Outline

- Property diagrams involving entropy
- What is entropy?
- T-ds relations
- Entropy change of substances
  - Pure substances (near wet dome)
  - Solids and liquids
  - Ideal gases

Property diagrams involving entropy

- Recall on a P-v diagram the area under the curve represents the boundary work for a quasi-equilibrium process

$$w = \int P dv$$

- Recall equality part of Clasius inequality or definition of entropy

$$dS = \left(\frac{\delta Q}{T} \right)_{\substack{int \\ rev}} \rightarrow \delta Q = T dS \underset{integrate}{\rightarrow} Q = \int_{1}^{2} T dS$$

Heat transfer for internally reversible process

- On a T-s diagram the area under the curve represents the heat transfer for an internally reversible process


T

Internally reversible process

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

$\text{Area} = \int_{1}^{2} T\,dS = Q$

S
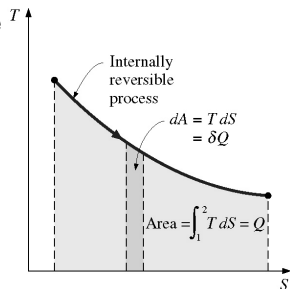
T-S diagram of a Carnot cycle

- Two reversible isothermal (T=constant) and two reversible adiabatic (s=constant) processes
- Recall area under curve on T-s diagram represents heat transfer for internally reversible process
- For cycle, net heat transfer equals net work
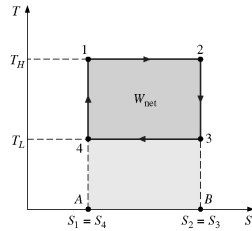
What is entropy?

- Level of molecular disorder (entropy) of substance increases as it melts or evaporates
- Entropy is related to total number of possible microscopic states for a given macroscopic state
- How certain are we about molecular position?
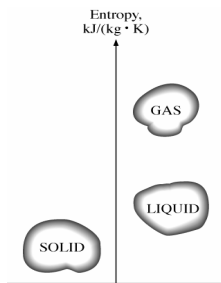
Disorder (entropy) increases during heat transfer

- Heat is form of disorganized energy
- During heat transfer net entropy increases
- Increase in entropy of cold body more than offsets decrease in entropy of hot body
- There is no entropy transfer associated with work
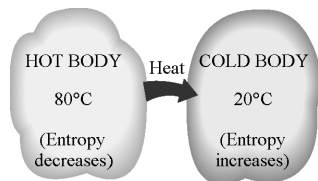
Third law of thermodynamics and absolute entropy

- Third law of thermodynamics
  - Entropy of a pure crystalline substance at absolute zero temperature is zero (no uncertainty about molecular state)
- Entropy determined relative to this state is called absolute entropy
- Use of entropy (disorganization, uncertainty) is not limited to thermodynamics e.g. studying for exam, library, textbooks, army, friction at work, angry words, etc.

Derivation of T-ds relations

- Consider closed, stationary system and differential form of first law

$$\delta Q - \delta W = dU$$

- Consider quasiequilibrium boundary work and recall

$$\delta W = PdV$$

- Substitute work expression into first law

$$\delta Q = dU + PdV$$

T-ds relations (cont.)

- Consider an internally reversible process

$$TdS = \delta Q$$

- Substitute heat expression into first law

$$TdS = dU + PdV$$

- Divide through by system mass

$$Tds = du + Pdv$$

T-ds relations (cont.)

- Recall definition of enthalpy

$$dh = d(u + Pv) = du + Pdv + vdP$$
$$= Tds + vdP \therefore Tds = dh - vdP$$

- In summary, we have two T-ds relations:

$$\boxed{\begin{aligned} Tds &= du + Pdv \\ Tds &= dh - vdP \end{aligned}}$$

Implications of T-ds relations

- Entropy is a property
- T-ds relations express change in entropy in terms of changes in other properties
- Properties are process path independent
- Hence, T-ds relations relate entropy changes to changes in other properties for any process between any two states
- T-ds relations very useful for evaluating change in entropy when property relations (v, T, P, u, and h) are available
- This is true for incompressible substances (solids and liquids) and ideal gases

Entropy change and isentropic relations – pure substances
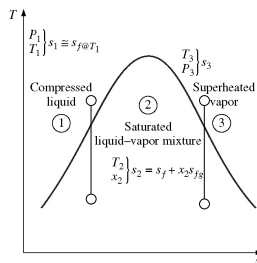
- Pure substances (near wet dome)

Any process:

$$\Delta s = s_2 - s_1$$

$$\left[kJ / (kg - K) \right]$$

Isentropic proces:

$$\Delta s = 0 \therefore s_2 = s_1$$

Entropy change and isentropic process – incompressible substances

- Incompressible substances (solids/liquids)

$$v = \text{constant} \Rightarrow dv = 0 \therefore ds = \frac{du}{T} = \frac{CdT}{T}$$

Liquids/solids: $\Delta s = s_2 - s_1 = \int_1^2 C(T)\frac{dT}{T} \cong C_{av} \ln\frac{T_2}{T_1} \; \left[kJ/(kg-K) \right]$

Isentropic proces: $\Delta s = 0 \therefore s_2 = s_1 = C_{av} \ln\frac{T_2}{T_1} = 0 \rightarrow T_2 = T_1$

- Temperature of incompressible substance remains constant during isentropic process
- Isentropic process of an incompressible substance is also isothermal (model for solids/liquids)

Entropy change and isentropic process – ideal gas

$$Tds = du + Pdv \underset{\substack{ideal \\ gas}}{=} C_v dT + RT\frac{dv}{v}$$

$$\rightarrow ds = C_v \frac{dT}{T} + R\frac{dv}{v} \Rightarrow \Delta s = \int_1^2 C_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1}$$

$$Tds = dh - vdP \underset{\substack{ideal \\ gas}}{=} C_P dT - RT\frac{dP}{P}$$

$$\rightarrow ds = C_P \frac{dT}{T} - R\frac{dP}{P} \Rightarrow \Delta s = \int_1^2 C_P(T)\frac{dT}{T} - R\ln\frac{P_2}{P_1}$$

Entropy change and isentropic process – ideal gas (cont.)

- Recall we derived two entropy change formulas for ideal gas

$$\Delta s = \int_1^2 C_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1}$$

$$\Delta s = \int_1^2 C_P(T)\frac{dT}{T} - R\ln\frac{P_2}{P_1}$$

- Further evaluations depends upon whether or not you assume constant or variable specific heats

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Entropy change – ideal gas

- Constant specific heats

$$\Delta s = \int_1^2 C_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1} \cong C_{v,av}\ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$$

$$\Delta s = \int_1^2 C_P(T)\frac{dT}{T} - R\ln\frac{P_2}{P_1} \cong C_{P,av}\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

- Variable specific heats

$$\int_{T_1}^{T_2} C_P\frac{dT}{T} = \int_{T=0}^{T_2} C_P\frac{dT}{T} - \int_{T=0}^{T_1} C_p\frac{dT}{T} = s^o(T_2) - s^o(T_1) = s_2^o - s_1^o$$

$$\therefore s_2 - s_1 = s_2^o - s_1^o - R\ln\frac{P_2}{P_1} \quad (s^o(T) \text{ in A-22/23})$$

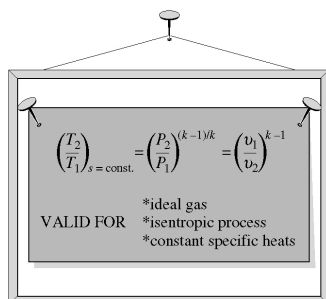## Entropy change and isentropic process – ideal gas; constant specific heat

$$\Delta s = C_{v,av}\ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1} \;\underset{isentropic}{\rightarrow}\;$$

$$\ln\frac{T_2}{T_1} = -\frac{R}{C_v}\ln\frac{v_2}{v_1} = \ln\left(\frac{v_1}{v_2}\right)^{\frac{R}{C_v}}$$

$$\left(\frac{T_2}{T_1}\right)_{s=const} = \left(\frac{v_1}{v_2}\right)^{k-1}$$

$$\Delta s = C_{P,av}\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} \rightarrow \left(\frac{T_2}{T_1}\right)_{s=const} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

Validity of isentropic relations

$$\left(\frac{T_2}{T_1}\right)_{s=const.} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} = \left(\frac{v_1}{v_2}\right)^{k-1}$$

VALID FOR *ideal gas *isentropic process *constant specific heats

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Entropy change and isentropic process – ideal gas; variable specific heat

$$s_2 - s_1 = s_2^o - s_1^o - R \ln \frac{P_2}{P_1} \xrightarrow{isentropic} 0 = s_2^o - s_1^o - R \ln \frac{P_2}{P_1}$$

$$s_2^o = s_1^o - R \ln \frac{P_2}{P_1} \rightarrow \frac{P_2}{P_1} = \exp \frac{s_2^o - s_1^o}{R} = \frac{\exp(s_2^o / R)}{\exp(s_1^o / R)} = \frac{P_{r2}}{P_{r1}}$$

$$\left(\frac{P_2}{P_1} \right)_{s=const} = \frac{P_{r2}}{P_{r1}} \quad \text{(A-17 for air)};$$

$$\left(\frac{v_2}{v_1} \right)_{s=const} = \frac{v_{r2}}{v_{r1}} \quad \left(v_r = T / P_r \right)$$

Use of isentropic relations – variable specific heats

Process: isentropic
Given: P_1, T_1, and P_2
Find: T_2

T	P_r
.	.
.	.

$T_2 \xleftarrow{read} P_{r2} = \frac{P_2}{P_1} P_{r1}$

$T_1 \xrightarrow{read} P_{r1}$

Process: isentropic
Given: v_1, T_1, and v_2
Find: T_2

T	v_r
.	.
.	.

$T_2 \xleftarrow{read} v_{r2} = \frac{v_2}{v_1} v_{r1}$

$T_1 \xrightarrow{read} v_{r1}$

Isentropic relation formula summary

• Constant specific heats

$$\left(\frac{T_2}{T_1} \right)_{s=const} = \left(\frac{v_1}{v_2} \right)^{k-1} ; \left(\frac{T_2}{T_1} \right)_{s=const} = \left(\frac{P_2}{P_1} \right)^{(k-1)/k} ; \left(\frac{P_2}{P_1} \right)_{s=const} = \left(\frac{v_1}{v_2} \right)^{k}$$

• Variable specific heats

$$\left(\frac{P_2}{P_1} \right)_s = \frac{P_{r2}}{P_{r1}} ; \quad \left(\frac{v_2}{v_1} \right)_s = \frac{v_{r2}}{v_{r1}}$$

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Example

- A 12 kg block initially at 350C is quenched in an insulated tank that contains 100 kg of water at 22C. Assuming the water that vaporizes during the process condenses back in the tank, determine the entropy change during this process.

Solution 1

- Model tank as closed system
- Model iron and water (initial and final states) as incompressible substances
- Find final equilibrium temperature using 1st law

$$Q - W = \Delta U \therefore \Delta U = 0 = \Delta U_{iron} + \Delta U_{water}$$

$$0 = \left[mC(T_2 - T_1) \right]_{iron} + \left[mC(T_2 - T_1) \right]_{water}$$

$$(12)(0.45)(T_2 - 350C) + (100)(4.18)(T_2 - 22) = 0$$

$$T_2 = 26.2C$$

Solution 2

- Second law for entropy change

$$\Delta S_{iron} = mC_{ave} \ln\left(\frac{T_2}{T_1}\right) = (12)(0.45)\ln\left(\frac{299.2}{623}\right) = -3.96 kJ/K$$

$$\Delta S_{water} = mC_{ave} \ln\left(\frac{T_2}{T_1}\right) = (100)(4.18)\ln\left(\frac{299.2}{295}\right) = 5.91 kJ/K$$

$$\Delta S_{total} = \Delta S_{iron} + \Delta S_{water} = -3.96 + 5.91 = S_{gen}$$

- Improve accuracy using specific heats at average temperature

Example

- Oxygen gas is compressed in a piston-cylinder device from an initial state of 0.8m3/kg and 25C to a final state of 0.1m3/kg and 287C. Determine the entropy change of the oxygen during this process. Assume constant specific heats.

Solution

- Assume ideal gas; use constant specific heat at average temperature

$$T_{ave} = \frac{298+560}{2} = 429K \rightarrow C_{v,ave} = 0.69kJ/kg - K$$

$$\Delta s = C_{v,ave} \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{v_2}{v_1}\right)$$

$$= (0.69)\ln\left(\frac{560K}{298K}\right) + (0.2598)\ln\left(\frac{0.1}{0.8}\right)$$

$$= -0.105kJ/kg - K$$

Example

- Air is compressed steadily by a 5-kW compressor from 100kPa and 17C to 600kPa and 167 C at a rate of 1.6kg/min. During this process, some heat transfer takes place between the compressor and the surrounding medium at 17C. Determine the rate of entropy change of the air during this process.

Solution

- Use variable specific heats

$$\left. \begin{array}{l} T_1 = 290K \\ P_1 = 100kPa \end{array} \right\} s_1^o = 1.6882 \quad (A-22)$$

$$\left. \begin{array}{l} T_2 = 440K \\ P_2 = 600kPa \end{array} \right\} s_2^o = 2.0887 \quad (A-22)$$

$$\Delta \dot{S}_{sys} = \dot{m} \left(s_2^o - s_1^o - R \ln \left(\frac{P_2}{P_1} \right) \right)$$

$$= (1.6/60) \left(2.0887 - 1.66802 - (0.287) \ln(600/100) \right)$$

$$= -0.00250 kW/K$$

Summary

- T-s diagram important! Area under curve represents heat transfer only for an internally reversible process
- Entropy is related to disorder
- T-ds relations
- Entropy change . . .
  - Pure substance near wet dome – use tables
  - Incompressible substances (solids/liquids)
  - Ideal gases

Summary

- Key formulas (where did they come from?)
- Pure substances $\qquad \Delta s = s_2 - s_1$
- Solids/liquids
- Ideal gases $\qquad \Delta s = s_2 - s_1 = \int_1^2 C(T) \frac{dT}{T} \cong C_{av} \ln \frac{T_2}{T_1}$
  - Constant specific heats

$$\Delta s = C_{v,av} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \text{ or } \Delta s = C_{P,av} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

  - Variable specific heats

$$\Delta s = s_2^o - s_1^o - R \ln \frac{P_2}{P_1} \quad (s^o(T) \text{ in A-17})$$

Summary

- Isentropic relations $\Delta s = s_2 - s_1 = 0$
- Constant specific heats

$$\left(\frac{T_2}{T_1}\right)_{s=const} = \left(\frac{v_1}{v_2}\right)^{k-1} ; \left(\frac{T_2}{T_1}\right)_{s=const} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} ; \left(\frac{P_2}{P_1}\right)_{s=const} = \left(\frac{v_1}{v_2}\right)^{k}$$

- Variable specific heats

$$\left(\frac{P_2}{P_1}\right)_s = \frac{P_{r2}}{P_{r1}} ; \qquad \left(\frac{v_2}{v_1}\right)_s = \frac{v_{r2}}{v_{r1}}$$