Entropy and The Second Law of Thermodynamics

- Explain and manipulate the second law [Ch 3.3-3.6]
  ◦ State and illustrate by example the second law of thermodynamics
  ◦ Write both the integral and differential forms of the second law
  ◦ Identify when the open and closed forms of the second law are applicable
  ◦ Determine when each term in the second law is zero or negligible
- Identify, formulate, and solve simple engineering problems (such as expansion/compression and power cycles) [Ch 3.5-3.9]
- Derive and use the mechanical energy balance equation to solve engineering problems [Ch 3.8]
- Devise and use strategies for entropy change calculations
  ◦ Develop hypothetical reversibile paths between two states in order to calculate entropy changes [Ch 3.1-3.2]
  ◦ Use the heat capacity to calculate entropy changes
  ◦ Use tables to calculate entropy changes
  ◦ Calculate entropy changes for materials undergoing phase changes and/or reaction
- Perform power cycle problems [Ch 3.9]
  ◦ Solve for the net power obtained and efficiency of reversible power cycles
  ◦ Calculate the coefficient of performance of a reversible refrigeration cycle
  ◦ Correct reversible calculations for real systems using isentropic efficiencies

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SL: The need for the second law

The need for the Second Law of Thermodynamics

Processes have directionality:

EXAMPLE:

An 100g ice cube at -10C is added to a 500g cup of coffee at 80C in an insulated (adiabatic) cup. What will happen? Perform a first law analysis of this process to obtain the final temperature.

EXAMPLE:

A 600 g cup of lukewarm coffee in an insulated (adiabatic) cup is made to separate into a 100 g cube of ice at -10C and 500 ml of 80C coffee. Perform a first law analysis.

OBSERVATION:

Thermal directionality: heat goes from high T to low

Two gases at 100C and 1 atm -- water/steam and ethanol -- are in either side of a partitioned box. What will happen when the partition between water and ethanol is opened.

EXAMPLE:

Gasoline and oxygen are mixed in a container at 500C. What do you expect will happen? What if they are mixed at 2000C? How about 25C?

OBSERVATION:

Chemical directionality: concentration gradients and chemical potential "gradients" get "smoothed out".

EXAMPLE:

A partition divides a box in half. One half contains 100 molecules of nitrogen; the other half is empty. What will happen if a hole is made in the partition? How many molecules will be in each half when the system comes to equilibrium?

OBSERVATION:

Mechanical directionality: pressure gradients drive flow.

NOTE:

Conservation of mass + conservation of energy (first law) are exact but incomplete → No inherent direction; Spontaneity is not predicted. Need something else

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SL: Heat and Directionality vs Reversibility

Heat and Directionality vs Reversibility

Few caveats about directionality:
- Work $\sim$ potential energy or kinetic energy or electrical
- Work $\sim$ heat (100%)
- Heat $\neq$ work (not 100%, anyway)

NOTE:

Reversible processes do not exhibit directionality (consider the piston-cylinder with small and large weights).

DEFINITION:

***Second Law**: No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.*

DEFINITION:

***Second Law**: It is impossible for a cyclic process to convert the heat absorbed by a system completely into work done by the system.*
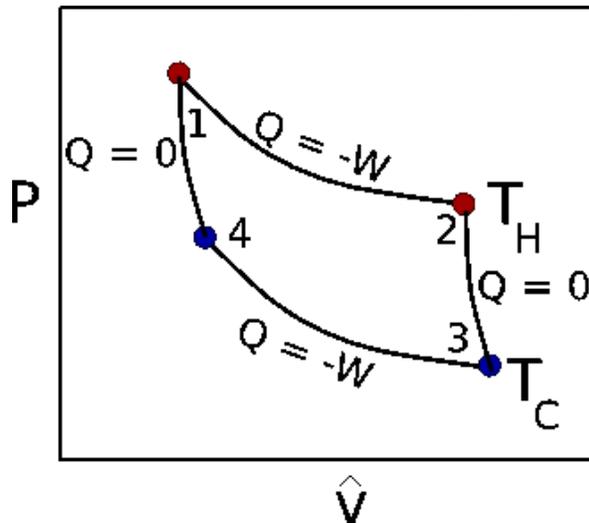
*The **second law** states that for any irreversible (real) process the entropy of the universe increases, while for any reversible process the entropy of the universe remains unchanged.*

DEFINITION:

$\Delta s_{univ} \geq 0$

SL: Motivating the mathematical form of S

Thermodynamic Cycles

Entropy is a state function so, just like:

$$\Delta U_{cycle} = 0$$

so is

$$\Delta S_{cycle} = 0$$

The two steps that are not adiabatic yield:

$$Q_H = Q_{12} = -W_{12} = nRT_H \ln\left(\frac{V_2}{V_1}\right)$$

$$Q_C = Q_{34} = -W_{34} = nRT_C \ln\left(\frac{V_4}{V_3}\right)$$

The two adiabatic steps yield:

$$\Delta U_{41} = W_{41} = \int_1^4 c_v dT = -\int_1^4 PdV$$

Noting that $P = \frac{RT}{V}$, so:

$$\int_1^4 \frac{c_v}{R}\frac{dT}{T} = -\int_1^4 \frac{dV}{V} = \ln\left(\frac{V_1}{V_4}\right)$$

by similar logic:

$$\int_2^3 \frac{c_v}{R}\frac{dT}{T} = -\int_2^3 \frac{dV}{V} = \ln\left(\frac{V_2}{V_3}\right)$$

since $T_1 = T_2$ and $T_3 = T_4$ both c_v-related (i.e., left-hand-side) integrals are the same, so:

$$\ln\left(\frac{V_2}{V_3}\right) = \ln\left(\frac{V_1}{V_4}\right)$$

rearranging:

$$\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_3}{V_4}\right)$$

Combining this result with our non-adiabatic steps:

$$Q_H = Q_{12} = -W_{12} = nRT_H \ln\left(\frac{V_2}{V_1}\right) = nRT_H \ln\left(\frac{V_3}{V_4}\right)$$

$$Q_C = Q_{34} = -W_{34} = nRT_C \ln\left(\frac{V_4}{V_3}\right) = -nRT_C \ln\left(\frac{V_3}{V_4}\right)$$

Taking the ratio $\frac{Q_C}{Q_H}$, gives:

$$\frac{Q_C}{Q_H} = \frac{-nRT_C \ln\left(\frac{V_3}{V_4}\right)}{nRT_H \ln\left(\frac{V_3}{V_4}\right)}$$

$$\frac{Q_C}{Q_H} = \frac{-T_C}{T_H}$$

or

$$\frac{|Q_C|}{Q_H} = \frac{T_C}{T_H}$$

This tells us two interesting things:

- $\eta = \frac{W_{net}}{Q_{in}} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$

- $\frac{Q_H}{T_H} = -\frac{Q_C}{T_C}$, so that $\oint \frac{\delta Q}{T} = \sum \frac{Q}{T} = 0$!

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NOTE:

*This suggests that, despite the fact that Q is a path function, the **ratio** of $\frac{Q}{T}$ (at least for reversible processes) is a state function.*

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SL: Entropy of a Reversible Isothermal Expansion

Entropy of a Reversible Isothermal Expansion
EXAMPLE:

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Consider a reversible, isothermal (T=962K), expansion from a pressure of 2 bar and a specific volume of $0.04 m^3/mol$ to a pressure of 1 bar and a specific volume of $0.08 m^3/mol$. Calculate the change in entropy of the system, the surroundings, and the universe.

$$\Delta S_{sys} = \int_{initial}^{final} \frac{\delta Q}{T}$$

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RECALL:

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Out first law analysis of this problem yields:

$$Q = -W = -\left(-\int P_E dV\right) = nRT_1 \ln\left(\frac{P_1}{P_2}\right)$$

$$\Delta S_{sys} = \int_{initial}^{final} \frac{nRT_1 \ln\left(\frac{P_1}{P_2}\right)}{T}$$

$$\Delta S_{sys} = nR \ln\left(\frac{P_1}{P_2}\right) = (1mol)(8.314 J/molK) \ln(2) = 5.76 J/K$$

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NOTE:

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For a reversible process the entropy change of the universe does not change. Thus, $\Delta S_{sys} = -\Delta S_{surround}$

Identify, formulate, and solve simple engineering problems (such as expansion/compression and power cycles)

SL: Entropy of a Irreversible Isothermal Expansion

Entropy of a Irreversible Isothermal Expansion
EXAMPLE:

The same piston-cylinder assembly is now loaded with a single weight to yield the same initial pressure of 2 bar. The weight is removed all at once. The initial and final P,V,T are the same as the previous example. Represent this on a PV and PT diagram. Find the total heat transfer, and the entropy change of the system, the surroundings, and the universe.
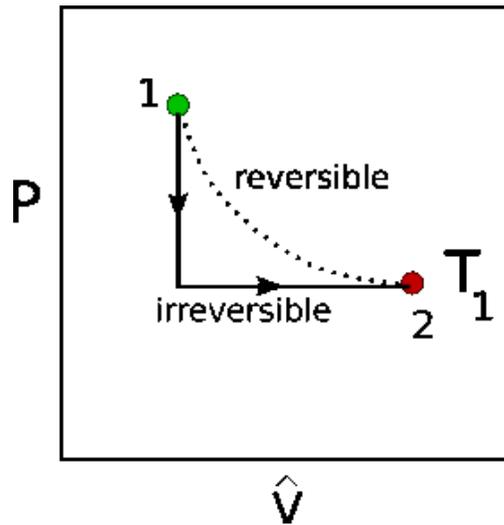
NOTE:

*In order to calculate ΔS_{sys} we must always use the **reversible** process, so even for the irreversible process, we get*

$$\Delta S_{sys} = 5.76 J/K$$

$$\Delta S_{surr} = \int_{initial}^{final} \frac{\delta Q_{surr}}{T}$$

RECALL:

Our first law analysis of this problem yields:

$$Q_{sys} = -W = -\left(-\int P_E dV\right) = nP_2\left(\hat{V}_2 - \hat{V}_1\right)$$

$$\Delta S_{surr} = -\int_{initial}^{final} \frac{nP_2\left(\hat{V}_2 - \hat{V}_1\right)}{T}$$

$$\Delta S_{surr} = -\frac{nP_2}{T_1}\left(\hat{V}_2 - \hat{V}_1\right) = -\frac{(1mol)(1bar)}{962K}(0.08 m^3/mol - 0.04 m^3/mol) = -4.16 J/K$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = 5.75 J/K - 4.16 J/K = 1.59 J/K$$


SL: Entropy of a Rev/irreversible Isothermal Compression

Entropy of a Rev/irreversible Isothermal Compression
EXAMPLE:

The gas in the previous examples is compressed back isothermally and (ir)reversibly. Represent this on a PV and PT diagram. Find the total heat transfer, and the entropy change of the system, the surroundings, and the universe.

NOTE:

For both the reversible and irreversible case, ΔS_{sys} must use the **reversible** process.
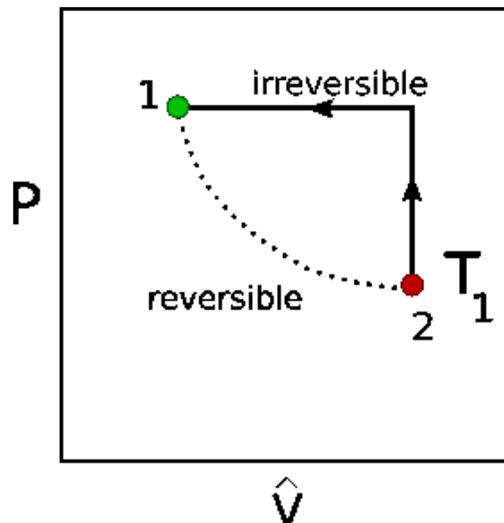
$$\Delta S_{sys(ir)rev} = \int_{initial}^{final} \frac{\delta Q_{sys}}{T}$$

RECALL:

Our first law analysis of this problem (reversible) yields:

$$Q = -W = -\left(-\int P_E dV\right) = nRT_1 \ln\left(\frac{P_2}{P_1}\right)$$

$$\Delta S_{sys(ir)rev} = \int_{initial}^{final} \frac{nRT_1 \ln\left(\frac{P_2}{P_1}\right)}{T}$$

$$\Delta S_{sys(ir)rev} = nR\ln\left(\frac{P_2}{P_1}\right) = -(1mol)(8.314 J/molK)\ln(2) = -5.76 J/K$$

$$\Delta S_{surr_{rev}} = -\Delta S_{sys_{rev}} = 5.76 J/K$$

$$\Delta S_{univ_{rev}} = 0$$

RECALL:

In contrast, our first law analysis of this problem (irreversible) yields:

$$Q_{sys} = -W = -\left(-\int P_E dV\right) = nP_1\left(\hat{V}_1 - \hat{V}_2\right)$$

$$\Delta S_{surr_{irrev}} = -\int_{initial}^{final} \frac{nP_1\left(\hat{V}_1 - \hat{V}_2\right)}{T}$$

$$\Delta S_{surr_{irrev}} = -\frac{nP_1}{T_1}\left(\hat{V}_1 - \hat{V}_2\right) = -\frac{(1mol)(1bar)}{962K}(0.04 m^3/mol - 0.08 m^3/mol) = 8.31 J/K$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr_{irrev}}$$

$$\Delta S_{univ} = -5.75 J/K + 8.31 J/K = 2.56 J/K$$
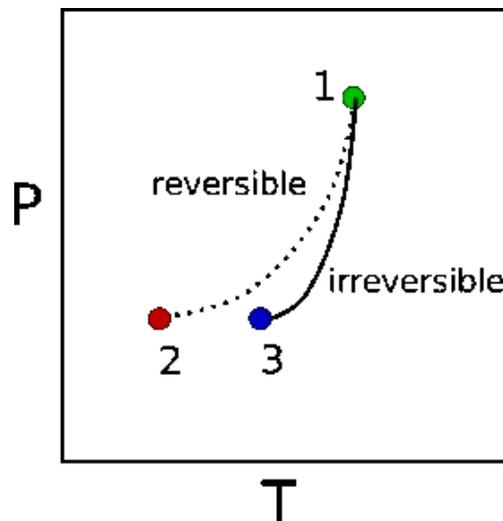
OUTCOME:

Identify, formulate, and solve simple engineering problems (such as expansion/compression and power cycles)

SL: Entropy of a Rev/irreversible Adiabatic Expansion/Compression

Entropy of a Rev/irreversible Adiabatic Expansion/Compression
EXAMPLE:

What is the entropy change of the system and surroundings in the (ir)reversible adiabatic expansion from P_1, T_1 to a final pressure P_2?

$$\Delta S = \int_{initial}^{final} \frac{\delta Q_{sys}}{T}$$

RECALL:

By definition adiabatic means $Q = 0$!

$$\Delta S_{sys_{rev}} = \Delta S_{surr_{rev}} = \Delta S_{univ_{rev}} = 0$$

For irreversible:

$$\Delta S_{surr} = 0$$

$$\Delta S_{sys} = \Delta S_{univ} \neq 0. \text{ Why?}$$

OUTCOME:

Identify, formulate, and solve simple engineering problems (such as expansion/compression and power cycles)
EXAMPLE:

Let's try it with numbers now.

*Compare the entropy change of the system, the surroundings, and the universe when you alternatively expand an ideal gas (assume $c_p = \frac{7}{2}R$) **adiabatically** by:*

- a reversible expansion from $P_1 = 2$ bar and $T_1 = 962$K to $P_2 = 1$ bar
- an irreversible expansion from $P_1 = 2$ bar and $T_1 = 962$K to $P_2 = 1$ bar and $T_2 = 820$K

SL: The entropy "balance" equations

Entropy equations: Open/Closed Integrated/Differential
CLOSED, DIFF:

$$nds - \frac{\delta Q}{T} = nds + \frac{\delta Q_{surr}}{T} \geq 0$$

CLOSED, INT:

$$\Delta S - \int \frac{\delta Q}{T} \geq 0$$

OPEN, DIFF:

$$\left(\frac{dS}{dt}\right)_{surr} + \left(\frac{dS}{dt}\right)_{sys} = \left(\frac{dS}{dt}\right)_{sys} + \sum_{out} \dot{n}_{out} s_{out} - \sum_{in} \dot{n}_{in} s_{in} + \frac{\dot{Q}_{surr}}{T_{surr}} \geq 0$$

OPEN, SS, 1IN/OUT:

$$\Delta S + \frac{\dot{Q}_{surr}}{T_{surr}} \geq 0$$

NOTE:

Often, we make an equality out of these expressions by calculating the (rate of) entropy generation, S_G, which must be greater than or equal to zero at all times.

OUTCOME:
Write both the integral and differential forms of the second law
OUTCOME:
Identify when the open and closed forms of the second law are applicable
OUTCOME:
Determine when each term in the second law is zero or negligible
TEST YOURSELF:
Calculate the rate of entropy generation for a steady flow process where 1 mol/s of air at 600K and 1 atm is continuously mixed with 2 mol/s of air at 450K and 1 atm to yield a stream of air at 400K and 1 atm. Take air to be an ideal gas with $c_P = 7/2R$ and the surroundings to be at 300K.

SL: Use tables to calculate entropy changes

Use tables to calculate entropy changes
RECALL:

Entropy is a state function! By the state postulate (and/or the Gibbs phase rule), it is uniquely determined once we know enough information (intensive variables) to fix the system's state.

OUTCOME:

Use tables to calculate entropy changes

TEST YOURSELF:

Superheated water vapor at a pressure of 200bar, a temperature of 500C, and a flow rate of 10 kg/s is brought to a saturated vapor state at 100bar by mixing it adiabatically with a stream of liquid water at 20C and 100bar. The flow rate of the liquid is 1.95 kg/s. What is the rate of entropy generation?

SL: Calculating entropy changes for ideal gases

Entropy calculations for ideal gases

For **one mole** of ideal gas undergoing a closed, reversible process:

$$dU = \delta Q_{rev} + \delta W = \delta Q_{rev} - PdV$$

Recall:

$$dH = dU + d(PV) = dU + PdV + VdP$$

Combining yields:

$$dH = \delta Q_{rev} - PdV + PdV + VdP = \delta Q_{rev} + VdP$$

$$\delta Q_{rev} = dH - VdP$$

Using $dH = c_P dT$ and $V = RT/P$ gives:

$$\delta Q_{rev} = c_P dT - \frac{RTdP}{P}$$

Dividing by T:

$$dS = \frac{\delta Q_{rev}}{T} = \frac{c_P dT}{T} - \frac{RdP}{P}$$

Integrating:

$$\frac{\Delta S}{R} = \int_{T_1}^{T_2} \frac{c_P}{R} \frac{dT}{T} - \ln\frac{P_2}{P_1}$$

Alternatively:

$$\frac{\Delta S}{R} = \int_{T_1}^{T_2} \frac{c_V}{R} \frac{dT}{T} + \ln\frac{V_2}{V_1} \text{ (Why?)}$$

NOTATION:

*Because ΔS is a state function, which is calculated from the reversible path anyway (for the system), and this equation depends only on state functions, **this equation is general for ideal gases**.*

OUTCOME:

Develop hypothetical reversible paths between two states in order to calculate entropy changes

Use the heat capacity to calculate entropy changes
TEST YOURSELF:

Use these expressions to calculate the entropy changes for each step of a carnot cycle operated between $P_1 = 2bar, P_2 = 1bar, P_3 = 0.05bar, and P_4 = 0.1bar$ and $T_1 = 1000K, T_2 = 1000K, T_3 = 300K, and T_4 = 300K$. (Assume $c_P = (5/2)R$.) Plot the results on a TS diagram.

SL: Entropy of Mixing (Ideal Gases)

Ideal Gas Mixtures

If you have n_i moles of each species (for example n_A moles of A), you can try to calculate the pressure or volume that that gas alone (i.e., ignoring the other gases that are around) exerts/occupies.

DEFINITION

Partial pressure refers to the pressure that would be exerted by a species (in a mixture) if there were no other species present.

DEFINITION

The pure component volume, V_A, refers to the volume that would be occupied by a species (in a mixture) if there were no other species present.

So, in an ideal gas mixture EACH COMPONENT satisfies the ideal gas law provided the partial pressure or pure component volumes are used!

$$p_A V = n_A RT$$

or

$$PV_A = n_A RT$$

In this way, the sum of the component pressures (partial pressures) or volumes (pure component volumes) should sum to the total pressure or volume:

$$p_A + p_B + ... = P$$
$$V_A + V_A + ... = V$$

This is easy to see if you divide either the partial pressure equation or the pure component volume equation by the ideal gas law for the total mixture:

$$\frac{p_A V = n_A RT}{PV = nRT}$$

$$\frac{PV_A = n_A RT}{PV = nRT}$$

Note that RT cancels in both equations and that V cancels in the first and P cancels in the second, also that $n_A / n = y_A$. We can then rearrange the result to get:

$$p_A = y_A P$$
$$V_A = y_A V$$

So The volume fraction (or pressure fraction) of an ideal gas is equal to the mol fraction! $(V_A/V = n_A/n)$

NOTE:

Since ideal gas molecules do not interact, isobaric mixing of ideal gases is effectively the same as reducing the pressure or specific volume of each component (since the partial pressure will be lowered). Not surprisingly, you simply use the same ideal gas expressions that we derived earlier.

TEST YOURSELF:

1 mol of nitrogen and 2 mol oxygen, both initially at 1 bar and 298 K are mixed at constant P and T in an insulated container. Find the entropy change of the system.

SL: Ideal Work in an Open System

To calculate the ideal/maximum amount of work that can be obtained from a open, steady-state fluid stream, one first performs a first law analysis:

$$\Delta \dot{H} = \dot{Q} + \dot{W}_s$$

The maximum work will be obtained from a reversible process, where we know the following will be true:

$$\Delta \dot{S} = \frac{\dot{Q}_{rev}}{T_{surr}}$$

or

$$Q_{rev} = T_{surr} \Delta \dot{S}$$

so

$$\dot{W}_{s_{ideal}} = \Delta \dot{H} - T_{surr} \Delta \dot{S}$$

DEFINITION:

*The **isentropic efficiency** is the ratio of the actual power obtained relative to the power that would be obtained in a reversible process.*

$$\eta_{isetropic} = \frac{\dot{W}_{actual}}{\dot{W}_{rev}} = \frac{\dot{W}_{actual}}{\dot{W}_{ideal}}$$

OUTCOME:

Correct reversible calculations for real systems using isentropic efficiencies

NOTE:

The isentropic efficiency of a power cycle (like a Rankine cycle) is the ratio of the actual power obtained in the cycle, relative to the power that would be obtained in a reversible power cycle.

TEST YOURSELF:

Calculate the maximum amount of work (i.e., the "ideal work") that can be obtained from a steady-state flow of N_2 at 800K and 50bar

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SL: Real Power Cycles

A more "realistic" power cycle: the ideal Rankine Cycle

The problem with compressing a mixture of liquid and vapor is that the work required to compress a liquid is considerably smaller than that of a vapor (or mixture). Why?
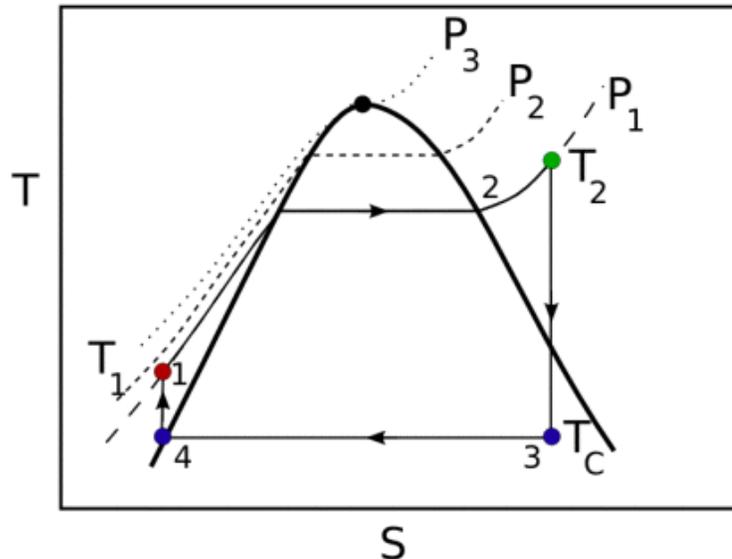
NOTE:

Again, the most convenient choice for the boiler operation is isobaric; therefore, the compression is typically to a sub-critical pressure.

OUTCOME:

Identify the key issues in choosing a working fluid

Obviously, the efficiency calculation used for a Carnot engine is no longer applicable. Why?

Instead we must explicitly calculate:

$$\eta = \frac{\dot{W}_{net}}{\dot{Q}_H} = \frac{|\dot{W}_{turbine}| - |\dot{W}_{compressor}|}{\dot{Q}_H}$$

OUTCOME:

Solve for the net power obtained and efficiency of reversible power cycles

OUTCOME:

Calculate the coefficient of performance of a reversible refrigeration cycle

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SL: A "mechanical" Energy Balance

A "mechanical" Energy Balance

Now that we are comfortable with both the first and the second law, it is often required that we combine them. Consider an open system that is at steady state and undergoing a reversible process.

The first law yields:

$$0 = -\dot{n}[d(h + e_k + e_p)] + \delta \dot{Q}_{sys} + \delta \dot{W}_s$$

The second law yields:

$$0 = \dot{n}ds + \frac{\delta \dot{Q}_{surr}}{T_{surr}} = \dot{n}ds - \frac{\delta \dot{Q}_{sys}}{T_{surr}}$$

Eliminating $\dot{Q}_{sys}$ gives:

$$0 = -\dot{n}[d(h + e_k + e_p)] + \dot{n}Tds + \delta \dot{W}_s$$

Solving for $\dot{W}_s$:

$$\frac{\dot{W}_s}{\dot{n}} = [dh - Tds + de_k + de_p]$$

Noting that for a reversible process:

$$du = \delta q_{rev} + \delta w_{rev} = Tds - Pdv$$

and that dh can be written as:

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

combining this with earlier:

$$\frac{\dot{W}_s}{\dot{n}} = [vdP + de_k + de_p]$$

which, for 1in/1out gives:

$$\frac{\dot{W}_s}{\dot{n}} = \int vdP + (e_{k_2} - e_{k_1}) + + (e_{p_2} - e_{p_1})$$

NOTE:

This is related to the Bernoulli equation (when $W_s = 0$).

TEST YOURSELF:

Calculate the work extracted from a turbine that is fed an ideal gas at 250 mol/s at 125 bar and a volume of 500 cm³/mol. The final pressure is 8 bar. Take $c_P = \frac{7}{2}R$

SL: Entropy and Spontaneity/Equilibrium

Entropy and Spontaneity/Equilibrium

Positive Entropy change of the universe → spontaneous process

For equilibrium: $dS_{univ} →$ "maximum"

$$dS_{univ} = dS_{sys} + dS_{surr} = dS_{sys} + \frac{\delta Q_{surr}}{T_{surr}} = dS_{sys} - \frac{\delta Q_{sys}}{T_{surr}} \geq 0$$

- Closed System: Constant T,V
- ◦ First Law: $dU = \delta Q_{rev} + \delta W_{rev} \rightarrow dU = \delta Q_{rev}$
  - ◦ Second Law: $dS_{sys} - \frac{Q_{sys}}{T_{surr}} = dS_{sys} - \frac{dU}{T_{surr}} \geq 0$
    - (constant T) $T_{surr} = T_{sys}$
    - $T_{sys}dS_{sys} - dU \geq 0$
    - (constant T) $d(T_{sys}S_{sys}) = T_{sys}dS_{sys} + S_{sys}dT_{sys} = T_{sys}dS_{sys}$
    - For equilibrium: $d(T_{sys}S_{sys} - U) \geq 0$

DEFINITION:

*The **Helmholtz Free Energy**, A, is defined as $A \equiv U - TS$.*
- For equilibrium: $dA \leq 0$ ("minimum")

- Closed System: Constant T,P
- ◦ First Law: $dU = \delta Q_{rev} + \delta W_{rev} \rightarrow dU = \delta Q_{rev} - PdV$
  - ◦ Second Law: $dS_{sys} - \frac{Q_{sys}}{T_{surr}} = dS_{sys} - \frac{dU + PdV}{T_{surr}} \geq 0$
    - (constant T) $T_{surr} = T_{sys}$
    - $T_{sys}dS_{sys} - (dU + PdV) \geq 0$
    - (constant T) $d(T_{sys}S_{sys}) = T_{sys}dS_{sys} + S_{sys}dT_{sys} = T_{sys}dS_{sys}$
    - (constant P) $d(PV) = PdV + VdP = PdV$, so $(dU + PdV) = dH$
    - For equilibrium: $d(T_{sys}S_{sys} - H) \geq 0$

DEFINITION:

*The **Gibbs Free Energy**, G, is defined as $G \equiv H - TS$.*
- For equilibrium: $dG \leq 0$ ("minimum")