Ideal Gases and the 2nd Law
(Understanding Engineering Thermo—Octave Levenspiel)

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BATCH OF IDEAL GAS

- Recall the 1st and 2nd law,

$$d\!\!\;E \quad = \quad d\!\!\!/\,Q \quad + \quad d\!\!\!/\,W$$

$$d\,S \quad = \quad (\,1\,/\,T\,)\,d\,E \quad - \quad (\,\underline{f}\,/\,T\,) \;\cdot\; d\,\underline{X}$$

- therefore,

$$\boxed{\Delta S = \int \frac{dQ_{rev}}{T}}$$

- Constant volume process

$$W_{rev} \quad = \quad 0\,, \quad \boxed{Q \;=\; \Delta U}$$

$$\Delta S = \int \frac{dQ_{rev}}{T} = \int \frac{nc_v dT}{T} = nc_v \ln\frac{T_2}{T_1} = nc_v \ln\frac{p_2}{p_1}$$

- Constant pressure process

$$W_{rev} = \int p\,dv = p\,\Delta v = nR\,\Delta T$$

$$\Delta U = nc_v\,\Delta T$$

$$Q_{rev} = \Delta U + W_{rev} = nc_v\Delta T + nR\,\Delta T = nc_p\,\Delta T$$

$$\Delta S = \int \frac{dQ_{rev}}{T} = \int \frac{nc_p dT}{T} = nc_p\ln\frac{T_2}{T_1} = nc_p\ln\frac{v_2}{v_1}$$

$$W_{rev} = nR\left(T_2 - T_1\right)$$

- Constant temperature process

$$Q_{rev} = W_{rev} = \int p\,dv$$

$$dQ_{rev} = p\,dv = \frac{nRT}{V}\,dv$$

$$\Delta S = \int \frac{dQ_{rev}}{T} = \int \frac{nRT}{vT}\,dv = nR\ln\frac{v_2}{v_1} = -nR\ln\frac{p_2}{p_1}$$

$$W_{rev} = -nR\ln\frac{p_2}{p_1}$$

- Going from $p_1 \, v_1 \, T_1$ to $p_2 \, v_2 \, T_2$ in general
  - Constant p_1, T_1 to T_2
  - Constant T_2, p_1 to p_2

  This is specific, why ?

- Recall

$$\Delta S = \int \frac{dQ_{rev}}{dT} = \int \frac{nc_p dT}{T} = nc_p \ln \frac{T_2}{T_1} = nc_p \ln \frac{v_2}{v_1} \quad \boxed{\textbf{Const p}}$$

$$\Delta S = \int \frac{dQ_{rev}}{dT} = \int \frac{nRT}{vT} dv = nR \ln \frac{v_2}{v_1} = -nR \ln \frac{p_2}{p_1} \quad \boxed{\textbf{Const T}}$$

- Therefore,

$$\boxed{\Delta S = nc_p \ln \frac{T_2}{T_1} - nR \ln \frac{p_2}{p_1}} \qquad \boxed{\Delta S = nc_v \ln \frac{T_2}{T_1} + nR \ln \frac{v_2}{v_1}}$$

$$\boxed{\Delta S = nc_v \ln \frac{p_2}{p_1} + nc_p \ln \frac{v_2}{v_1}}$$

- Reversible work

- Going from p_1 T_1 to p_2 T_2 , one can take various paths, two are as follow,

  - Constant p_1, T_1 to T_2 + Constant T_2, p_1 to p_2
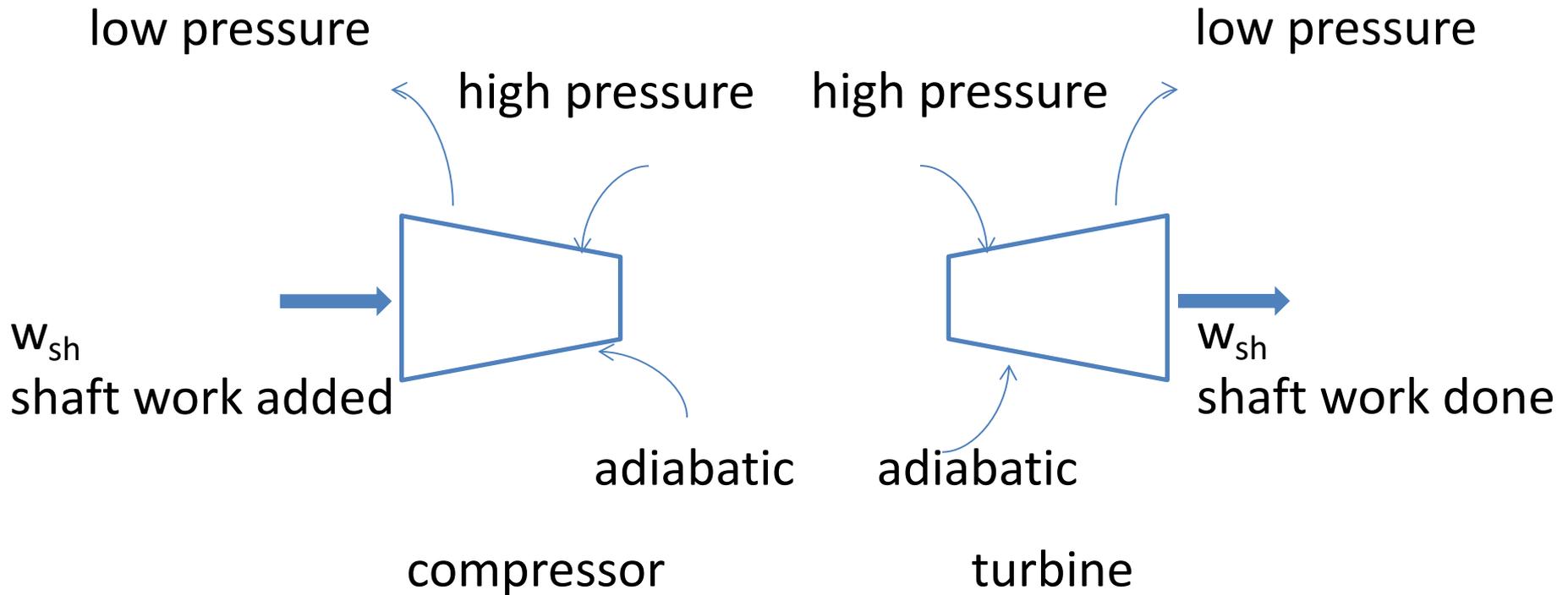 - Constant T_1, p_1 to p_2 + Constant p_2, T_1 to T_2

$$W_{1+2} = nR(T_2 - T_1) - nRT_2 \ln \frac{p_2}{p_1}$$

$$W_{3+4} = -nRT_1 \ln \frac{p_2}{p_1} + nR(T_2 - T_1)$$

  - they are clearly different—path dependent ! So is the heat !
  - However, $\Delta S = \int \frac{dQ_{rev}}{dT}$ is independent of the path taken

- Adiabatic reversible processes (Q = 0; ΔS = 0)

low pressure

high pressure　　high pressure

low pressure

w_{sh}
shaft work added

adiabatic　　adiabatic

compressor

w_{sh}
shaft work done

turbine

- From 1st law

$q_{actual} = 0$

- And flow systems
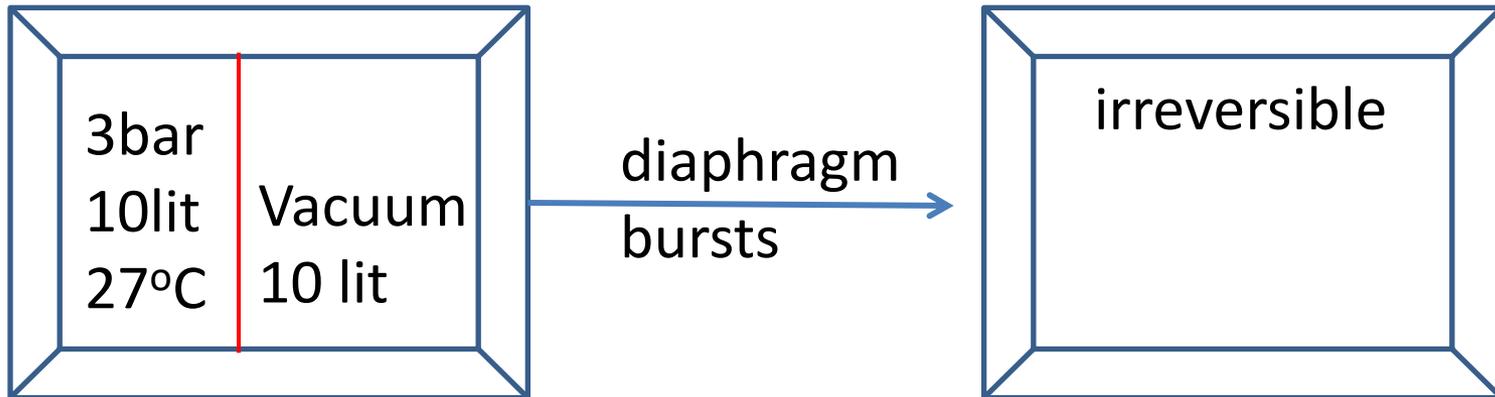
$- w_{sh} = \Delta h + \Delta e_p + \Delta e_k$

- From 2nd law

$$\Delta s = \int \frac{dq_{rev}}{T} = 0$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{(k-1)}{k}}$$

Example I

- Rupture of a diaphragm in an insulated tank
- Find ΔS for this process

- From the 1st law, $Q = 0$ and $W = 0$

- Therefore $\Delta U = 0$, so for ideal gas, $T_{final} = 300$ K, $V_{final} = 20$ lit, $p_{final} = 1.5$ bar and $n = 1.2$ mol

$$Q_{rev} = W_{rev} = nRT\ln\frac{V_{final}}{V_{initial}}$$

$$\Delta S = \int \frac{dQ_{rev}}{dT} = nR\ln\frac{V_{final}}{V_{initial}}$$

$$= (1.2\,\text{mol}) \left(8.314\,\frac{J}{mol \cdot K}\right)\ln\frac{20}{10} = 6.92\ JK^{-1}$$

- $Q_{actual} = 0$ because the process is adiabatic and irreversible. We had to devise a reversible path and use the Q_{rev} for ΔS. $Q_{rev} \neq 0$.

Example II

- Making money from wasted air

- Presently, high-pressure air (v=20 lit/s, T=300 K, p=10 atm) is vented to one atmosphere.

- We considering installing a turbine with an electricity generator to recover some of the available energy presently being lost.

- Find the ideal power generated for adiabatic reversible operations of the turbine, and the money recovered per 30 day month, if energy is worth 7¢/kWhr.

v=20 lit/s
$T_1 = 300\ K$
$p_1 = 10$ atm

$T_2 = ?$
$P_2 = 1$ atm

w_{sh} ?

adiabatic

- For adiabatic reversible

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{(k-1)}{k}}$$

$$= 300\left(\frac{1}{10}\right)^{\frac{0.4}{1.4}} = 155\ K$$

$$\dot{W}_{rev} = -\Delta\dot{H}$$

$$= -\dot{n}c_p(T_2 - T_1) = 34283\,W$$

$$= (34283\,W)\left(\frac{3600 \times 24 \times 30\,s}{month}\right)$$

$$\left(\frac{0.2778\ kW \cdot hr}{10^6\ J}\right) = \$1728/month$$
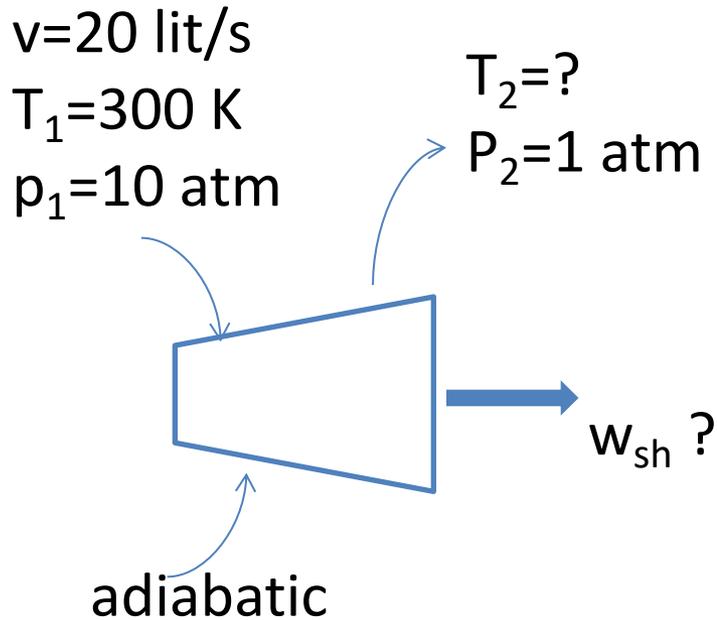
- The molar flow rate

$$n = \frac{p\dot{v}}{RT}$$

$$= \frac{(1013250)(0.020)}{(8.314)(300)}$$

$$= 8.125\ mol \cdot s^{-1}$$

- T_2=155 K, which is very cold, this leads us to suspect.

- How about a reversible isothermal expansion ?

v=20 lit/s
T_1=300 K
p_1=10 atm

T_2= T_1
P_2=1 atm

w_{sh} ?

Q_{in}
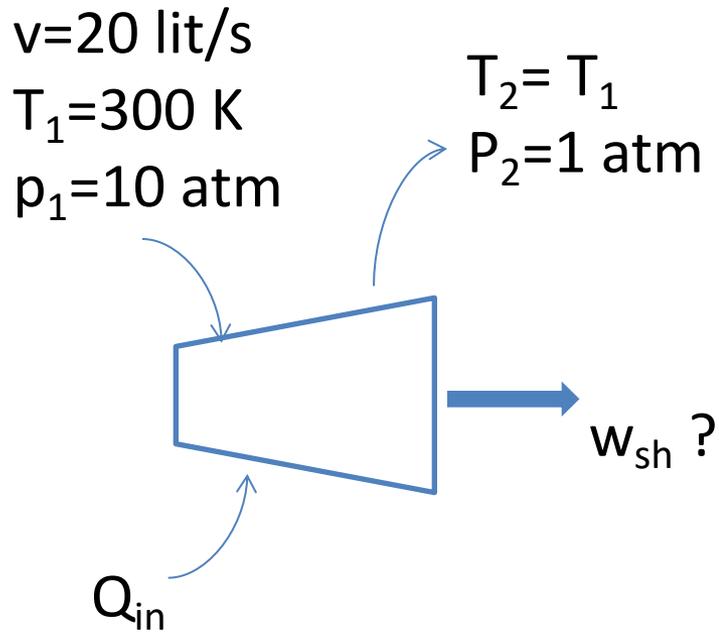
$$\dot{W}_{sh} = -\dot{n}RT\ln\frac{p_2}{p_1}$$

$$= -(8.125)(8.314)(300) \ln\frac{1}{10}$$

$$= 46662 \text{ W}$$

46.6/34.2=1.36, 36% more.

Example III

- A Hilsch tube, a "tricky" device that splits a of high-pressure air (p_1=1.5 bar, T_1=27°C) into two equimolar streams, one hot and one cold, both at lower pressure (p_2=p_3=1 bar). The salesman claims that the cold air is at -123°C. I don't believe that the air could get that cold with so simple a device. Would you please determine whether his claim violates the laws of thermodynamics.

high pressure

p_1 T_1

cold
low pressure

p_2 T_2

hot
low pressure

p_3 T_3
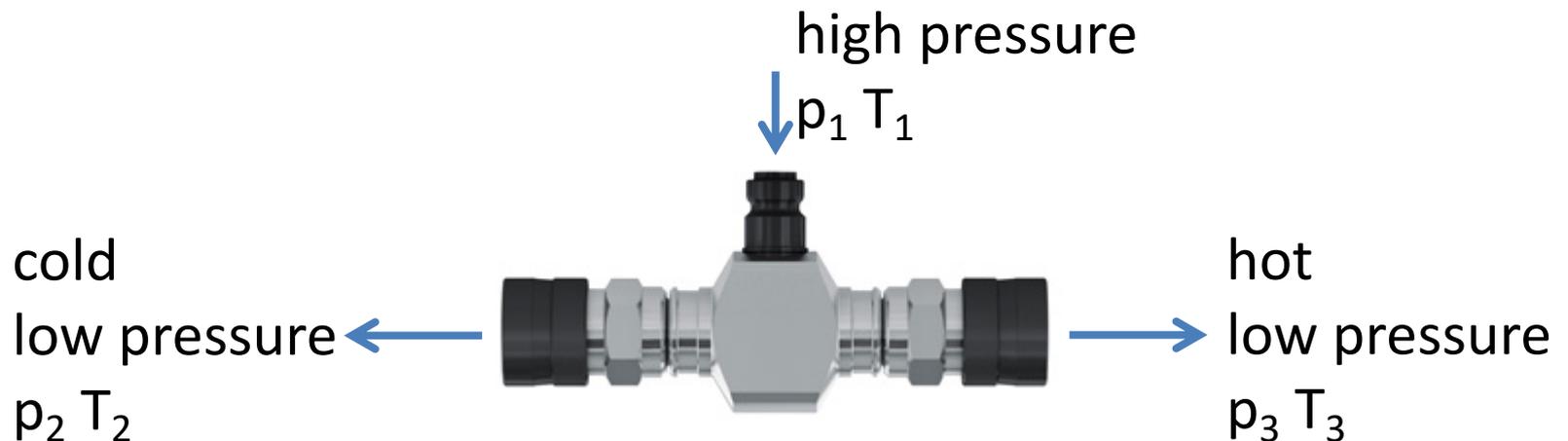
- From the 1st law,

  $n_1 h_1 = n_2 h_2 + n_3 h_3$

  $n_1 c_p T_1 = n_2 c_p T_2 + n_3 c_p T_3$

  $2(200) = 1(150) + 1(T_3), \quad T_3 = 450$

- From the second law,

$$\Delta S_{total} = \Delta S_{coldside} + \Delta S_{hot\,side}$$

$$= \left[n_2 c_p \ln \frac{T_2}{T_1} - n_2 R \ln \frac{p_2}{p_1} \right] + \left[n_3 c_p \ln \frac{T_3}{T_1} - n_3 R \ln \frac{p_3}{p_1} \right]$$
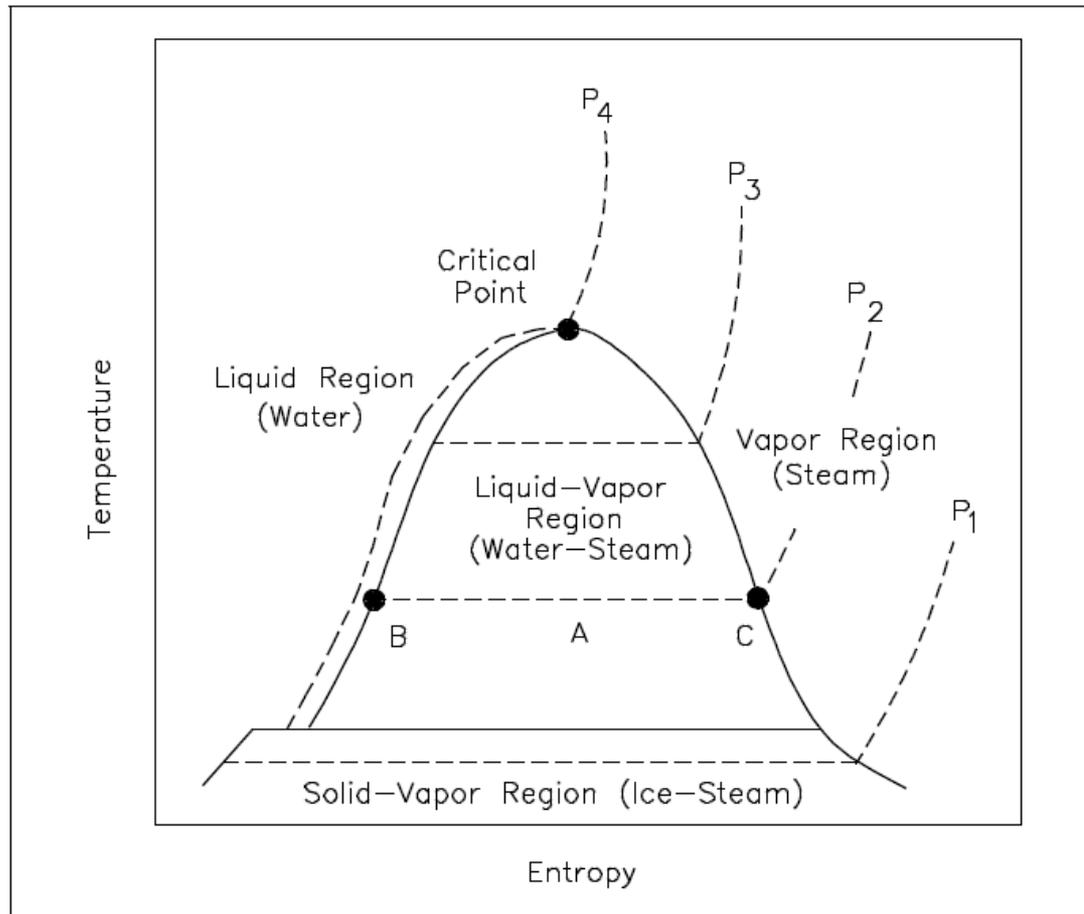
$$\Delta S_{total} = \Delta S_{coldside} + \Delta S_{hot\,side}$$

$$= \left[29.1 \ln \frac{150}{300} - 8.314 \ln \frac{1}{1.5} \right] + \left[29.1 \ln \frac{450}{300} - 8.314 \ln \frac{1}{1.5} \right]$$

$$= -1.63 \text{ Jmol}^{-1}\text{K}^{-1} \quad < 0$$

ENTROPY OF ENGINEERING FLUIDS

Temperature-Entropy (T-s) Diagram

$$\Delta S = \int \frac{dQ_{rev}}{T}, \quad \left[JK^{-1} \right]$$

$$= \int_{T_1}^{T_2} \frac{mc_p dT}{T} \quad \longleftarrow \quad \text{constant pressure}$$
$$\text{no phase change}$$

$$= \frac{m\Delta h_{lg}}{T} \quad \longleftarrow \quad \text{a phase change}$$
$$\text{at } T$$

Vertical lines are isentropic lines, adiabatic

Example I

- Find the work needed to compress adiabatically and reversibly to 500 kPa a stream of saturated HFC-134a gas at -40°C

saturated
HFC-134a
$T_1 = -40°C$

$P_2 = 500$ kPa

$-w_{sh}$

adiabatic

$$-w_{sh} = (h_2 - h_1) - q^{\,0}$$

$$p_1 = 51.14 \text{ kPa} \quad v_1 = 0.3614 \text{ m}^3\text{kg}^{-1}$$
$$h_1 = 374.3 \text{ kJkg}^{-1} \quad s_1 = 1.7655 \text{ kJkg}^{-1}\text{K}^{-1}$$

$$\Delta S = \int \frac{dQ_{rev}}{T} = 0 \quad \text{or} \quad s_2 = s_1$$

$$p_2 = 500 \text{ kPa} \quad \text{and}$$
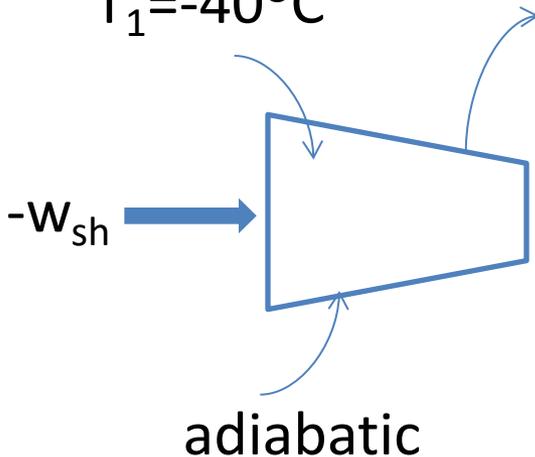$$s_2 = s_1 = 1.7655 \text{ kJkg}^{-1}\text{K}^{-1}$$

$$T_2 = 30°C \quad v_2 = 0.04434 \text{ m}^3\text{kg}^{-1},$$

$$h_2 = 421.3 \text{kJkg}^{-1}$$

$$-w_{sh} = h_2 - h_1 = 47 \text{ kJkg}^{-1}$$

Example II

steam
$T_1 = 600^oC$
$p_1 = 10$ bar

$v_2 = 200$ m/s
$P_2 = 1$ bar

w_{sh} ?

adiabatic
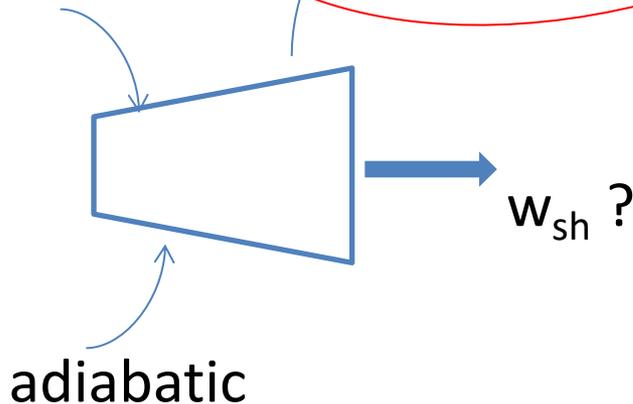
$$h_2 + \frac{v_2^2}{2} - h_1 = \cancel{q}^{0} - w_{sh}$$

$h_1 = 3697.9$ kJkg^{-1}

$s_1 = 8.0290$ kJkg^{-1}K^{-1}

$$\Delta S = \int \frac{dQ_{rev}}{T} = 0 \quad \text{or } s_2 = s_1$$

$p_2 = 100$ kPa

$s_2 = s_1 = 8.0290$ kJkg^{-1}K^{-1}

$T_2 = 250^oC \quad v_2 = 2.406$ m^{3}kg^{-1},

$h_2 = 2974.3$ kJkg^{-1}

$$w_{sh} = h_1 - h_2 - \frac{v_2^2}{2} = 703.6 \text{ kJkg}^{-1}$$

WORK FROM HEAT

The Carnot heat engine

- Sadi Carnot wrestled with the problem of finding the maximum efficiency of a heat engine. He cracked this problem by brilliant deductive reasoning, but no experimenting or tinkering with real steam engines.

- Carnot did this analysis and gave a mathematical representation of the 2nd law in 1811, long before the 1st law was clarified and properly expressed (about 1840 to 1850). Shouldn't the 2nd law be called the 1st law and vice versa ?

- Carnot's analysis let to the concept of entropy.

- Consider a "heat engine" does only three kinds of operations
  - The absorption of heat from a hot constant temperature reservoir, at T_1
  - The removal of heat to a cold temperature sink at T_2
 - Doing work or receiving work
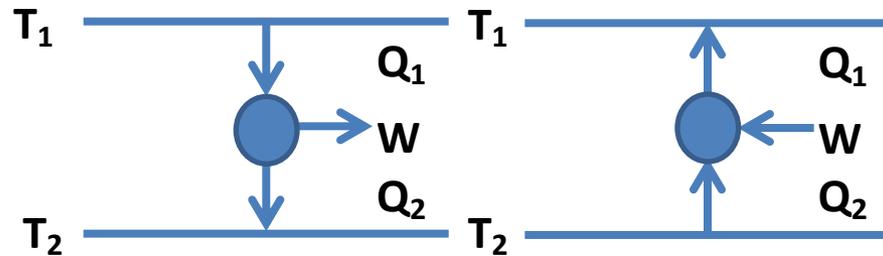
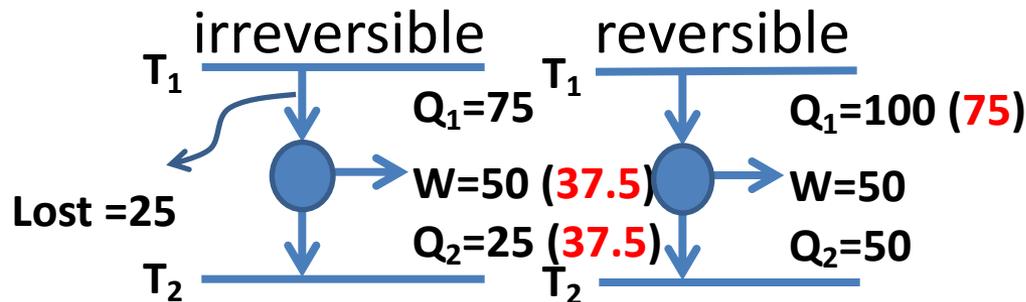- The former one call Carnot heat engine, latter one call Carnot heat pump.

- Theorem 1. All reversible heat engines operation between the same two temperatures, T_1 and T_2 must have the same efficiency.

- Proof. Let us assume the contradictory, the following two reversible engines have different efficiencies,
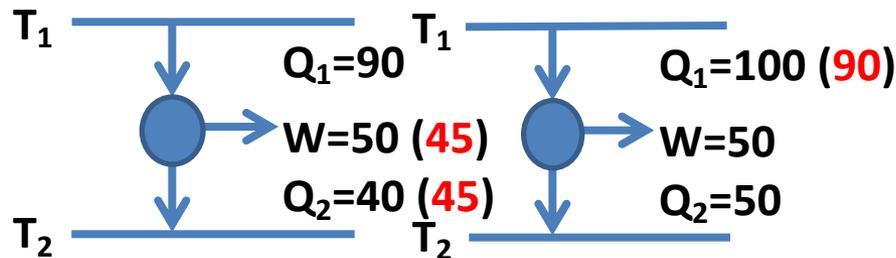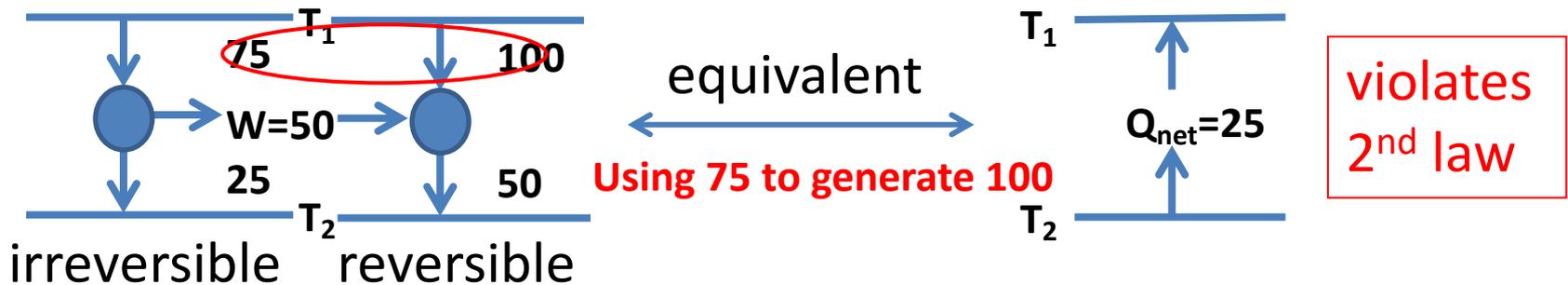

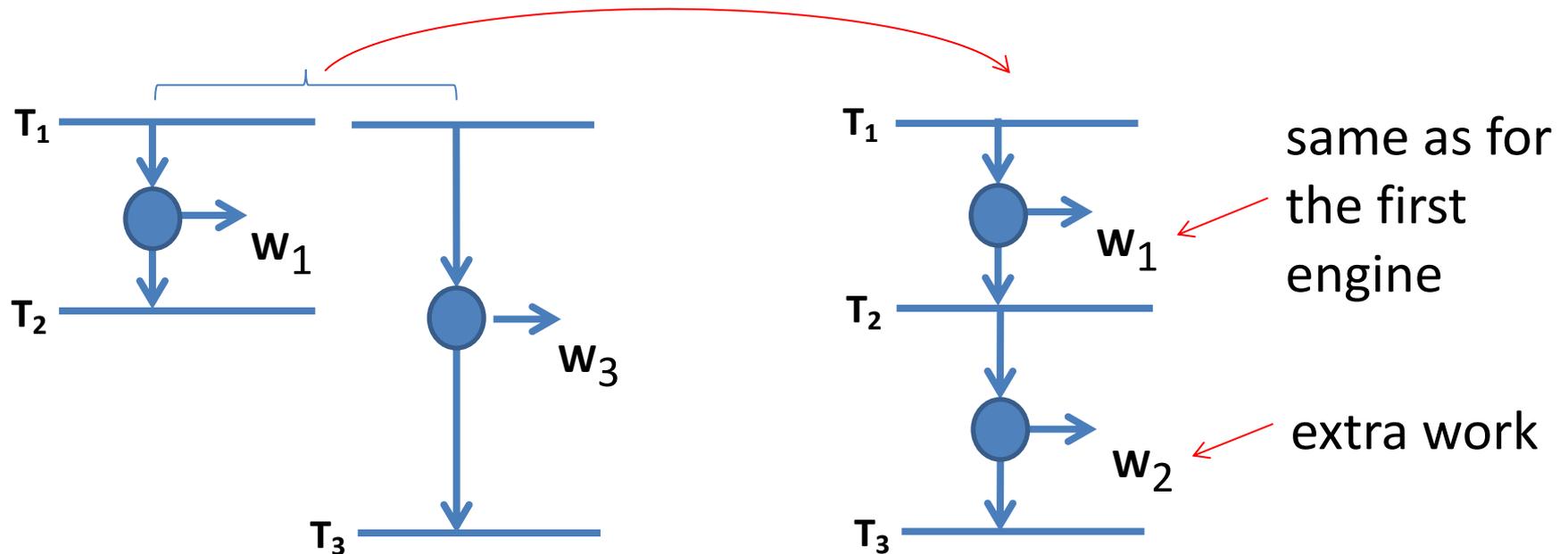say $\eta_1 = 56\%$, $\eta_2 = 50\%$. Reverse the second and interconnect,
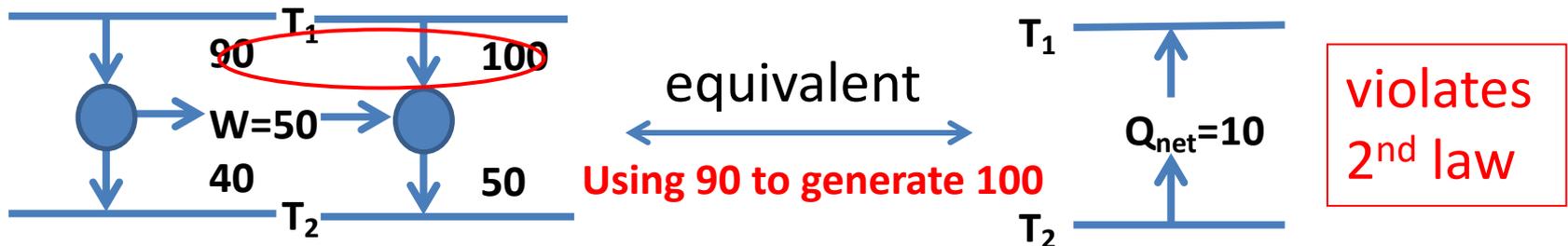
- Theorem 2. Reversible heat engines have the highest efficiency between any two temperatures.

- Proof. Assume that the irreversible engine has the higher efficiency, higher efficiency,

irreversible   reversible

T_1 T_1

$Q_1=75$ $Q_1=100$ **(75)**

Lost =25   W=50 **(37.5)**   **W=50**

$Q_2=25$ **(37.5)** $Q_2=50$

T_2 T_2

say η_1=67%, η_2=50%. Reverse the second and interconnect,

T_1 75   100   equivalent T_1

W=50 Q_{net}=25   **violates 2nd law**

25   50   **Using 75 to generate 100**

T_2

irreversible   reversible

- Theorem 3. For the same high temperature T_1, the engine that the larger ΔT has the higher efficiency and produces more work.

- Proof. $W_3 = W_1 + W_2 \geq W_1$.

T_1

W_1

T_2

W_3

T_3

T_1

W_1

T_2

W_2

T_3

same as for the first engine

extra work

Quiz VII

A reversible power cycle receives Q_H from a hot reservoir at temperature T_H and rejects energy by heat transfer to the surroundings at temperature T_0. The work developed by the power cycle is used to drive a refrigeration cycle that removes Q_C from a cold reservoir at temperature T_C and discharges energy by heat transfer to the same surroundings at T_0. Develop an expression for the ratio Q_C/Q_H in terms of the temperature ratios T_H/T_0 and T_C/T_0.

The kelvin temperature scale

T'=100

$100=Q_1$

W=10

$90=Q_2$

90

90

10

80

80

80

10

70

70

10

10

10

0

0
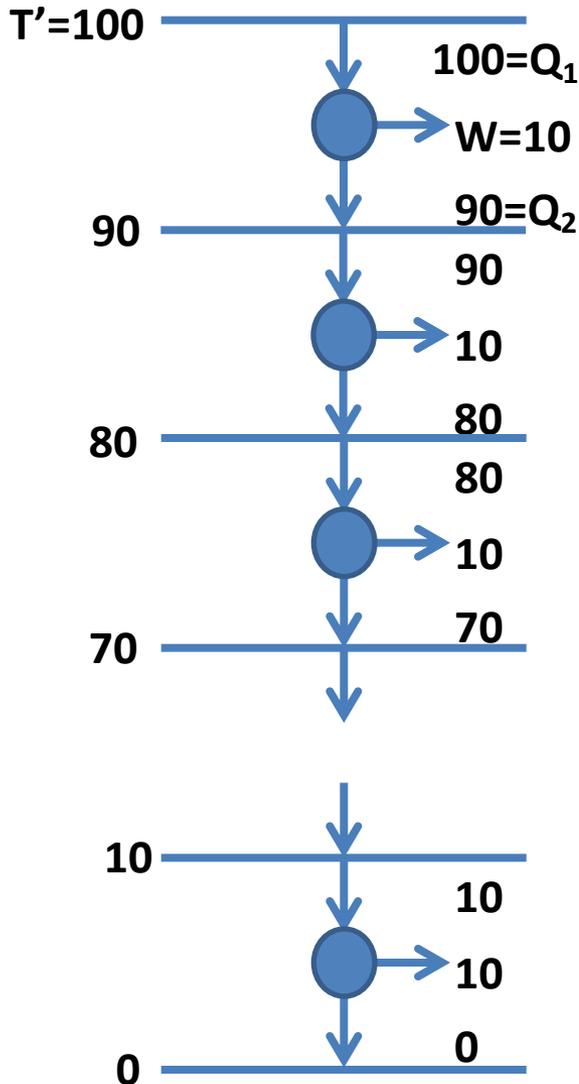
- Kelvin derived a temperature scale not based on the expansion of gases or liquids, but based on Carnot's heat engines. Consider a series of Carnot engines, each producing the same amount of work, say 10 units, as in the figure.

- and

$$T_1' \propto Q_1 \quad \text{and} \quad \frac{T_2'}{T_1'} = \frac{Q_2}{Q_1}$$

- Therefore,

$$\frac{|W|}{|Q_1|} = \frac{|Q_1| - |Q_2|}{|Q_1|} = 1 - \frac{|Q_2|}{|Q_1|} = 1 - \frac{T_2'}{T_1'} = \frac{T_1' - T_2'}{T_1'}$$

$$\frac{|W|}{|Q_2|} = \frac{T_1' - T_2'}{T_2'} \quad \text{or} \quad \frac{|Q_2|}{|Q_1|} = \frac{T_2'}{T_1'}$$

- This temperature scale is measured in terms of work and heat in a Carnot engine, and is known as Kelvin work scale, T'.

- This scale is defined and derived straight from thermodynamics, no reason to suspect that it has anything to do with our arbitrary scales, Fahrenheit, Celsius, …

- Fahrenheit temperature scale
- 0° F was established as the temperature of a solution of "brine" made from equal parts of ice, water and salt (ammonium chloride)
- 32° F as melting point of ice
- 96° F as the average human body temperature
- In this scale the boiling point of water is defined to be 212° F, 180° F separation from melting point, 32° F .

Carnot cycle revisit

Let us take one mole of an ideal gas, put it in a cylinder with piston and operate it in a four-step cycle as a Carnot engine.

Carnot Cycle
Ideal gas working fluid
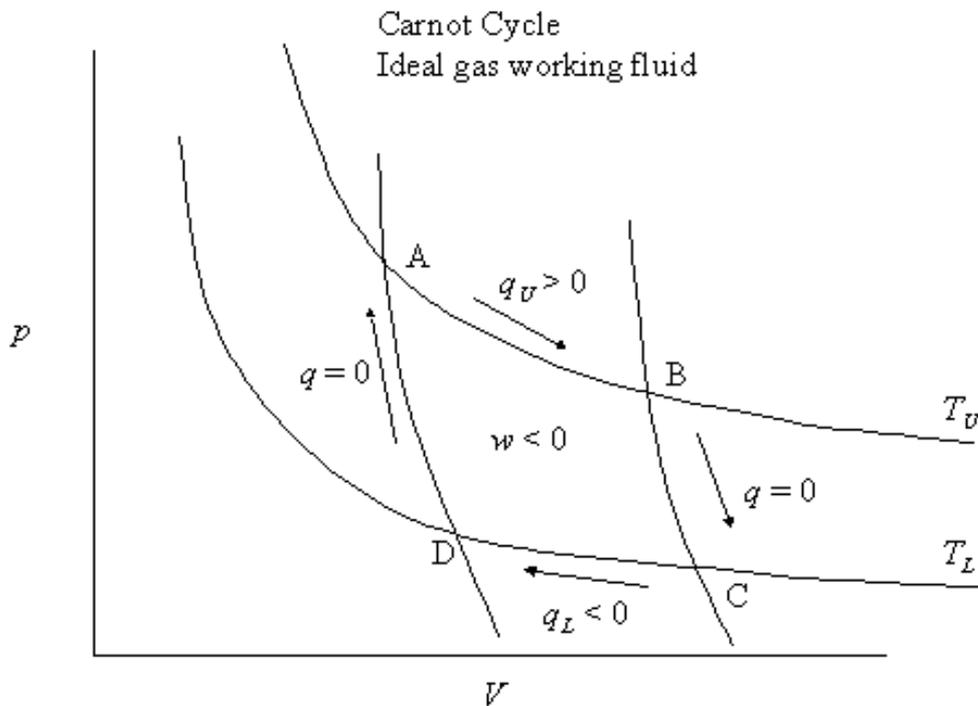
- AB: isothermal expansion at T_1
- BC: adiabatic reversible expansion
- CD: isothermal contraction at T_2
- DA: adiabatic reversible contraction back to A.

For ideal gas

- AB: isothermal expansion at T_1

$$\left| w_1 \right| = \left| q_1 \right| = RT_1 \ln \frac{p_A}{p_B}$$

- BC: adiabatic reversible expansion

$$\left| w \right| = c_v (T_2 - T_1)$$

- CD: isothermal contraction at T_2

$$\left| w_2 \right| = \left| q_2 \right| = RT_2 \ln \frac{p_C}{p_D}$$

- DA: adiabatic reversible contraction back to A.

$$\left| w \right| = c_v (T_1 - T_2)$$

- For the adiabatic reversible

$$\left. \begin{array}{l} \dfrac{p_A}{p_D} = \left(\dfrac{T_1}{T_2} \right)^{\frac{k}{k-1}} \\[3em] \dfrac{p_B}{p_C} = \left(\dfrac{T_1}{T_2} \right)^{\frac{k}{k-1}} \end{array} \right\} \quad \text{or} \quad \frac{p_A}{p_B} = \frac{p_D}{p_C}$$

For the four step cycle,

$$\frac{\left| w_{cycle} \right|}{\left| q_1 \right|} = \frac{\left| w_{AB} \right| + \left| w_{BC} \right| - \left| w_{CD} \right| - \left| w_{DA} \right|}{\left| q_1 \right|}$$

$$= \frac{R(T_1 - T_2)\ln \dfrac{p_B}{p_A}}{RT_1 \ln \dfrac{p_B}{p_A}} = \frac{T_1 - T_2}{T_1}$$

This shows that the ideal gas temperature scale is equivalent to the Kelvin work scale, That T = T'.

Because Kelvin made this discovery, we name our absolute temperature scale in his honor.

- For the heat lost from our Carnot engine, -Q,

<div style="border: 1px solid red;">Kelvin work scale</div>
$$\frac{-Q_2}{Q_1} = \frac{T_2}{T_1} \quad \text{or} \quad \frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0$$

- For any reversible Carnot engine that uses any number of sources and sinks,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \cdots = 0$$

- Or
$$\sum \frac{Q_i}{T_i} = 0 \quad \text{or} \quad \int \frac{Q_{rev}}{T} = 0$$

- This quantity always enters in cyclical reversible processes, it represents a change in a property of the system as is the enthalpy or internal energy change. This is entropy change, ΔS. Carnot's !
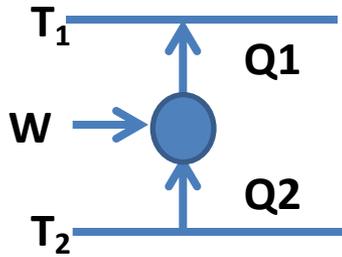
T-s diagram of Carnot engine

T

q_1 w_1

T_1 A B

steps BC and DA
Are adiabatic
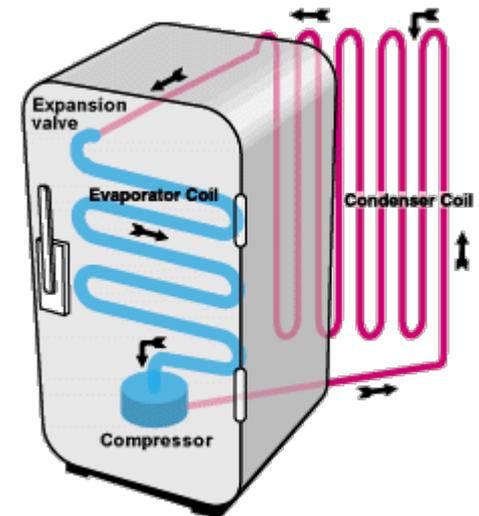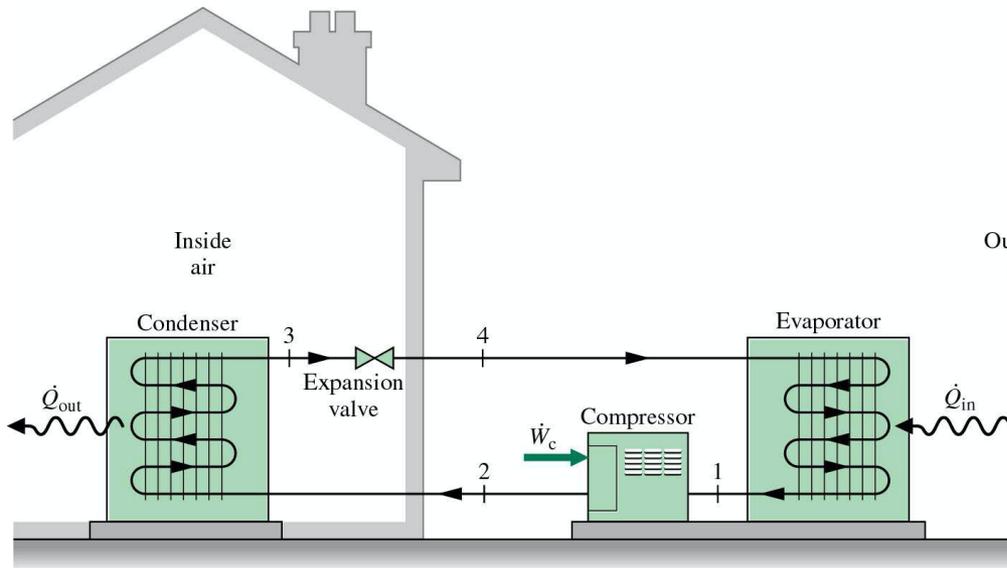
w w

T_2 D C

q_2 w_2

s, J/mol/K
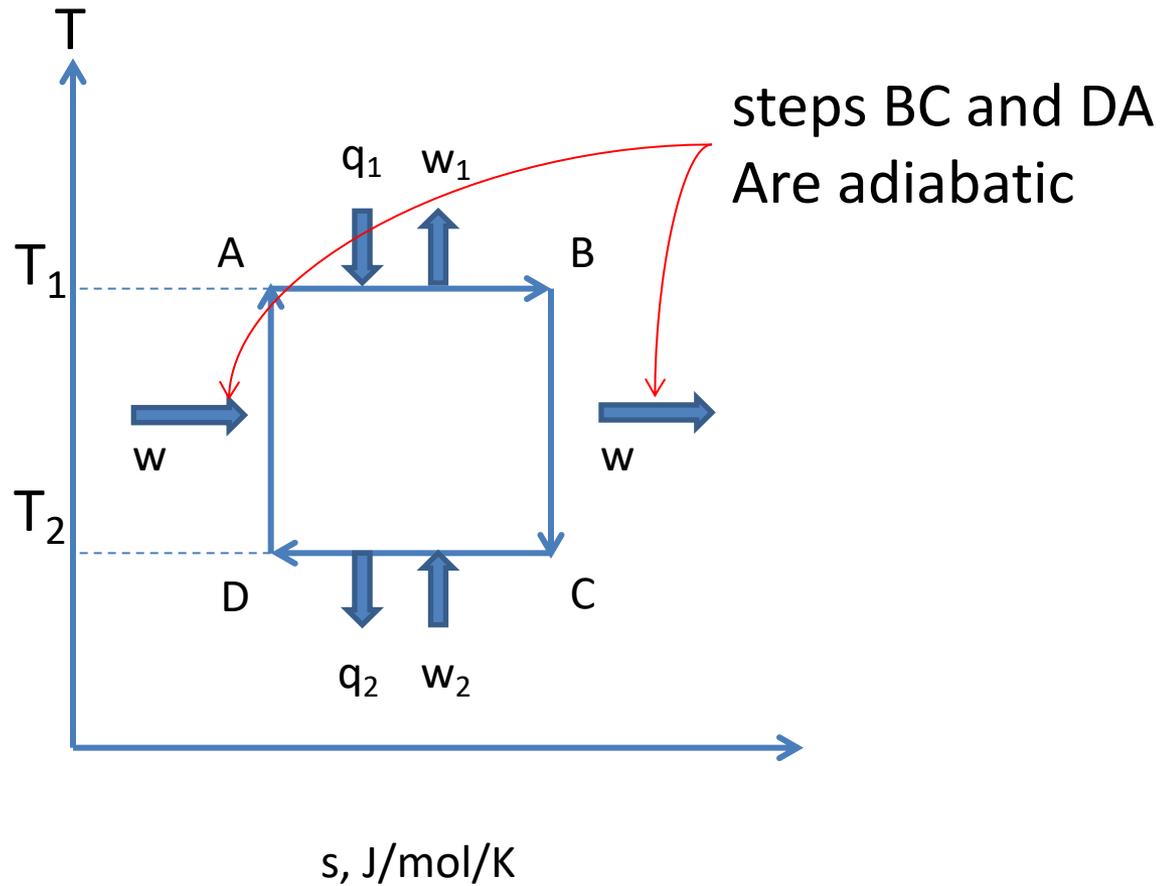
THE IDEAL OR REVERSIBLE HEAT PUMP

Coefficient of performance, COP

$$\text{cop} = \frac{|Q_2|}{|W|} = \frac{T_2}{T_1 - T_2} \quad \text{refrigeration}$$
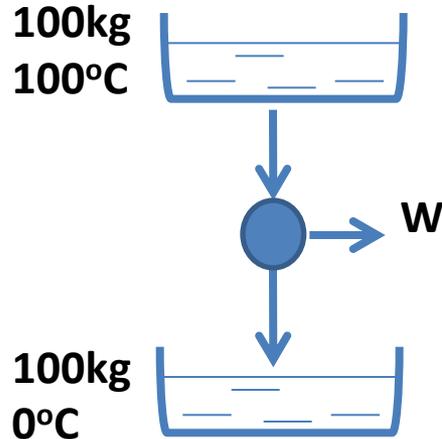
$$\text{cop}' = \frac{|Q_2|}{|W|} = \frac{T_1}{T_1 - T_2} \quad \text{heater}$$

Example

- 100 kg of water at 100°C furnishes heat to a Carnot engine that discards heat to a sink consisting of 100 kg of cold water at 0°C. Source cools, sink heats, and eventually both end at the same temperature. Calculate

100kg
100°C

W

100kg
0°C

1. The final temperature of the 200 kg of water
2. The work obtainable

- If we just cooled the hot water with the cold without doing work,

$$\Delta H_{hot} + \Delta H_{cold} = 0$$

$$m_{hot}c_p(T_f - T_1) + m_{cold}c_p(T_f - T_2) = 0$$

$$100(100 - T_f) + 100(0 - T_f) = 0$$

$$T_f = \frac{10000}{200} = 50^o C$$

- With work withdraw,

$$\Delta S_{total} = \Delta S_{hot} + \Delta S_{cold} = 0$$

$$\Delta S_{hot} = \int_{T_1}^{T_f} \frac{mc_p dT}{T} = m_{hot}c_p \ln \frac{T_f}{373}$$

$$\Delta S_{cold} = \int_{T_2}^{T_f} \frac{mc_p dT}{T} = m_{cold}c_p \ln \frac{T_f}{273}$$

$$m_{hot}c_p \ln \frac{T_f}{373} + m_{cold}c_p \ln \frac{T_f}{273} = 0$$

$$T_f = \sqrt{(273)(373)} = 319\,\text{K} = 46^\circ\text{C}$$

- Work done is the energy lost in going from 50°C to 46°C.

$$W = mc_p(50 - 46) = 200(4184)(4) = 3.347 \times 10^6 \text{ J}$$