8.21 The Physics of Energy
Fall 2009

8.21 Lecture 10

Phase Change Energy Conversion I

September 30, 2009

- Why this now?

- Thermodynamics of heat extraction
- Phase change in pure substances

Part I

- The vapor compression cycle: heat pumps, refrigeration, air conditioners
- The Rankine steam cycle and steam turbines
- Some implementations of the Rankine cycle

Part II

Several aims

- Explain how simple thermodynamic cycles can move heat from low to high temperatures
- Explain why cycles that make a fluid change from vapor to liquid and back dominate practical applications, and how they work
- Construct and evaluate the dominant cooling ("vapor compression") and power ("Rankine") cycles in use today

Heat extraction devices are everywhere

- Household air conditioning — 5.1% of all U. S. energy use (2001)
- Household refrigeration — 4.4%
- Commercial AC and refrigeration — 7%
- Plus industrial cooling and "actively cooled transport"!

Household energy use

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Similar graph can be found on web page http://www.homeauto.com/_SiteElements/images/EnergyMgt/EnergyPieChart_500.jpg

Kitchen energy use

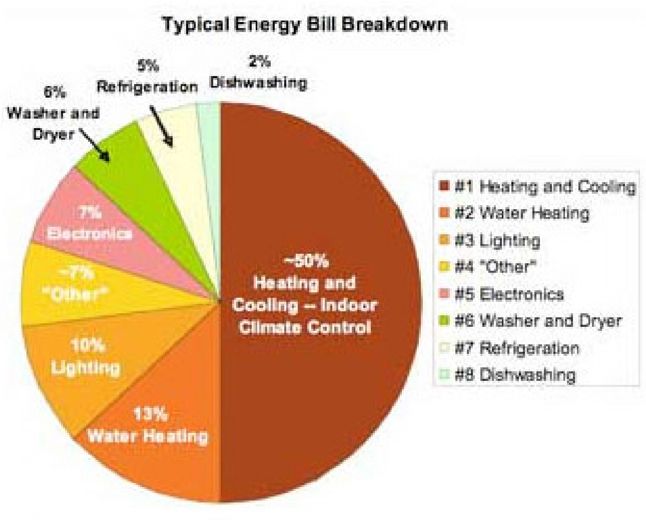

Image courtesy of EPA.

Heat pumps are gaining popularity for home heating

- ⋆ Use work to move heat from cold environment to warm environment
- ⋆ Same principle as refrigerator, except aim is to warm rather than to cool!

Heat pump image removed due to copyright restrictions.

Could describe heat extraction devices absent phase change, but

- ⋆ Heat extraction devices almost universally employ phase change thermodynamic cycle
- ⋆ Which are chosen for thermodynamic properties (eg. liquid ⇔ vapor near ambient temperatures) eg. Freon
- ⋆ And phase change power generation is ubiquitous

Turbine generator image removed due to copyright restrictions.

Please see: http://geothermal.marin.org/Geopresentation/images/img038.jpg

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Please see:
http://www.nytimes.com/2009/09/30/business/energy-environment/30water.html

Many projects involve building solar thermal plants, which use cheaper technology than the solar panels often seen on roofs. In such plants, mirrors heat a liquid to create steam that drives an electricity-generating turbine. As in a fossil fuel power plant, that steam must be condensed back to water and cooled for reuse.

But then things got messy. The company revealed that its preferred method of cooling the power plants would consume 1.3 billion gallons of water a year, about 20 percent of this desert valley's available water.

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Heat engines and heat extraction devices with flowing fluids

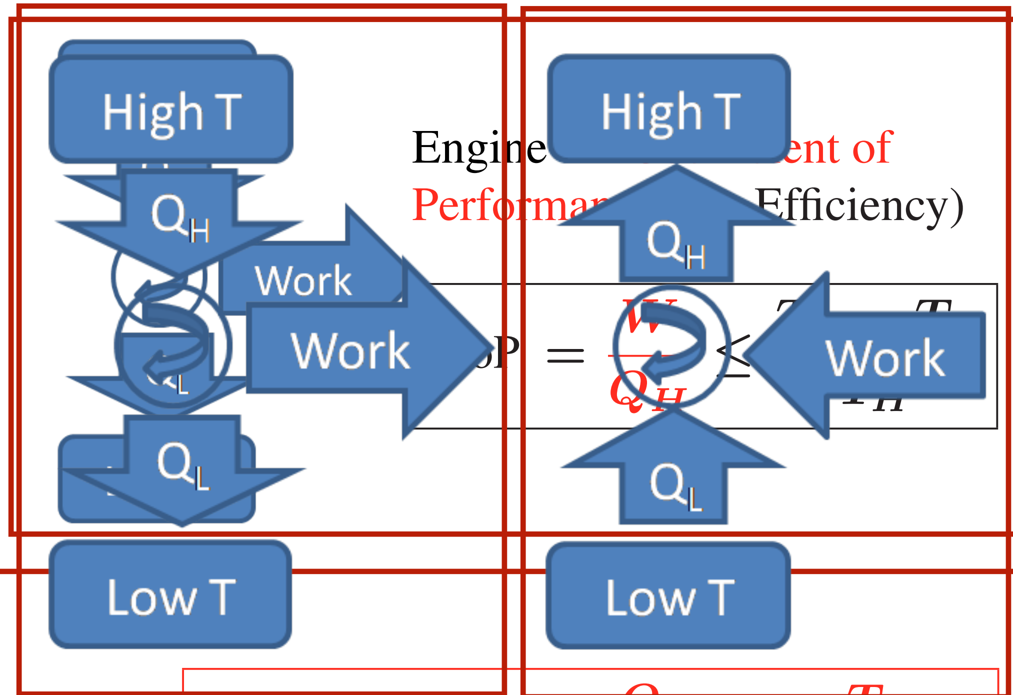
- Fluid flows in, bringing heat, flows out removing heat, work gets done, but
- In a cycle, the machine returns to its original state and does not store energy or entropy

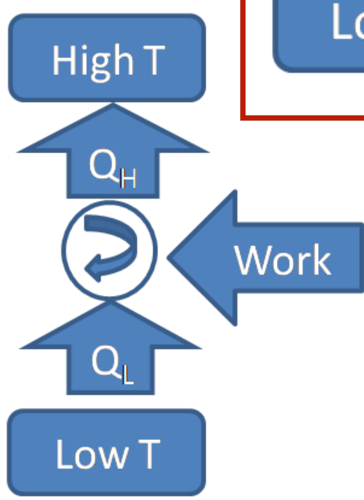
Conservation of energy around a cycle: machine does not store energy

$$Q_H = Q_L + W$$

Best possible: Entropy is conserved around a cycle if it's performed reversibly: "machine does not store entropy"

$$\frac{Q_L}{T_L} - \frac{Q_H}{T_H} = 0$$

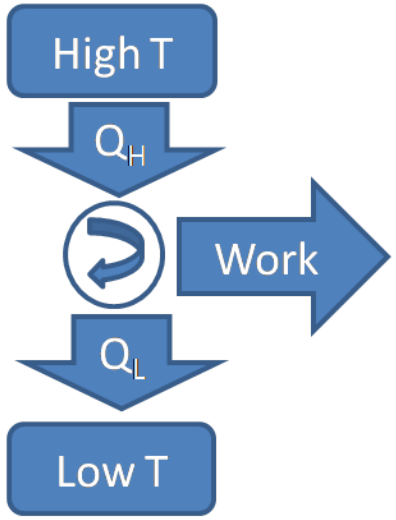




$$\mathrm{CoP}|_{\mathbf{refrigeration}} = \frac{Q_L}{W} \leq \frac{T_L}{T_H - T_L}$$

$$\mathrm{CoP}|_{\mathbf{heat\ pump}} = \frac{Q_H}{W} \leq \frac{T_H}{T_H - T_L}$$

Reminder: Thermodynamics of an ideal engine



- ⋆ Based on fluid executing a cycle

  Fluid begins and ends in the same state

- ⋆ Fluid must have same energy and entropy at beginning and end of cycle
  - Absorbs heat Q_H at T_H.
  - Does work W
  - Expels heat Q_L at T_L

- ⋆ First Law

  Change in internal energy of fluid around cycle must vanish

$$\boxed{Q_H = Q_L + W}$$

- ⋆ Second Law

  The entropy of the universe can never decrease

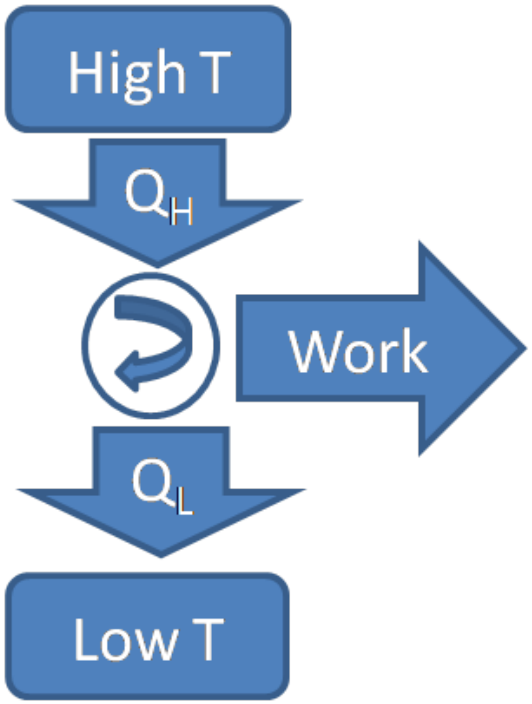
- ⋆ When a system absorbs heat Q at temperature T, then it gains entropy $\Delta S \geq \frac{Q}{T}$. When it loses heat Q at temperature T it loses entropy $|\Delta S| \leq \frac{Q}{T}$
- ⋆ With entropy: "You always get more than you want and get rid of less than you hope."
- ⋆ And the equality holds only when heat transfer is reversible
- ⋆ Compute $\Delta S_{\text{universe}}$

$$\Delta S_{\text{universe}} \geq \boxed{\frac{Q_L}{T_L} - \frac{Q_H}{T_H} \geq 0}$$

Combine 1st and 2nd laws

$$\boxed{Q_H = Q_L + W}$$

$$\boxed{\frac{Q_L}{T_L} - \frac{Q_H}{T_H} \geq 0}$$



Substitute and rearrange

$$\boxed{\frac{W}{Q_H} \leq \frac{T_H - T_L}{T_H}}$$

"Efficiency" = " Coefficient of Performance "

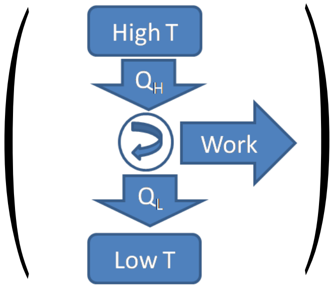
$$\boxed{\text{CoP} \leq \frac{T_H - T_L}{T_H}}$$

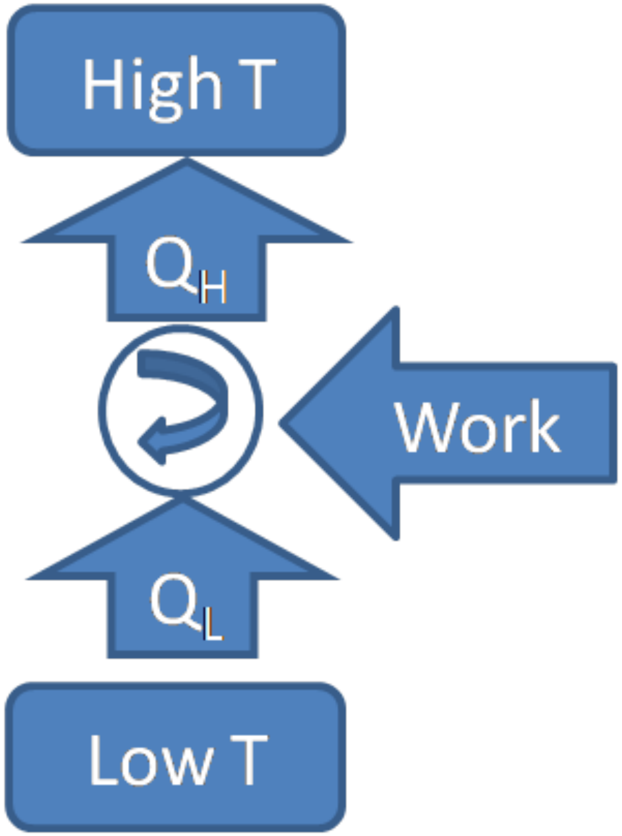
And maximum CoP is only reached when heat transfer is reversible:

- ★ **Minimize temperature and pressured gradients**

Thermodynamics of an ideal heat extraction device

- ⋆ Same as engine: fluid executes cycle; begins and ends in same state.
- ⋆ Direction of heat and work flows are reversed:
  - Absorbs heat Q_L at T_L.
  - Work done on it, W
  - Expels heat Q_H at T_H





- ⋆ First Law

$$\boxed{Q_H = Q_L + W}$$

- ⋆ Second Law

$$\Delta S_{\text{universe}} = \boxed{\frac{Q_H}{T_H} - \frac{Q_L}{T_L} \geq 0}$$

Note signs: Here Q_H/T_H is entropy delivered to universe and Q_L/T_L is entropy removed from universe

Coefficient of Performance? It depends what you're trying to accomplish

- ⋆ **Air conditioning/refrigeration: remove heat from low temperature reservoir:**

$$\boxed{\mathrm{CoP}|_{\mathrm{refrigeration}} = \frac{Q_L}{W} \leq \frac{T_L}{T_H - T_L}}$$

- ⋆ **Heat pump: provide heat to high temperature reservoir:**

$$\boxed{\mathrm{CoP}|_{\text{heat pump}} = \frac{Q_H}{W} \leq \frac{T_H}{T_H - T_L}}$$

Relations among ideal CoP's

$$\mathrm{CoP}|^{\mathrm{ideal}}_{\text{heat pump}} = \frac{1}{\mathrm{CoP}|^{\mathrm{ideal}}_{\mathrm{engine}}}$$

$$\mathrm{CoP}|^{\mathrm{ideal}}_{\text{heat pump}} = \mathrm{CoP}|^{\mathrm{ideal}}_{\mathrm{refrigerator}} + 1$$

$$\mathrm{CoP}|^{\mathrm{ideal}}_{\text{heat pump}}$$

is always greater than unity and can be very large

Carnot cooling cycle

- ⋆ [1 ⟶ 2] **Isentropic compression: Work is done on the gas.**

  It heats up to T_H.

- ⋆ [2 ⟶ 3] **Isothermal compression: Work is done on the gas.**

  Heat equal to work is expelled as Q_H

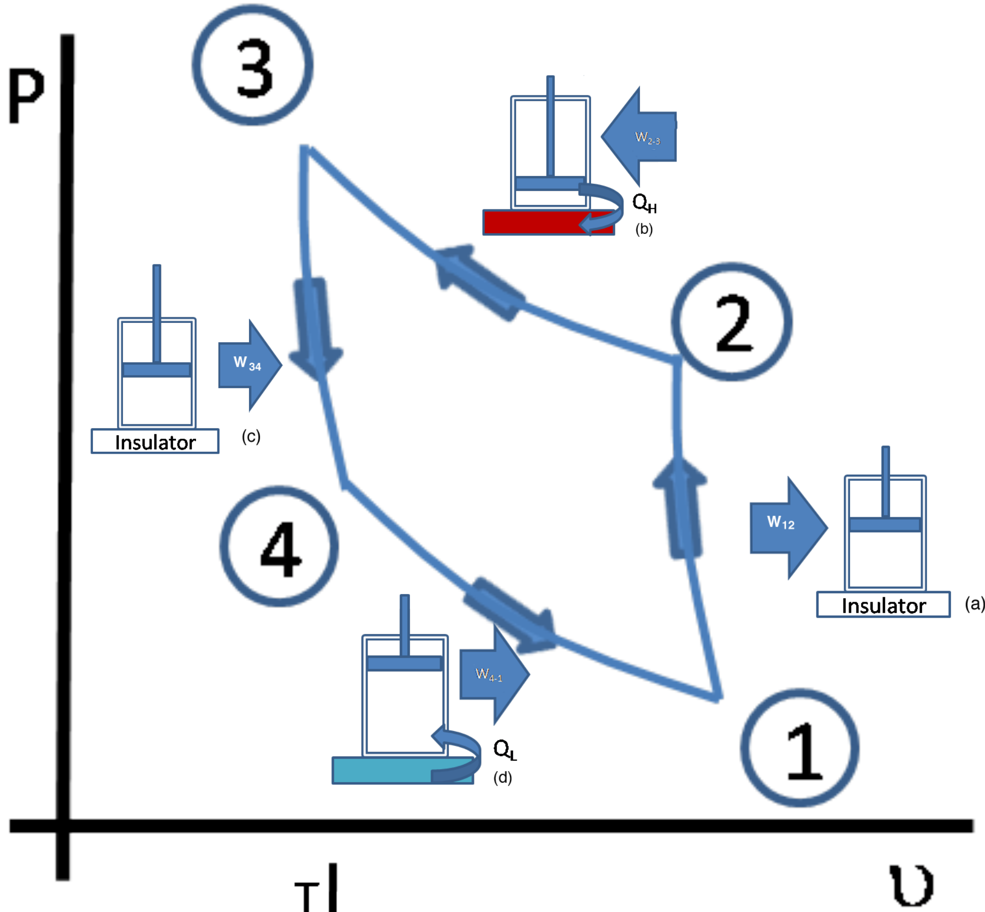
- ⋆ [3 ⟶ 4] **Isentropic expansion: Gas does work.**

  It cools to T_L

- ⋆ [4 ⟶ 1] **Isothermal expansion: Gas does work.**

  Heat equal to work is absorbed as Q_L.

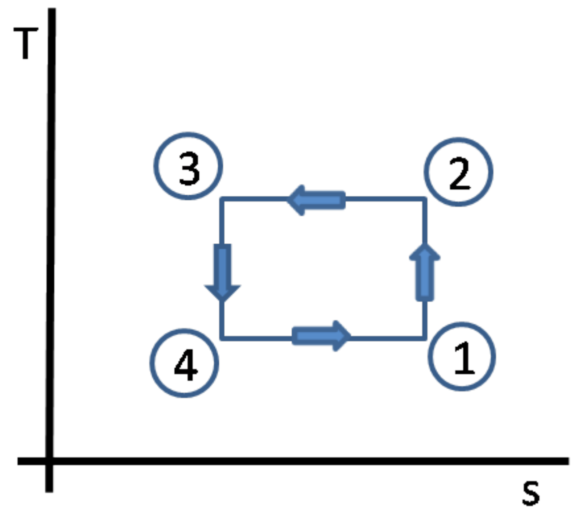
  - ⋆ If steps are carried out reversibly, then it's guaranteed to reach thermodynamic limit for CoP



Example: A refrigerator

- $T_L = 20°F$
- $T_H = 70°F$

$$\text{CoP} = \frac{266}{294 - 266} = 9.6$$



Cooling based on phase change

- ⋆ **Goes back to Michael Faraday in $\sim$ 1820: Liquid ammonia left to evaporate in air cools the air!**
- ⋆ **Make cyclic by condensing ammonia elsewhere and expelling heat**
- ⋆ **Commercialized by Willis Carrier $\sim$ 1930.**
- ⋆ **Must review thermodynamics of phase change**
  - **Liquid/vapor**
  - **Phases separated by boiling or condensation curve**
  - $T_{\text{boiling}}(P)$ **or** $P_{\text{boiling}}(T)$
  - **Other important points: Triple Point and Critical Point**

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http://www.kaushik.net/avinash/wp-content/uploads/2007/11/water_drop_causing_a_ripple.jpg

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Phase Diagram

- Water — but other substances are similar
- Phase changes
  - Solid/liquid Enthalpy (latent heat) of melting/solidification
  - Liquid/gas Enthalpy (latent heat) of vaporization/condensation
  - Solid/gas Enthalpy of sublimation
- Special points
  - Triple point: $T = 273.16\text{K}$, $P = 611.73\text{Pa}$
  - Critical point: $T = 647\text{K}$, $P = 22.064\text{MPa}$

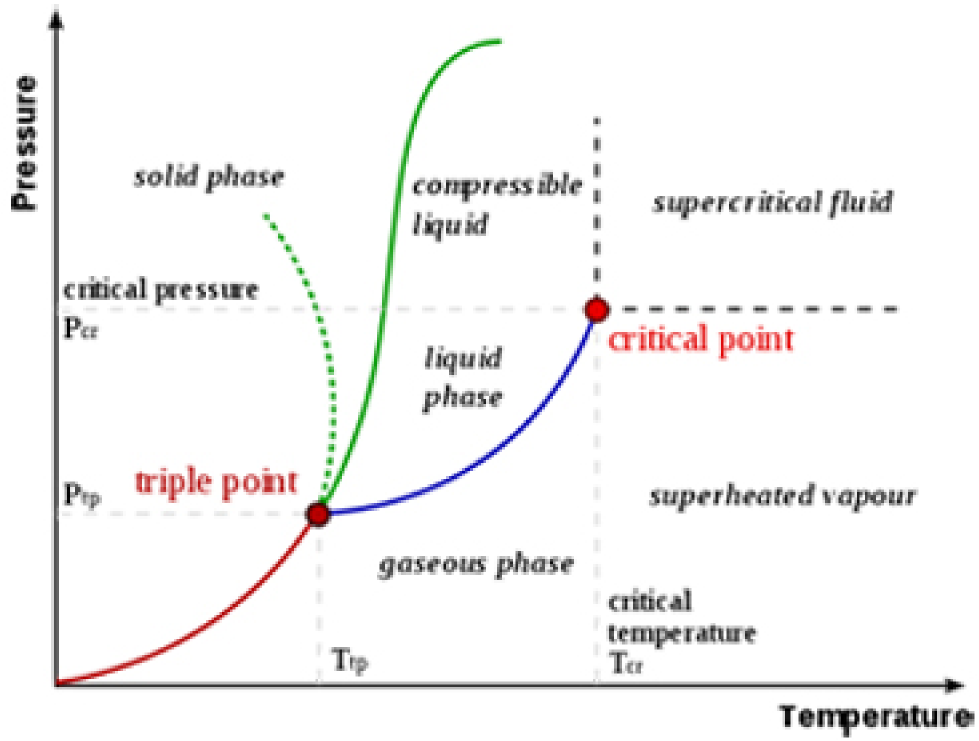

Image from http://commons.wikimedia.org/wiki/File:Phase-diag.svg

- Enthalpies of phase change
  - Enthalpy of melting (at $0°\text{C}$) $\approx$ 334 kJ/kg
  - Enthalpy of vaporization (at $100°\text{C}$) $\approx$ 2.26 MJ/kg

Why use phase change?

1. **Large energy storage potential**

   2.26 MJ to vaporize 1 kg H_2O at 100°C

2. **Energy transfer at constant temperature and pressure!**

   Bring liquid to boiling point, then T and P stay fixed until all liquid $\longrightarrow$ vapor!

   Copious heat transfer under reversible conditions!

3. **Flexibility in inducing phase transition.**

   Adjust pressure to select working T, for example.

4. **Enhanced heat transfer in boiling**

1. and 2. Large energy storage potential and constant T and P energy transfer.

- **Take 1 kg water at 1 atm and 100° and add heat (example: resistive heating element)**

  Temperature and pressure stay the same until 2.26 MJ has been added and all liquid $\Rightarrow$ vapor.

  Conditions are $\approx$ reversible: Phase change ceases as soon as heat is removed (turn off current)

  Most added heat goes into internal energy of vapor (small amount in $p\,dV$ work).

- **Compare adding heat to 1 kg of water vapor at 100°.**

  Heat capacity at constant pressure: $\sim$ 2kJ/kg K.

  So to add same amount of heat to water vapor at constant pressure would raise temperature by

$$\sim 2.26\,\mathrm{MJ}/2\,\mathrm{kJ} \sim 1000^\circ\ \mathrm{K!}$$

3. Choice of operating set points (T and P)

Vapor pressure graph removed
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Please see:
http://www.chem.purdue.edu/gchelp/liquids/vpvst.gif

Vapor pressure chart removed
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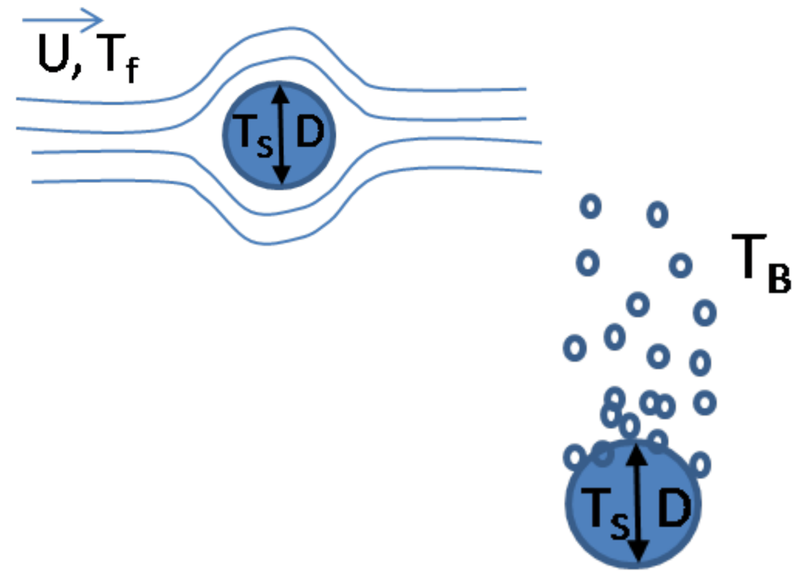
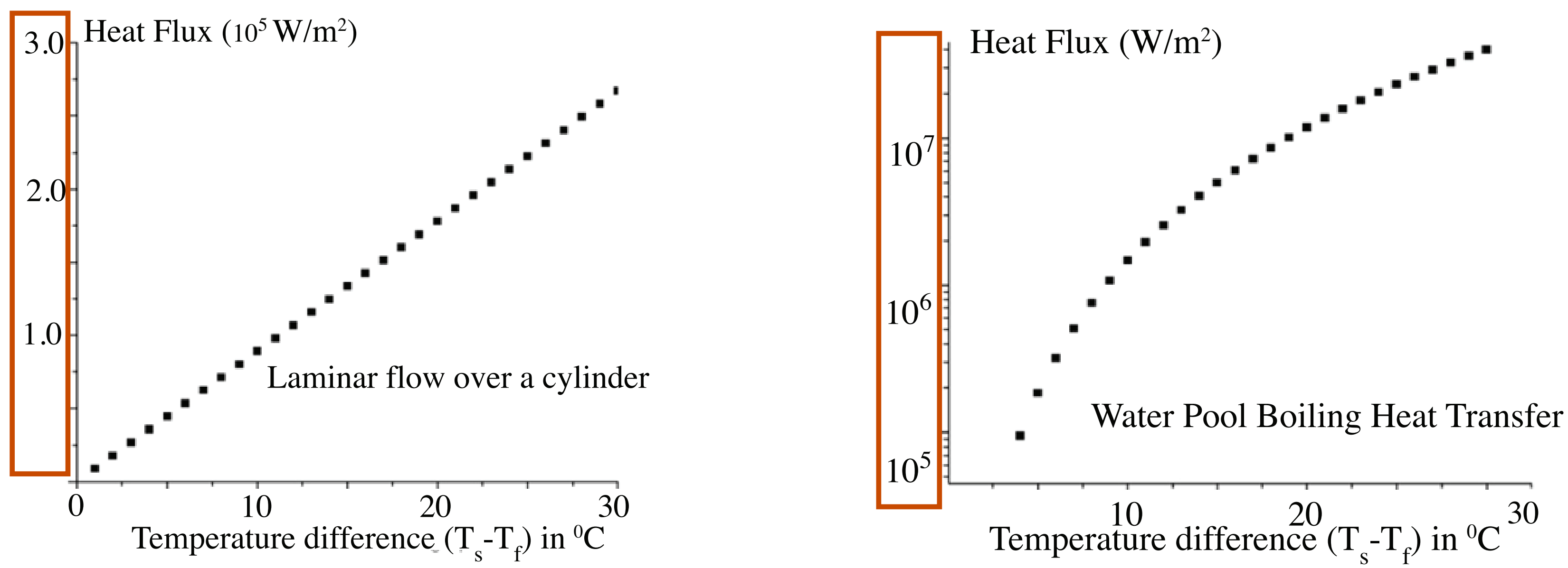
4. Enhanced heat transfer in boiling



- **Compare resistively heated wire in asymptotically laminar liquid flow with same wire in boiling pool**
- **Two advantages: (1) vapor bubble spontaneously migrate away from surface, whereas fluid flow is minimal near surface due to viscosity**
- **(2) Each vapor molecule carries full enthalpy of vaporization with it as it leaves the heated surface.**



Following phase change in pV, ST, and “quality”

- So far we looked at phase change in the pT plane.
- Need to look at it in the pV and ST planes to get full description
- Why? Because one point in the pT plane covers whole process of boiling (or melting)

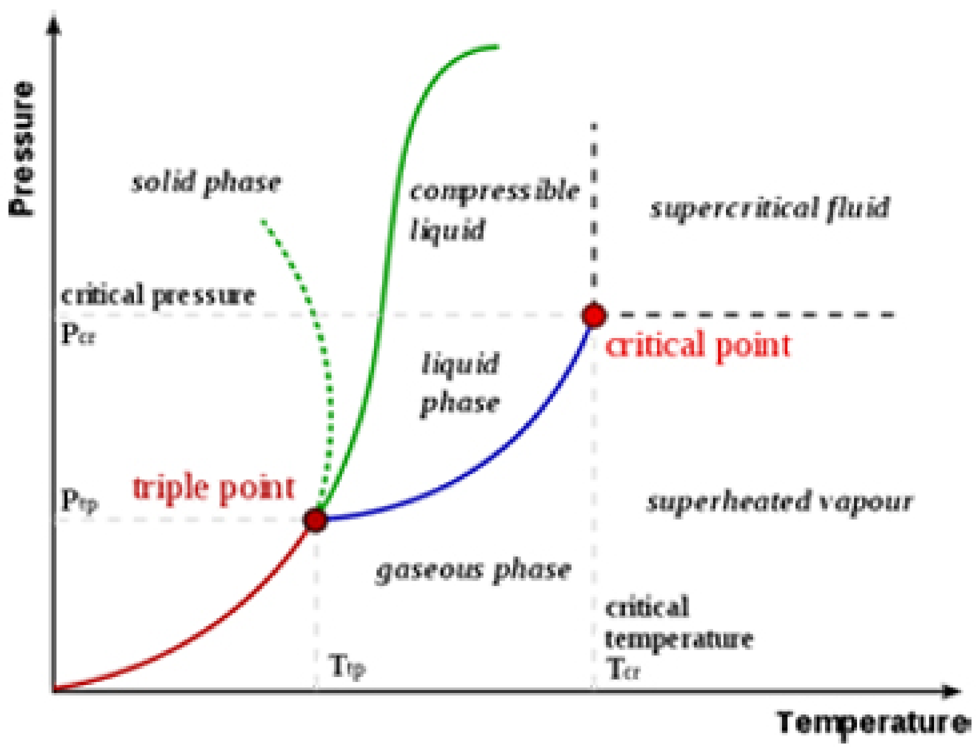


Image from http://commons.wikimedia.org/wiki/File:Phase-diag.svg

Lee Carkner, Department of Physics and Astronomy, Augustana College

Phase change in the pV-plane

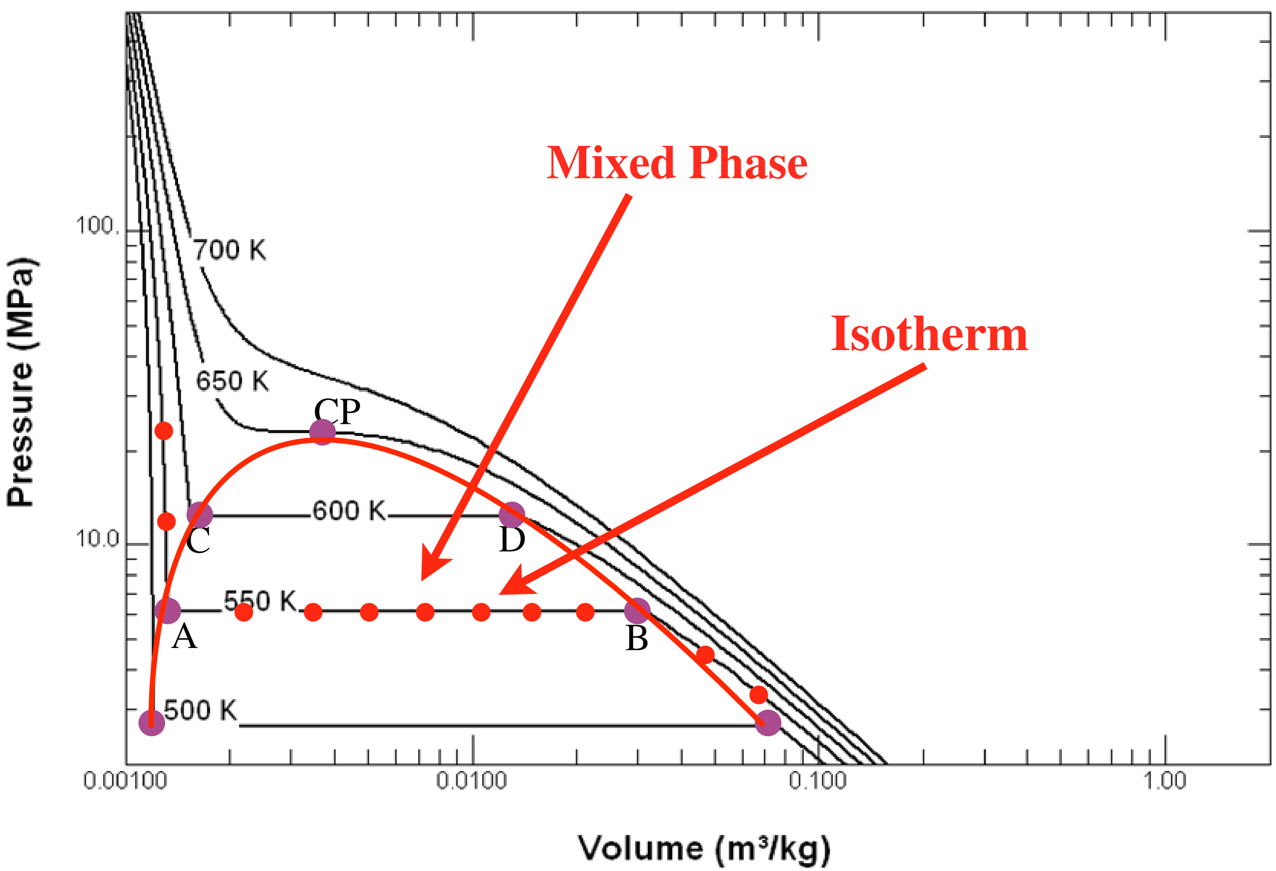
Walk along the isotherms

- ⋆ 550°K
- ⋆ 600°K
- ⋆ 650°K

- Choose a T
- Slowly lower P
- V increases a little
- Until you reach $P_{\text{boiling}}(T)$
- Then all liquid turns to vapor

  With dramatic increase in volume at fixed P

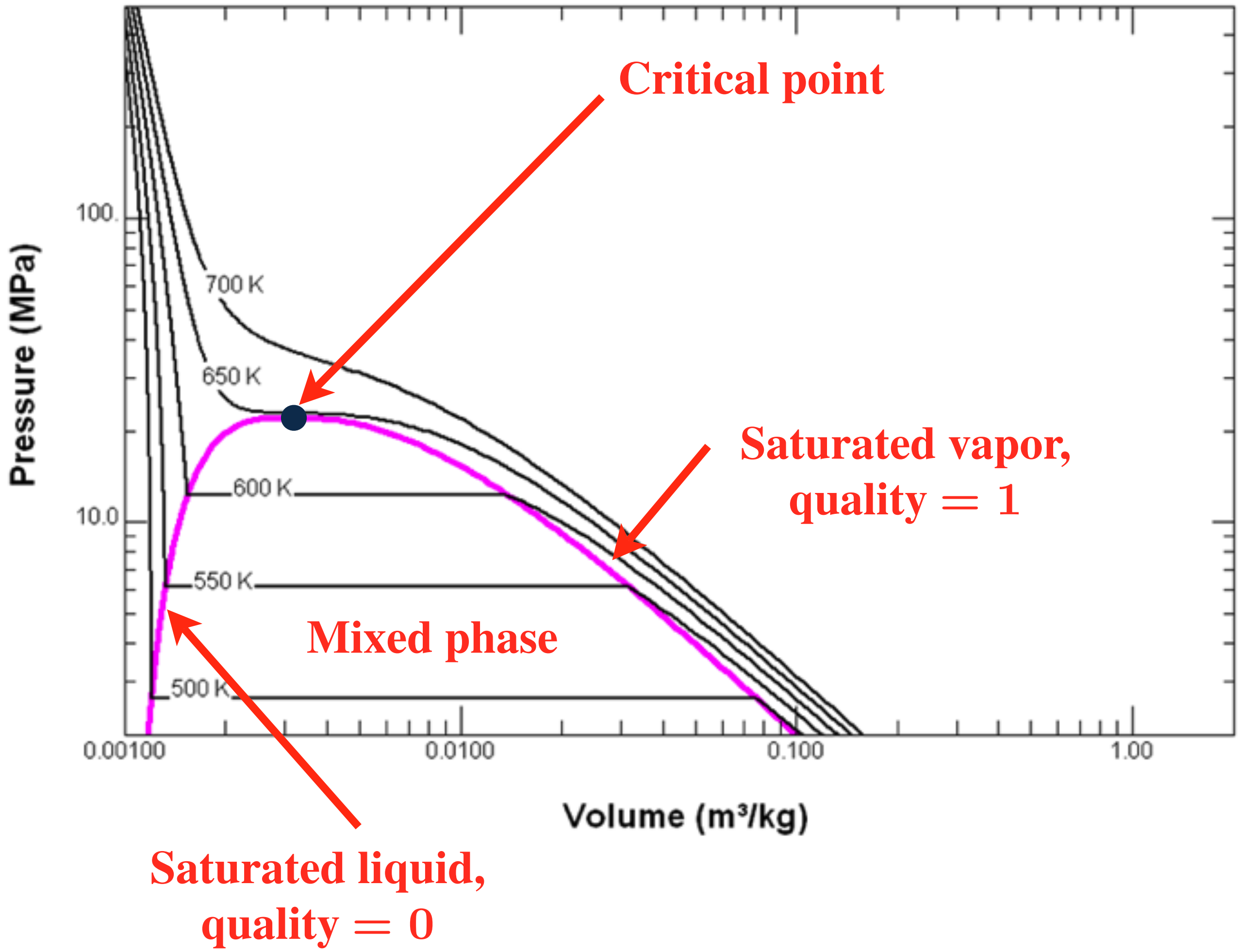
- Then P again can decrease



Saturation dome for water

- Phase change curve
- Mixed phase below the "dome"
- "Saturated vapor" on the right part of curve
- "Saturated liquid" on the left part of curve
- **Quality**:

$$\chi = \frac{m_v}{m_v + m_l}$$



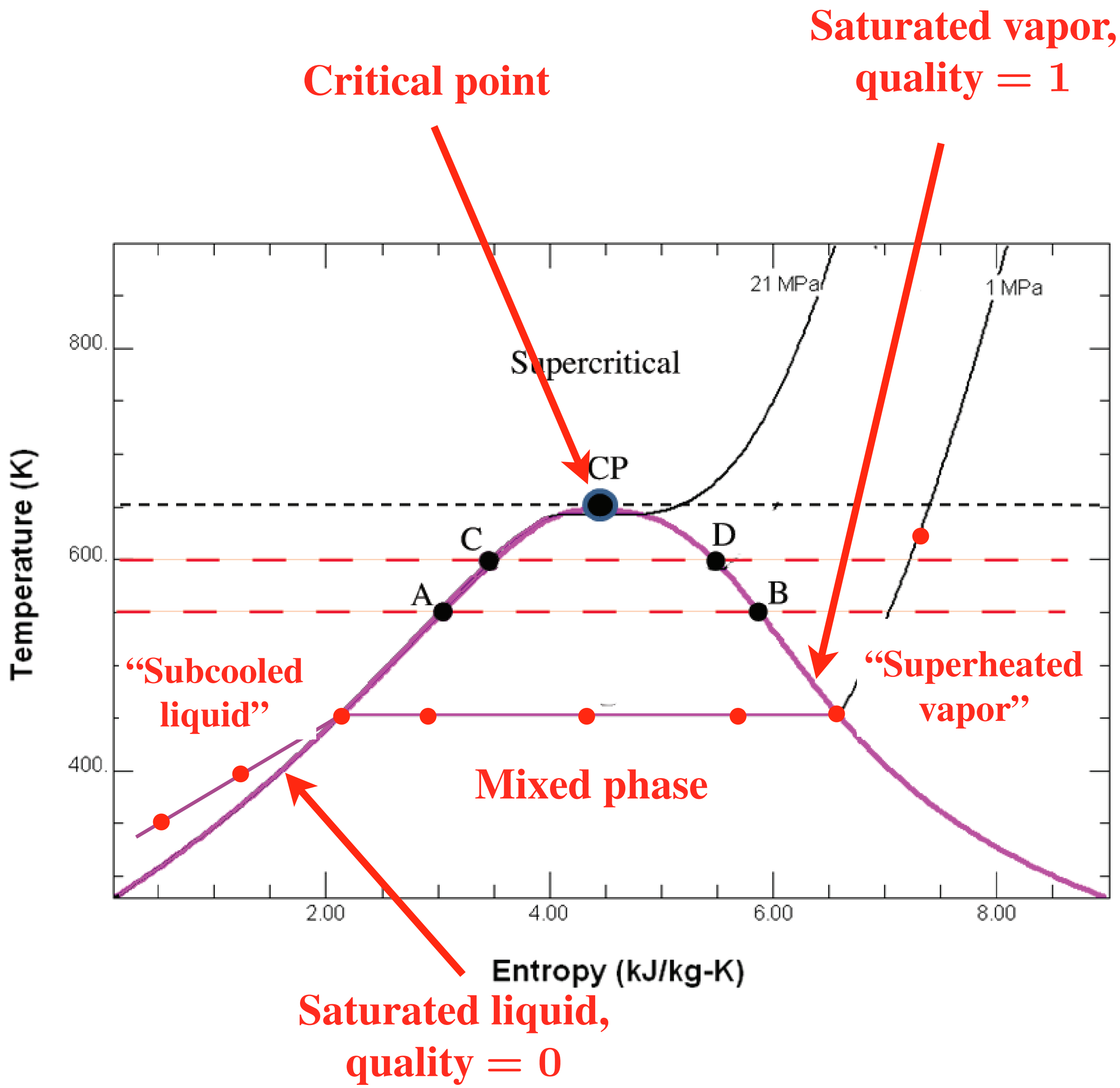
Phase change in the TS-plane

Walk along the isobars

- **Choose a P**
- **Slowly add heat (entropy)**
- **System does work against constant P**

  And T increase (C_p)
- **Until you reach $T_{\text{boiling}}(P)$**
- **Then all liquid turns to vapor**

  With dramatic increase in heat (enthalpy) at fixed T
- **Then T again can increase**



Properties of the mixed phase

- ⋆ To a very good approximation, entensive properties of mixed phase are merely

  The proportional sum of the liquid and vapor properties.

- ⋆ For example, entropy

$$S = \frac{m_v S_v + m_l S_l}{m_v + m_l} = \chi S_v + (1-\chi) S_l$$

- ⋆ Applies to energy, entropy, enthalpy, volume
- ⋆ Why not exact? Interface properties: 50/50 mix of liquid and vapor water has slightly different properties than a fog.
- ⋆ Where to get properties of saturated liquid and vapor?

  Not from perfect gas law!

  Thermodynamic tables!

Steam tables: For each pressure

- ⋆ The saturation temperature

  $\equiv$ boiling point

- ⋆ Properties of saturated liquid and saturated vapor at the boiling point

- ⋆ Table of properties at other temperatures

Subcooled liquid

Superheated vapor

$P(T_{sat})$	1 x 10^5 N/m² (99.61 C)				1.2 x 10^5 N/m² (104.78 C)			
Temp [C]	v [m³/kg]	u [kJ/kg]	h [kJ/kg]	s [kJ/kg K]	v [m³/kg]	u [kJ/kg]	h [kJ/kg]	s [kJ/kg K]
Sat. Liq.	1.0432E-03	417.40	417.50	1.3028	1.0473E-03	439.23	439.36	1.3609
Evap.	1.6929	2088.2	2257.4	6.0560	1.4274	2072.5	2243.7	5.9368
Sat. Vap.	1.6939	2505.6	2674.9	7.3588	1.4284	2511.7	2683.1	7.2977
0.00	*1.0002E-03*	*-0.0404*	*0.0597*	*-0.0001*	*1.0001E-03*	*-0.0400*	*0.0800*	*-0.0001*
10	1.0003E-03	42.018	42.118	0.1511	1.0003E-03	42.017	42.137	0.1511
20	1.0018E-03	83.906	84.006	0.2965	1.0018E-03	83.905	84.025	0.2965
30	1.0044E-03	125.72	125.82	0.4367	1.0044E-03	125.72	125.84	0.4367
40	1.0078E-03	167.51	167.62	0.5724	1.0078E-03	167.51	167.63	0.5724
50	1.0121E-03	209.32	209.42	0.7038	1.0121E-03	209.31	209.43	0.7038
60	1.0171E-03	251.15	251.25	0.8313	1.0171E-03	251.14	251.26	0.8312
70	1.0227E-03	293.02	293.12	0.9551	1.0227E-03	293.02	293.14	0.9551
80	1.0290E-03	334.95	335.05	1.0755	1.0290E-03	334.95	335.07	1.0755
90	1.0359E-03	376.96	377.06	1.1928	1.0359E-03	376.95	377.08	1.1928
100	1.6959	2506.2	2675.8	7.3610	1.0435E-03	419.05	419.18	1.3072
120	1.7932	2537.3	2716.6	7.4678	1.4906	2535.7	2714.6	7.3794
140	1.8891	2567.8	2756.7	7.5672	1.5712	2566.5	2755.1	7.4800
160	1.9841	2598.0	2796.4	7.6610	1.6508	2597.0	2795.1	7.5745
180	2.0785	2628.1	2836.0	7.7503	1.7299	2627.3	2834.9	7.6643
200	2.1724	2658.2	2875.5	7.8356	1.8085	2657.5	2874.5	7.7499
220	2.2661	2688.4	2915.0	7.9174	1.8867	2687.8	2914.2	7.8320

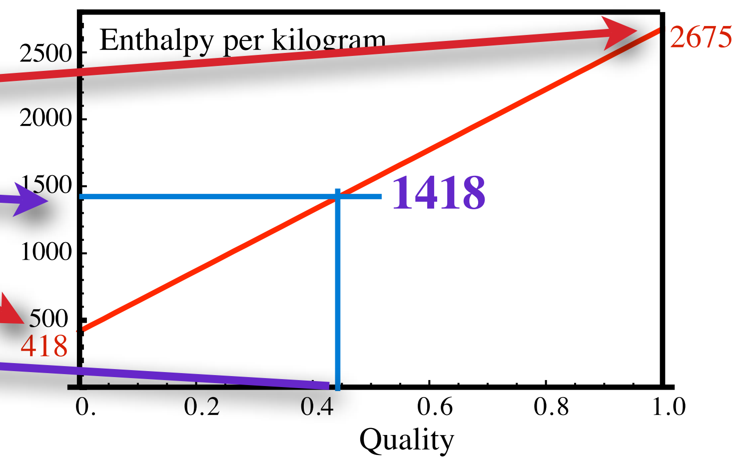
Example

A kilojoule of heat is added to a kilogram of liquid water at 1 atmosphere pressure and 100° C.

What are the properties of the resultant mixture?

$P(T_{sat})$	$\boxed{1 \times 10^5 \text{ N/m}^2 \text{ (99.61 C)}}$			
Temp [C]	v [m³/kg]	u [kJ/kg]	h [kJ/kg]	s [kJ/kg K]
Sat. Liq.	1.0432E-03	417.40	417.50	1.3028
Evap.	1.6929	2088.2	2257.4	6.0560
Sat. Vap.	1.6939	2505.6	2674.9	7.3588

- ⋆ **Since the system is at constant pressure, the heat is added as enthalpy.**
- ⋆ **1 atmosphere is close enough to 1×10^5 N/m ^{2} to use tables on last slide**
  - $h_{\text{liq}} = 418$ **kJ/kg**
  - $h_{\text{vap}} = 2675$ **kJ/kg**
  - $h_{\text{mixture}} = 418 + 1000$ **kJ/kg,**
  - **Which corresponds to a quality of** $\chi = 0.44$



- ⋆ **Once we know $\chi = 0.44$, (and $1 - \chi = 0.56$),**

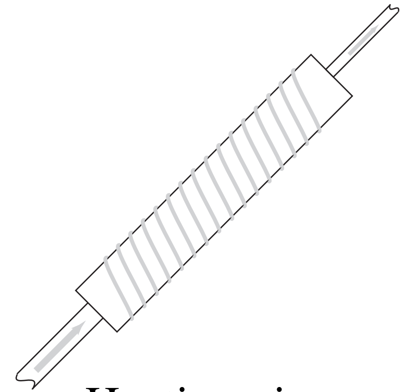
$$
\begin{aligned}
v &= 0.44(1.69) + 0.56(1.04 \times 10^{-3}) = 0.744\,\text{m}^3/\text{kg} \\
s &= 0.44(7.36) + 0.56(1.30) = 3.97\,\text{kJ/kg K}
\end{aligned}
$$

Digression: Thermodynamics with flowing fluids

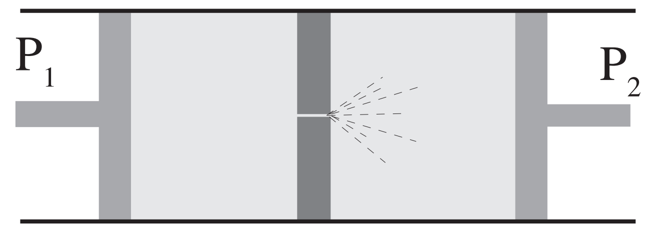
- ⋆ **Need to deal with devices where materials flow in and out!**

  Pipe heated by resistive coil: fluid flows in, heats, flows out.

  "Throttle": fluid pushed through nozzle



Heating pipe



Throttle

- ⋆ **Fluid enters:** $\rho_1, p_1, T_1, u_1, h_1, s_1$

  Leaves: $\rho_2, p_2, T_2, u_2, h_2, s_2$

- ⋆ **These are density (ρ), pressure (p), temperature (T), specific energy (u), enthalpy (h), and entropy (s)**

  Specific energy $\equiv$ energy per unit mass, ...

- ⋆ **Concept: control volume**

  In a time Δt, apply first (and second) laws on a fixed domain

- ⋆ **In a time Δt, mass $\Delta m_1 = \rho_1 A_1 \, (v_1 \Delta t)$ enters and $\Delta m_2 = \rho_2 A_2 \, (v_2 \Delta t)$ leaves**

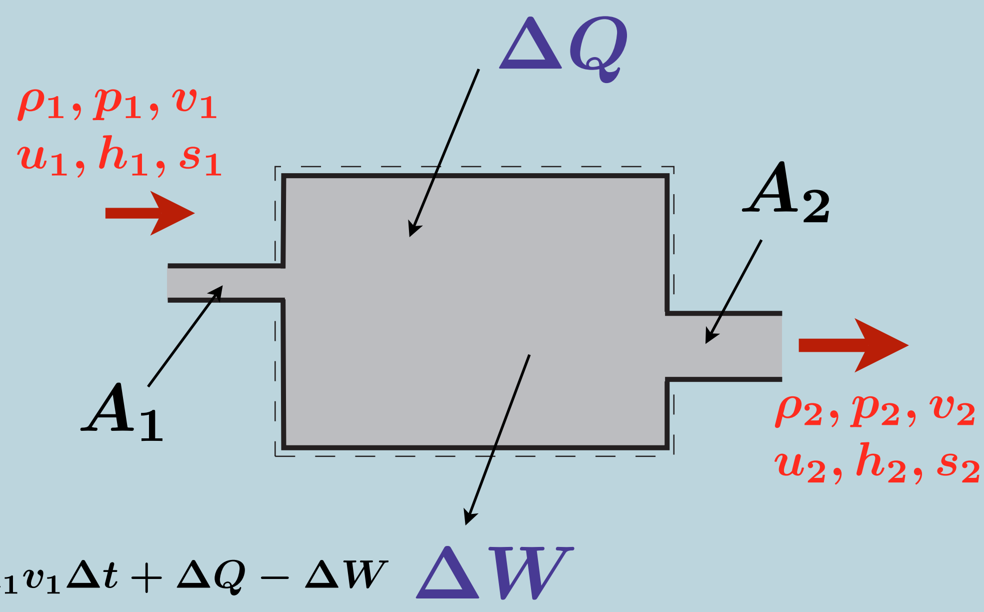
- ⋆ **And $\Delta m_1 = \Delta m_2$**

- ⋆ **Entering mass brings energy $\Delta U = u_1 \rho_1 A_1 v_1 \Delta t$**

  And similarly for enthalpy and entropy entering and leaving

★ **Apply first law to control volume**

$$\begin{aligned}\Delta E_{\text{in}} &= \text{Internal energy}|_{\text{in}} + pdV\ \text{work}|_{\text{in}}\\ &= u_1\rho_1 v_1 A_1 \Delta t + p_1 A_1 v_1 \Delta t\\ \Delta E_{\text{out}} &= \text{Internal energy}|_{\text{out}} + pdV\ \text{work}|_{\text{out}}\\ &= u_1\rho_2 v_2 A_2 \Delta t + p_2 A_2 v_2 \Delta t\end{aligned}$$



★ **First law**

$$\begin{aligned}\Delta E_{\text{out}} &= \Delta E_{\text{in}} + \Delta Q - \Delta W\\ u_2\rho_2 v_2 A_2\Delta t + p_2 A_2 v_2 \Delta t &= u_1\rho_1 v_1 A_1 \Delta t + p_1 A_1 v_1 \Delta t + \Delta Q - \Delta W\end{aligned}$$

Divide out $\Delta m = \boxed{\rho_2 v_2 A_2 \Delta t} = \rho_1 v_1 A_1 \Delta t$

$$u_2 + \frac{p_2}{\rho_2} = u_1 + \frac{p_1}{\rho_1} + \frac{\Delta Q}{\Delta m} - \frac{\Delta W}{\Delta m}$$

$$h_2 = h_1 + \frac{dQ}{dm} - \frac{dW}{dm}$$

$$u + \frac{p}{\rho} = \frac{U}{m} + \frac{p}{m/V} = \frac{1}{m}(U + PV) = h$$

Result: Enthalpy out = Enthalpy in + Heat in − Work out

$$\begin{aligned}h_2 &= h_1 + \frac{dQ}{dm} - \frac{dW}{dm}\\ &= h_1 + q - w\end{aligned}$$

Some examples!

- ⋆ **Heat exchanger (evaporator): Heat in, no work**

  $h_2 = h_1 + q$

- ⋆ **Heat exchanger (condensor): Heat out, no work**

  $h_2 = h_1 - q$

- ⋆ **Throttle: No heat, no work**

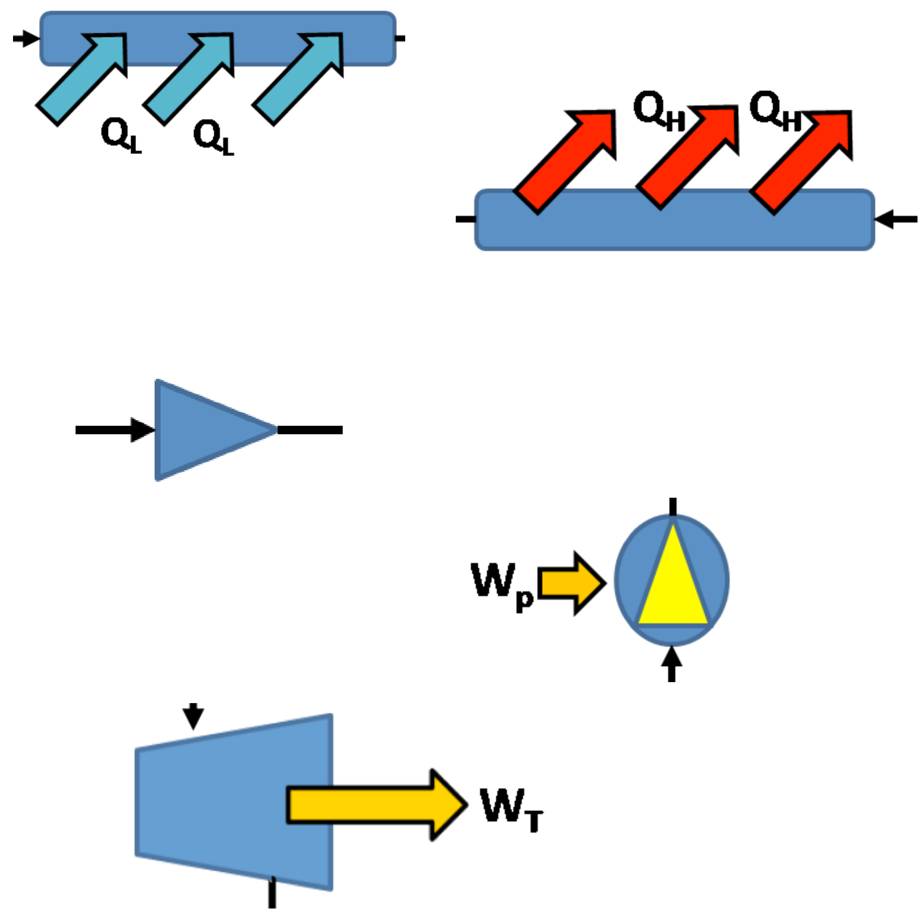
  $h_2 = h_1$

- ⋆ **Pump (adiabatic): Work in, no heat**

  $h_2 = h_1 + w$

- ⋆ **Turbine (adiabatic): Work out, no heat**

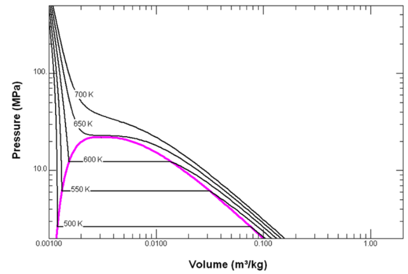
  $h_2 = h_1 - w$

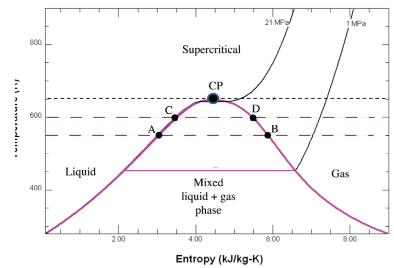


Summary

- An engine cycle run backwards $\Rightarrow$ a refrigerator or a heat pump
- CoP $|_{\text{heat pump}} = T_H / (T_H - T_L) = 1 / \text{CoP}|_{\text{engine}}$ CoP $|_{AC} = T_L / (T_H - T_L)$
- Phase change takes place at constant temperature and pressure
- Phase change working fluid: (1) High heat capacity; (2) heat transfer at constant T; (3) wide range of (T, p) set points; (4) rapid energy transfer.
- Phase change in (T, p), (p,V) and (S,T) planes.
- Quality

$$\chi = \frac{m_v}{m_v + m_l}$$





- Saturated vapor, saturated liquid, superheated vapor, subcooled liquid
- Quality calculations: properties of the mixed phase are additive (enthalpy for example)

$$h_{\text{mixed}}(\chi) = \chi h_{\text{vapor}} + (1 - \chi) h_{\text{liquid}}$$

- When fluid moves through a device follow the enthalpy!

$$h_{\text{out}} = h_{\text{in}} + \frac{\Delta Q}{\Delta m} - \frac{\Delta W}{\Delta m}$$

WORK DONE

HEAT ADDED