## Week 12

## Lecture 1

- Final Exam will be open book. Discussed this with Prof. Wilson.
- Entropy and the Second Law of Thermodynamics (SLOT)
- Read Chapter 6: Sections 1 through 5.
- See ECE 309 Web site for notes on Entropy.
- S[J/K], extensive property
- $s = S/M [J/(kg \cdot K], \text{ intensive property}]$
- Perfect crystal (pure substance) at 0 K, molecules are motionless and perfectly arranged; entropy is zero, i.e., S = 0
- Discuss T s diagram
- For mixture:

$$s = (1-x)s_f + xs_g$$

• See example in text.

• Isolated system (system plus surroundings); (boundary closed to energy transfer in the form of heat and work):

$$(\Delta S)_{\text{isolated system}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}} \ge 0$$

- Reversible process  $\Delta S = 0$  and irreversible process  $\Delta S > 0$
- Production  $\mathcal{P}$

CE	$\mathcal{P}_M = M_2 - M_1 = 0$
FLOT	$\mathcal{P}_E = E_2 - E_1 = 0$
SLOT	$\mathcal{P}_S = S_2 - S_1 \ge 0$

- Chapter 7 Consequences of the Second Law
- S = S(U, V) and s = s(u, v)
- Thermodynamic Definition of Temperature

$$T = \frac{1}{\left(\frac{\partial S}{\partial U}\right)_V}$$

• Thermodynamic Definition of Pressure

$$P = \left(\frac{\partial S}{\partial V}\right)_U$$

• Definitions of T and P in terms of s = s(u, v)

$$\frac{1}{T} = \left(\frac{\partial s}{\partial u}\right)_v, \qquad \frac{P}{T} = \left(\frac{\partial s}{\partial v}\right)_u$$

## Lecture 2

• Gibbs equation for SCS based on s = s(u, v)

$$ds = \left(rac{\partial s}{\partial u}
ight)_v du + \left(rac{\partial s}{\partial v}
ight)_u dv$$

or

$$ds = \frac{du}{T} + \frac{P}{T}dv$$
 or  $Tds = du + Pdv$ 

• Macroscopic Evaluation of Entropy

$$s_2 - s_1 = \int_1^2 \frac{du}{T} + \int_1^2 \frac{P}{T} dv$$

- See example in Text for entropy change from saturated liquid to saturated vapor at constant pressure and temperature.
- Entropy change of solid or liquid. If SCS is incompressible, dv = 0, then

$$ds = \frac{du}{T}$$

If dv is small (liquid) or negligible (solid), then

$$ds \approx rac{du}{T} pprox c rac{dT}{T}$$

where c is the specific heat capacity. Assuming that c = constant:

$$s_2 - s_1 pprox c \ln rac{T_2}{T_1}$$

• Example: One kilogram of water is heated from  $T_1 = 20^{\circ}C + 273 = 293K$  to  $T_2 = 90^{\circ}C + 273 = 363K$ . Calculate the change in the entropy assuming constant specific heat capacity. Compare the result against the steam table value.

• Solution:

$$s_2 - s_1 \approx c \, \ln \frac{T_2}{T_1} \, \left[ \frac{kJ}{kg \cdot K} \right]$$

 $\operatorname{But}$ 

$$\int_{1}^{2} du = c_{v} \int_{1}^{2} dT \quad \text{and} \quad u_{2} - u_{1} = c_{v} (T_{2} - T_{1})$$

Therefore

$$c_v = \frac{u_2 - u_1}{T_2 - T_1}$$

¿From Table B.1a, page 622 we find

At 
$$T_1 = 293 K$$
,  $u_2 = 83.9 \left[\frac{kJ}{kg \cdot K}\right]$   
At  $T_2 = 363 K$ ,  $u_1 = 376.8 \left[\frac{kJ}{kg \cdot K}\right]$ 

This gives

$$c_v = \frac{376.8 - 83.9}{363 - 293} = 4.184 \left[\frac{kJ}{kg \cdot K}\right]$$

 $\quad \text{and} \quad$ 

$$s_2 - s_1 = 4.184 \ln\left(\frac{363}{293}\right) = 0.8964 \left[\frac{kJ}{kg \cdot K}\right]$$

and a better estimate is

$$s_2 - s_1 = 4.184 \ln\left(\frac{363.2}{293.2}\right) = 0.8958 \left[\frac{kJ}{kg \cdot K}\right]$$

¿From steam tables:

$$s_2 - s_1 = s_{90°C} - s_{20°C} = 1.1927 - 0.2965 = 0.8962 \left[\frac{kJ}{kg \cdot K}\right]$$

The agreement is good. Water (liquid) can be approximated as an incompressible substance.

• Chapter 8:

- 8.2 The Gibbs Equation
- 8.3 Equation of State for Perfect Gas
- 8.4 Other P v T Equations for Gases

- Entropy Change for Ideal Gas
- Gibbs Equation:

$$Tds = du + Pdv$$

For ideal gas

$$du = c_v dT$$
 and  $\frac{P}{T} = \frac{R}{v}$ 

 $\operatorname{Now}$ 

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

and the change in entropy is

$$s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} + R \ln \frac{v_2}{v_1}$$
 and  $c_v = c_v(T)$ 

Assuming that  $c_v = \text{constant}$ , gives

$$s_2 - s_1 \approx c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

Similarly

$$Tds = dh - vdP$$

For ideal gas

$$dh = c_p dT$$
 and  $\frac{v}{T} = \frac{R}{P}$ 

Now

$$ds = c_p \frac{dT}{T} - R \frac{dP}{P}$$

and the change in entropy is

$$s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$
 and  $c_p = c_p(T)$ 

Assuming that  $c_p = \text{constant}$ , gives

$$s_2 - s_1 \approx c_p \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

## Lecture 3

• 15 minutes at end of lecture to do Project 2 Part 2, and to hand in Part 1.

• Relationship between specific heat capacities

$$c_p - c_v = R$$

• Approximate Polynomial Fit to Experimental Data

$$c_p = a + b T + c T^2$$

where a, b, c are correlation coefficients fitted to data. Average deviation is  $\pm 1\%$  and maximum deviation is  $\pm 2\%$ . See Table B.16 for values for several gases.

• Definition

$$\phi(T) = \int_{T_0}^T \frac{c_p(T)}{T} dT, \quad T_0 = \text{some reference temperature}$$

Entropy can now be expressed as

$$s_2 - s_1 = \phi_2 - \phi_1 - R \ln \frac{P_2}{P_1}$$

See Table B.9 for properties of air. Note that  $T_0 = 0 R$ .

• Section 7.7 Two Idealized Systems

- Thermal Energy Reservoir (TER) is a reservoir for disorganized energy. It has a fixed volume dV = 0, and its temperature is  $T_{TER}$  for all time. The TER is a non-isolated system.

• Gibbs Equation for TER

$$T_{TER} dS = dU$$
 and  $PdV = 0$ 

• FLOT for TER

$$dU = dQ$$
 and  $dS = \frac{dQ}{T_{TER}}$ 

where Q enters the TER.