Chapter 6 - Entropy

Lecture 20

Sections 6.5-6.7

MEMS 0051 Introduction to Thermodynamics

Mechanical Engineering and Materials Science Department
University of Pittsburgh

Student Learning Objectives

At the end of the lecture, students should be able to:

- Derive the Thermodynamic Property Relations (Gibbs equations)
- Apply Gibbs equations to incompressible substances (solids and liquids)
- Apply Gibbs equations to Ideal Gases
- Define standard entropy for Ideal Gases

Thermodynamic Property Relation

- It is our goal to relate entropy to other state properties (U, P, H, etc.)
- To do such, recall the 1st Law formulation

$$\delta Q = dU + \delta W$$

- Considering a compressible substance undergoing a *reversible* process, the heat added is

$$\delta Q = T\,dS$$

- The work done during this process is

$$\delta W = P\,d\forall$$

Thermodynamic Property Relation

- Substituting these expressions back into the 1st Law

$$\delta Q = dU + \delta W \implies \boxed{T\,dS = dU + P\,d\forall}$$

- This formulation is valid for both a reversible and irreversible process, since the formulation only depends on properties at states and not the paths between states

Thermodynamic Property Relation

- Re-examining the 1$^{\text{st}}$ Law formulation, but recalling the definition of enthalpy

$$H \equiv U + P\forall \implies dH = dU + P\,d\forall + \forall\,dP$$

- Substituting this back into the Conservation of Energy equation

$$\delta Q = dU + \delta W \implies \delta Q = dH - P\,d\forall - \forall\,dP + P\,d\forall$$

- Recalling the expression for heat addition, the Conservation of Energy becomes

$$\boxed{T\,dS = dH - \forall\,dP}$$

Gibbs equations

- These two equations are known as the **Thermodynamic Property Relation** or **Gibbs equations**

$$\boxed{T\,dS = dU + P\,d\forall}$$

$$\boxed{T\,dS = dH - \forall\,dP}$$

- These equations can be evaluated on a per mass basis

Example #1

- Determine the change of specific entropy of R-134a from saturated liquid to saturated vapor at a temperature of 0 °C

Entropy Change for Incompressible Substance

- Solids and liquids are assumed incompressible, that is, $C \approx C_\forall \approx C_P$
- Recall the change of internal energy for incompressible substances

$$du = C\, dT$$

- Recalling the first formulation of Gibbs equations

$$T\, dS = dU + P\, d\forall \implies ds \approx \frac{du}{T} \approx \frac{C\, dT}{T}$$

- Integrating

$$\boxed{ds = s_2 - s_1 \approx C \ln\left(\frac{T_2}{T_1}\right)}$$

Example #2

- Determine the change of specific entropy of copper heated from 20 to 100 °C

Entropy Change for Ideal Gases - $C_{\forall 0}$

- Recall for an Ideal Gas the change of internal energy is

$$du = C_{\forall 0}\, dT$$

- On a per mass basis, the pressure is expressed as

$$P = \frac{RT}{\nu}$$

- Substituting these expressions in the first formulation of Gibbs equations

$$T\, ds = du + P\, d\nu = C_{\forall 0}\, dT + \frac{RT}{\nu} d\nu$$

- Dividing by T

$$ds = C_{\forall 0} \frac{dT}{T} + R \frac{d\nu}{\nu}$$

Entropy Change for Ideal Gases - $C_{\forall 0}$

- Integrating, assuming $C_{\forall 0}$ is a function of T

$$ds = C_{\forall 0}\frac{dT}{T} + R\frac{d\nu}{\nu} \rightarrow \boxed{ds = \int_1^2 C_{\forall 0}\frac{dT}{T} + R\ln\left(\frac{\nu_2}{\nu_1}\right)}$$

- If $C_{\forall 0}$ is constant

$$\boxed{ds = C_{\forall 0}\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{\nu_2}{\nu_1}\right)}$$

- A similar expression can be formulated in terms of C_{P0}

Entropy Change for Ideal Gases - C_{P0}

- Recall for an Ideal Gas the change of enthalpy

$$dh = C_{P0}\,dT$$

- On a per mass basis, the specific volume of an Ideal Gas is

$$\nu = \frac{RT}{P}$$

- Substituting these expressions in the second formulation of Gibbs equations

$$T\,ds = dh - \nu\,dP = C_{P0}\,dT - \frac{RT}{P}\,dP$$

Entropy Change for Ideal Gases - C_{P0}

- Dividing by T

$$ds = C_{P0}\,\frac{dT}{T} - R\,\frac{dP}{P}$$

- Integrating, and assuming C_{P0} is a function of T

$$\boxed{ds = \int_1^2 C_{P0}\,\frac{dT}{T} - R\ln\left(\frac{P_2}{P_1}\right)}$$

- If C_{P0} is a constant

$$\boxed{ds = C_{P0}\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)}$$

Standard Entropy

- To avoid the integration of C_{P0}, we define **standard entropy**, which allows use to use tabulated values for entropy changes
- The value of standard s at 0 [K] is set to 0 [kJ/kg-K] at 1 [atm], and is defined as

$$s^o(T) = \int_0^T C_{P0} \ln\left(\frac{T_2}{T_1}\right)$$

- Thus, the change of entropy is expressed as

$$\boxed{ds = s_2 - s_1 = (s^o(T_2) - s^o(T_1)) - R\ln\left(\frac{P_2}{P_1}\right)}$$

- Table A.7.1 gives said values for air, A.8 for other gases

Example #3

- Determine the change of specific entropy of air going from T_1=300 [K] and P_1=1 [bar] to T_2=1,000 [K] and P_2=3 [bar] 1.) assuming constant $C_{\forall 0}$ or C_{P0} and 2.) using standard entropy

Example #3

Student Learning Objectives

At the end of the lecture, students should be able to:

- Derive the Thermodynamic Property Relations (Gibbs equations)
  - The Gibbs equations relate the change of entropy to that of internal energy, volume, enthalpy and pressure such that

$$T\,dS = dU + P\,d\forall; \quad T\,dS = dH - \forall\,dP$$

- Apply Gibbs equations to incompressible substances (solids and liquids)
  - The Gibb's equations for incompressible substances relate the change of entropy to that of the temperature between the final and initial state using specific heat such that

$$ds = C\ln\left(\frac{T_2}{T_1}\right)$$

Student Learning Objectives

At the end of the lecture, students should be able to:

- Apply Gibbs equations to Ideal Gases
  - Gibbs equations for Ideal Gases take various forms, depending upon how $C_{\forall 0}$ and C_{P0} are treated:

$$ds = \begin{cases} \int_1^2 C_{\forall 0} \dfrac{dT}{T} + R \ln\left(\dfrac{\nu_2}{\nu_1}\right), \; C_{\forall 0} = C_{\forall 0}(T) \\ C_{\forall 0} \ln\left(\dfrac{T_2}{T_1}\right) + R \ln\left(\dfrac{\nu_2}{\nu_1}\right), \; C_{\forall 0} = c \\ \int_1^2 C_{P0} \dfrac{dT}{T} - R \ln\left(\dfrac{P_2}{P_1}\right), \; C_{P0} = C_{P0}(T) \\ C_{P0} \ln\left(\dfrac{T_2}{T_1}\right) - R \ln\left(\dfrac{P_2}{P_1}\right), \; C_{P0} = c \end{cases}$$

Student Learning Objectives

At the end of the lecture, students should be able to:

- Define standard entropy for Ideal Gases
  - Standard entropy sets s equal to zero at 0 [K], allowing for the evaluation of the integral of the temperature dependent constant-pressure specific heat such that

$$s^o(T) = \int_0^T C_{P0} \ln\left(\frac{T_2}{T_1}\right)$$

The evaluation of the integral of specific heat is then

$$\int_1^2 C_{P0} \frac{dT}{T} = s^o(T_2) - s^o(T_1)$$

Suggested Problems

- 6.60, 6.61, 6.63, 6.77, 6.78, 6.85, 6.92, 6.93, 6.95, 6.97