# Ideal Gases and the 2nd Law

(Understanding Engineering Thermo—Octave Levenspiel)

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# BATCH OF IDEAL GAS

- Recall the $1^{st}$ and $2^{nd}$ law,

$$dE = đQ + đW$$

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

- therefore,

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

- Constant volume process

$$w_{rev} = 0, \; Q = \Delta U$$

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

- Constant pressure process

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

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

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

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

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

- 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 $p_2$
- Recall

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

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

- Therefore,

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

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

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

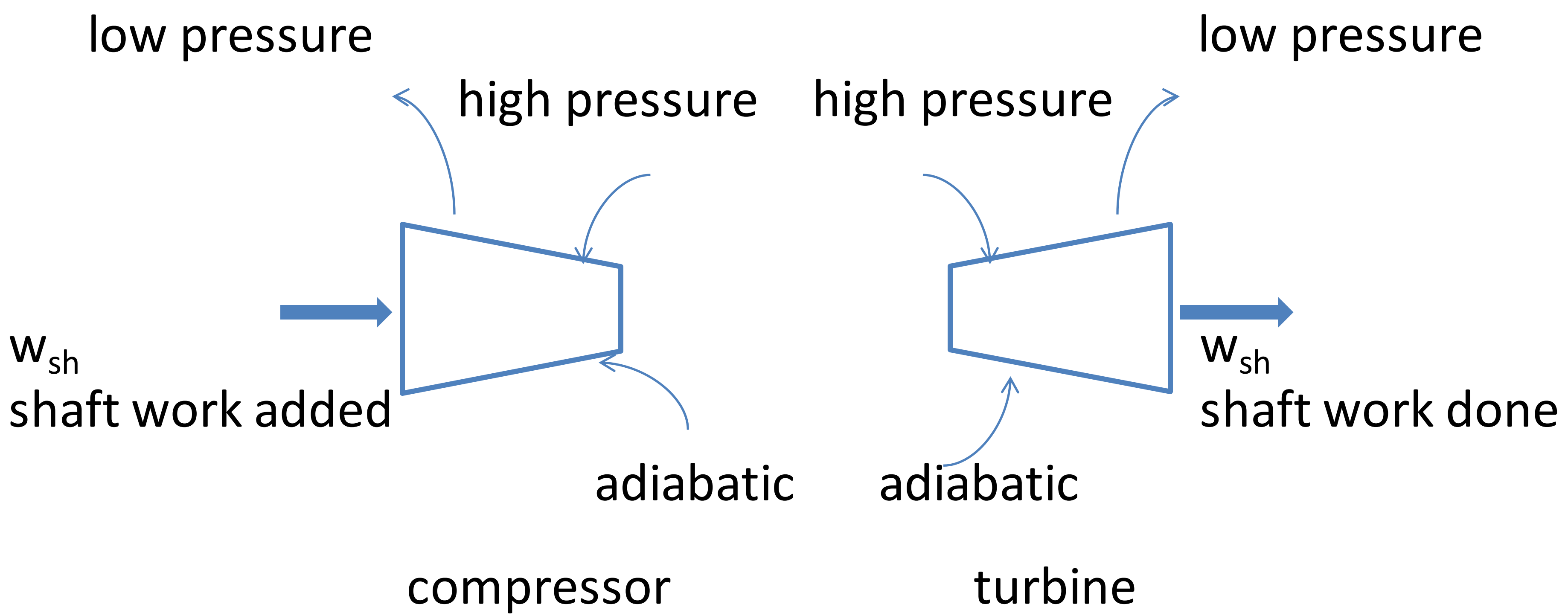
- Reversible work
- Going from $p_1$ $T_1$ to $p_2$ $T_2$ , one can take various paths, two are as follow,
  - Constant $p_1$, $T_1$ to $T_2$ + Constant $T_2$, $p_1$ to $p_2$
  - Constant $T_1$, $p_1$ to $p_2$ + Constant $p_2$, $T_1$ to $T_2$

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

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

  - 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; $\Delta S = 0$)



- From 1st law
- And flow systems

$$q_{actual} = 0$$

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

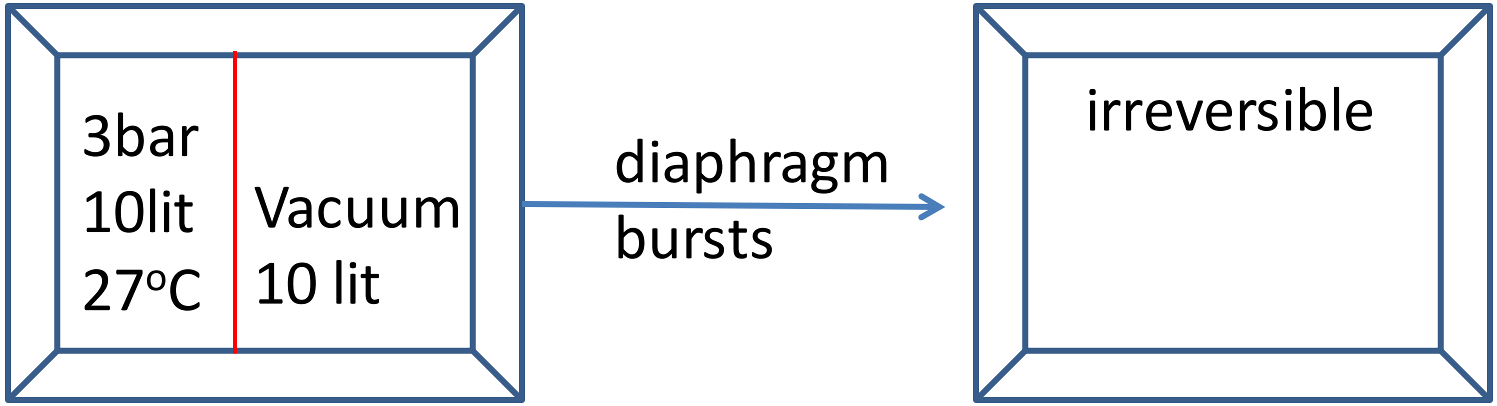
- From 2nd law

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

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

# Example I

- Rupture of a diaphragm in an insulated tank
- Find $\Delta S$ 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

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

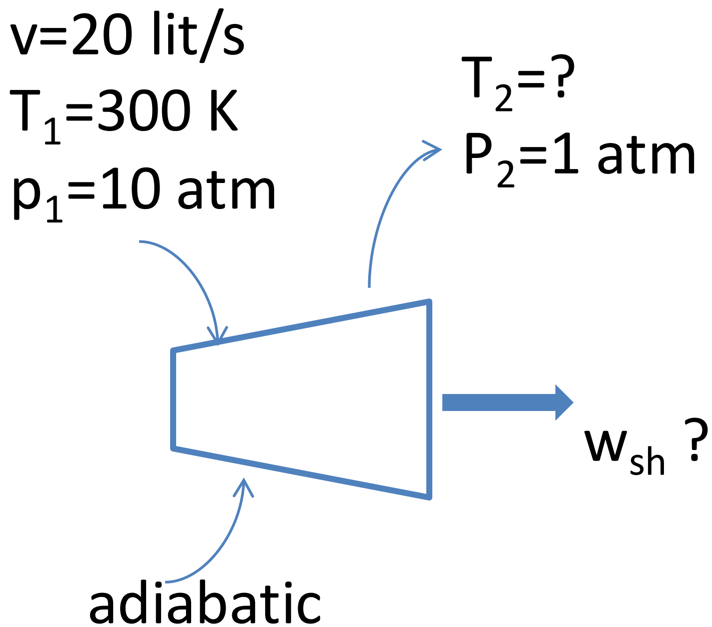
$$\Delta S = \int\frac{dQ_{rev}}{dT} = nR\ln\frac{V_{final}}{V_{initial}}$$

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

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

# 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.




- For adiabatic reversible

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

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

- The molar flow rate

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

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

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

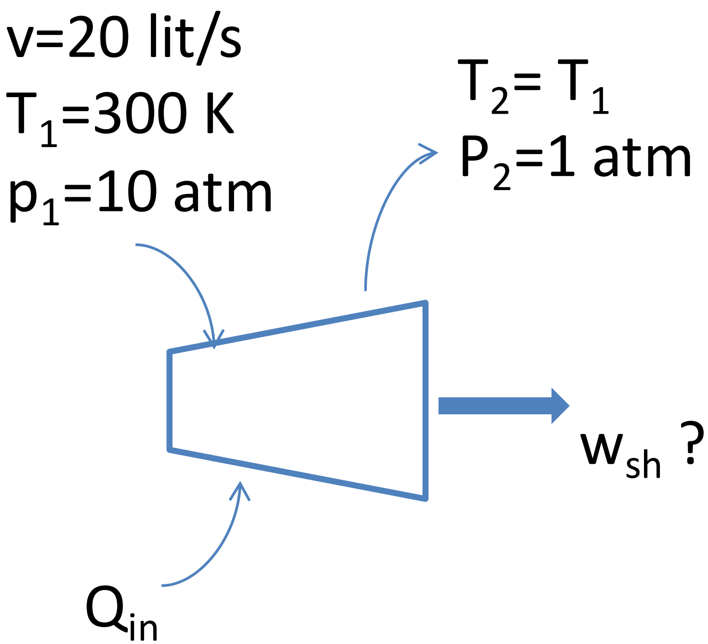
$$\dot{W}_{rev} = -\Delta\dot{H}$$

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

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

$$\left(\frac{0.2778\ \mathrm{kW \cdot hr}}{10^6\ \mathrm{J}}\right) = \$1728/\mathrm{month}$$

- $T_2$=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% more.

# Example III

- A Hilsch tube, a "tricky" device that splits a of high-pressure air ($p_1$=1.5 bar, $T_1$=27$^o$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$^o$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,

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

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

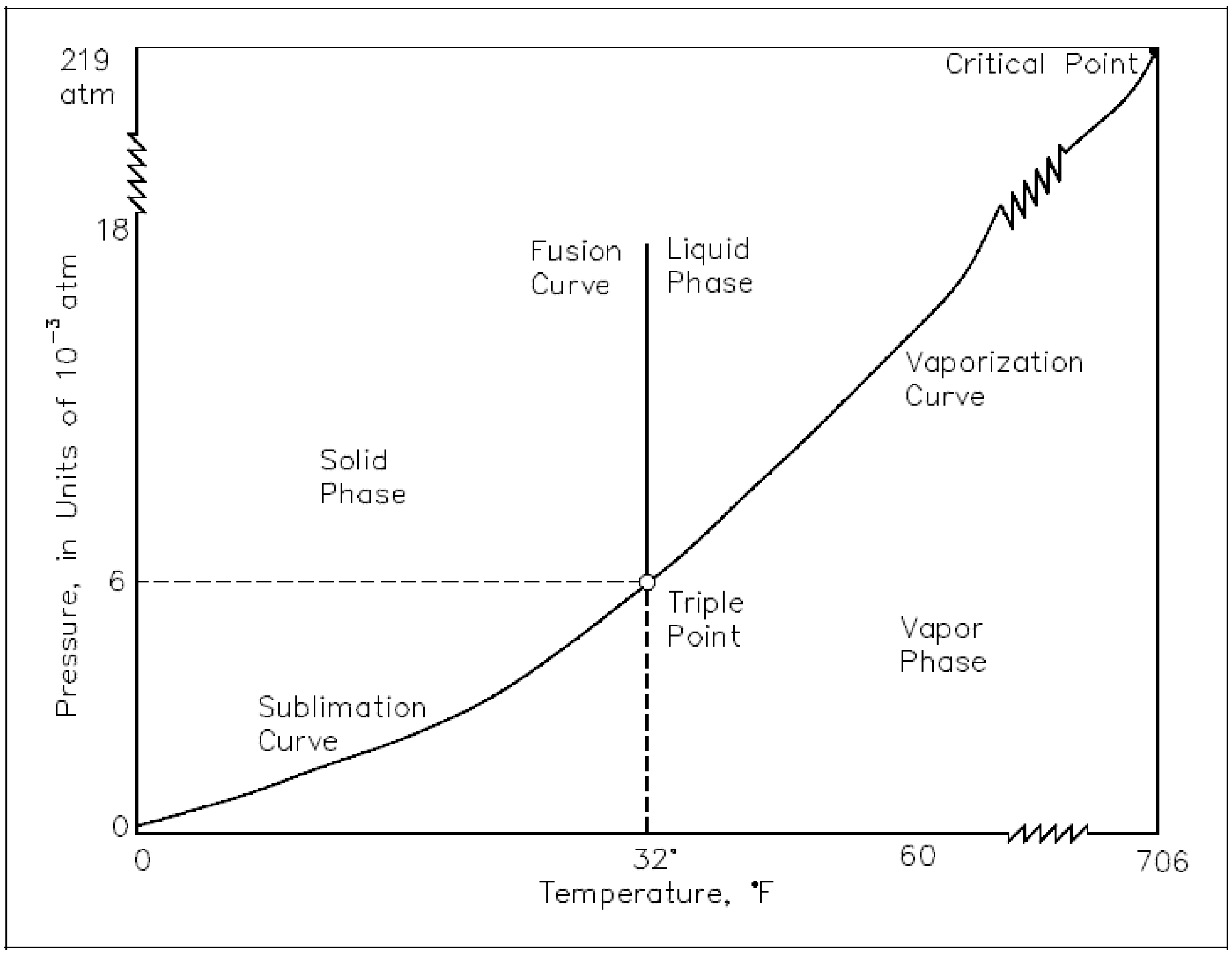
$$\boxed{\begin{aligned} \Delta S_{total} &= \Delta S_{cold\,side} + \Delta S_{hot\,side} \\ &= \left[ 29.1 \ln \frac{150}{300} - 8.314 \ln \frac{1}{1.5} \right] + \left[ 29.1 \ln \frac{450}{300} - 8.314 \ln \frac{1}{1.5} \right] \\ &= -1.63 \ \mathrm{J mol^{-1} K^{-1}} \quad < 0 \end{aligned}}$$

# ENTROPY OF ENGINEERING FLUIDS

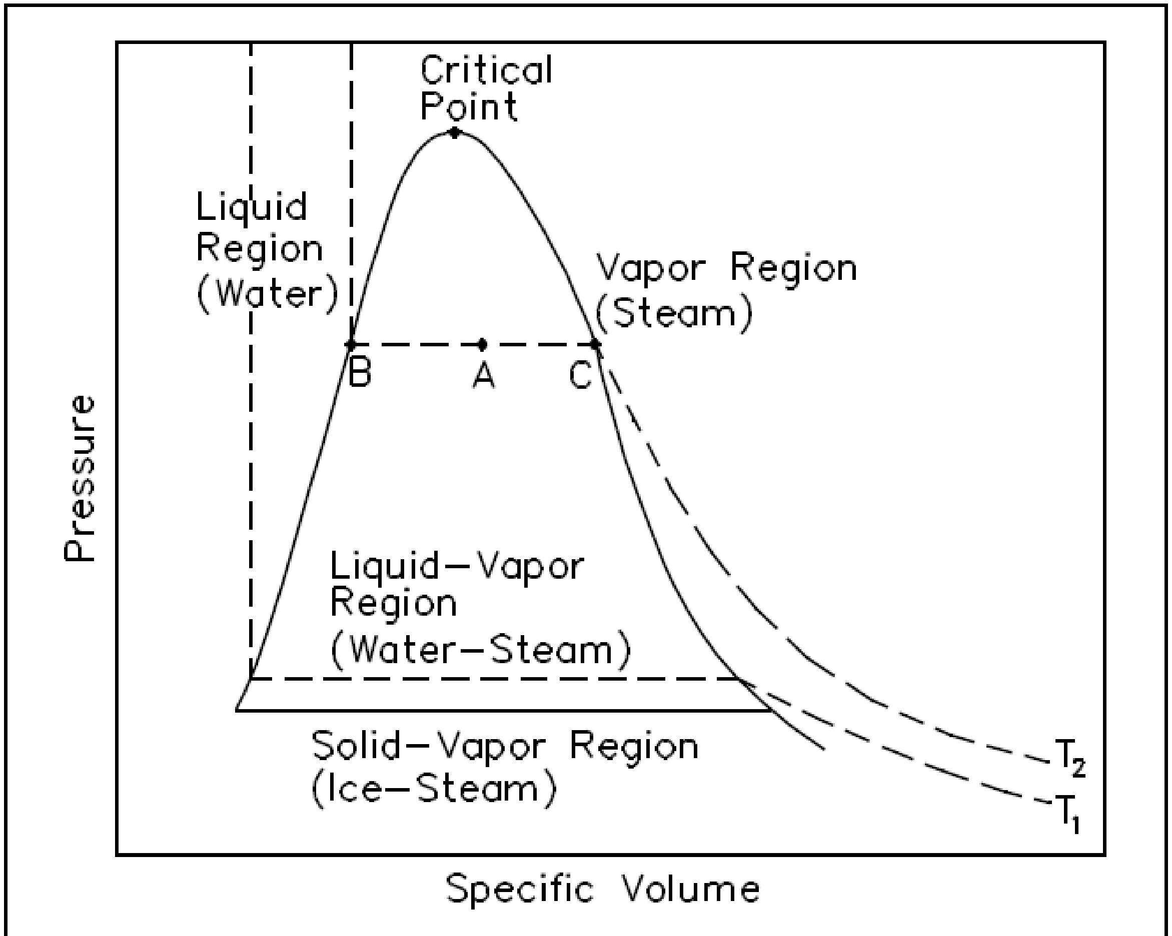
# Property Diagrams

- 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.

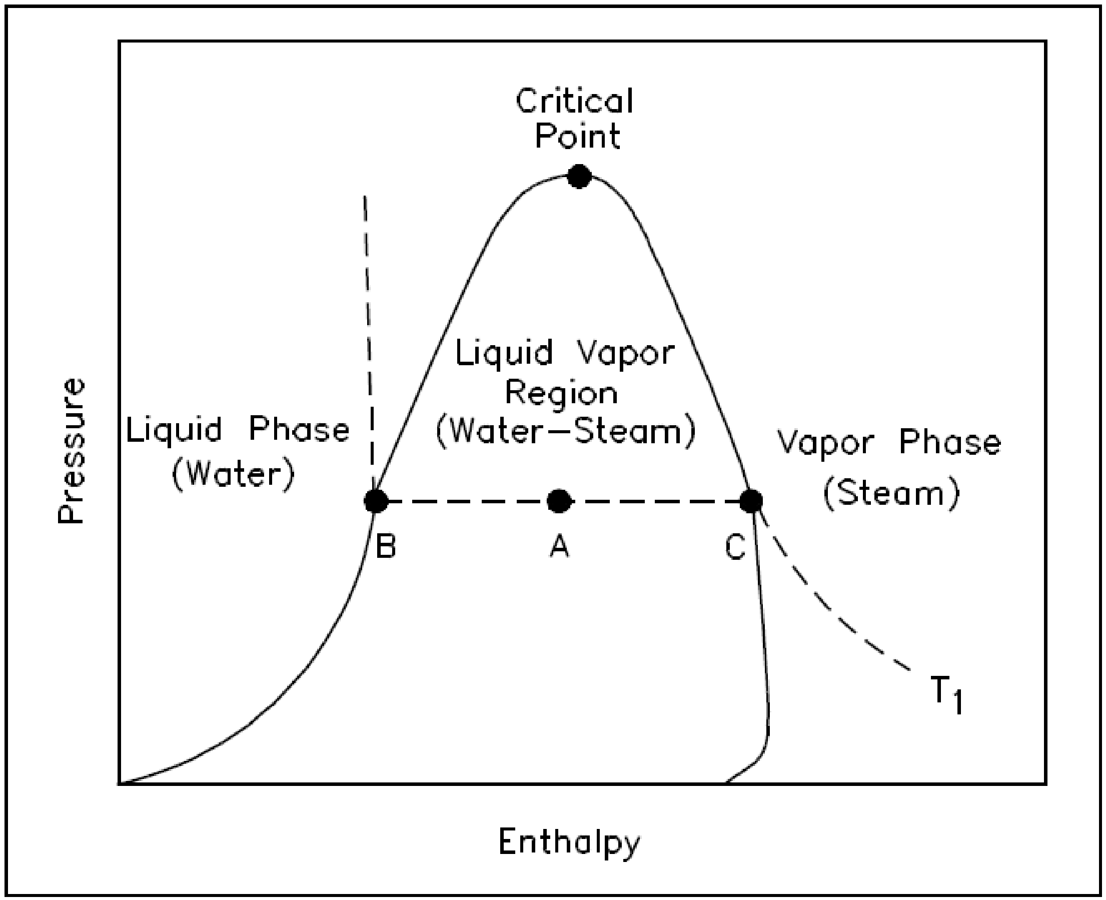
# Pressure- Temperature (P-T) diagram



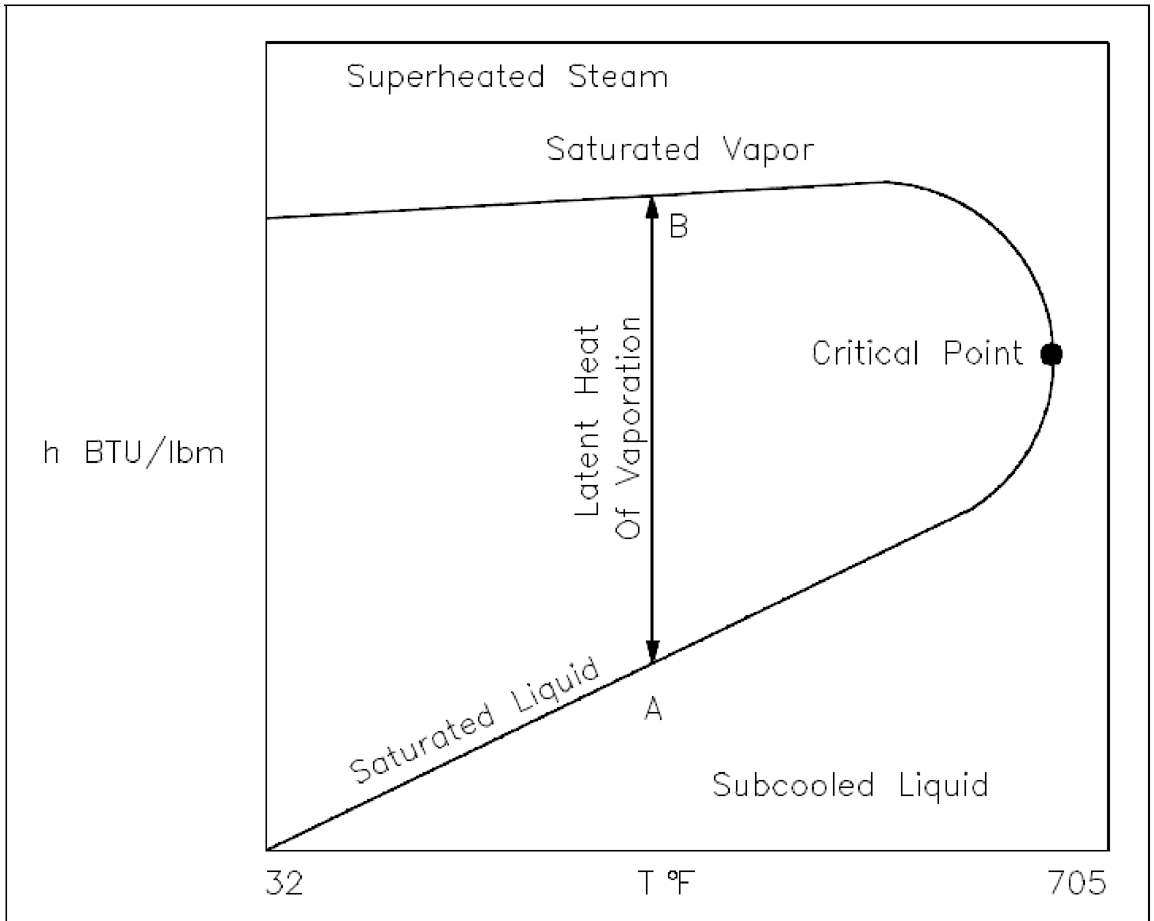
# Pressure-Specific Volume (P-v) Diagram



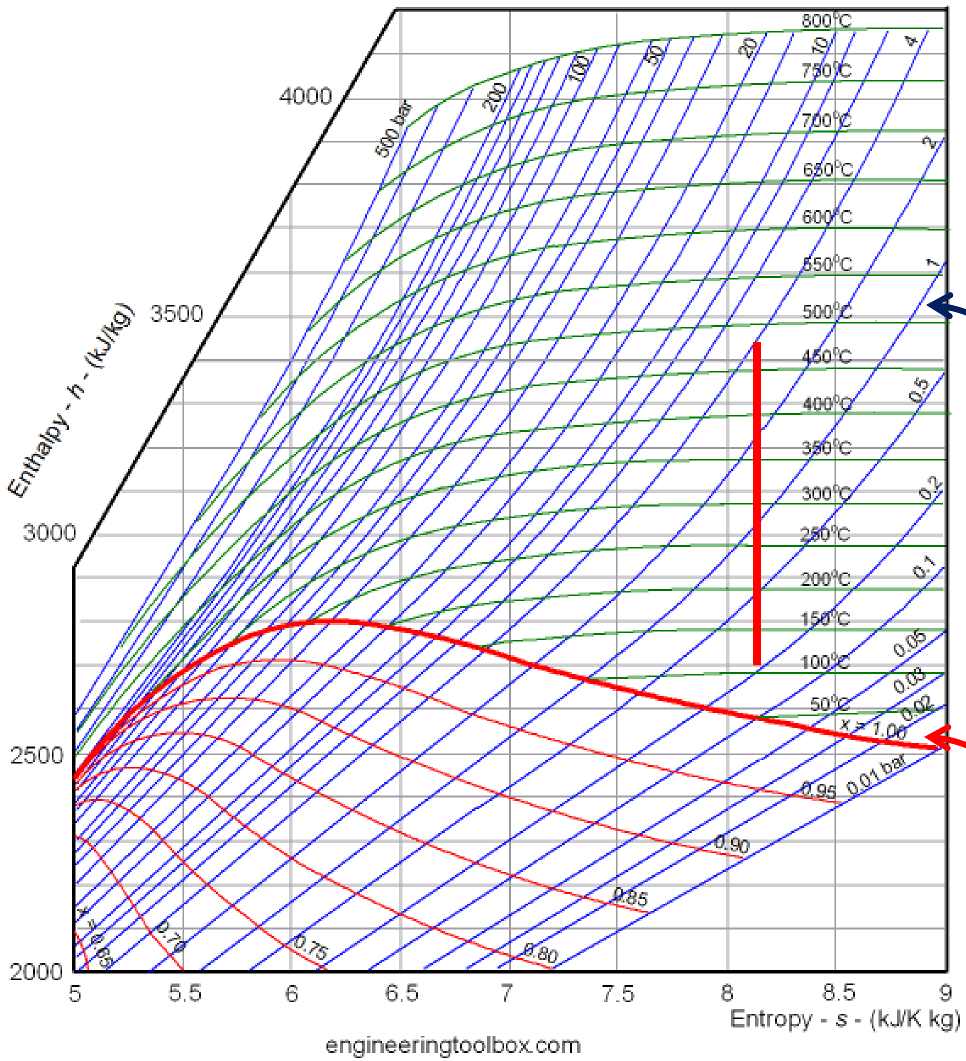
# Pressure-Enthalpy (P-h) Diagram



# Enthalpy-Temperature (h-T) Diagram



# Enthalpy-Entropy (h-s) or Mollier Diagram

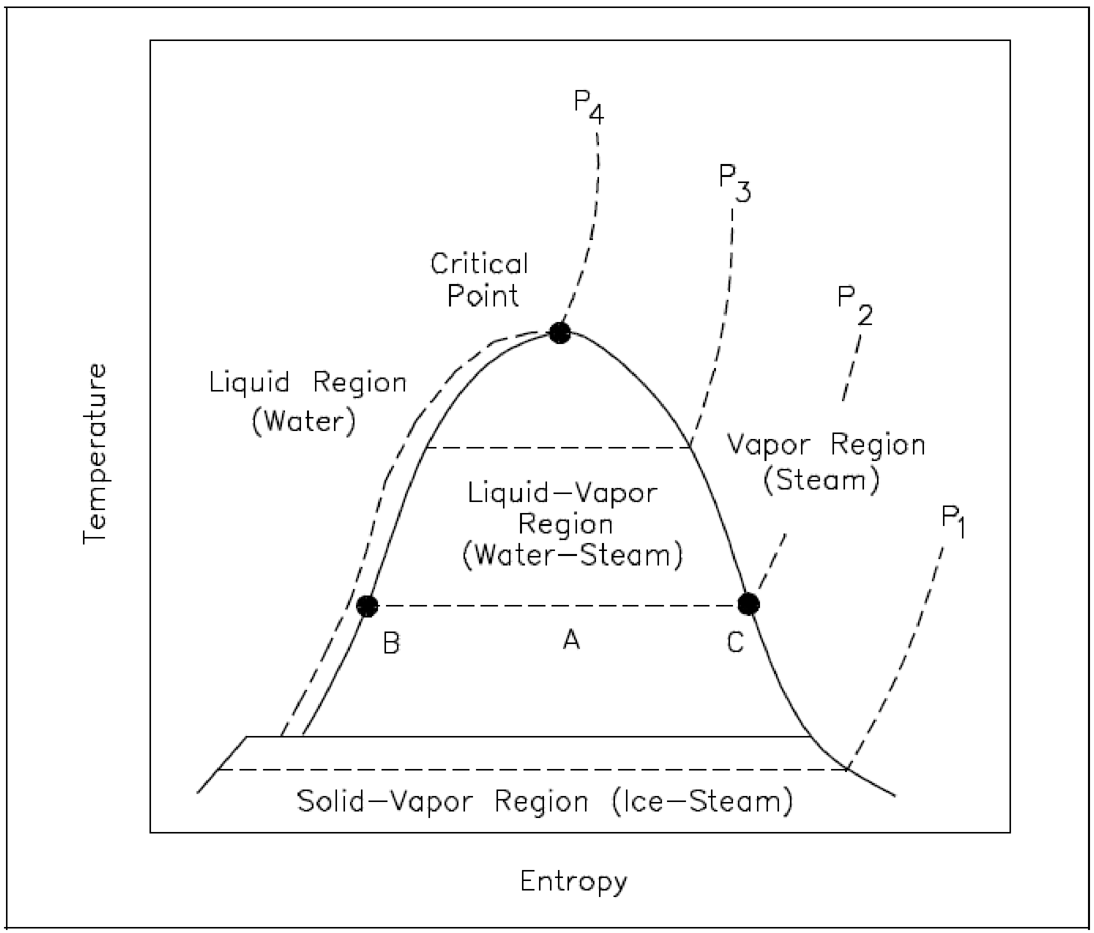



constant
p line

saturated
vapor line

- 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



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

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

$$= \frac{m\Delta h_{lg}}{T}$$ ← 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

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

$$\boxed{\begin{aligned} p_1 &= 51.14\ \text{kPa} \qquad v_1 = 0.3614\ \text{m}^3\text{kg}^{-1} \\ h_1 &= 374.3\ \text{kJ kg}^{-1} \quad s_1 = 1.7655\ \text{kJ kg}^{-1}\text{K}^{-1} \end{aligned}}$$

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

$$\boxed{\begin{aligned} p_2 &= 500\ \text{kPa} \ \ \text{and} \\ s_2 = s_1 &= 1.7655\ \text{kJ kg}^{-1}\text{K}^{-1} \end{aligned}}$$

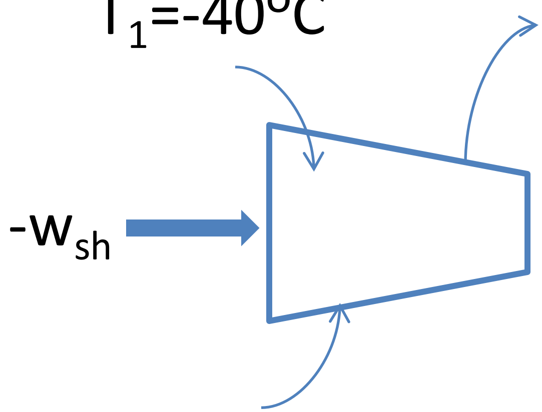
$$T_2 = 30^\circ\text{C} \quad v_2 = 0.04434\ \text{m}^3\text{kg}^{-1},$$

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

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

saturated
HFC-134a
$T_1$=-40°C

$P_2$=500 kPa

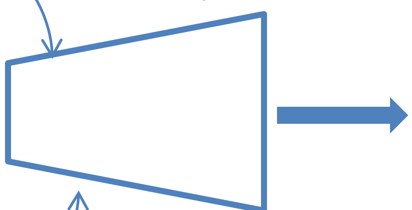



adiabatic

# Example II

steam
$T_1$=600°C
$p_1$=10 bar

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



$w_{sh}$ ?

adiabatic

$$\boxed{\begin{aligned} h_1 &= 3697.9\ \text{kJkg}^{-1} \\ s_1 &= 8.0290\ \text{kJkg}^{-1}\text{K}^{-1} \end{aligned}}$$

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

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

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

$$\boxed{\begin{aligned} &T_2 = 250^\circ\text{C} \quad v_2 = 2.406\ \text{m}^3\text{kg}^{-1}, \\ &h_2 = 2974.3\ \text{kJkg}^{-1} \\ &w_{sh} = h_1 - h_2 - \frac{v_2^2}{2} = 703.6\ \text{kJkg}^{-1} \end{aligned}}$$

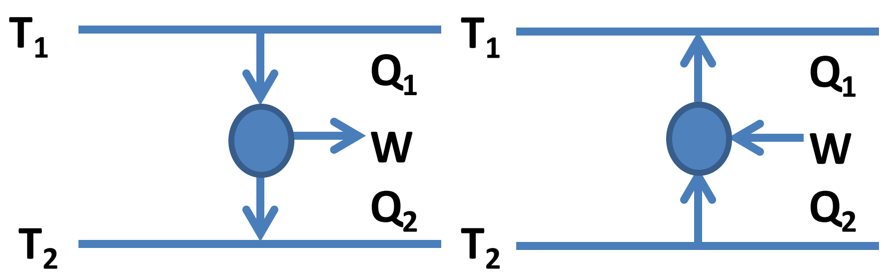
$$h_2 + \frac{v_2^2}{2} - h_1 = \cancelto{0}{q} - w_{sh}$$

# WORK FROM HEAT

# The Carnot heat engine

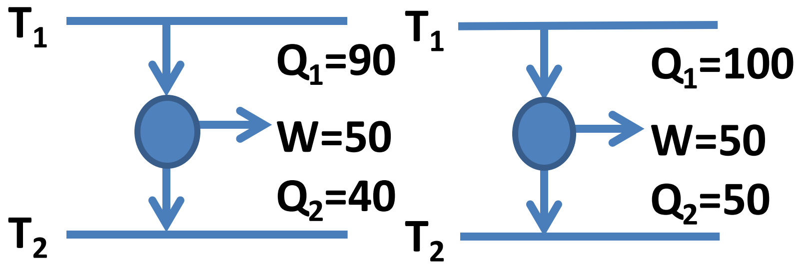
- Sadi Carnot wrestled with the problem of finding the maximum efficiency of a heat engine. He cracked this problem by brilliant deductive reasoning, but no experimenting or tinkering with real steam engines.
- Carnot did this analysis and gave a mathematical representation of the 2$^{nd}$ law in 1811, long before the 1$^{st}$ law was clarified and properly expressed (about 1840 to 1850). Shouldn't the 2$^{nd}$ law be called the 1$^{st}$ 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

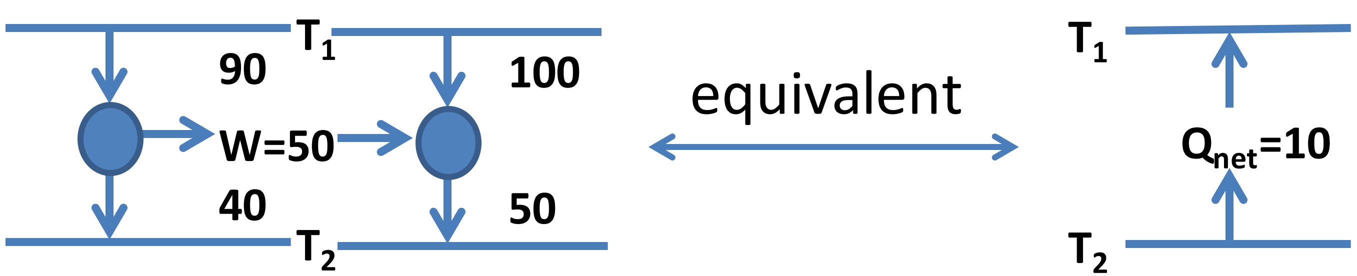



- The former one call Carnot heat engine, latter one call Carnot heat pump.

- 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,

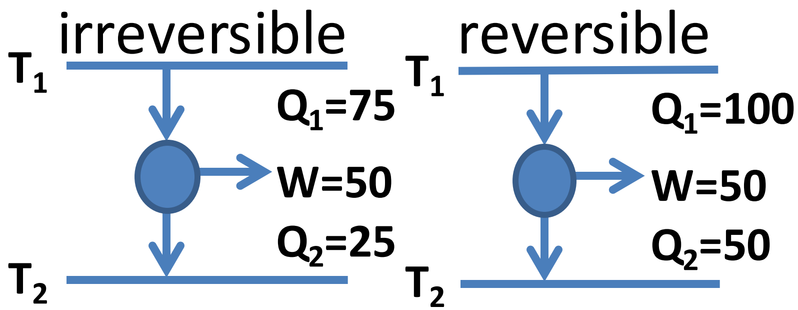



say $\eta_1$=56%, $\eta_2$=50%. Reverse the second and interconnect,

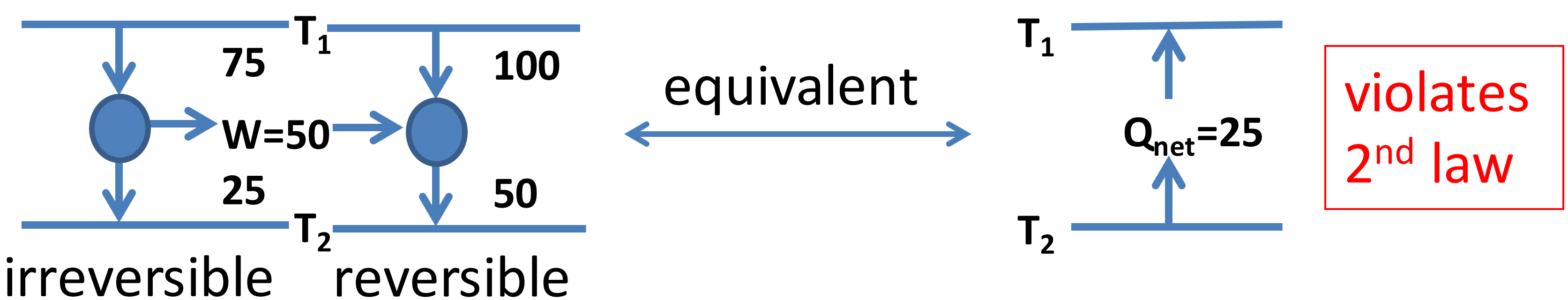



violates $2^{nd}$ law

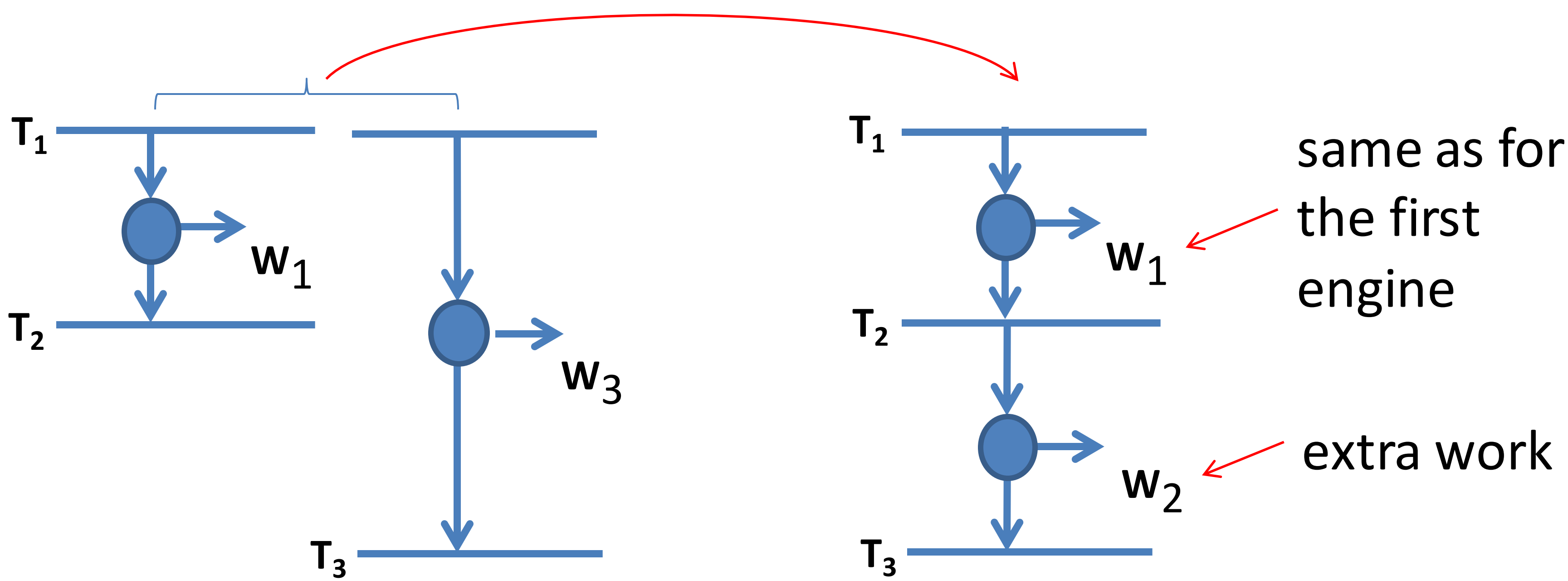
- Theorem 2. Reversible heat engines have the highest efficiency between any two temperatures.
- Proof. Assume that the irreversible engine has the higher efficiency,



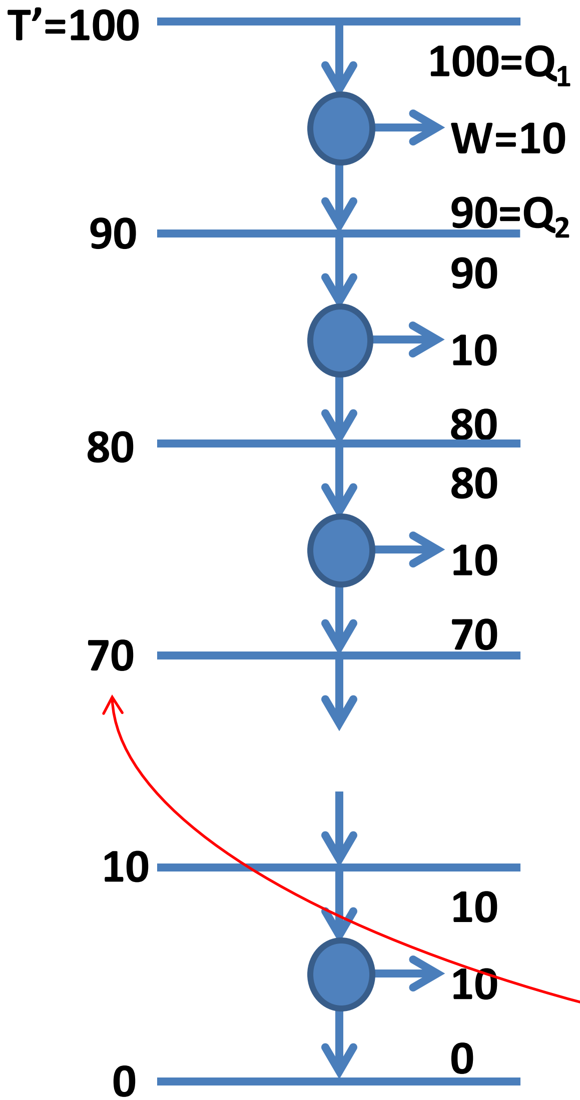

say $\eta_1$=67%, $\eta_2$=50%. Reverse the second and interconnect,



- Theorem 3. For the same high temperature $T_1$, the engine that the larger $\Delta T$ 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,

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

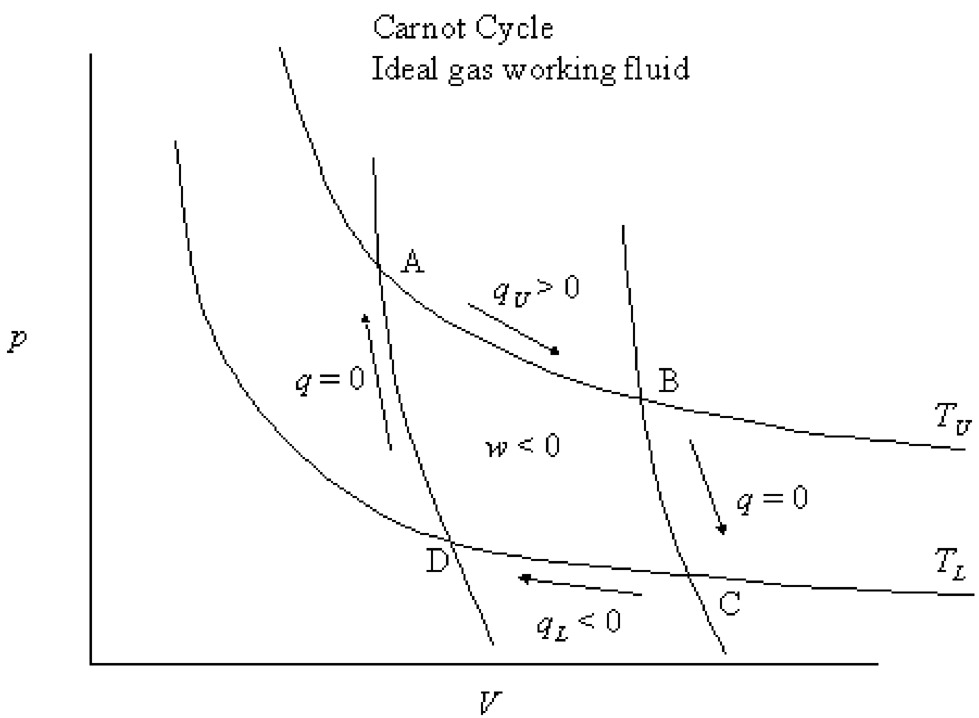
$$\frac{|W|}{|Q_2|} = \frac{T_1' - T_2'}{T_2'} \quad \text{or} \quad \frac{|Q_2|}{|Q_1|} = \frac{T_2'}{T_1'}$$

- 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
- $0^o$ F was established as the temperature of a solution of “brine” made from equal parts of ice, water and salt (ammonium chloride)
- $32^o$ F as melting point of ice
- $96^o$ F as the average human body temperature
- In this scale the boiling point of water is defined to be $212^o$ F, $180^o$ 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 $T_1$
- BC: adiabatic reversible expansion
- CD: isothermal contraction at $T_2$
- DA: adiabatic reversible contraction back to A.

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

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

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

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

- For the adiabatic reversible

$$\left.\begin{aligned} \frac{p_A}{p_D} &= \left(\frac{T_1}{T_2}\right)^{\frac{k}{k-1}} \\ \frac{p_B}{p_C} &= \left(\frac{T_1}{T_2}\right)^{\frac{k}{k-1}} \end{aligned}\right\} \text{ or } \frac{p_A}{p_B} = \frac{p_D}{p_C}$$

For the four step cycle,

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

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

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,

Kelvin work scale

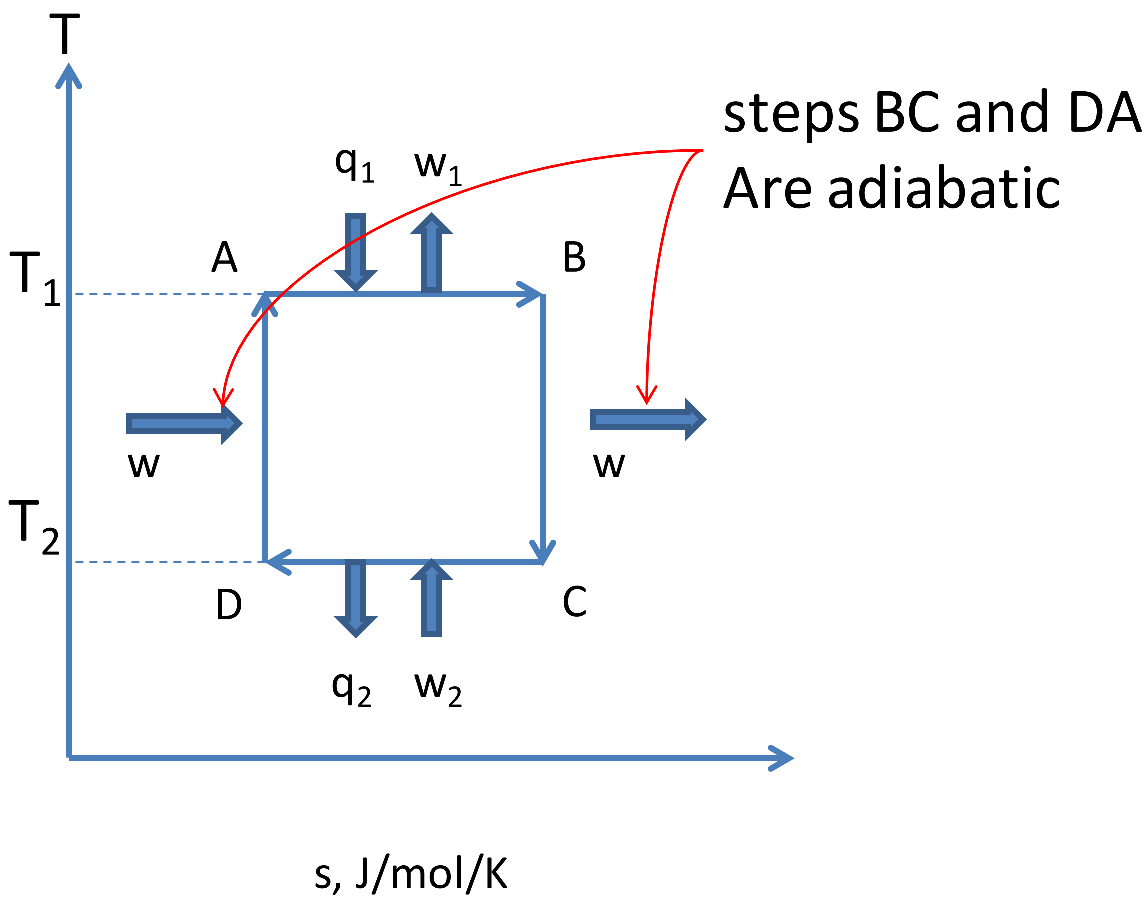
$$\frac{-Q_2}{Q_1} = \frac{T_2}{T_1} \quad \text{or} \quad \frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0$$

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

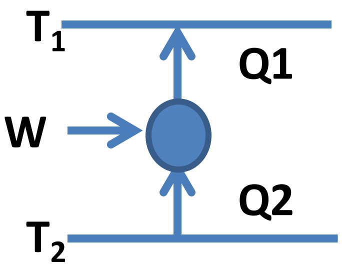
$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \cdots = 0$$

- Or $$\boxed{\sum \frac{Q_i}{T_i} = 0 \quad \text{or} \quad \int \frac{Q_{rev}}{T} = 0}$$
- 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, $\Delta S$. Carnot's !

# T-s diagram of Carnot engine



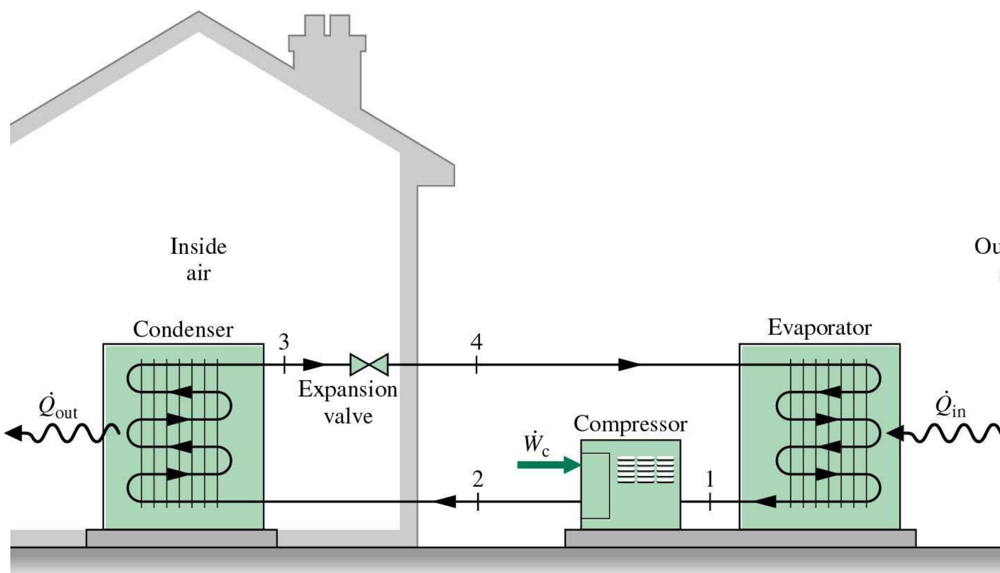
# THE IDEAL OR REVERSIBLE HEAT PUMP

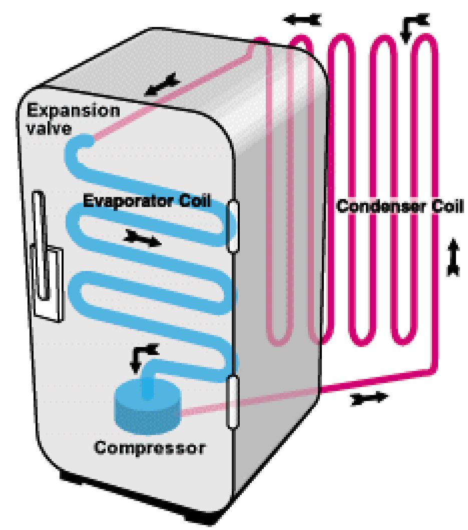



## Coefficient of performance, COP

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

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

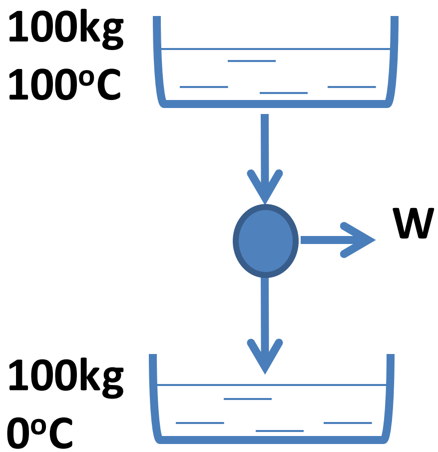


# Example

- 100 kg of water at 100$^oC$ furnishes heat to a Carnot engine that discards heat to a sink consisting of 100 kg of cold water at 0$^oC$. 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,

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

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

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

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

- With work withdraw,

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

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

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

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

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

- Work done is the energy lost in going from 50$^{o}$C to 46$^{o}$C.

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