Lecture 4

- 2nd law
  - different statements of 2nd law
  - Carnot theorem
- Entropy
  - Clausius theorem
  - definition of entropy
- Mathematical statement of 2nd law – Clausius inequality
- Entropy change of a heat reservoir
- Calculating entropy change

Read Ch. 4 Sandler, Chs. 1 and 2 Callen

Objectives

- Know the common statements of 2nd law
- Have appreciation for how the concept of entropy came about
- Use entropy change as criterion for whether a process is thermodynamically feasible
- Distinguish entropy change for system, reservoir, the universe
- Calculate entropy change by connecting to changes in other state variables
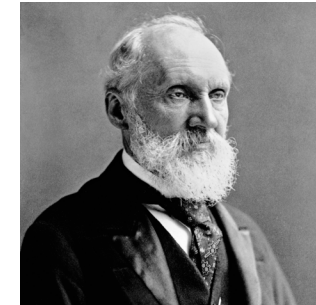
Read Ch. 4 Sandler

Statements of Second Law

Clausius – It's impossible for heat to transfer spontaneously from a colder to a hotter body without causing other changes

Kelvin – It is impossible to convert heat taken from a hot body of uniform temperature completely into work without causing other changes.

Caratheodory – In the neighborhood of any initial state, there are states which cannot be accessed arbitrarily close through adiabatic changes of state, i.e. two adiabatic lines can't cross

Carnot Theorem

(1) The efficiency of a reversible Carnot cycle operating between two constant heat reservoirs R_1 and R_2 depends only on the temperatures of the reservoirs and is independent of the working substance.

(2) Furthermore, the efficiency of any irreversible cycle operating between the same heat reservoirs is less than that of the reversible cycle

→ All reversible Carnot cycles have the same efficiency (operating between the same reservoirs) which is maximum

Clausius Theorem

Given any reversible process in which the temperature changes in any prescribed manner, it is always possible to find a reversible process consisting of adiabatic-isothermal-adiabatic steps, such that the heat interaction in the isothermal step is equal to the heat interaction in the original process.
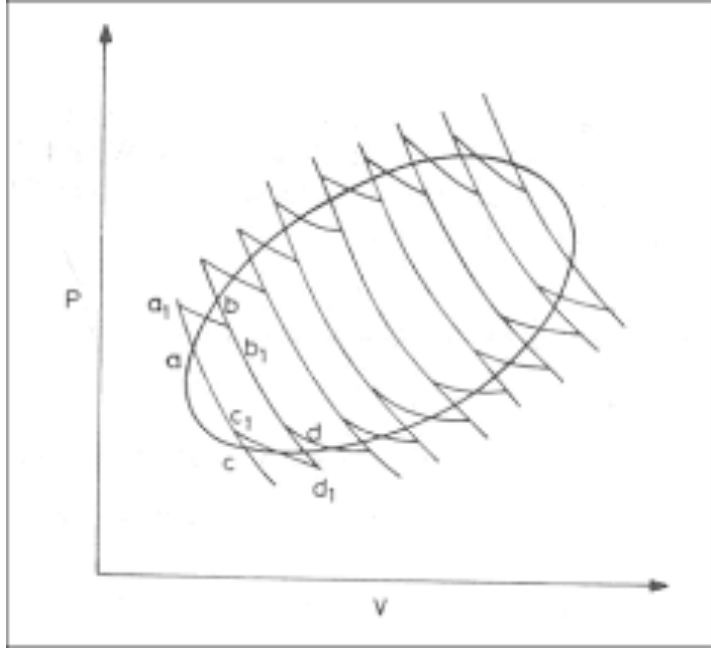
P

i

g

h

f
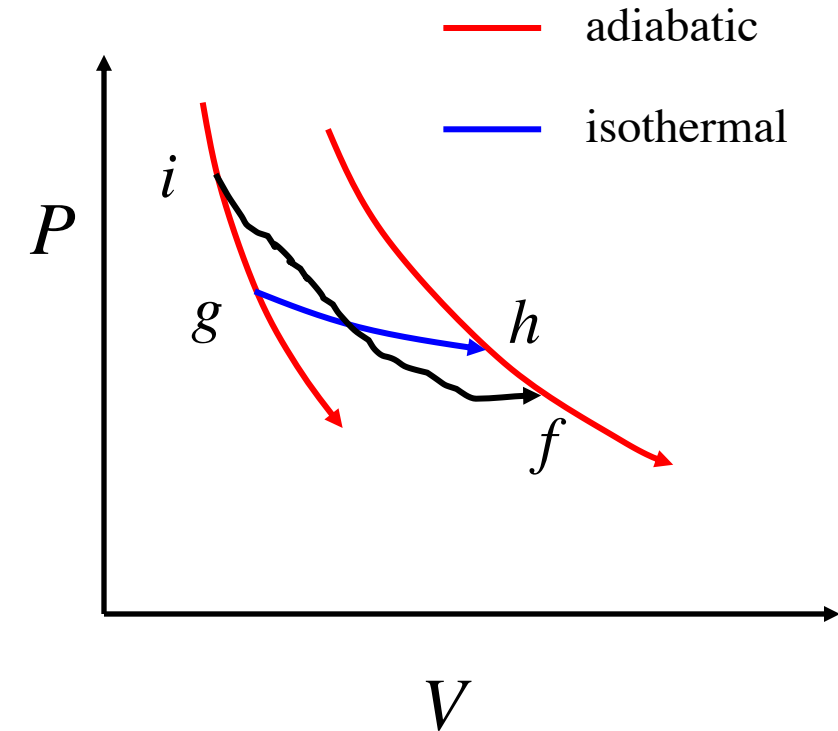
(i) Draw two adiabatic lines passing i and f

V

(ii) Draw an isothermal line to make area above and below equal $W_{if} = W_{ighf}$

$$Q_{if} = \Delta U_{if} - W_{if} = \Delta U_{ig} + \Delta U_{gh} + \Delta U_{hf} - W_{ig} - W_{gh} - W_{hf}$$

$$Q_{if} = \Delta U_{gh} - W_{gh} = Q_{gh}$$

Reversible Cycle

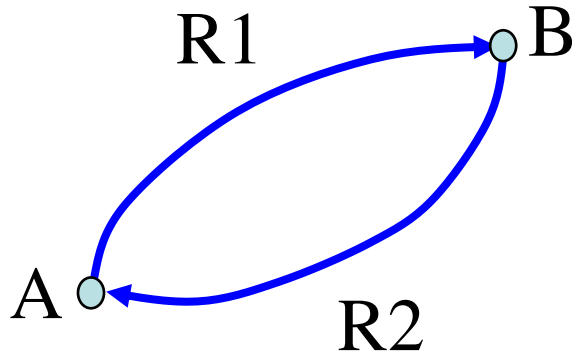A reversible cycle can be approximated by n small Carnot cycles

Since for each Carnot cycle we have
$$\frac{Q_H}{T_H} + \frac{Q_c}{T_c} = 0$$

$$\sum_{i=1}^{2n} \frac{\delta Q_i}{T_i} = 0$$

In the limit $n \to \infty$

$$\oint \left(\frac{\delta Q}{T}\right)_R = 0$$

https://physics.stackexchange.com/questions/388385/demonstration-of-clausius-theorem-for-irreversible-cycles

A New State Function

$$\oint \left(\frac{\delta Q}{T}\right)_R = 0$$

$$\int_A^B \left(\frac{\delta Q}{T}\right)_{R1} + \int_B^A \left(\frac{\delta Q}{T}\right)_{R2} = 0$$

$$\int_A^B \left(\frac{\delta Q}{T}\right)_{R1} = -\int_B^A \left(\frac{\delta Q}{T}\right)_{R2} = \int_A^B \left(\frac{\delta Q}{T}\right)_{R2} \qquad \text{Independent of path!}$$
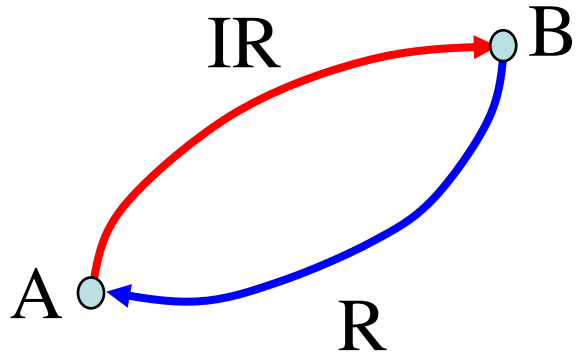
Suggest defining a state function S, *entropy*: $\qquad S_B - S_A = \int_A^B \left(\frac{\delta Q}{T}\right)_R$

For infinitesimal process, differentia form $\qquad dS = \left(\frac{\delta Q}{T}\right)_R$

(Rudolf Clausius, 1865)

Clausius Inequality

IR

B

A

R

Carnot theorem

$$\eta' = \frac{Q_H + Q_C}{Q_H} < 1 - \frac{T_C}{T_H} \qquad \Longrightarrow \qquad \frac{Q_H}{T_H} + \frac{Q_C}{T_C} < 0$$

generalize $\qquad \oint \left(\frac{\delta Q}{T}\right) < 0 \qquad \Longrightarrow \qquad \int_A^B \left(\frac{\delta Q}{T}\right)_{IR} + \int_B^A \left(\frac{\delta Q}{T}\right)_R < 0$

$$\Longrightarrow \qquad \int_A^B \left(\frac{\delta Q}{T}\right)_{IR} < \int_A^B \left(\frac{\delta Q}{T}\right)_R$$

$$S_B - S_A > \int_A^B \left(\frac{\delta Q}{T}\right)_{IR}$$

Entropy and 2nd Law

$$S_B - S_A \geq \int_A^B \left(\frac{\delta Q}{T} \right)$$

"=" only applies for reversible process

Differential form

$$dS \geq \frac{\delta Q}{T}$$

Mathematical statement of 2nd law!

For isolated system or adiabatic process

$$dS \geq 0 \quad \text{or} \quad \Delta S \geq 0$$

The entropy of the universe will always increase

Entropy and 2nd Law

$$S_B - S_A \geq \int_A^B \left(\frac{\delta Q}{T} \right)$$

"=" only applies for reversible process

Differential form $$dS \geq \frac{\delta Q}{T}$$ Mathematical statement of 2nd law!

For isolated system or adiabatic process

$$dS \geq 0$$ or $$\Delta S \geq 0$$

Die Entropie der Welt strebt einem Maximum zu.

Entropy Change of Heat Bath

Since heat bath is infinitely large and is always maintained at internal equilibrium, any finite change is infinitesimal, i.e., quasi-static

$$dS_{res} = \frac{\delta Q_{res}}{T_{res}}$$

Entropy change of the universe: $dS_{sys} + dS_{res} \geq 0$

$$dS \geq -dS_{res} = \frac{\delta Q}{T_{res}}$$ Clausius inequality!

(notation w/o subscript by default refers to system)

Entropy Generation

Any irreversible process leads to entropy generation and contributes to the entropy increase in the universe

- Friction (lost work)
- Temperature gradient
- Concentration gradient
- Pressure gradient

$$dS_{gen} = \delta W_{lost} + \left(1 - \frac{T}{T_{res}}\right) \delta Q_{irr}$$

Second law in terms of entropy generation:

$$dS = \frac{\delta Q}{T_{res}} + dS_{gen} \quad \text{with} \quad dS_{gen} \geq 0$$

Calculating System Entropy Change

From definition: $$dS = \left(\frac{\delta Q}{T}\right)_R$$

Using 1st law: $$\delta Q = dU - \delta W$$

Simple system, only PV work: $$\delta Q = dU + PdV$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \qquad S = S(U,V)$$

fundamental eqn.

$$dU = TdS - PdV \qquad U = U(S,V)$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

Calculating System Entropy Change

$$dS = \frac{dU}{T} + \frac{p}{T}dV = \frac{C_V}{T}dT + \left[\frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T + \frac{p}{T}\right]dV$$

$$dS = \frac{dH}{T} - \frac{V}{T}dp = \frac{C_p}{T}dT + \left[\frac{1}{T}\left(\frac{\partial H}{\partial p}\right)_T - \frac{V}{T}\right]dp$$

Using Maxwell relations

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{C_P}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

Simplifications

Const-V
$$dS = \frac{C_V}{T}\, dT$$

Const-P
$$dS = \frac{C_p}{T}\, dT$$

Ideal gas
$$dS = \frac{C_V}{T}\, dT + \frac{P}{T}\, dV = \frac{C_P}{T}\, dT - \frac{V}{T}\, dP$$

Calculating Entropy Change

Examples:

- Isothermal expansion of ideal gas

$$\Delta S = \frac{Q}{T} = -\frac{W}{T} = nR\ln\frac{V_2}{V_1} \quad (\Delta S)_{res} = \frac{Q_{res}}{T} = -\frac{Q}{T} = -nR\ln\frac{V_2}{V_1} \quad (\Delta S)_{univ} = 0$$

- Free expansion of ideal gas

$$\Delta S = \frac{Q}{T} = -\frac{W}{T} = nR\ln\frac{V_2}{V_1} \qquad \text{same as above, but} \quad (\Delta S)_{univ} = nR\ln\frac{V_2}{V_1} > 0$$

- Metal bar cooling

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} = C_p\ln\frac{T_2}{T_1} \qquad (\Delta S)_{res} = \frac{Q_{res}}{T_2} = \frac{C_p(T_1 - T_2)}{T_2}$$
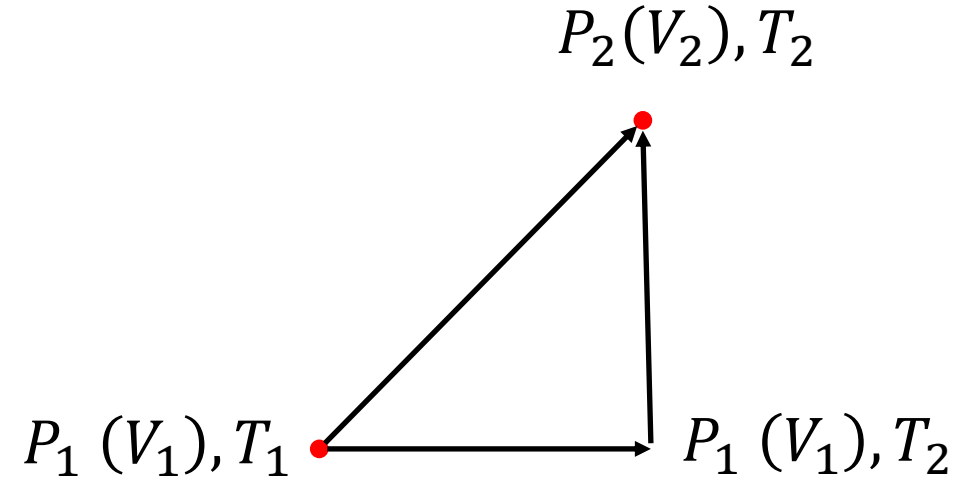
$$(\Delta S)_{univ} = C_p\left(\frac{T_1 - T_2}{T_2} + \ln\frac{T_2}{T_1}\right) > 0$$

Entropy Change for Ideal Gas

$$dS = \frac{C_V}{T} dT + \frac{P}{T} dV = \frac{C_P}{T} dT - \frac{V}{T} dP$$

For constant C_P, C_V

$$\Delta S = C_V \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1} = C_P \ln\frac{T_2}{T_1} - nR \ln\frac{P_2}{P_1}$$

$P_2(V_2), T_2$

$P_1(V_1), T_1$

$P_1(V_1), T_2$

Questions to Think about

- What's the condition for isentropic process?

- Show that the adiabats can be simply obtained from $\Delta S=0$?

- For the 1-step isothermal expansion we discussed in Lecture 2 (Example 3.4-7 of Sandler), what's the entropy change of the system, the surrounding, and the universe?