

Lecture 13

Topic 3

Second Law of Thermodynamics

Topics

- 3.4 Entropy changes for various processes

Reading:

Ch 6: 6.5 – 6.11 Borgnakke & Sonntag Ed. 8
Ch 7: 7-9 – 7-9 & 7-13 Cengel and Boles Ed. 7

3.4 Revisiting Second Law thus far



Lecture 12: Introduction to Entropy

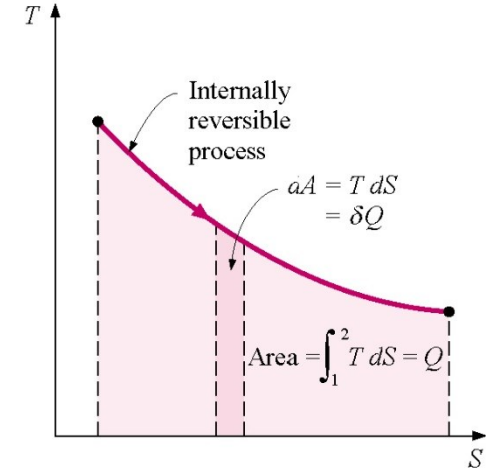
- $S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{reversible}}$
- Entropy is a thermodynamic property
- $q = \int T ds \rightarrow$ heat is area under T-s curve
 - Reversible processes only

TABLE B.1.1 (continued)
Saturated Water

Temp. (°C)	Press. (kPa)	Entropy, kJ/kg·K		
		Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g
0.01	0.6113	0	9.1562	9.1562
5	0.8721	0.0761	8.9496	9.0257
10	1.2276	0.1510	8.7498	8.9007
15	1.705	0.2245	8.5569	8.7813

Lecture 13

- Change of entropy (Δs) for various processes: $s_2 - s_1 \geq \int_1^2 \frac{\delta q}{T}$
 - Solid / Liquid
 - Ideal gas
 - Reversible polytropic
- $s_2 - s_1$
- Entropy balance equation: $s_2 - s_1 = \int_1^2 \frac{\delta q}{T} + S_{\text{gen}}$
 - Entropy generation



3.4.1 ΔS for Reversible Processes



• Pure substance

- $\Delta s = s_2 - s_1$
- Thermodynamic tables
- Reversible & adiabatic = Isentropic

$$\bullet \quad s_2 - s_1 = \int_1^2 \left(\frac{\delta q}{T} \right)_{\text{reversible}}$$

$$\bullet \quad s_1 = s_2 \quad q = 0$$

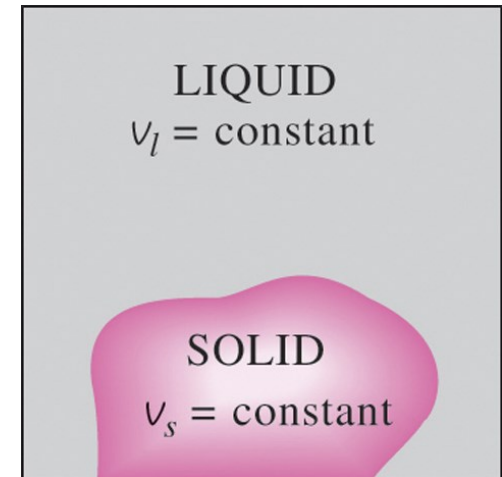
$$s_2 - s_1 \geq \int_1^2 \frac{\delta q}{T}$$

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• Solids and Liquids

- $ds = dq/T$
- First law analysis gives: $du = dq - \cancel{dw} \rightarrow du = dq$ $Pdv = 0$ (incompressible)
- Specific heat
 - $du = CdT$ (lecture 6)
- $ds \simeq du/T \simeq \frac{C}{T} dT$
- $s_2 - s_1 \simeq C \ln(T_2/T_1)$
- If isentropic ($s_2 - s_1 = 0$) $\rightarrow T_2 = T_1$



3.4.1 ΔS for Reversible Processes



- **Ideal Gas**

- Closed system

- $du = dq - dw$

- Where: $dq = Tds$ & $dw = Pdv$

- $dq = du + dw \rightarrow Tds = du + Pdv$

- Ideal gas with specific heats

- $du = C_v dT$ (see lecture 6)

- $Pv = RT$

- $Tds = C_v dT + (RT/v)dv$

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

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

- Recall: $dh = du + d(Pv)$

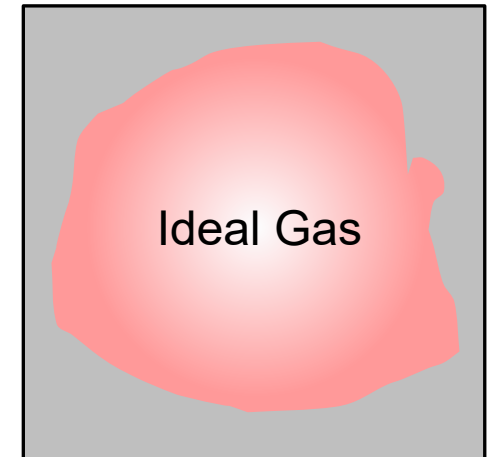
- $dq = du + dw \rightarrow dq = dh - vdP - Pdv + Pdv$

- $dh = C_p dT$

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

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

$$s_2 - s_1 \geq \int_1^2 \frac{\delta q}{T}$$



3.4.1 ΔS for Reversible Processes



Ideal Gas

- Evaluating specific heat (see lecture 6)

– Option 1: Constant Specific Heat

- C_p and C_v do not change
- $s_2 - s_1 = C_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right)$
- $s_2 - s_1 = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right)$

– Option 2: Variable specific heat

- Empirical formula (table A.6)
- $s_2 - s_1 = \int_1^2 C_{p\theta} \frac{dT}{T} - R \ln \left(\frac{P_2}{P_1} \right)$

– Option 3:

- 'Standard entropy' values: $s_T^0 = \int_{T_0}^T \frac{C_p}{T} dT$
- s_T^0 resulting from statistical thermodynamics
- s_T^0 values WRT temperature (Table A.7.1 (air) A.8 (gases))

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

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

TABLE A7.1

Ideal Gas Properties of Air, Standard Entropy s_T^0

T (K)	u (kJ/kg)	h (kJ/kg)	s_T^0 (kJ/kg-K)
280	200.02	280.39	6.79998
290	207.19	290.43	6.83521
298.15	213.04	298.62	6.86305
300	214.36	300.47	6.86926
320	228.73	320.58	6.93413

$$s_2 - s_1 = (s_{T2}^0 - s_{T1}^0) - R \ln \left(\frac{P_2}{P_1} \right)$$

3.4.1 ΔS for Reversible Processes



Example 3.4: Entropy change for Ideal Gas

Air is heated from 300K to 2000K. During this process, the pressure increases from 100 kPa to 800 kPa. Calculate the change in entropy per kg assuming:

- (a) Constant specific heats with $C_{p,\text{air}} = 1.004 \text{ kJ/kgK}$, $R_{\text{air}} = 0.287 \text{ kJ/kgK}$
- (b) Variable specific heats

Solution:

$$(a) \quad s_2 - s_1 = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right)$$

$$\circ \quad 1.004 \frac{\text{kJ}}{\text{kgK}} \ln \left(\frac{2000\text{K}}{300\text{K}} \right) - 0.287 \frac{\text{kJ}}{\text{kgK}} \ln \left(\frac{800\text{kPa}}{100\text{kPa}} \right) = 1.308 \frac{\text{kJ}}{\text{kgK}}$$

$$(b) \quad s_2 - s_1 = (s_{T2}^0 - s_{T1}^0) - R \ln \left(\frac{P_2}{P_1} \right)$$

$$\circ \quad (8.96611 - 6.86926) \frac{\text{kJ}}{\text{kgK}} - 0.287 \frac{\text{kJ}}{\text{kgK}} \ln \left(\frac{800\text{kPa}}{100\text{kPa}} \right) = 1.500 \frac{\text{kJ}}{\text{kgK}}$$

- Difference of 15%

TABLE A7.1

Ideal Gas Properties of Air, Standard Entropy s^0

T (K)	u (kJ/kg)	h (kJ/kg)	s_T^0 (kJ/kg-K)
298.15	213.04	298.62	6.86305
300	214.36	300.47	6.86926
320	228.73	320.58	6.93413
1900	1581.59	2126.95	8.90219
1950	1629.47	2189.19	8.93452
2000	1677.52	2251.58	8.96611

3.4.1 ΔS for Reversible Processes



Ideal Gas

- If process is adiabatic & reversible (isentropic)

- Option 1: Constant Specific Heat

- $s_2 - s_1 = 0 = C_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right) \quad \rightarrow \quad C_v \ln \left(\frac{T_2}{T_1} \right) = R \ln \left(\frac{v_1}{v_2} \right)$

- $s_2 - s_1 = 0 = C_P \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right) \quad \rightarrow \quad C_P \ln \left(\frac{T_2}{T_1} \right) = R \ln \left(\frac{P_2}{P_1} \right)$

- Expressions lead to isentropic ideal gas relations

- $\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{k-1} \quad \& \quad \frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(k-1)/k}$

isentropic ideal gas relations

- Where $k = \frac{C_P}{C_v}$ & $R = C_P - C_v$

- We can also rearrange: $\frac{P_2}{P_1} = \left(\frac{v_1}{v_2} \right)^k \rightarrow$ form of $Pv^k = \text{Const}$

- Polytropic with exponent k

3.4.1 ΔS for Reversible Processes



Ideal Gas

- If process is adiabatic & reversible (isentropic)
 - Option 3: Variable Specific Heats
 - $s_2 - s_1 = 0 = (s_{T2}^0 - s_{T1}^0) - R \ln \left(\frac{P_2}{P_1} \right)$
 - Expressions can be used to solve for s_{T2}^0 or s_{T1}^0
 - e.g. $s_{T2}^0 = s_{T1}^0 + R \ln \left(\frac{P_2}{P_1} \right)$
 - s_{T2}^0 or s_{T1}^0 can then be used to find u , h , T , etc.
 - Similar approach to solving problems with steam or refrigerant tables (i.e. pure substances)

TABLE A7.1

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3.4.1 ΔS for Reversible Processes



Ideal Gas – Reversible Polytropic Processes

- $PV^n = \text{Constant}$
- $P_1 V_1^n = P_2 V_2^n$ (see book or lecture 6 example)
- Polytropic relations

$$- \frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^n$$

$$- \frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(n-1)/n} = \left(\frac{V_1}{V_2} \right)^{n-1}$$

Process

Constant pressure

Constant volume

Isothermal & ideal gas

Adiabatic, reversible & ideal gas

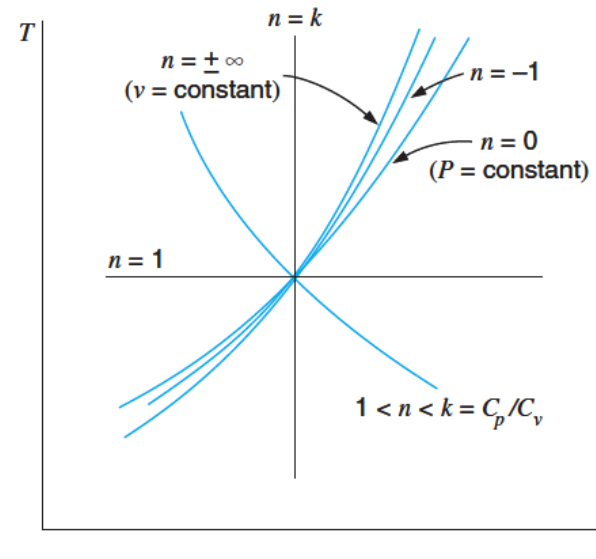
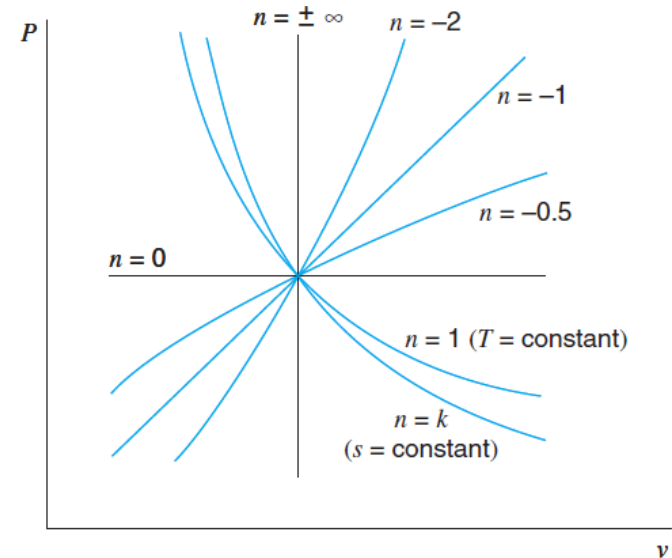
Exponent (n)

0

∞

1

$k = C_p/C_v$



3.4.1 ΔS for Reversible Processes



Ideal Gas – Reversible, Isothermal ($n = 1$)

- $PV^n = \text{Constant}; n = 1$
- $P_1V_1 = P_2V_2 = \text{Constant}$

- $s_2 - s_1 = \int_1^2 C_v \frac{dT}{T} + R \ln \left(\frac{v_2}{v_1} \right)$
- $s_2 - s_1 = \int_1^2 C_p \frac{dT}{T} - R \ln \left(\frac{P_2}{P_1} \right)$

– Option 1: Constant Specific Heat

- $s_2 - s_1 = C_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right) \rightarrow s_2 - s_1 = R \ln \left(\frac{v_2}{v_1} \right)$
- $s_2 - s_1 = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right) \rightarrow s_2 - s_1 = R \ln \left(\frac{P_1}{P_2} \right)$

– Option 3: Variable Specific Heats

- $s_2 - s_1 = (s_{T2}^0 - s_{T1}^0) + R \ln \left(\frac{v_2}{v_1} \right) \rightarrow s_2 - s_1 = R \ln \left(\frac{v_2}{v_1} \right)$
- $s_2 - s_1 = (s_{T2}^0 - s_{T1}^0) - R \ln \left(\frac{P_2}{P_1} \right) \rightarrow s_2 - s_1 = R \ln \left(\frac{P_1}{P_2} \right)$

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3.4.2 ΔS for Irreversible Process

Consider a control mass (closed system)

- Process path A and B are reversible
- Process path C is irreversible
- Clausius Inequality

$$- \oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T} \right)_A - \int_2^1 \left(\frac{\delta Q}{T} \right)_B = 0 \text{ (reversible)}$$

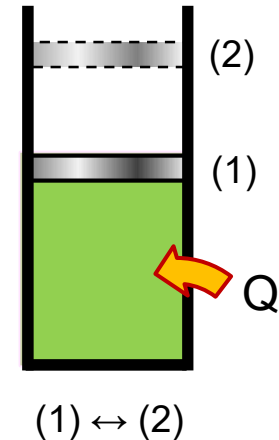
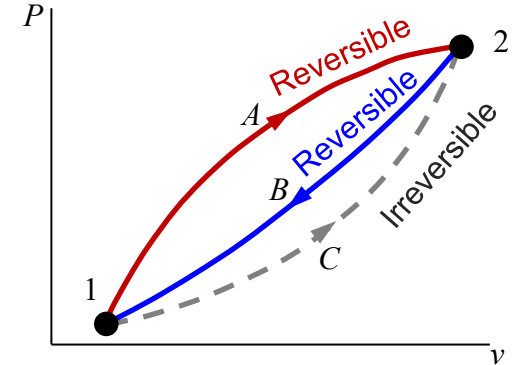
$$- \oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T} \right)_C - \int_2^1 \left(\frac{\delta Q}{T} \right)_B < 0 \text{ (irreversible)}$$

$$- \int_1^2 \left(\frac{\delta Q}{T} \right)_A > \int_2^1 \left(\frac{\delta Q}{T} \right)_C$$

- States 1 & 2 are the same and entropy is a state property

$$- (S_2 - S_1)_A = \int_1^2 \left(\frac{\delta Q}{T} \right)_A$$

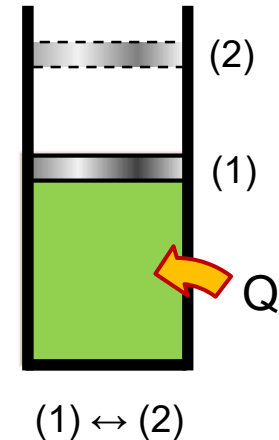
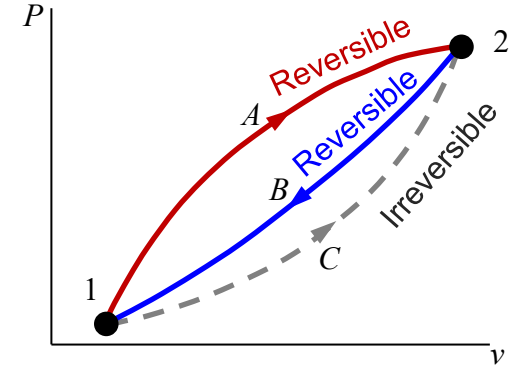
$$- (S_2 - S_1)_C > \int_1^2 \left(\frac{\delta Q}{T} \right)_C$$



3.4.2 ΔS for Irreversible Process

Consider a control mass (closed system)

- $S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$
- Reversible processes
 - $S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$
- Irreversible processes
 - $S_2 - S_1 > \int_1^2 \frac{\delta Q}{T}$



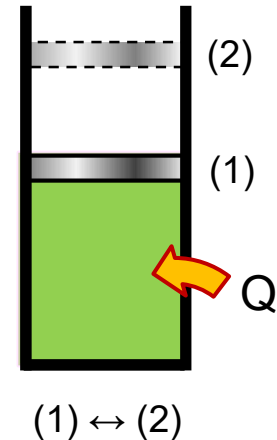
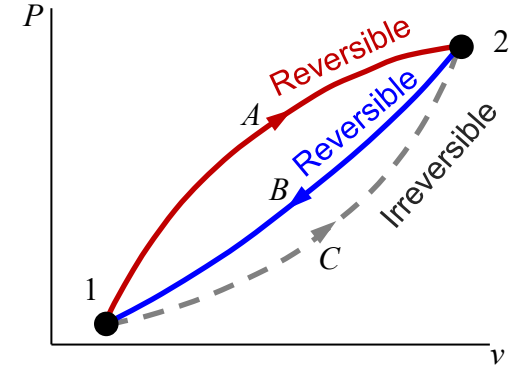
3.4.3 Entropy Equation

Consider a control mass (closed system)

- $S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$

Entropy Equation

- $S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}$
- $\Delta \text{Entropy} = +\text{in} - \text{out} + \text{generation}$
- Entropy generation
 - Entropy generation from irreversibilities
 - E.g. friction, mixing, chemical reaction
 - S_{gen} : positive value or zero
 - S_{gen} : process dependent (i.e. not a property)



3.4.3 Entropy Equation

General Notes about Entropy

1. Processes only occur such that $S_{\text{gen}} \geq 0$
2. Entropy is a non-conserved property (it can be generated)
3. $S_{\text{gen}} = 0$ for reversible systems
4. $S_{\text{gen}} > 0$ for irreversible systems
5. Performance is degraded by irreversibilities.
 - a) S_{gen} : measure of the magnitude of irreversibilities during a process
6. Lost work opportunity: $\delta W = PdV - T\delta S_{\text{gen}}$

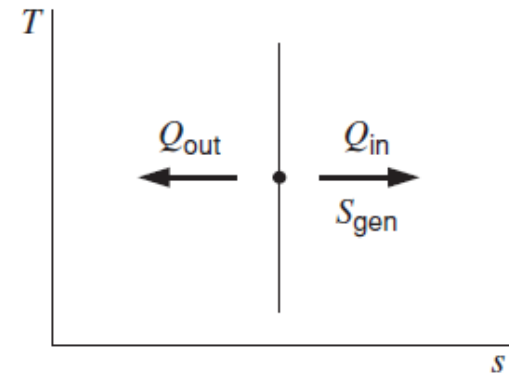
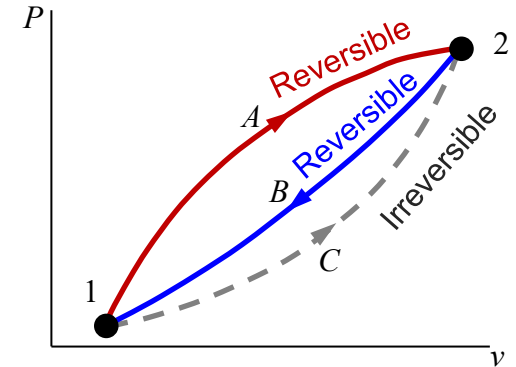


FIGURE 6.16

Change of entropy due to heat transfer and entropy generation.

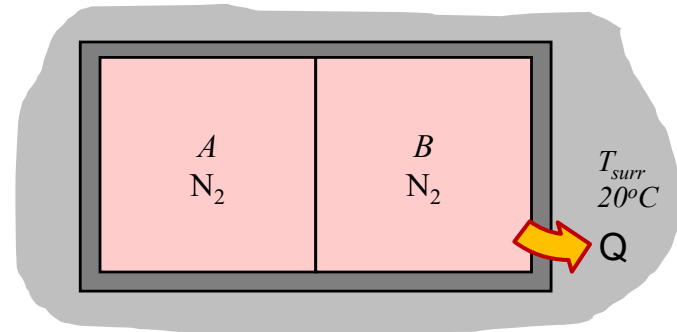
3.4.4 Example



Example 3.5 (2016 exam Q2):

A rigid container with volume 0.2 m^3 is divided into two equal volumes by a partition. Both sides contain nitrogen, on side at 2 MPa , 200°C and the other side at 200 kPa , 100°C . The partition ruptures and the nitrogen comes to a uniform state at 70°C . The temperature of the surroundings is 20°C . Assume ideal gas with constant specific heats $C_v = 0.745 \text{ kJ/kgK}$, $C_p = 1.042 \text{ kJ/kgK}$, and $R_{\text{N}_2} = 0.2968 \text{ kJ/kg K}$. Determine:

- a) The work done
- b) The heat transfer to the surroundings
- c) The entropy generated during this process
- d) Describe two methods for which entropy can be generated
- e) Is entropy a conserved property?

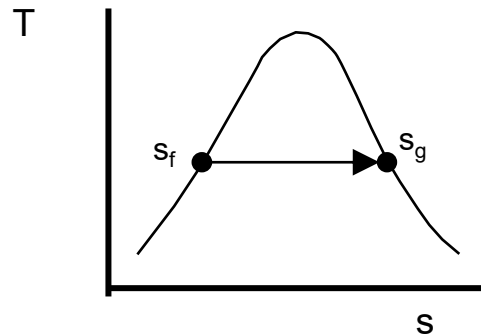
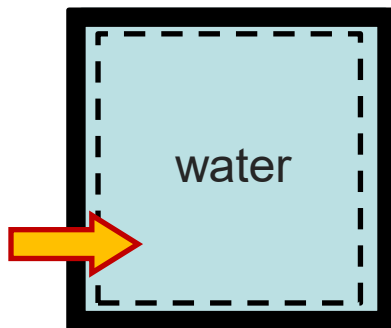


3.4.5 Exercises



Exercise 3-2

- (a) Determine the entropy change of water contained in a closed system as it changes phase from saturated liquid to saturated vapor when the pressure is 0.1 MPa and constant.
- (b) Why is the entropy change positive for this process?
- (c) If the heat transferred to the cylinder is 1000 kJ, what is the entropy generated in the system during this process?



ans: a) 6.057 kJ/kgK, b) $\Delta s > 0$ because heat is added to the water,
c) $S_{\text{gen}} = 3.38$ kJ/kgK

3.4.5 Exercises



Exercise 3-3

Air initially at 0.1 MPa, 27°C, is compressed reversibly to a final state.

- a) Find the entropy change of the air when the final state is 0.5 MPa, 227°C.
- b) Find the entropy change when the final state is 0.5 MPa, 180°C.
- c) Find the temperature at 0.5 MPa that makes the entropy change zero.

Show these processes on a T - s diagram.

Assume air is an ideal gas with constant specific heats.

($C_p=1.005\text{kJ/kgK}$, $R=0.287\text{kJ/kgK}$, $k=1.4$)

(Solutions are shown on the following slides)

3.4. EXTRA – Thermodynamic Relations



- Thermodynamic relations

- $\Delta S = S_2 - S_1$
- Consider a first law analysis: $du = dq - dw$
 - $dq = du + dw$
 - $dq = Tds$; $dw = Pdv$
 - $Tds = du + Pdv$
- Recall: $h = u + Pv \rightarrow u = h - Pv$
 - $Tds = dh - d(Pv) + Pdv$
 - $Tds = dh - vdP$

- $Tds = du + Pdv$ & $Tds = dh - vdP$

- Known as Gibbs equations
- Important for further thermodynamic processes that will be covered in further thermodynamic courses or in chemistry
- $\Delta G = \Delta H - T\Delta S$

$$S_2 - S_1 \leq \int_1^2 \frac{\delta q}{T}$$



To create a human out of nothing and place it on the table, the magician need not summon up the entire enthalpy, $H = U + PV$. Some energy, equal to TS , can flow in spontaneously as heat; the magician must provide only the difference, $G = H - TS$, as work.

<http://www.eoht.info/page/Gibbs+free+energy>