – Ideal Gas

• If $Pv = RT$

\[
\left( \frac{\partial v}{\partial T} \right)_P = \frac{R}{P} ; \quad \left( \frac{\partial^2 v}{\partial T^2} \right)_P = 0
\]

\[
\frac{\partial C_P}{\partial P} = -T \left( \frac{\partial^2 v}{\partial T^2} \right)_P = 0
\]

• So $C_P$ is NOT a function of pressure for an Ideal Gas

• So $h$ is not a function of pressure for an Ideal Gas
Joule-Thomson Coefficient

- When we were dealing with refrigeration cycles, we considered throttling valves or capillary tubes to have refrigerants undergo isenthalpic pressure drops.
- The temperature of some fluids drop when they undergo an isenthalpic pressure drop.
- What we’re concerned with is

$$
\left( \frac{\partial T}{\partial P} \right)_h \equiv \mu_{JT} = \text{Joule-Thomson coefficient}
$$
Joule-Thomson Coefficient

• If the temperature goes down ($\Delta T$ is negative) when the pressure decreases ($\Delta P$ is negative)

$$\left( \frac{\partial T}{\partial P} \right)_{h} \equiv \mu_{JT} = \text{Joule-Thomson coefficient}$$

• the Joule-Thomson coefficient is positive and the fluid can be used as a refrigerant.
Joule-Thomson Coefficient

• We found a general expression for enthalpy change

$$\text{dh} = C_p \text{dT} + \left( v - T \left( \frac{\partial v}{\partial T} \right)_P \right) \text{dP}$$

• We’re interested in throttling processes, when the enthalpy change is zero.

$$0 = C_p \text{dT} + \left( v - T \left( \frac{\partial v}{\partial T} \right)_P \right) \text{dP}$$
Joule-Thomson Coefficient

\[ 0 = C_p \, dT + \left( v - T \left( \frac{\partial v}{\partial T} \right)_p \right) \, dP \]

\[ \left[ C_p \, dT = \left( T \left( \frac{\partial v}{\partial T} \right)_p - v \right) \, dP \right]_h \]

\[ \mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_h = \frac{1}{C_p} \left( T \left( \frac{\partial v}{\partial T} \right)_p - v \right) \]
Can we use an ideal gas, like air, $Pv = RT$, as a refrigerant? Can we throttle air and make its temperature drop?

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_h = \frac{1}{C_p} \left( T \left( \frac{\partial v}{\partial T} \right)_p - v \right)$$

$$v = \frac{RT}{P} \rightarrow \left( \frac{\partial v}{\partial T} \right)_p = \frac{R}{P} \rightarrow T \left( \frac{\partial v}{\partial T} \right)_p = \frac{RT}{P} = v$$

$$\mu_{JT, Ideal\ Gas} = \frac{1}{C_p} \left( T \left( \frac{\partial v}{\partial T} \right)_p - v \right) = 0$$
Collecting Results

• Entropy Change:

\[ s_2 - s_1 = \int_1^2 \frac{C_p}{T} \, dT - \int_1^2 \left( \frac{\partial v}{\partial T} \right)_p \, dP \]

\[ s_2 - s_1 = \int_1^2 \frac{C_v}{T} \, dT + \int_1^2 \left( \frac{\partial P}{\partial T} \right)_v \, dv \]

• Entropy Change, Ideal Gas, large \( \Delta T \):

\[ s_2 - s_1 = s_2^0 - s_1^0 - R \ln \left( \frac{P_2}{P_1} \right) \]
Collecting Results

• Entropy Change, Ideal Gas, small $\Delta T$:

$s_2 - s_1 = C_{p,\text{avg}} \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{P_2}{P_1} \right)$

$s_2 - s_1 = C_{v,\text{avg}} \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2}{V_1} \right)$

• Specific Heat, $C_p$:

$$\frac{\partial C_P}{\partial P} = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P$$
Collecting Results

• Joule-Thomson Coefficient

\[
\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_{h} = \frac{1}{C_p} \left( T \left( \frac{\partial v}{\partial T} \right)_p - v \right)
\]
Problems?

• To be solved in class!