

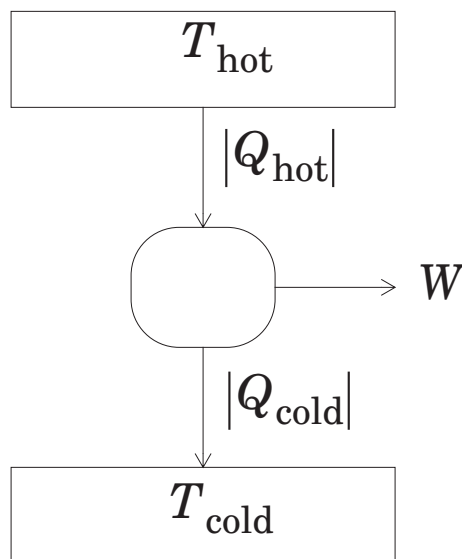
## Second Law of Thermodynamics

No apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat absorbed by a system completely into work.

It is impossible by a cyclic process to convert the heat absorbed by a system completely into work.

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

Imagine two isothermal heat reservoirs (they can absorb or provide an infinite amount of heat at a constant temperature) at temperatures  $T_{\text{hot}}$  and  $T_{\text{cold}}$ . Let's extract an amount of heat  $Q_{\text{hot}}$  from the hot reservoir and convert as much of the heat as possible into work and reject the remaining heat,  $Q_{\text{cold}}$ , into the cold reservoir. What is the maximum possible amount of work? What is the minimum amount of heat rejected?



Any engine which operates between these two reservoirs and produces the greatest possible work while rejecting the minimum amount of heat is called a Carnot engine. The efficiency of a Carnot engine is:

$$\eta \equiv \frac{W}{Q_{\text{hot}}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}.$$

What is the relationship between  $Q_{\text{hot}}$  and  $Q_{\text{cold}}$ ? Assume a cyclic process on a closed system with negligible kinetic and potential energy changes.

First law

$$\Delta U = Q - W = 0$$

$$W = Q_{\text{hot}} + Q_{\text{cold}}$$

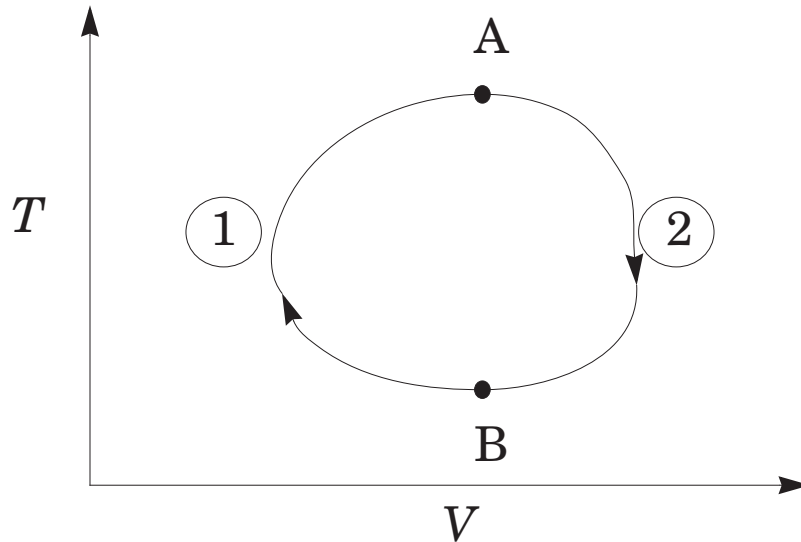
Combining with the efficiency

$$\frac{Q_{\text{hot}} + Q_{\text{cold}}}{Q_{\text{hot}}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$

Or

$$\frac{Q_{\text{hot}}}{T_{\text{hot}}} = -\frac{Q_{\text{cold}}}{T_{\text{cold}}}$$

Imagine an actual reversible cycle



Approximate the cycle with infinitesimal Carnot engines

$$\frac{dQ_{\text{hot}}}{dT_{\text{hot}}} + \frac{dQ_{\text{cold}}}{dT_{\text{cold}}} = 0$$

Integrate over all

$$\oint \frac{dQ}{T} = 0$$

Why?

Note that if the loop integral is zero,

$$\int_A^B \frac{dQ}{T} = \int_A^B \frac{dQ}{T}.$$

What kind of function is independent of path?

Let us define a new state function, called *entropy*.

$$\Delta S = \int_A^B \frac{dQ_{\text{Carnot}}}{T}$$

or

$$dS = \frac{dQ_{\text{Carnot}}}{T}.$$

If

$$Q \neq Q_{\text{Carnot}}$$

then

$$dS = \frac{dQ}{T} + \frac{dW_{\text{lost}}}{T}$$

Since  $S$  is a state function, any path can be used to evaluate  $\Delta \hat{S}$ .

## Mathematical Statement of the Second Law:

$$dW_{\text{lost}} \geq 0$$

or

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

$S$  can be thought of as the reversible normalized heat transfer or as the degree of randomness or disorder.

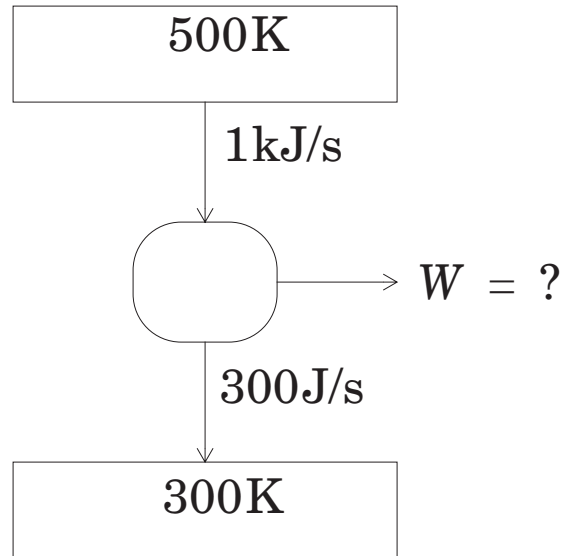
Remember:

$\Delta S_{\text{system}}$  or  $\Delta S_{\text{surroundings}}$  can be less than zero. But

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

What is  $\Delta S$  for a cyclic process?

**Example:** Analyze the following process. Is it possible?



## First Law

Closed system

$$\Delta U = 0 = Q - W$$

$$Q = 1 \text{ kJ} - 300 \text{ J}$$

$$0 = 700 \text{ J} - W$$

$$W = 700 \text{ J}$$

## Second Law

$$\Delta S_{\text{system}} = 0, \text{ Why?}$$

$$\Delta S_{\text{surroundings}} = ?$$

$$\Delta S_{500 \text{ K reservoir}} = \frac{-1000 \text{ J/s}}{500 \text{ K}} = -2 \frac{\text{J}}{\text{Ks}} = -2 \frac{\text{W}}{\text{K}}$$

$$\Delta S_{300 \text{ K reservoir}} = \frac{300 \text{ J/s}}{300 \text{ K}} = 1 \frac{\text{W}}{\text{K}}$$

$$\Delta S_{\text{total}} = 0 + (-2) + (1) = -1 \frac{\text{W}}{\text{K}} < 0$$

What is the maximum possible work?

## Calculation of $\Delta\hat{S}$ for an ideal gas

Assume closed system of  $n$  moles initially at  $T_1, P_1$  and finally at  $T_2, P_2$

First law

$$dU = dQ - dW$$

$$d\hat{U} = \frac{dQ}{n} - \frac{dW}{n}$$

Now follow a reversible path (why?).

$$d\hat{U} = C_v dT$$

$$dS = \frac{dQ}{T} \text{ or } Td\hat{S} = \frac{dQ}{n}$$

$$dW = PdV \text{ or } \frac{dW}{n} = Pd\hat{V}$$



Combining

$$C_v dT = T d\hat{S} - P d\hat{V}$$

$$d\hat{S} = \frac{C_v}{T} dT + \frac{P}{T} d\hat{V} = \frac{C_v}{T} dT + \frac{R}{\hat{V}} d\hat{V}$$

$$\Delta\hat{S} = \int_{T_1}^{T_2} \frac{C_v}{T} dT + \int_{\hat{V}_1}^{\hat{V}_2} \frac{R}{\hat{V}} d\hat{V} = \int_{T_1}^{T_2} \frac{C_v}{T} dT + R \ln \frac{\hat{V}_2}{\hat{V}_1}$$

Alternately

$$\Delta\hat{S} = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{T_1}^{T_2} \frac{R}{T} dT + R \ln \frac{\hat{V}_2}{\hat{V}_1}$$

$$= \int_{T_1}^{T_2} \frac{C_p}{T} dT - R \ln \frac{T_2 \hat{V}_1}{\hat{V}_2 T_1} = \int_{T_1}^{T_2} \frac{C_p}{T} dT - R \ln \frac{P_2}{P_1}$$

What is the minimum work required for an adiabatic compressor to compress 10 kg/s of air from 2kPa & 300 K to 6MPa? (Assume ideal gas,  $C_p = (7/2)R$ )

### First law (neglect kinetic & potential)

$$\Delta H = \overset{0}{\cancel{Q}} - W_s$$

$$m \int C_p dT = -W_s \approx m C_p \Delta T$$

### Second law

$$\Delta S_{\text{surroundings}} = 0. \text{ Why?}$$

$$\Delta \hat{S}_{\text{air}} = \int \frac{C_p}{T} dT - R \ln \frac{P_2}{P_1} \approx C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Minimum work for  $\Delta\hat{S} = 0$

$$R \ln \frac{P_2}{P_1} = C_p \ln \frac{T_2}{T_1}$$

$$\left(\frac{P_2}{P_1}\right)^{\frac{R}{C_p}} = \frac{T_2}{T_1}$$

$$T_2 = T_1 \left(\frac{6000 \text{ kPa}}{2 \text{ kPa}}\right)^{2/7}$$

$$-W_s = m C_p \Delta T$$

$$= \frac{10000 \text{ g/s}}{29 \text{ g/g-mol}} \left(\frac{7}{2}\right) (8.3145 \text{ J/g-mol K}) \left[\left(\frac{6000}{2}\right)^{2/7} - 1\right] (300 \text{ K})$$

$$= 26.64 \text{ MW}$$

## Calculation of $\Delta S$ for substances other than ideal gases

$$d\hat{S} = C_p \frac{dT}{T} - \left. \frac{\partial \hat{V}}{\partial T} \right|_P dP$$

or

$$d\hat{S} = C_p \frac{dT}{T} - \beta \hat{V} dP$$

where the volume expansivity (like a thermal expansion coefficient) is

$$\beta \equiv \left. \frac{1}{\hat{V}} \frac{\partial \hat{V}}{\partial T} \right|_P .$$

It is usually small for things other than gases.

## Air-standard Carnot cycle

### Carnot cycle

- 1) Adiabatic compression from  $T_{\text{cold}}$  to  $T_{\text{hot}}$ .
- 2) Isothermal heat addition.
- 3) Adiabatic expansion from  $T_{\text{hot}}$  to  $T_{\text{cold}}$ .
- 4) Isothermal heat removal.

For air-standard assume:

A) Ideal Gas

B)  $C_v = \frac{5}{2}R$

### For step 1

Closed system adiabatic reversible.

1st law

$$\Delta U = -W$$

$$nC_v \Delta T = -W$$

$$W = nC_v(T_{\text{cold}} - T_{\text{hot}})$$

How about  $P$  and  $\hat{V}$ ?

If  $\Delta S = 0$  (Why?)

$$\left(\frac{P_{\text{hot}}}{P_{\text{cold}}}\right)^{\frac{R}{C_p}} = \frac{T_{\text{hot}}}{T_{\text{cold}}}$$

$$P\hat{V} = RT$$

So

$$\frac{\hat{V}_1}{\hat{V}_2} = \left(\frac{P_2}{P_1}\right)^{\frac{C_p - R}{C_p}}$$

or

$$P_1(\hat{V}_1^\gamma) = P_2(\hat{V}_2^\gamma) = \text{constant}$$

where

$$\gamma \equiv \frac{C_p}{C_v} = \frac{C_p}{C_p - R}$$

## For Step 2

1st law

closed system isothermal

$$\Delta U = Q - W$$

$$\Delta U = 0 \text{ Why?}$$

$$Q = W$$

$$W = n \int P d\hat{V}$$

Since

$$P = \frac{RT}{\hat{V}}$$

$$W = nRT \int \frac{d\hat{V}}{\hat{V}}$$

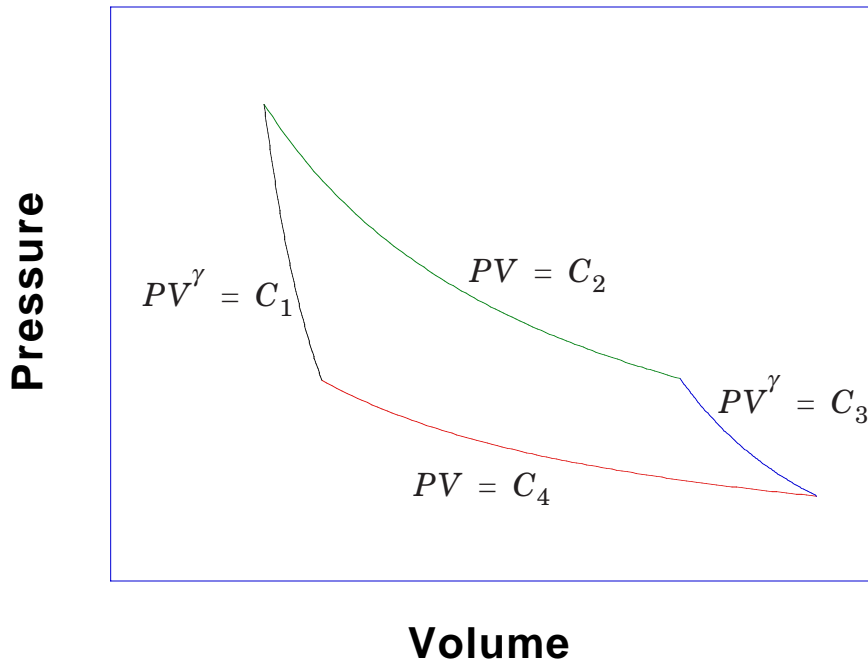
$$= nRT \ln \frac{\hat{V}_f}{\hat{V}_i} = nRT \ln \frac{P_i}{P_f} = Q$$

## Adiabatic expansion

$$W = nC_v(T_{\text{hot}} - T_{\text{cold}})$$

## Isothermal cooling

$$W = nRT \ln \frac{\hat{V}_f}{\hat{V}_i} = nRT \ln \frac{P_i}{P_f} = Q$$



Note that

$$\frac{P_b}{P_a} = \left( \frac{T_{\text{hot}}}{T_{\text{cold}}} \right)^{\frac{C_p}{R}}$$

and



$$\frac{P_c}{P_d} = \left( \frac{T_{\text{hot}}}{T_{\text{cold}}} \right)^{\frac{C_p}{R}}$$

so

$$\frac{P_b}{P_a} = \frac{P_c}{P_d}$$

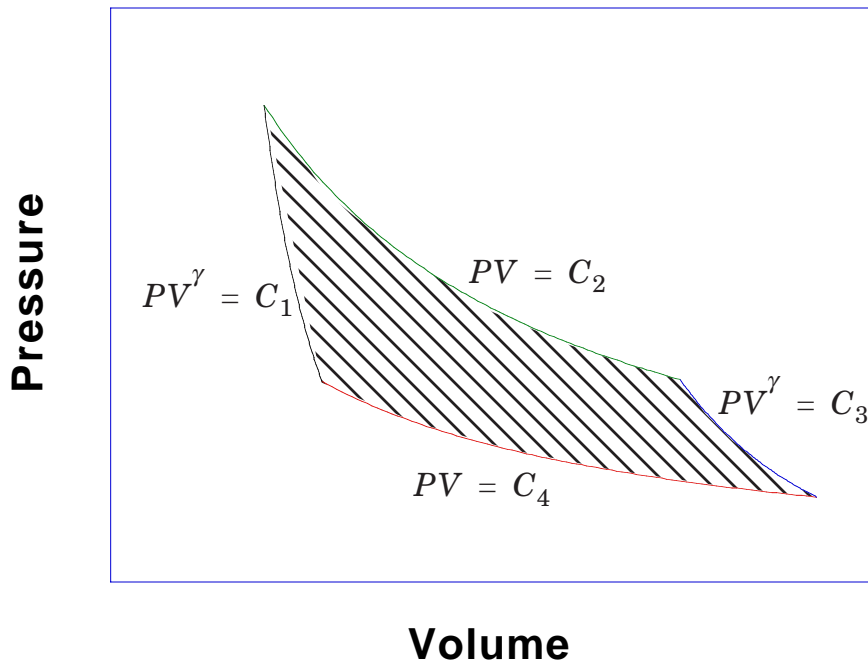
or rearranged

$$\frac{P_d}{P_a} = \frac{P_c}{P_b}$$

$$\begin{aligned} \frac{W_{\text{net}}}{n} &= C_v(T_{\text{cold}} - T_{\text{hot}}) + RT_{\text{hot}} \ln \frac{P_b}{P_c} \\ &\quad + C_v(T_{\text{hot}} - T_{\text{cold}}) + RT_{\text{cold}} \ln \frac{P_d}{P_a} \\ &= R(T_{\text{hot}} - T_{\text{cold}}) \ln \frac{P_b}{P_c} \\ \frac{Q_{\text{hot}}}{n} &= RT_{\text{hot}} \ln \frac{P_b}{P_c} \end{aligned}$$

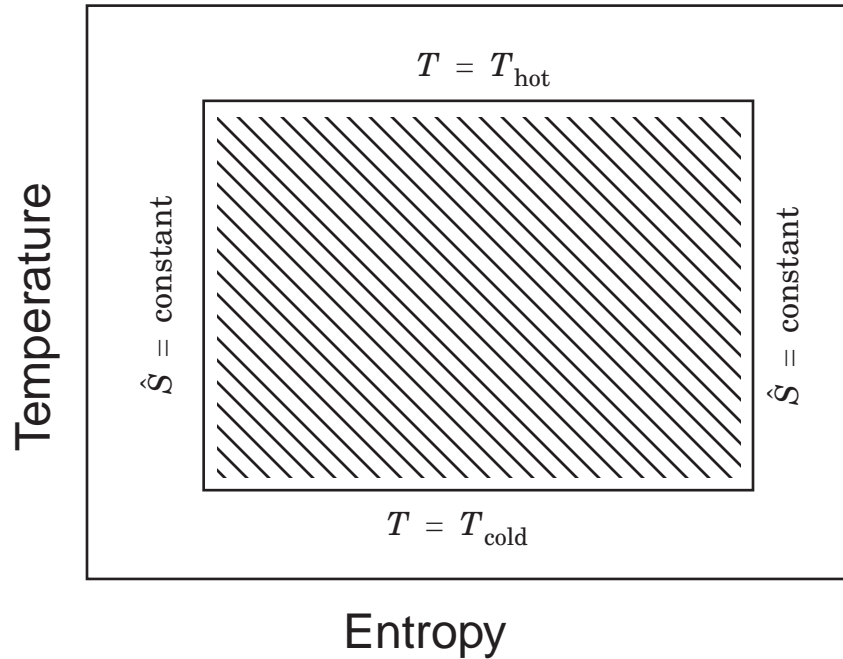
$$\eta = \frac{W_{\text{net}}}{Q_{\text{hot}}} = \frac{R(T_{\text{hot}} - T_{\text{cold}}) \ln \frac{P_b}{P_c}}{RT_{\text{hot}} \ln \frac{P_b}{P_c}} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$

Note area enclosed on  $P\hat{V}$  diagram is net work



What does a Carnot cycle look like on a T-S diagram?

## TS diagram



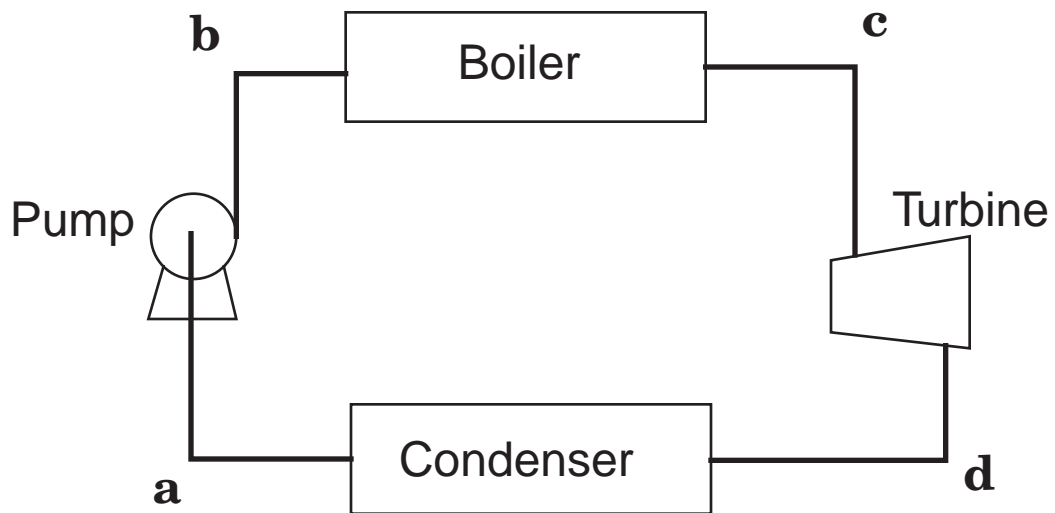
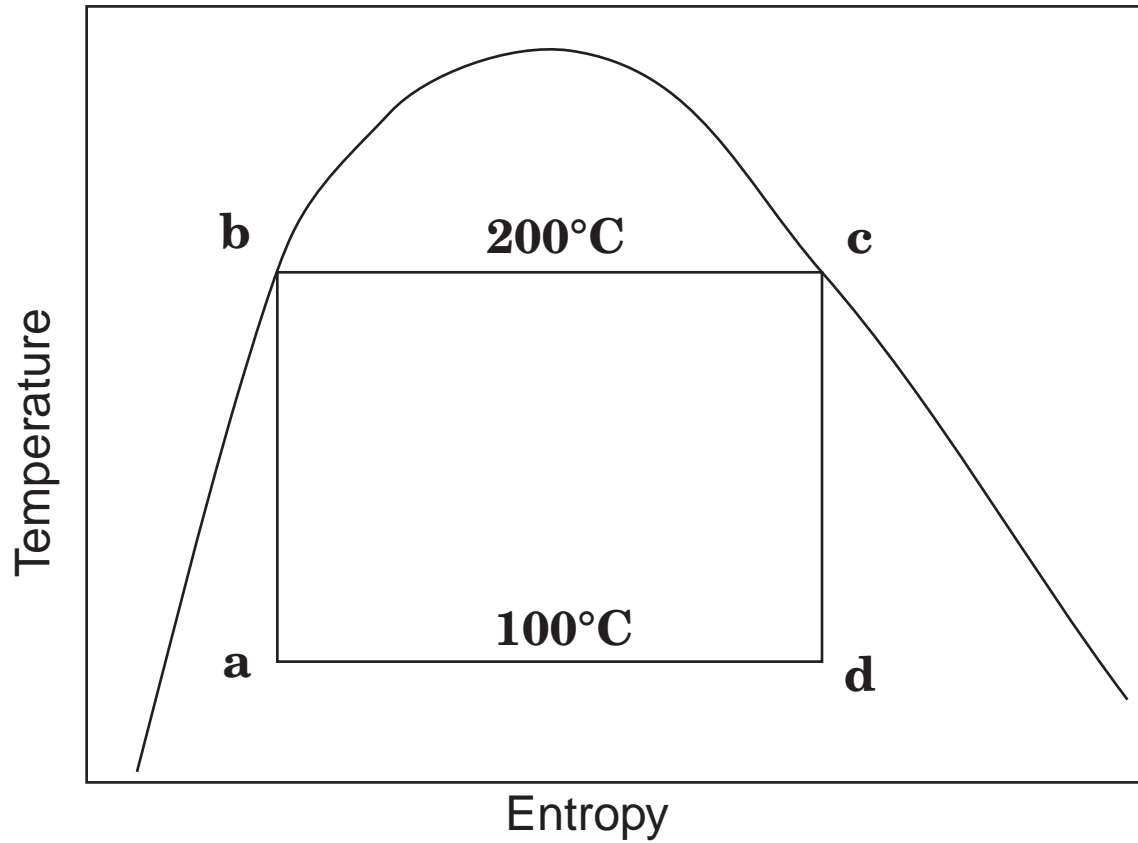
$$\text{enclosed area} = Q_{\text{net}}$$

For cycle

$$W_{\text{net}} = Q_{\text{net}}$$

The Carnot efficiency does not depend on the working fluid.

# Carnot steam cycle



## Boiler

1st law

$$\Delta H = Q = \dot{m}\Delta\hat{H} = \dot{m}(2792.0 - 852.3)$$

## Turbine

1st law

$$\Delta H = -W_s = \dot{m}\Delta\hat{H} = ?$$

2nd law

$$\Delta S = 0 = \dot{m}\Delta\hat{S}$$

so

$$\hat{S}_d = \hat{S}_c$$

$$\hat{S}_c = \hat{S}(\text{vapor}, 200^\circ\text{C}) = 6.4302$$

$$\hat{S}(\text{liquid}, 100^\circ\text{C}) = 1.3072$$

$$\hat{S}(\text{vapor}, 100^\circ\text{C}) = 7.3541$$

What is the specific entropy of a mixture of steam and water?

Define the mole- or mass-fraction of steam as the quality.

$$\text{quality} = x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

Then the specific entropy of a mixture is:

$$\hat{S}_{\text{mixture}} = x\hat{S}_v + (1 - x)\hat{S}_l$$

In our case

$$6.4302 = x(7.3541) + (1 - x)(1.3072)$$

$$x = \frac{(6.4302 - 1.3072)}{(7.3541 - 1.3072)} = 0.84721097$$

To calculate the enthalpy at point **d**

$$\hat{H} = x\hat{H}_v + (1 - x)\hat{H}_l$$

$$\hat{H}_{\mathbf{d}} = 2330.8$$

By a similar process

$$x(\text{at point a}) = 0.1692$$

$$\hat{H}_{\mathbf{a}} = 801.0$$

$$\eta = \frac{|Q_{\text{hot}}| - |Q_{\text{cold}}|}{|Q_{\text{hot}}|} = \frac{(2792.0 - 852.3) - (2330.8 - 801.0)}{(2792.0 - 852.3)}$$

$$\eta = 0.21132134$$

From formula for Carnot Efficiency

$$\eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} = 1 - \frac{373.15}{473.15} = 0.21134947$$

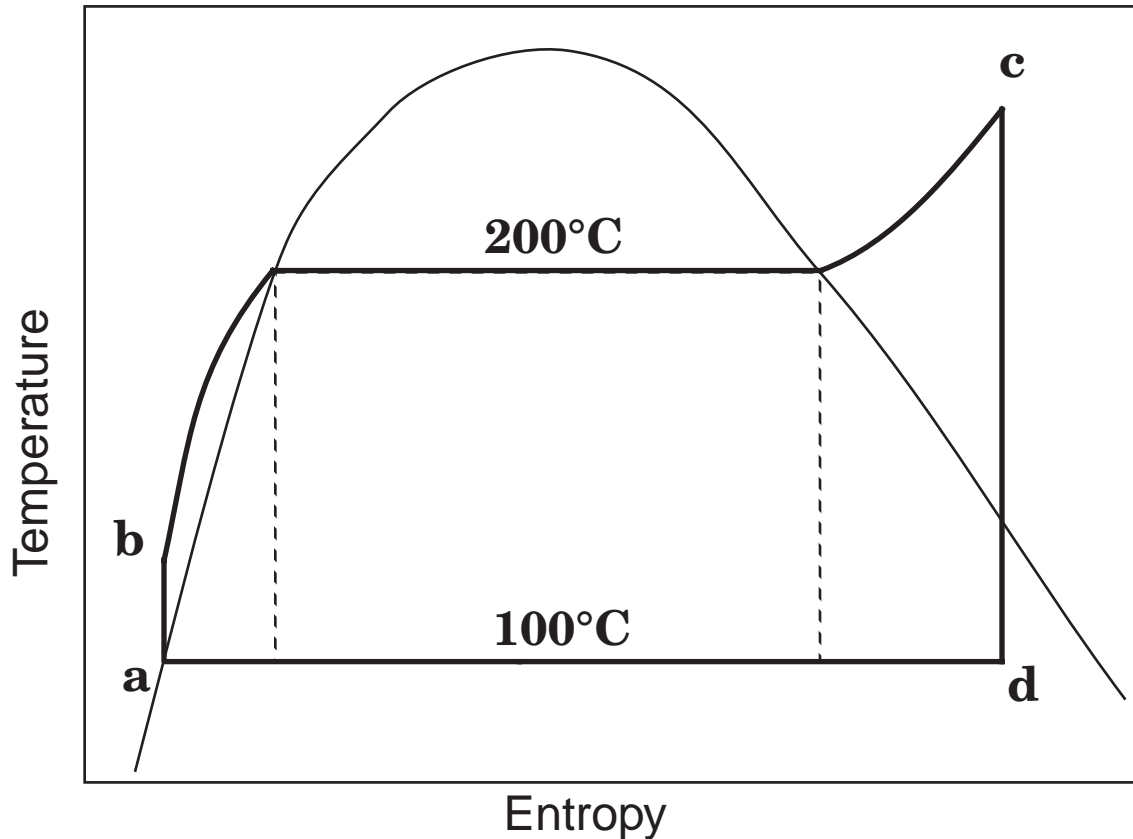
$$W_{\text{net}} = 409.9$$

$$Q_{\text{hot}} = 1939.7$$

$$Q_{\text{cold}} = -1529.8$$

What are the engineering problems with the Steam Carnot cycle?

## The Rankine cycle



The process from **b** to **c** is now isobaric instead of isothermal.

Pump from **a** to **b** now only compresses liquid.

$$\Delta H_{\text{pump}} = -W_s = V\Delta P$$

Why?

Recall

$$d\hat{U} = Td\hat{S} - Pd\hat{V}$$

and

$$d\hat{H} = d\hat{U} + Pd\hat{V} + \hat{V}dP$$



$$d\hat{U} = d\hat{H} - Pd\hat{V} - \hat{V}dP$$

So

$$d\hat{H} - Pd\hat{V} - \hat{V}dP = Td\hat{S} - Pd\hat{V}$$

or

$$d\hat{H} = Td\hat{S} + \hat{V}dP$$

Second law on pump (adiabatic and reversible)

$$\Delta S = 0$$

so

$$d\hat{S} = 0$$

For liquids  $\hat{V}$  is a very weak function of pressure.

$$\int d\hat{H} = \int \hat{V}dP = \hat{V} \int dP$$

$$\Delta H = V\Delta P$$

## Rankine Cycle Example

A steam power plant operates with steam entering the turbine at 80 bar and 500°C. The condenser operates at 44°C. Calculate the thermal efficiency. What is the water circulation rate for a net power generation of 80 kW?

Data needed from the steam tables

@ 44°C and 0.091124 bar:  $\hat{H}_l$ ,  $\hat{H}_v$ ,  $\hat{S}_l$ ,  $\hat{S}_v$ ,  $\hat{V}_l$

@ 500°C and 80 bar:  $\hat{H}$ ,  $\hat{S}$

At 44°C and 0.091124 bar

$$\hat{V}_l = 0.0010095 \frac{\text{m}^3}{\text{kg}}$$

$$\hat{H}_l = 184.25 \frac{\text{kJ}}{\text{kg}}$$

$$\hat{H}_v = 2580.6 \frac{\text{kJ}}{\text{kg}}$$

$$\hat{S}_l = 0.62545 \frac{\text{kJ}}{\text{kg K}}$$

$$\hat{S}_v = 8.1815 \frac{\text{kJ}}{\text{kg K}}$$

At 500°C and 80 bar

$$\hat{H} = 3399.5 \frac{\text{kJ}}{\text{kg}}$$

$$\hat{S} = 6.7266 \frac{\text{kJ}}{\text{kg K}}$$

## Pump

$$-W_s = \Delta H = V \Delta P$$

$$= 0.0010095 \frac{\text{m}^3}{\text{kg}} (8000 \text{ kPa} - 9.1124 \text{ kPa}) = 8.066801 \frac{\text{kJ}}{\text{kg}}$$

$$\hat{H}_b = \hat{H}_a + \Delta \hat{H} = 184.25 \frac{\text{kJ}}{\text{kg}} + 8.067 \frac{\text{kJ}}{\text{kg}} = 192.317 \frac{\text{kJ}}{\text{kg}}$$

## Boiler

$$\Delta H = Q = \hat{H}_c - \hat{H}_b = 3399.5 \frac{\text{kJ}}{\text{kg}} - 192.317 \frac{\text{kJ}}{\text{kg}} = 3207.183 \frac{\text{kJ}}{\text{kg}}$$

## Turbine

$$-W_s = \Delta H$$

$$\Delta S = 0$$

$$6.7266 = 8.1815x + (0.62545)(1 - x)$$

$$x = \frac{6.10115}{7.55605} = 0.80745231$$

$$\hat{H}_d = x\hat{H}_v + (1 - x)\hat{H}_l$$

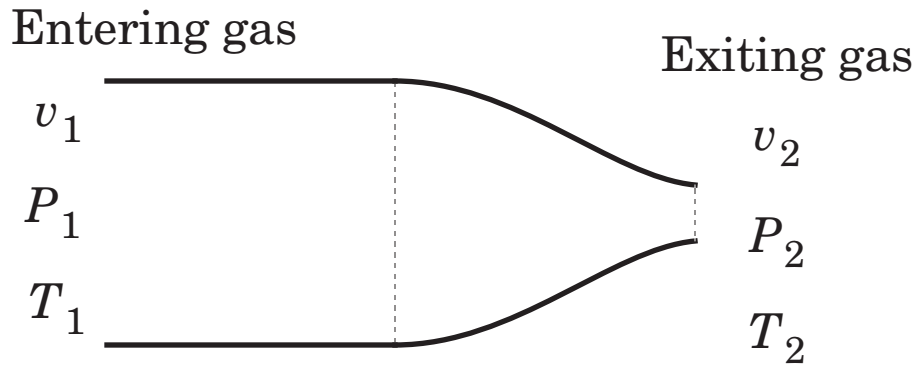
$$= 0.8075 \left( 2580.6 \frac{\text{kJ}}{\text{kg}} \right) + (1 - 0.8075) \left( 184.25 \frac{\text{kJ}}{\text{kg}} \right) = 2119.3 \frac{\text{kJ}}{\text{kg}}$$

$$\Delta H = 2119.3 \frac{\text{kJ}}{\text{kg}} - 3399.5 \frac{\text{kJ}}{\text{kg}} = -1280.2 \frac{\text{kJ}}{\text{kg}}$$

## Efficiency

$$\eta = \frac{W_{\text{net}}}{Q_{\text{hot}}} = \frac{1280.2 \frac{\text{kJ}}{\text{kg}} - 8.067 \frac{\text{kJ}}{\text{kg}}}{3207.183 \frac{\text{kJ}}{\text{kg}}} = 0.3966512 = 39.7\%$$

## Ideal Nozzle with Ideal Gas



The point of a nozzle is to get a huge increase in velocity.

### 1st Law

$$\Delta H + \Delta E_k = \overset{0}{\cancel{Q}} - \overset{0}{\cancel{W}_s}$$

$$\Delta \hat{H} + \frac{\Delta(v^2)}{2g_c} = 0$$

### 2nd Law

Assume  $C_p = \text{constant}$ .

$$\Delta \hat{S} = 0 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Then

$$C_p \ln \frac{T_2}{T_1} = R \ln \frac{P_2}{P_1}$$

or

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_p}}$$

Substitute in for  $\Delta T$ .

$$\Delta\hat{H} = C_p\Delta T = C_p(T_2 - T_1) = C_p T_1 \left[ \left(\frac{P_2}{P_1}\right)^{R/C_p} - 1 \right]$$

$$v_2^2 - v_1^2 = 2g_c C_p \Delta T = 2g_c C_p T_1 \left[ 1 - \left(\frac{P_2}{P_1}\right)^{R/C_p} \right]$$