

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,

$$dE = dQ + dW$$

$$dS = (1/T)dE - (f/T) \cdot d\underline{X}$$

- therefore,

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

- Constant volume process

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

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

- Constant pressure process

$$W_{\text{rev}} = \int p \, dv = p \Delta v = n R \Delta T$$

$$\Delta U = n c_v \Delta T$$

$$Q_{\text{rev}} = \Delta U + W_{\text{rev}} = n c_v \Delta T + n R \Delta T = n c_p \Delta T$$

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} = \int \frac{n c_p \, dT}{T} = n c_p \ln \frac{T_2}{T_1} = n c_p \ln \frac{v_2}{v_1}$$

$$W_{\text{rev}} = n R (T_2 - T_1)$$

- Constant temperature process

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

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

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

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

- 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

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

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

- Therefore,

$$\Delta S = nc_p \ln \frac{T_2}{T_1} - nR \ln \frac{p_2}{p_1}$$

$$\Delta S = nc_v \ln \frac{T_2}{T_1} + nR \ln \frac{v_2}{v_1}$$

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

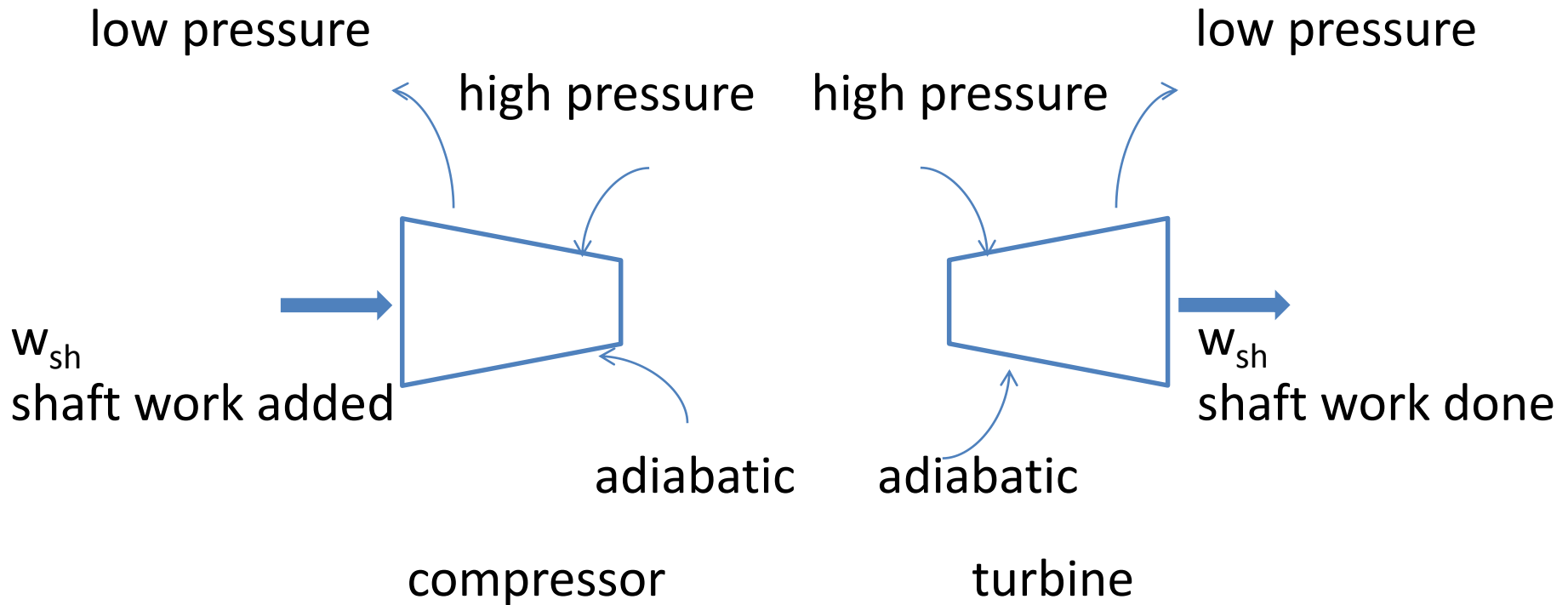
- Reversible work
- Going from p_1, T_1 to p_2, T_2 , one can take various paths, two are as follow,
 - Constant p_1, T_1 to T_2 + Constant T_2, p_1 to p_2
 - Constant T_1, p_1 to p_2 + Constant p_2, T_1 to T_2

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

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

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

- Adiabatic reversible processes ($Q = 0$; $\Delta S = 0$)



- From 1st law
- And flow systems

$$q_{\text{actual}} = 0$$

$$- w_{\text{sh}} = \Delta h + \Delta e_p + \Delta e_k$$

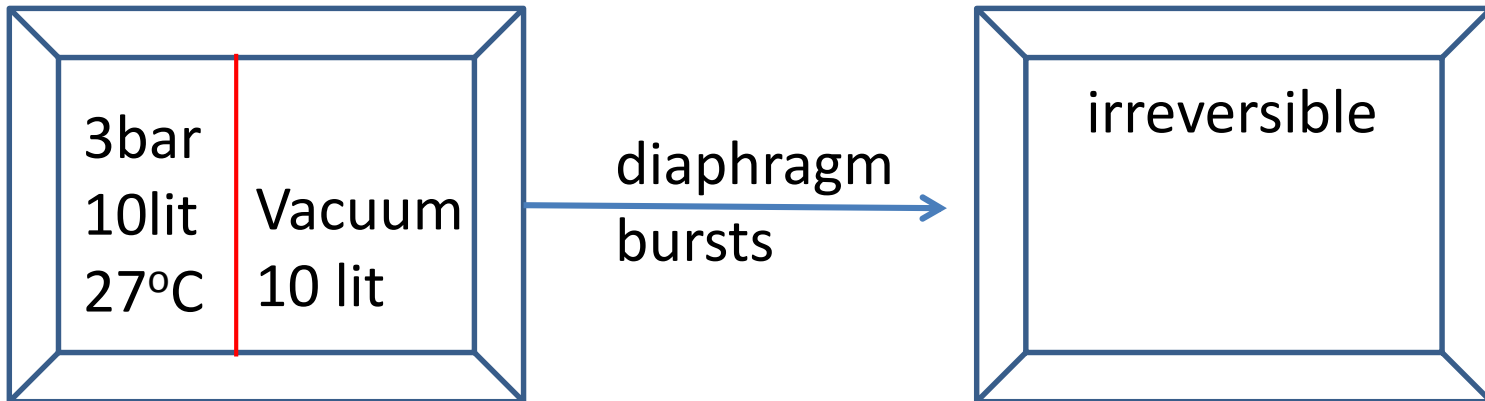
- From 2nd law

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

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

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, $T_{\text{final}} = 300 \text{ K}$, $V_{\text{final}} = 20 \text{ lit}$, $p_{\text{final}} = 1.5 \text{ bar}$ and $n = 1.2 \text{ mol}$

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

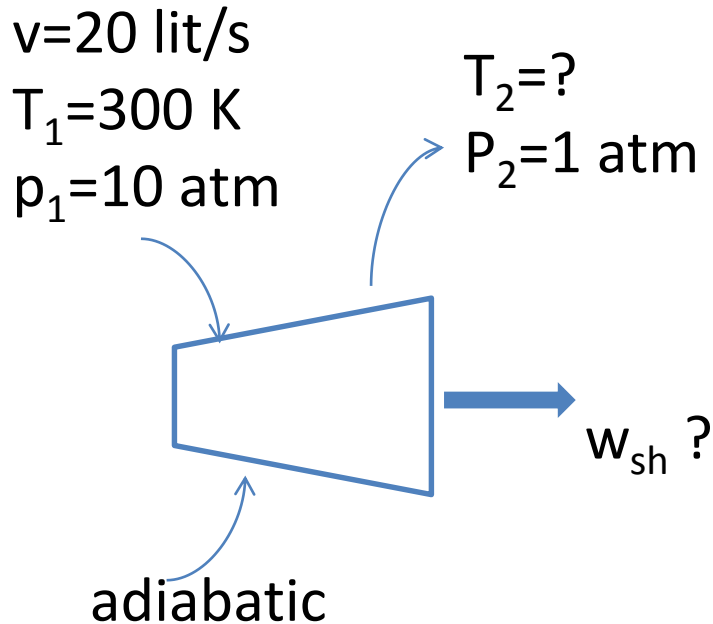
$$\Delta S = \int \frac{dQ_{\text{rev}}}{dT} = nR \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$$

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

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

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 $7\text{¢}/\text{kWhr}$.



- The molar flow rate

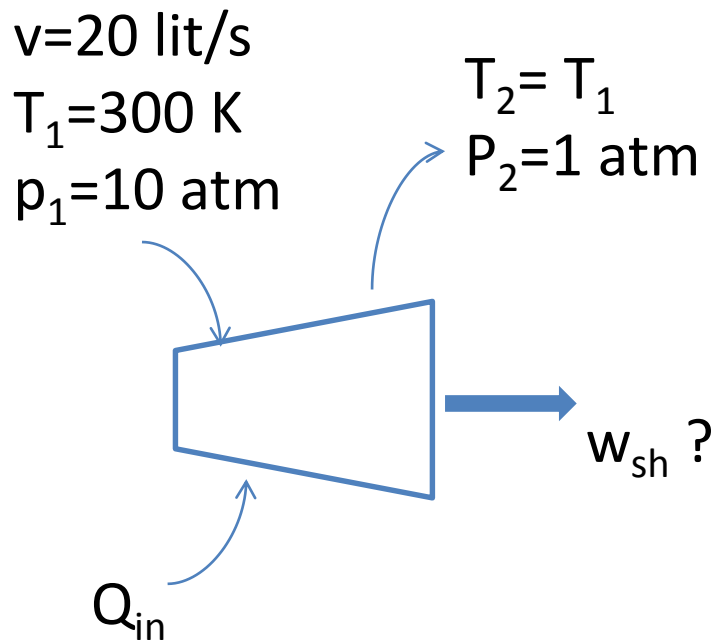
$$\begin{aligned}
 n &= \frac{p \dot{v}}{RT} \\
 &= \frac{(1013250)(0.020)}{(8.314)(300)} \\
 &= 8.125 \text{ mol} \cdot \text{s}^{-1}
 \end{aligned}$$

- For adiabatic reversible

$$\begin{aligned}
 \frac{T_2}{T_1} &= \left(\frac{p_2}{p_1} \right)^{\frac{(k-1)}{k}} \\
 &= 300 \left(\frac{1}{10} \right)^{\frac{0.4}{1.4}} = 155 \text{ K}
 \end{aligned}$$

$$\begin{aligned}
 \dot{W}_{rev} &= -\Delta \dot{H} \\
 &= -\dot{n} c_p (T_2 - T_1) = 34283 \text{ W} \\
 &= (34283 \text{ W}) \left(\frac{3600 \times 24 \times 30 \text{ s}}{\text{month}} \right) \\
 &= \left(\frac{0.2778 \text{ kW} \cdot \text{hr}}{10^6 \text{ J}} \right) = \$1728/\text{month}
 \end{aligned}$$

- $T_2=155$ K, which is very cold, this leads us to suspect.
- How about a reversible isothermal expansion ?



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

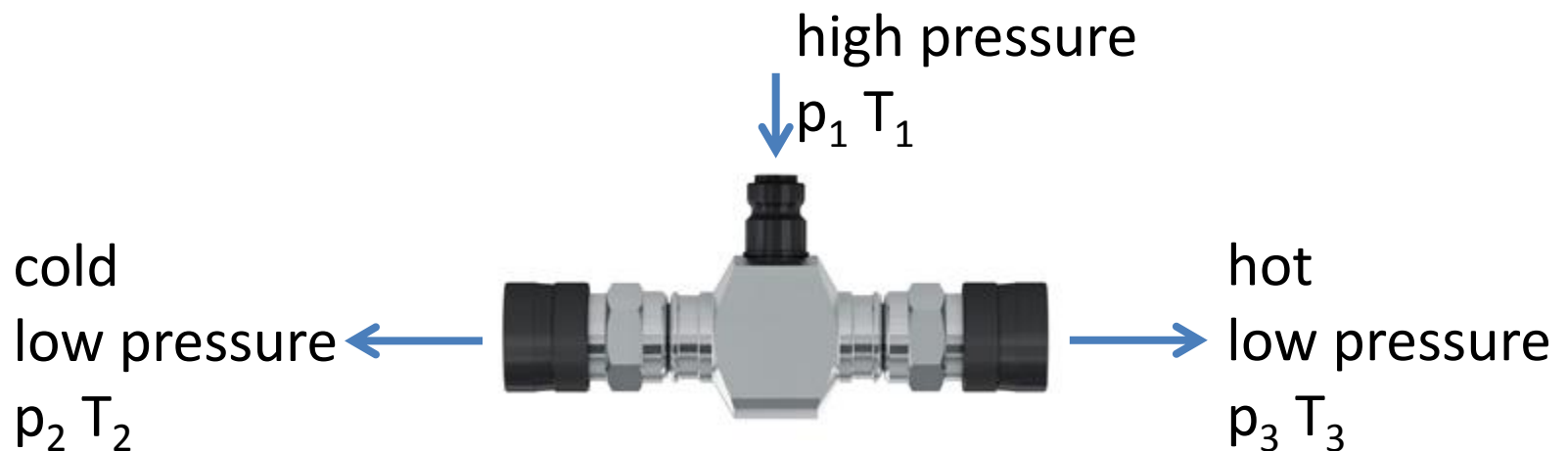
$$= -(8.125)(8.314)(300) \ln \frac{1}{10}$$

$$= 46662 \text{ W}$$

$$46.6/34.2=1.36, 36\% \text{ more.}$$

Example III

- A Hilsch tube, a “tricky” device that splits a of high-pressure air ($p_1=1.5$ bar, $T_1=27^\circ\text{C}$) 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.



- 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,

$$\Delta S_{\text{total}} = \Delta S_{\text{cold side}} + \Delta S_{\text{hot side}}$$

$$= \left[n_2 c_p \ln \frac{T_2}{T_1} - n_2 R \ln \frac{p_2}{p_1} \right] + \left[n_3 c_p \ln \frac{T_3}{T_1} - n_3 R \ln \frac{p_3}{p_1} \right]$$

$$\Delta S_{\text{total}} = \Delta S_{\text{cold side}} + \Delta S_{\text{hot side}}$$

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

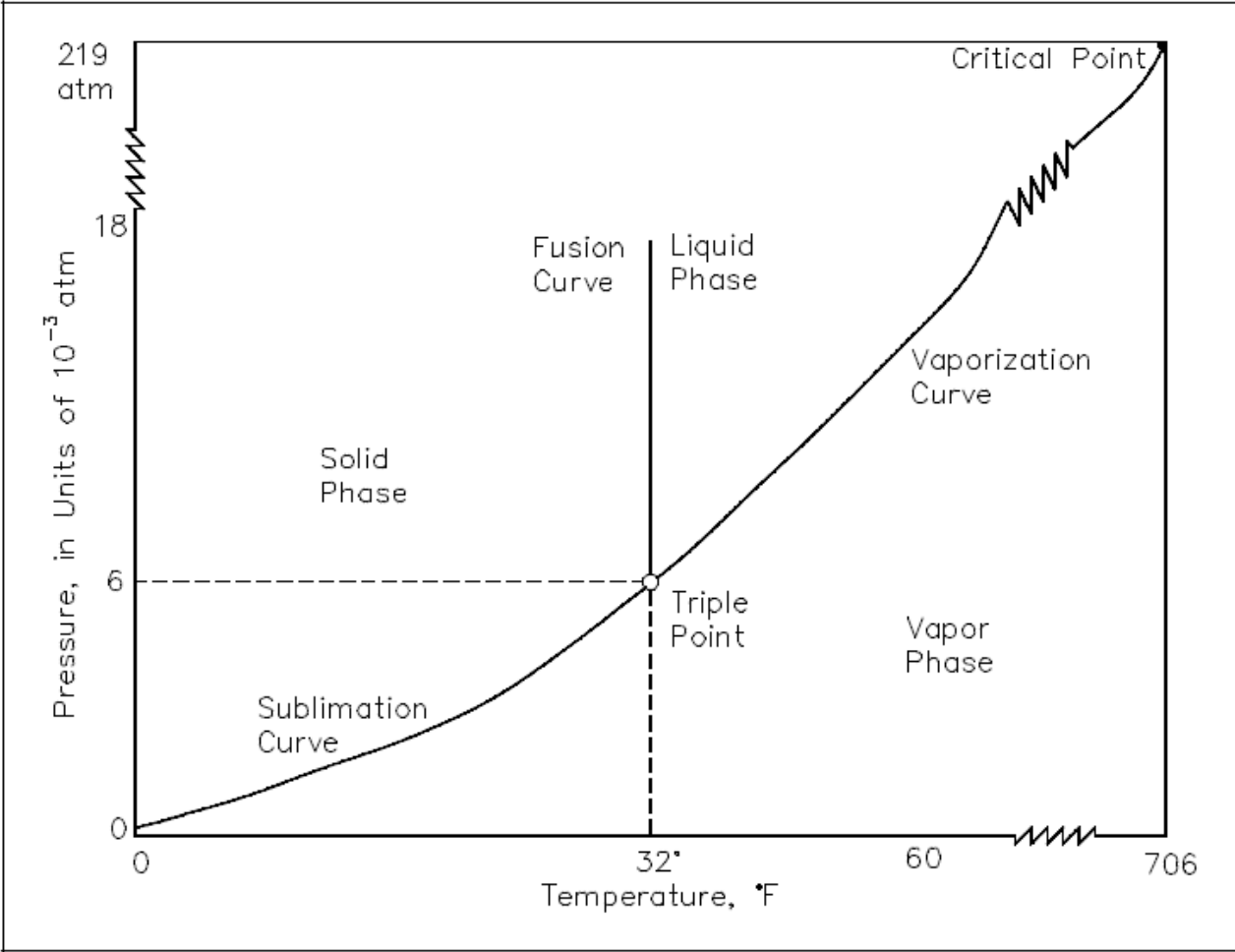
$$= -1.63 \text{ Jmol}^{-1} \text{K}^{-1} < 0$$

ENTROPY OF ENGINEERING FLUIDS

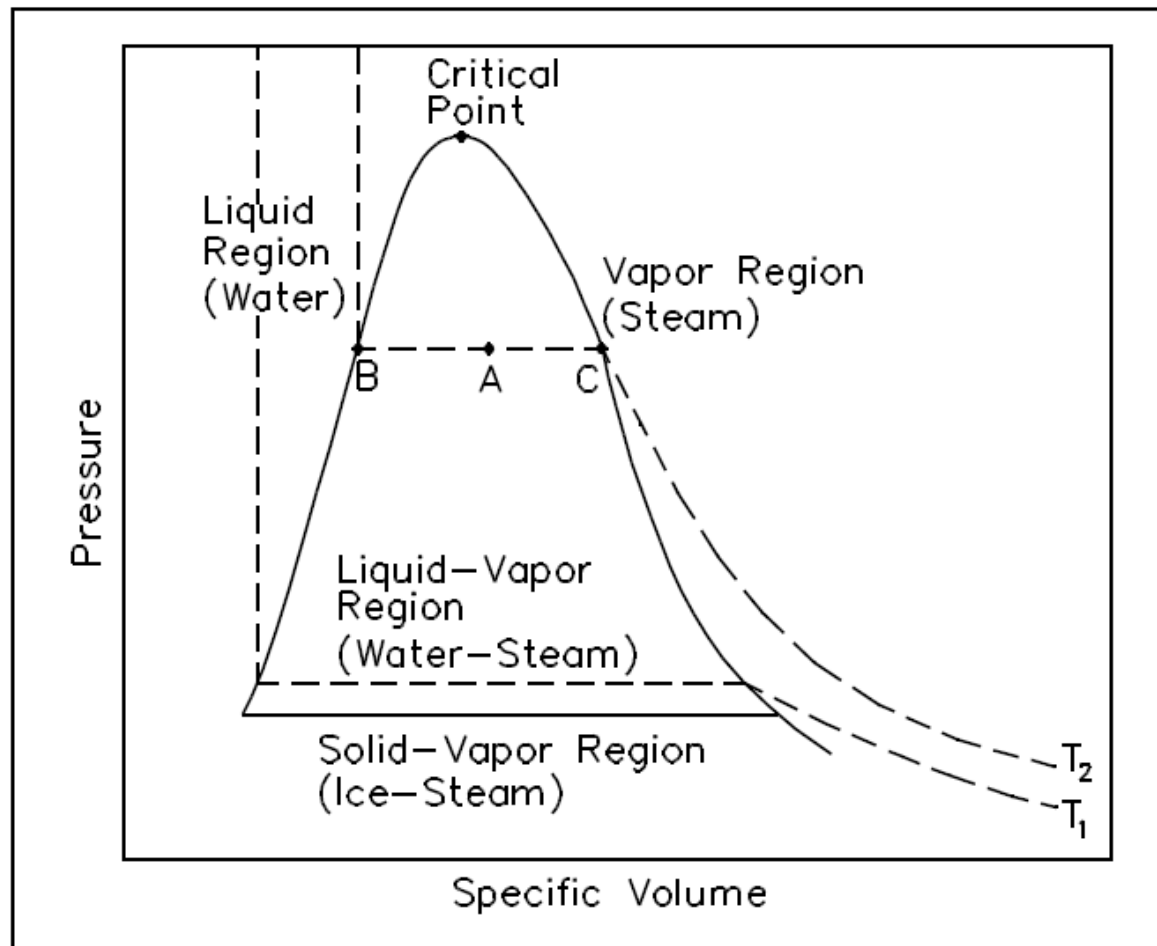
Property Diagrams

- Pressure- Temperature (P-T) diagrams
- Pressure-Specific Volume (P-v) diagrams
- Pressure-Enthalpy (P-h) diagrams
- Enthalpy-Temperature (h-T) diagrams
- Temperature-Entropy (T-s) diagrams
- Enthalpy-Entropy (h-s) or Mollier diagrams.

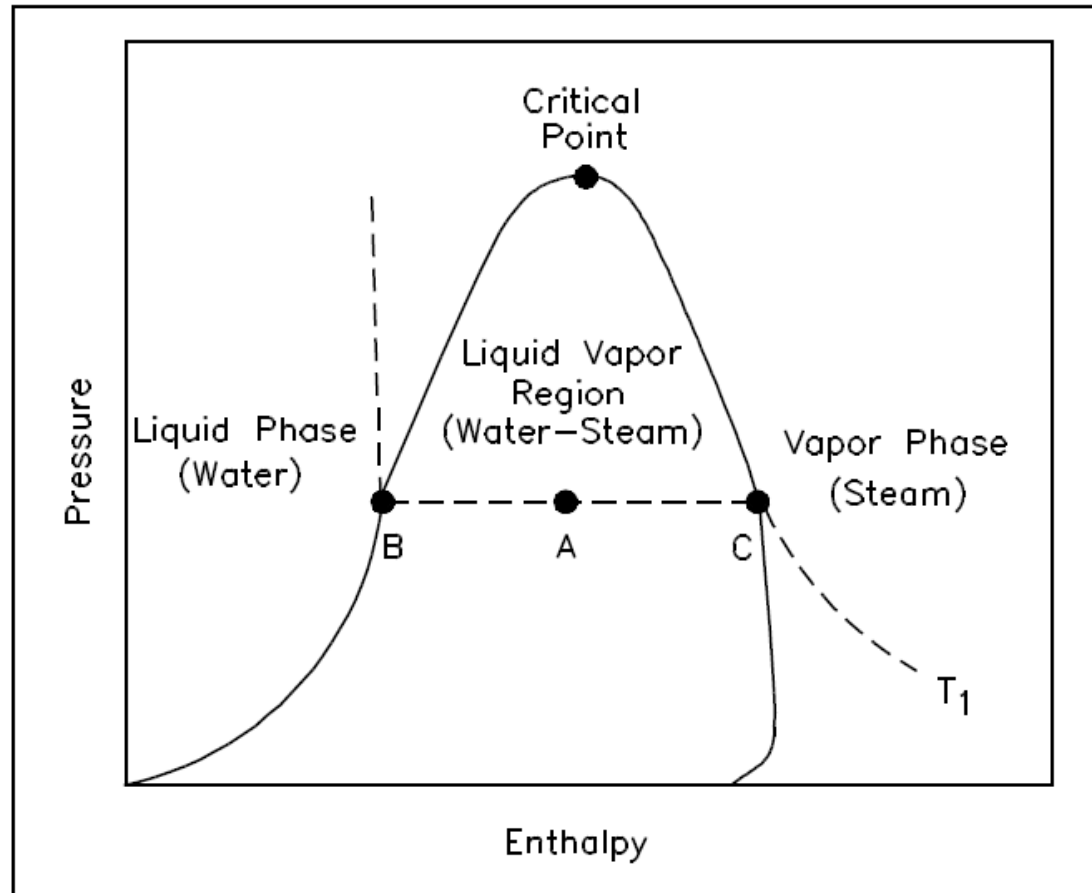
Pressure- Temperature (P-T) diagram



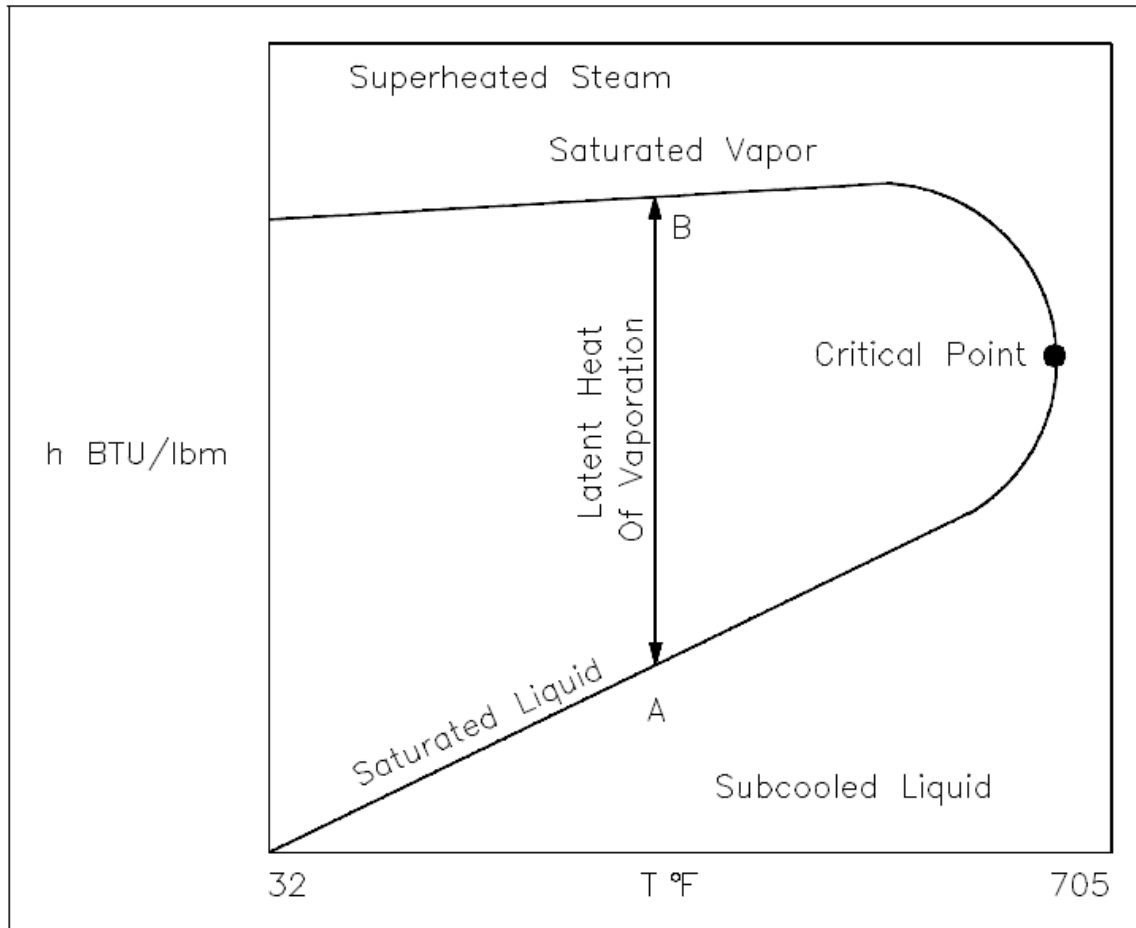
Pressure-Specific Volume (P-v) Diagram



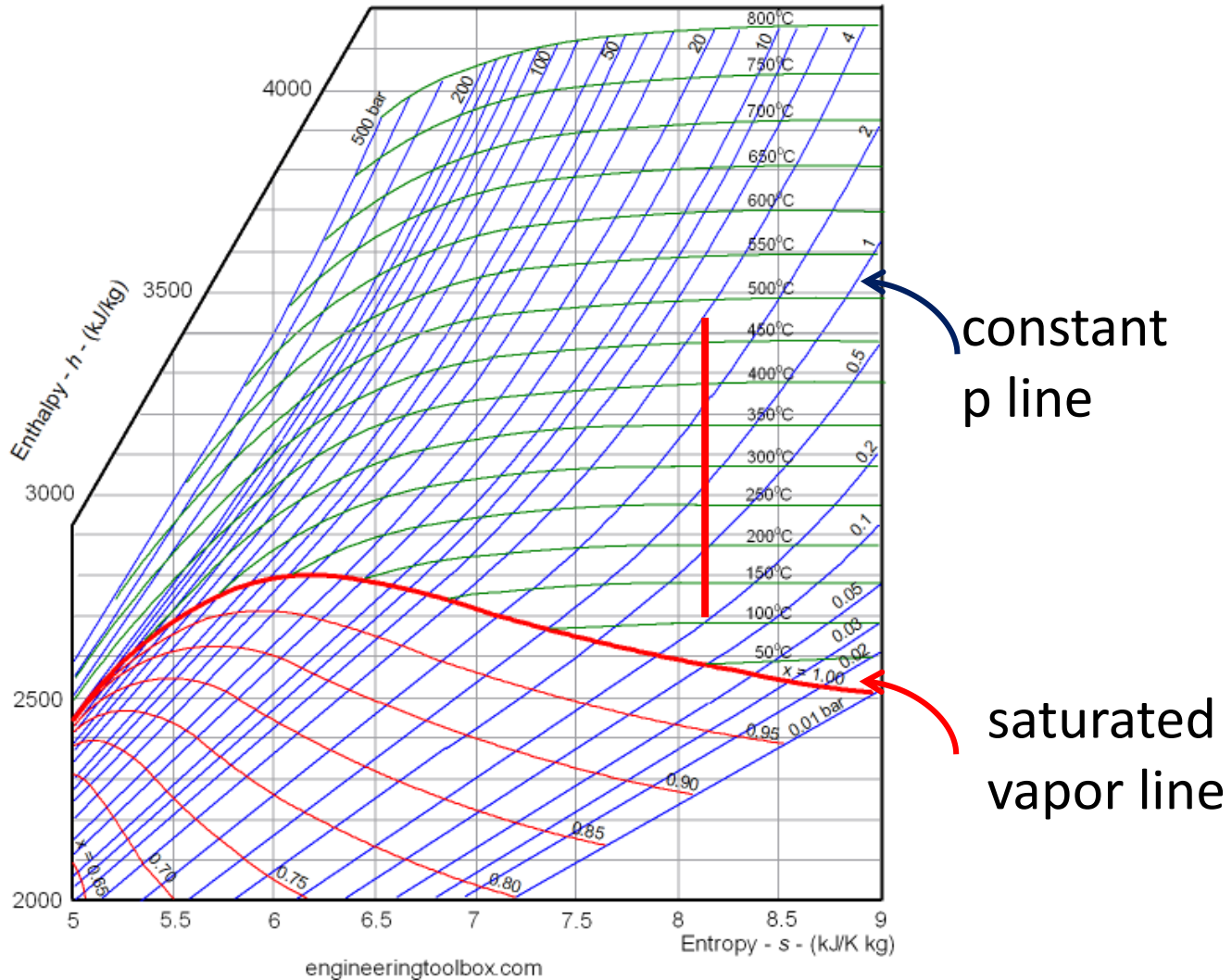
Pressure-Enthalpy (P-h) Diagram



Enthalpy-Temperature (h-T) Diagram

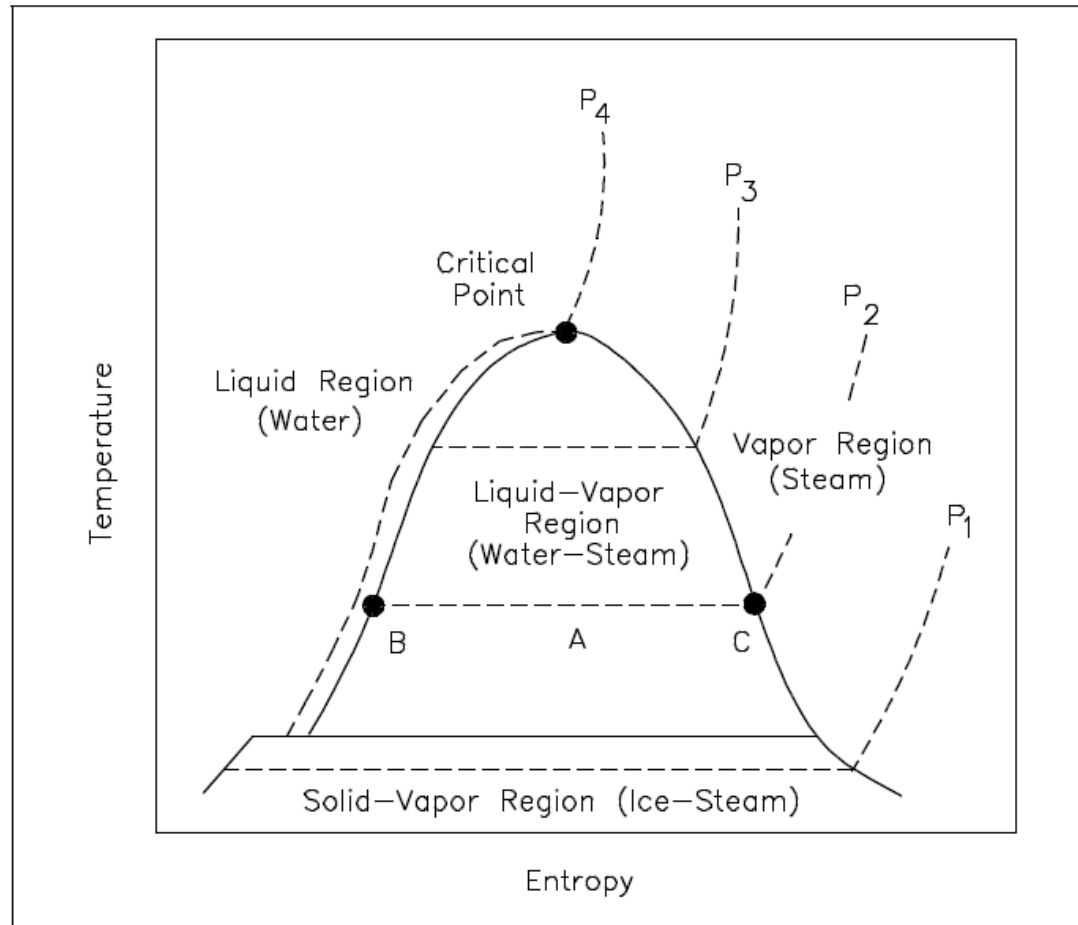


Enthalpy-Entropy (h-s) or Mollier Diagram



- This chart is particularly useful in evaluating the work involved in an adiabatic reversible step of an engine because
- From 1st law, $\Delta h=w$ (for adiabatic condition)
- From 2nd law, $\Delta s=0$ (for adiabatic condition)
- Therefore, **straight vertical line between p_{high} and p_{low}** gives the work done, simply and directly for a machine.

Temperature-Entropy (T-s) Diagram



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

$$= \int_{T_1}^{T_2} \frac{mc_p dT}{T} \quad \leftarrow \text{constant pressure}$$

no phase change

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

at T

Example I

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

$$-w_{sh} = (h_2 - h_1) - q \quad \text{with } q = 0$$

$$p_1 = 51.14 \text{ kPa} \quad v_1 = 0.3614 \text{ m}^3 \text{ kg}^{-1}$$

$$h_1 = 374.3 \text{ kJ kg}^{-1} \quad s_1 = 1.7655 \text{ kJ kg}^{-1} \text{ K}^{-1}$$

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

$$p_2 = 500 \text{ kPa} \quad \text{and}$$

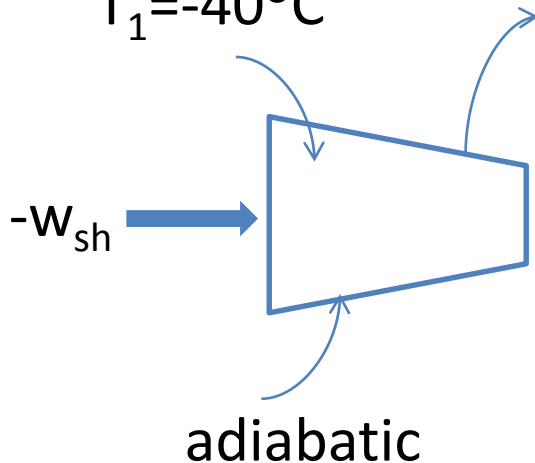
$$s_2 = s_1 = 1.7655 \text{ kJ kg}^{-1} \text{ K}^{-1}$$

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

$$h_2 = 421.3 \text{ kJ kg}^{-1}$$

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

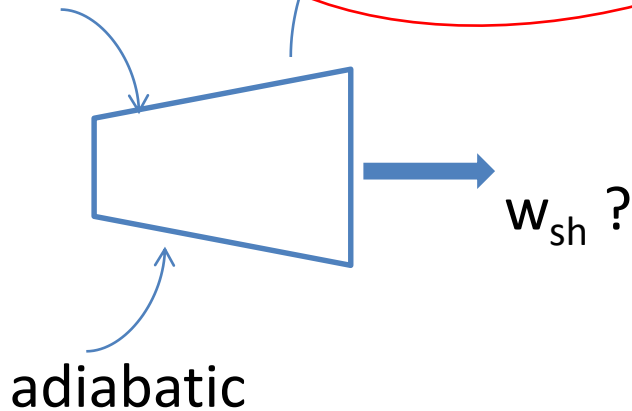
saturated
HFC-134a
 $T_1 = -40^{\circ}\text{C}$
 $P_2 = 500 \text{ kPa}$



Example II

steam
 $T_1 = 600^\circ\text{C}$
 $p_1 = 10 \text{ bar}$

$v_2 = 200 \text{ m/s}$
 $P_2 = 1 \text{ bar}$



$$h_1 = 3697.9 \text{ kJkg}^{-1}$$

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

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

$$p_2 = 100 \text{ kPa}$$

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

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

$$T_2 = 250^\circ\text{C} \quad v_2 = 240.6 \text{ m}^3 \text{ kg}^{-1},$$

$$h_2 = 2974.3 \text{ kJ kg}^{-1}$$

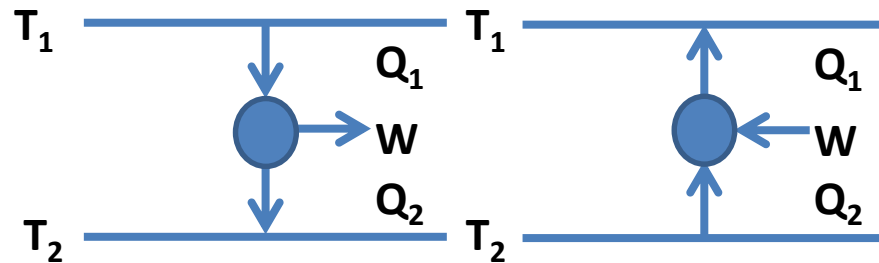
$$w_{sh} = h_1 - h_2 - \frac{v_2^2}{2} = 703.6 \text{ kJ kg}^{-1}$$

WORK FROM HEAT

The Carnot heat engine

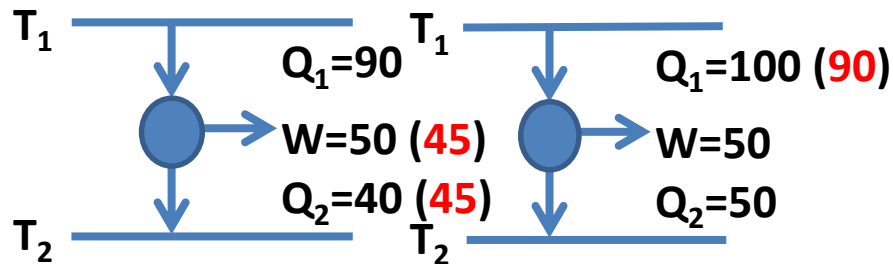
- Sadi Carnot wrestled with the problem of finding the maximum efficiency of a heat engine. He cracked this problem by brilliant deductive reasoning, but no experimenting or tinkering with real steam engines.
- Carnot did this analysis and gave a mathematical representation of the **2nd law** in 1811, 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 led 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

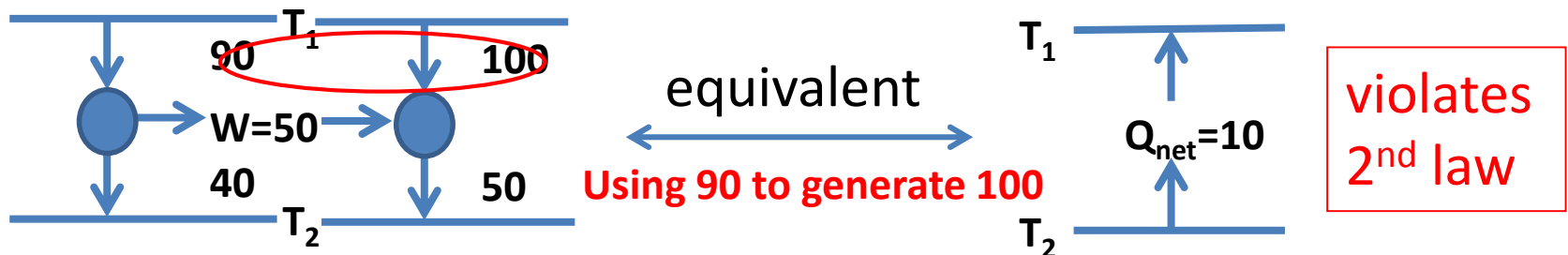


- The former one call **Carnot heat engine**, latter one call **Carnot heat pump**.

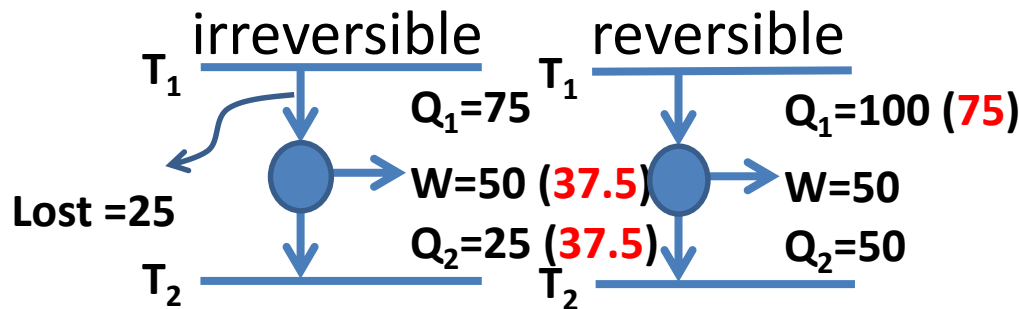
- **Theorem 1.** All reversible heat engines operation between the same two temperatures, T_1 and T_2 must have the same efficiency.
- **Proof.** Let us **assume the contradictory**, the following two reversible engines have different efficiencies,



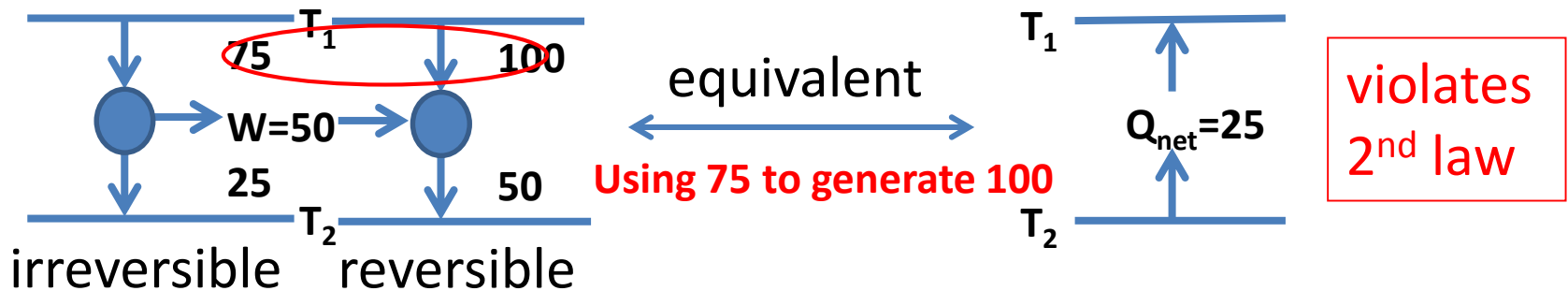
say $\eta_1 = 56\%$, $\eta_2 = 50\%$. Reverse the second and interconnect,



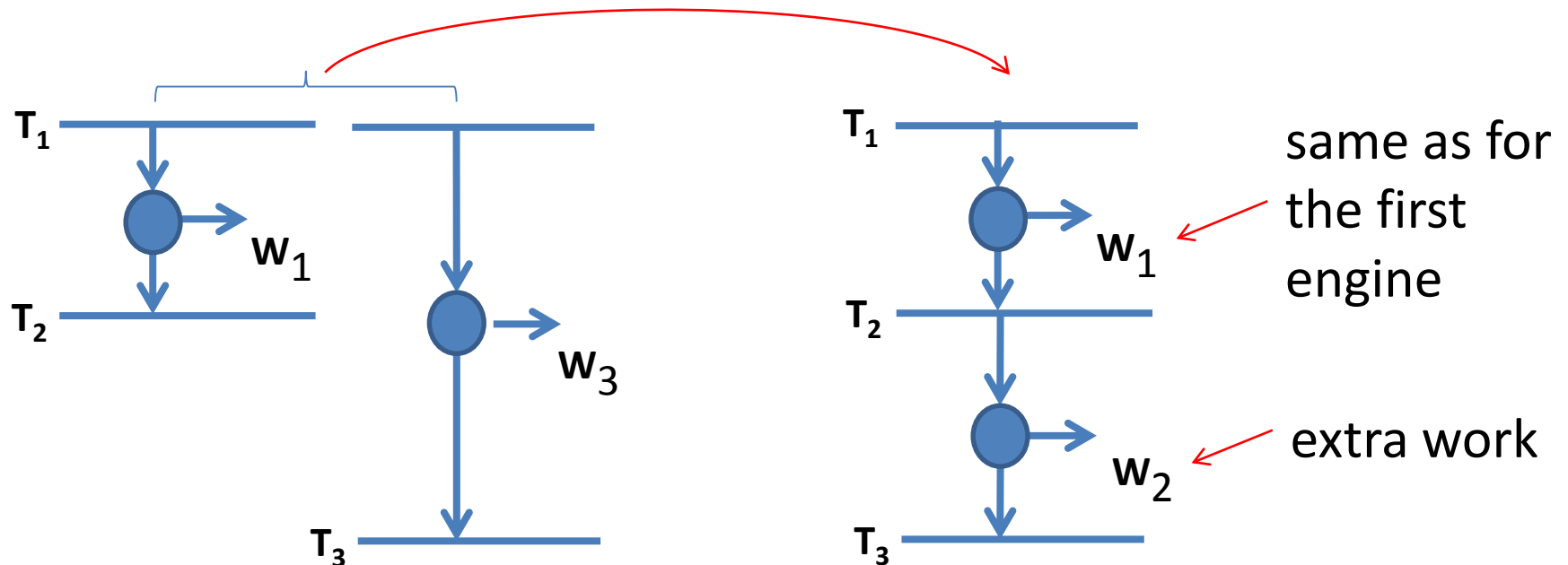
- **Theorem 2.** Reversible heat engines have the highest efficiency between any two temperatures.
- **Proof.** Assume that the irreversible engine has the higher efficiency,



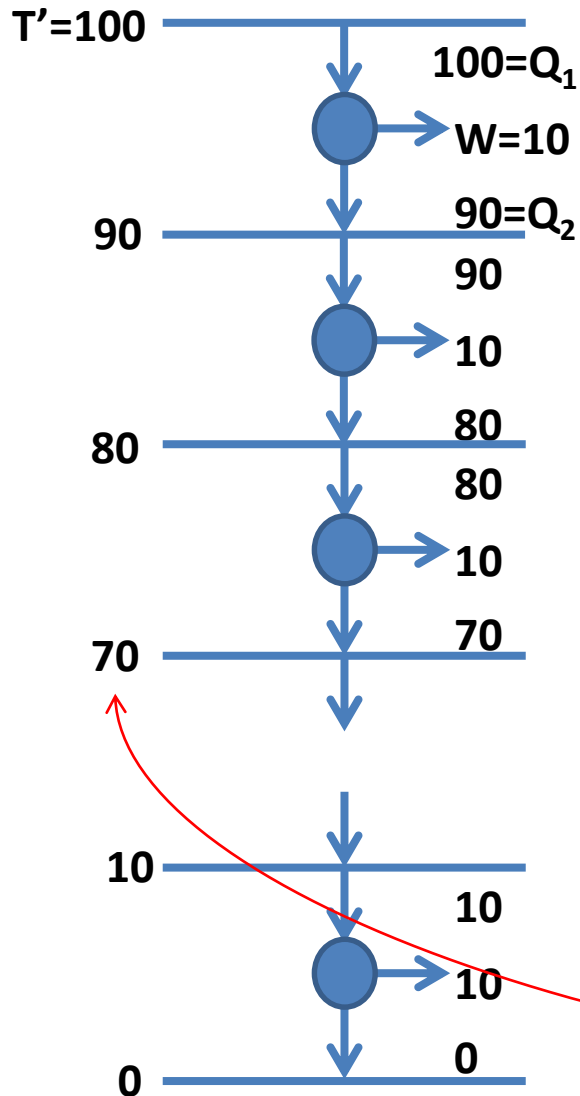
say $\eta_1 = 67\%$, $\eta_2 = 50\%$. Reverse the second and interconnect,



- **Theorem 3.** For the same high temperature T_1 , the engine that the larger ΔT has the higher efficiency and produces more work.
- **Proof.** $W_3 = W_1 + W_2 \geq W_1$.



The kelvin temperature scale



- 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,

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

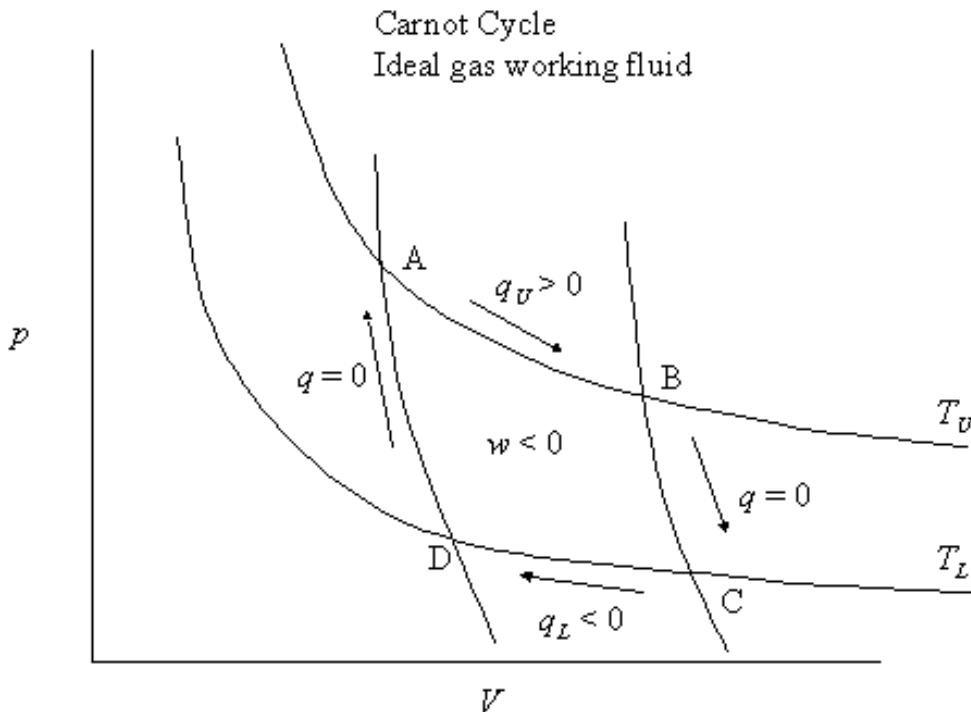
$$\frac{|W|}{|Q_2|} = \frac{T_1' - T_2'}{T_2'} \quad \text{or} \quad \frac{|Q_2|}{|Q_1|} = \frac{T_2'}{T_1'}$$

- 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.

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.



- 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

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

- BC: adiabatic reversible expansion

$$|w| = c_v (T_2 - T_1)$$

- CD: isothermal contraction at T_2

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

- DA: adiabatic reversible contraction back to A.

$$|w| = c_v (T_1 - T_2)$$

- For the adiabatic reversible

$$\frac{p_A}{p_D} = \left(\frac{T_1}{T_2} \right)^{\frac{k}{k-1}} \quad \text{or} \quad \frac{p_A}{p_B} = \frac{p_D}{p_C}$$

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

For the four step cycle,

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

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

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, $-Q_2$,

Kelvin
work scale

$$\frac{-Q_2}{Q_1} = \frac{T_2}{T_1} \quad \text{or} \quad \frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0$$

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

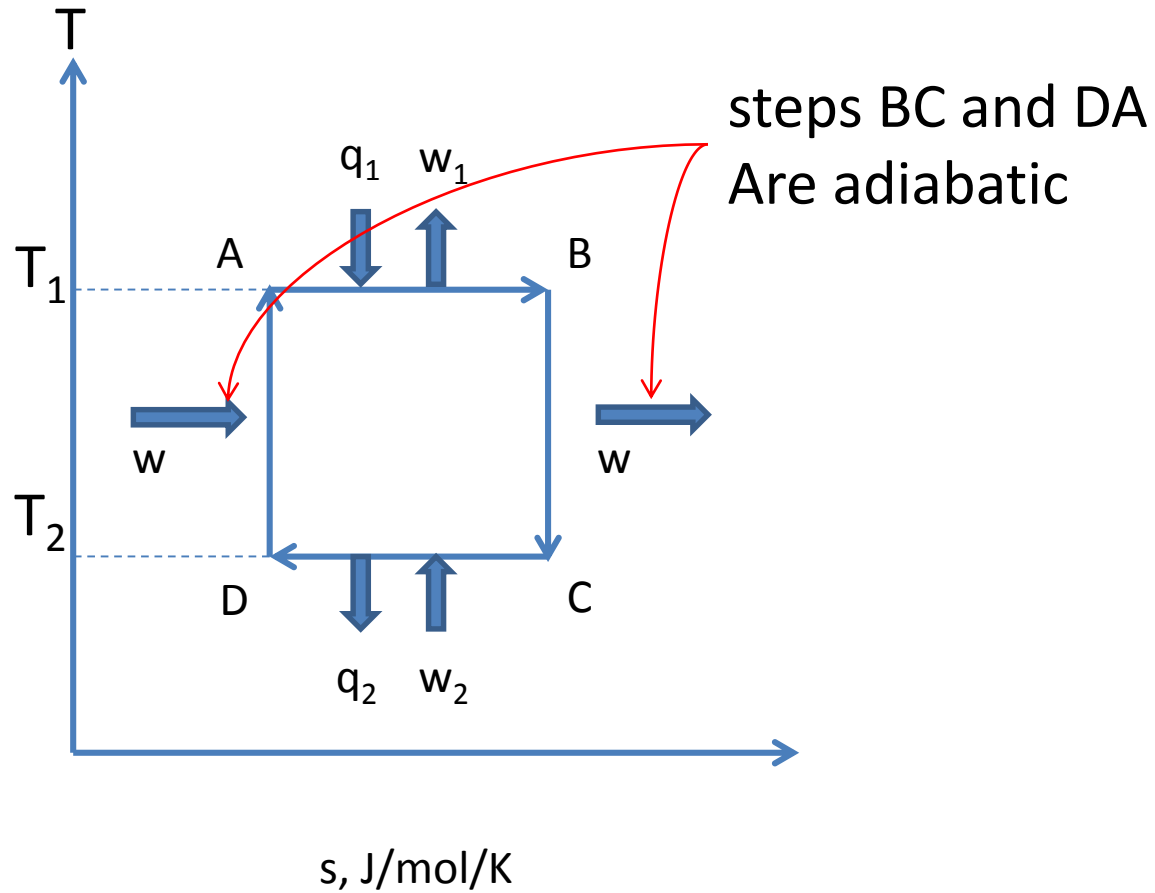
$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \dots = 0$$

- Or

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

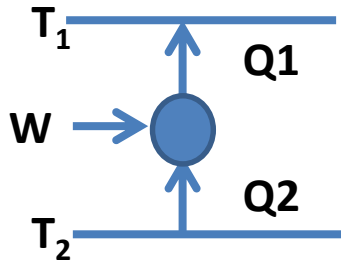
- This quantity always enters in cyclical reversible processes, it represents a change in a property of the system as is the enthalpy or internal energy change. This is **entropy change, ΔS** . Carnot's !

T-s diagram of Carnot engine



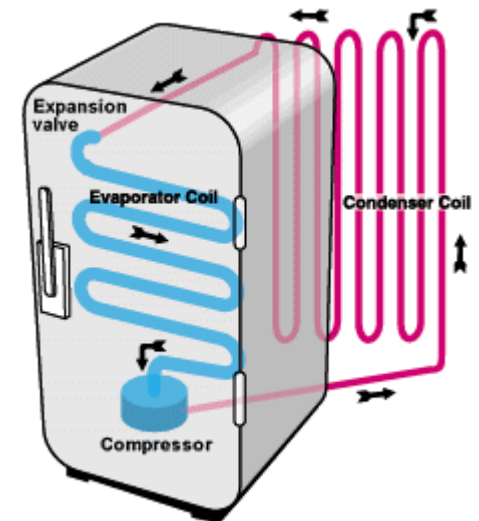
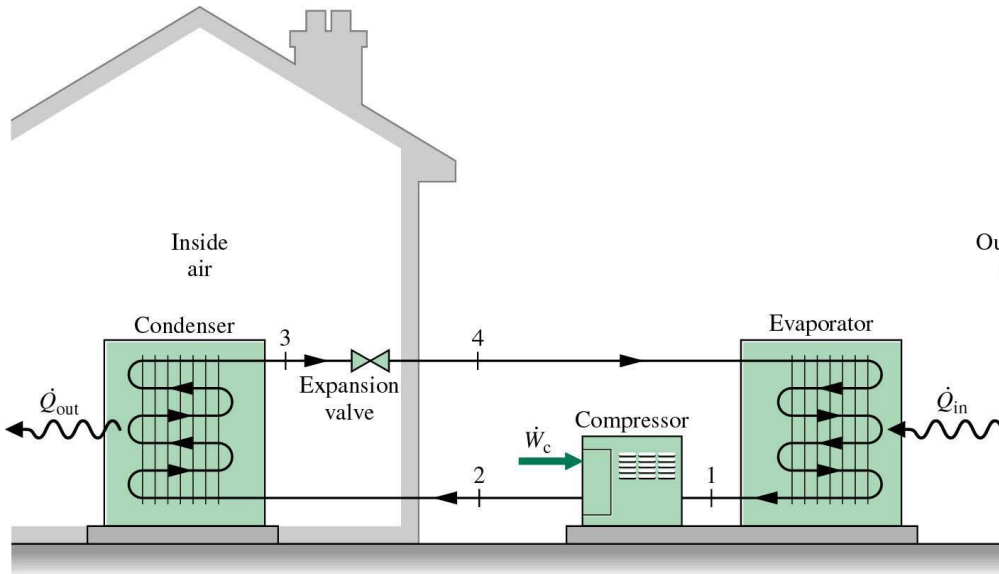
THE IDEAL OR REVERSIBLE HEAT PUMP

Coefficient of performance, COP



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

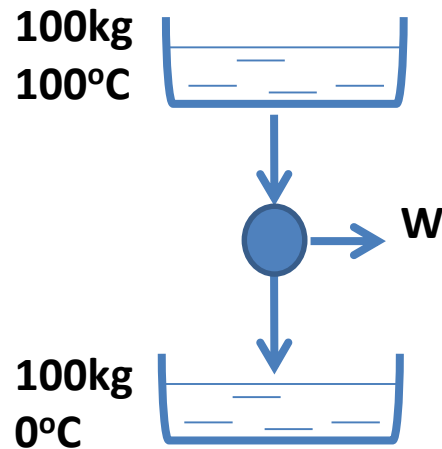
$$\text{cop}' = \frac{|Q_1|}{|W|} = \frac{T_1}{T_1 - T_2} \quad \text{heater}$$



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



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,

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

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

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

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

- With work withdraw,

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

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

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

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

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

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

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