Lecture 25 – Calculating entropy changes

Purdue ME 200, Thermodynamics I

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Outline

Using the TdS equations

Example #1

Using the incompressible substance model

Example #2

Motivations

- we showed last lecture that for closed systems,

$$\Delta S = \int \frac{\delta Q}{T} + \sigma$$

- this formula can be hard to use if T is not constant
- today, we'll develop handier formulas

The 1st $T\mathrm{d}S$ equation

- 1st law for stationary closed systems:

$$\mathrm{d}U = \delta Q - \delta W \implies \delta Q = \mathrm{d}U + \delta W$$

- for a closed system in an internally reversible process ($\delta\sigma = 0$),

$$\mathrm{d}S = \frac{\delta Q}{T} \implies \delta Q = T\mathrm{d}S$$

- for simple compressible systems (boundary work only),

$$\delta W = p\mathrm{d}V$$

- combining all of the above gives

$$T\mathrm{d}S = \mathrm{d}U + p\mathrm{d}V$$

The 2nd $T\mathrm{d}S$ equation

- since $H = U + pV$,

$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV)$$

- recall that the differential of $z = f(x, y)$ is

$$\mathrm{d}z = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

- therefore, $\mathrm{d}(pV) = V\mathrm{d}p + p\mathrm{d}V$, and so

$$\mathrm{d}H = \underbrace{\mathrm{d}U + p\mathrm{d}V}_{T\mathrm{d}S} + V\mathrm{d}p$$

- rearranging gives the 2nd $T\mathrm{d}S$ equation,

$$T\mathrm{d}S = \mathrm{d}H - V\mathrm{d}p$$

Summary

$$T\mathrm{d}S = \mathrm{d}U + p\mathrm{d}V$$
$$T\mathrm{d}S = \mathrm{d}H - V\mathrm{d}p$$

- the $T\mathrm{d}S$ equations apply to systems that are
  - ◇ stationary (constant KE and PE)
  - ◇ simple (only one type of work interaction)
  - ◇ compressible (the work interaction is boundary work)
- they relate entropy to familiar properties: T, V, p, U, H
- in the derivation, "$\delta Q = T\mathrm{d}S$" assumed internal reversibility
- but the $T\mathrm{d}S$ equations also apply to irreversible processes
- the $T\mathrm{d}S$ equations can be written per unit mass:

$$T\mathrm{d}s = \mathrm{d}u + p\mathrm{d}v$$
$$T\mathrm{d}s = \mathrm{d}h - v\mathrm{d}p$$

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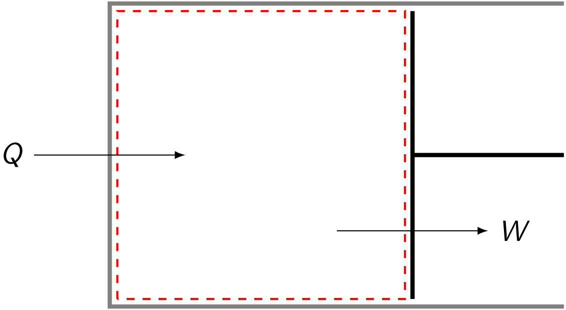
Problem statement

Find the change in specific entropy of 100 °C water that transitions from saturated liquid to saturated vapor. Use (a) a saturation table and (b) a $T\mathrm{d}S$ equation.

System diagram



Given and find

- **given:**
  - ◇ $T = 100\ ^\circ\mathrm{C}$
  - ◇ state 1 is saturated liquid
  - ◇ state 2 is saturated vapor
- **find:**
  - ◇ $\Delta s = s_2 - s_1$

Assumptions and basic equations

- **assume:**
    - ◇ closed system
    - ◇ stationary system ($\Delta \mathrm{KE} = \Delta \mathrm{PE} = 0$)
    - ◇ constant pressure and temperature during phase change
- **basic equations:**
    - ◇ $T \mathrm{d}s = \mathrm{d}h - v \mathrm{d}p$

Solution to part (a)

- saturation table: $s_1 = 1.3072$ kJ/K, $s_2 = 7.3541$ kJ/K, so

$$\begin{aligned}\Delta s &= (7.3541 - 1.3072)\text{kJ/kg/K} \\ &= 6.0469\text{kJ/kg/K}\end{aligned}$$

Solution to part (b)

- p is constant during phase changes, so $\mathrm{d}p = 0$
- the second $T\mathrm{d}S$ equation (per unit mass) simplifies to

$$T\mathrm{d}s = \mathrm{d}h - \cancelto{0}{V\mathrm{d}p} \implies \mathrm{d}s = \frac{\mathrm{d}h}{T}$$

- temperature is constant during phase changes, so

$$\Delta s = \frac{1}{T}\int_{h_1}^{h_2} \mathrm{d}h = \frac{h_2 - h_1}{T}$$

- saturation table: $h_1 = 419.17$ kJ/kg, $h_2 = 2675.6$ kJ/kg

$$\begin{aligned}\Delta s = \frac{h_2 - h_1}{T} &= \frac{(2675.6 - 419.17)\text{kJ/kg}}{373.15\text{K}} \\ &= 6.0470\text{kJ/kg/K}\end{aligned}$$

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Reminder: the incompressible substance model

- most liquids and solids are $\sim$incompressible:
  - $\diamond$ v is $\sim$constant
  - $\diamond$ u $\sim$depends on T only
- it follows that
  - $\diamond$ $\mathrm{d}v = 0$
  - $\diamond$ $\mathrm{d}u = c(T)\mathrm{d}T$

  (incompressible substances have only one specific heat, $c(T)$)

Entropy changes for incompressible substances

- for incompressible substances, 1st $T\mathrm{d}S$ equation simplifies to

$$T\mathrm{d}s = \underbrace{\mathrm{d}u}_{c(T)\mathrm{d}T} + \cancelto{0}{p\mathrm{d}v} = c(T)\mathrm{d}T$$

- to find Δs, integrate $\mathrm{d}s = (c(T)/T)\mathrm{d}T$:

$$\begin{aligned} s_2 - s_1 &= \int_{T_1}^{T_2} \frac{c(T)}{T}\mathrm{d}T \\ &\approx c_{\mathrm{av}} \int_{T_1}^{T_2} \frac{1}{T}\mathrm{d}T = c_{\mathrm{av}} \ln\left(\frac{T_2}{T_1}\right) \end{aligned}$$

- c_{av} is specific heat at average temperature, $c((T_1 + T_2)/2)$

Summary

- for incompressible substances,

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c(T)}{T} \mathrm{d}T$$

- if the temperature change $T_2 - T_1$ is not too large, then

$$s_2 - s_1 \approx c_{\mathrm{av}} \ln\left(\frac{T_2}{T_1}\right)$$

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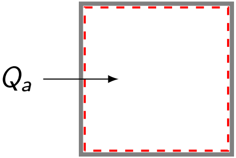
Problem statement

(a) Estimate the specific entropy change of water that transitions from compressed liquid at 0 °C to saturated liquid at 100 °C.

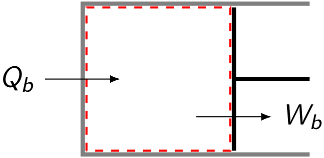
(b) If saturated water vapor at 100 °C is heated at constant pressure through the same specific entropy change as in part (a), what is its final temperature?

System diagrams

(a)



(b)



Given and find

- **given:**
  - ◇ for part (a),
    - ▶ state 1 is compressed liquid at $T_1 = 0$ °C
    - ▶ state 2 is saturated liquid at $T_2 = 100$ °C
  - ◇ for part (b),
    - ▶ state 1 is saturated vapor at $T_1 =$100 °C
    - ▶ state 2 is superheated vapor at unknown T_2
- **find:**
  - (a) Δs
  - (b) T_2

Assumptions and basic equations

- **assume:**
  - ◇ closed system
  - ◇ for part (a),
    - ▶ liquid water is ∼incompressible
    - ▶ and its specific heat is ∼constant over the process
- **basic equations:**
  - ◇ for incompressible substances,

$$\Delta s = \int_{T_1}^{T_2} \frac{c(T)}{T} \mathrm{d}T$$

Solution to part (a)

- liquid water is ∼incompressible, so

$$\Delta s = \int_{T_1}^{T_2} \frac{c(T)}{T} \mathrm{d}T$$

- specific heat table: $c_{\mathrm{av}} \approx 4.20$ kJ/kg/K between 0 and 100 °C
- specific heat is ∼constant, so entropy change is approximately

$$\begin{aligned}\Delta s &\approx c_{\mathrm{av}} \ln\left(\frac{T_2}{T_1}\right) \\ &= (4.20\mathrm{kJ/kg/K}) \ln\left(\frac{373.15\mathrm{K}}{273.15\mathrm{K}}\right) \\ &= 1.310\mathrm{kJ/kg/K}\end{aligned}$$

Solution to part (b)

- saturation table: at $T_{\mathrm{sat}} = 100\ ^\circ\mathrm{C}$, $p_{\mathrm{sat}} = 1$ bar and

$$s_1 = s_g = 7.3541 \mathrm{kJ/kg/K}$$

- final specific entropy is

$$s_2 = s_1 + \Delta s = (7.3541 + 1.310) \mathrm{kJ/kg/K} = 8.6641 \mathrm{kJ/kg/K}$$

- superheated vapor table at 1 bar: $s = 8.6653$ kJ/kg/K at

$$T_2 = 440\ ^\circ\mathrm{C}$$

Summary of examples (for water at 1 bar)

process	Δs (kJ/kg/K)
0 °C CL → 100 °C SL	1.31
100 °C SL → 100 °C SV	6.05
100 °C SV → 440 °C SHV	1.31