Lecture 12

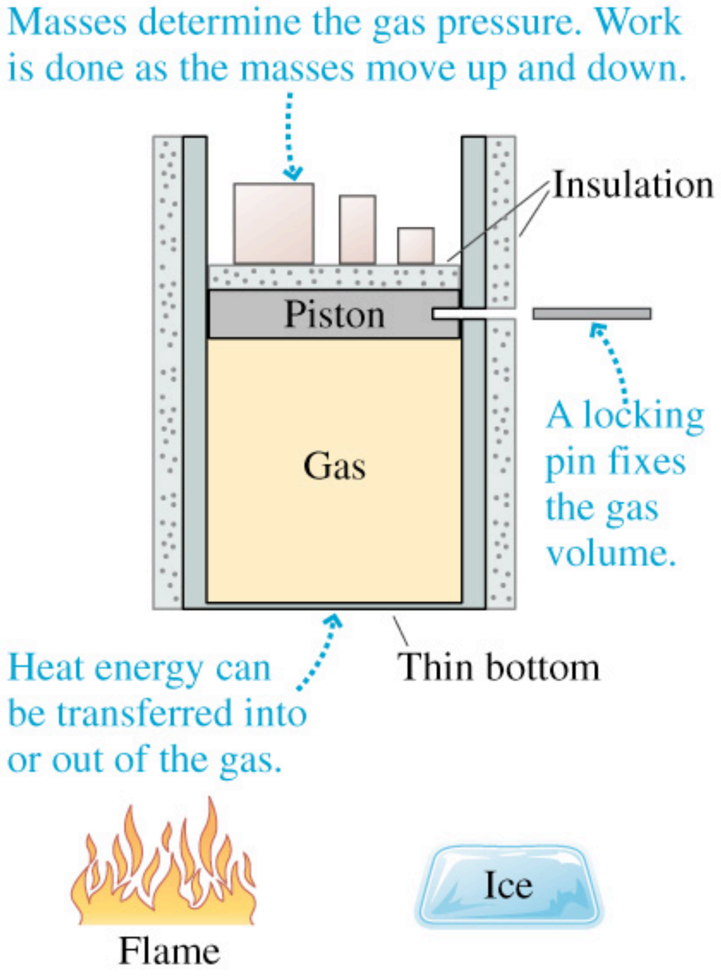
- 1st Law for isochoric, isothermal and adiabatic process
- Temperature change: specific heat
- Phase change: heat of transformation
- Calorimetry: calculating heat exchanges
- Specific heats of gases
- Heat transfer

Three special ideal gas processes: one of ΔE_{th}, W or Q is 0

- fix volume by locking pin (piston massless, frictionless)
- change pressure by masses
- heat transferred thru' bottom (piston/sides insulated)

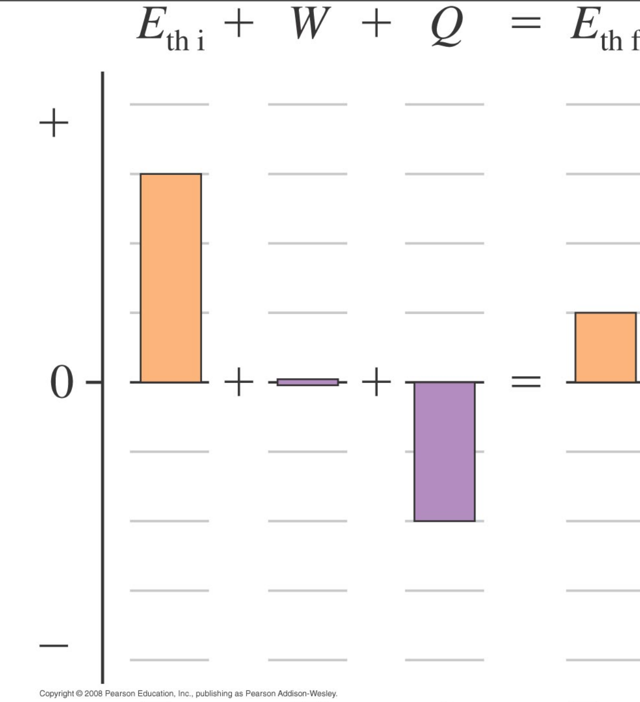
$$p_{gas} = p_{atm} + \frac{Mg}{A}$$

(invalid when locked)



(i) Isochoric (W = 0 $\Rightarrow Q = \Delta E_{th}$)

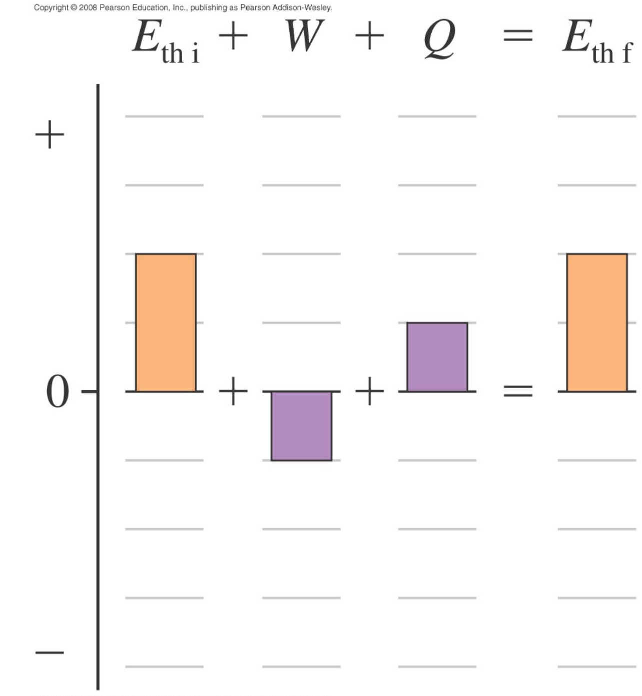
lock pin; cool by ice; remove ice when desired p reached; remove masses till new p balanced; unlock...



(ii) Isothermal ($\Delta T = 0,\ \Delta E_{th} = 0 \Rightarrow W = -Q$)

place over flame (gas expands); remove masses to match reduced p (pV = constant)....

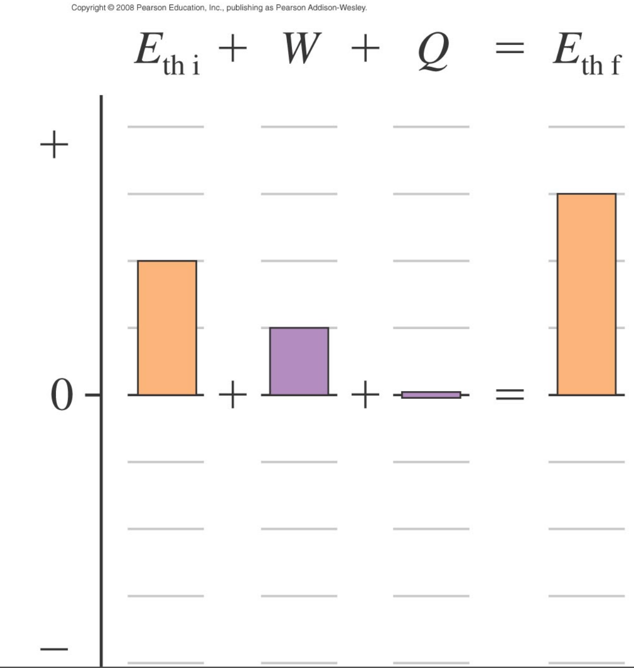
$$\Delta T = 0 \not\Rightarrow Q = 0$$



(iii) Adiabatic ($Q = 0 \Rightarrow W = \Delta E_{th}$)

insulate; add masses (p increases, V decreases)... work done on gas increases temperature (same effect as Q)

$$Q = 0 \not\Rightarrow \Delta T = 0$$



Thermal properties of matter (I)

Joule: heat and work are energy transferred; change in thermal energy $\longrightarrow$ change in temperature or phase

- Temperature change and Specific Heat

specific heat, c = energy to raise T of 1 kg by 1 K ("thermal inertia")

$$\Delta E_{th} = Mc\Delta T \text{ (temperature change)}$$

$$\Delta E_{th} = W + Q \text{ for solids/liquids, } W = 0 \Rightarrow$$

$$Q = Mc\Delta T \qquad \text{(temperature change)}$$

Molar specific heat, C: $Q = nC\Delta T$

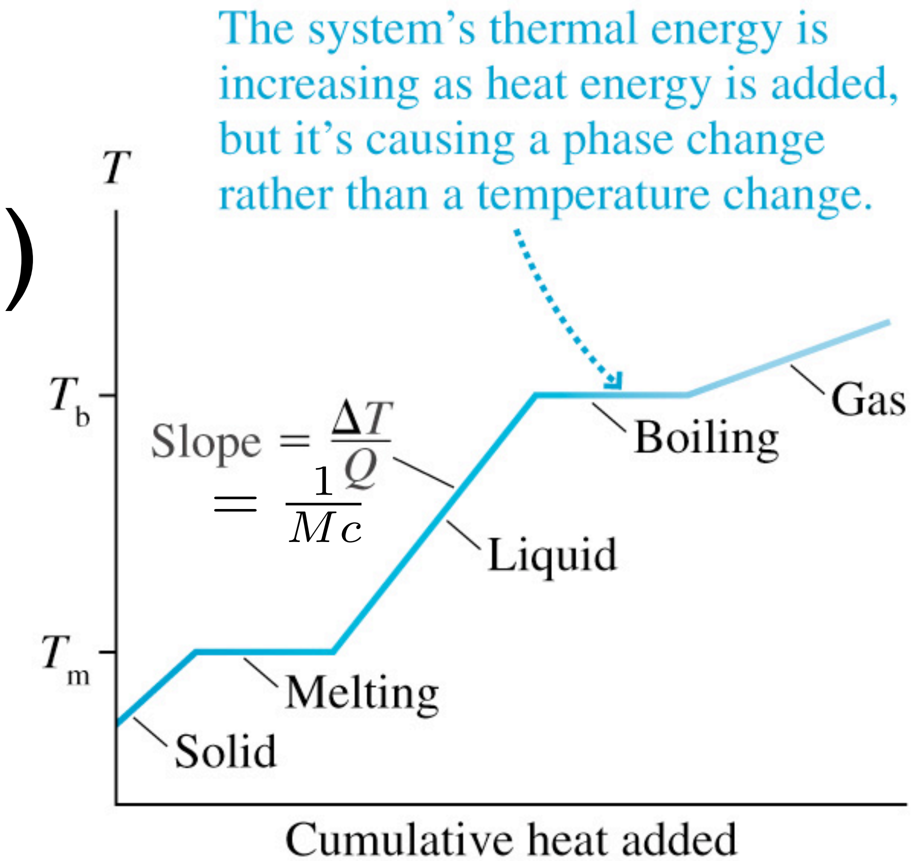
$$\text{Using } n = \frac{M(\text{in g})}{M_{mol}} = \frac{1000(\text{g/kg})}{M_{mol}(\text{in g/mol})} M(\text{in kg}):$$

$$C(\text{in J/mol/K}) = \frac{M_{mol}(\text{in g/mol})}{1000(\text{g/kg})} c(\text{in J/kg/K})$$

Thermal properties of matter (II)

- Phase change and <u>heat of transformation, L</u>

T same, heat transferred breaks bonds (instead of speeding up atoms)



L = heat energy for 1 kg to change phase

$$Q = \begin{cases} \pm ML_f & \text{melt/freeze} \\ \pm ML_v & \text{boil/condense} \end{cases}$$

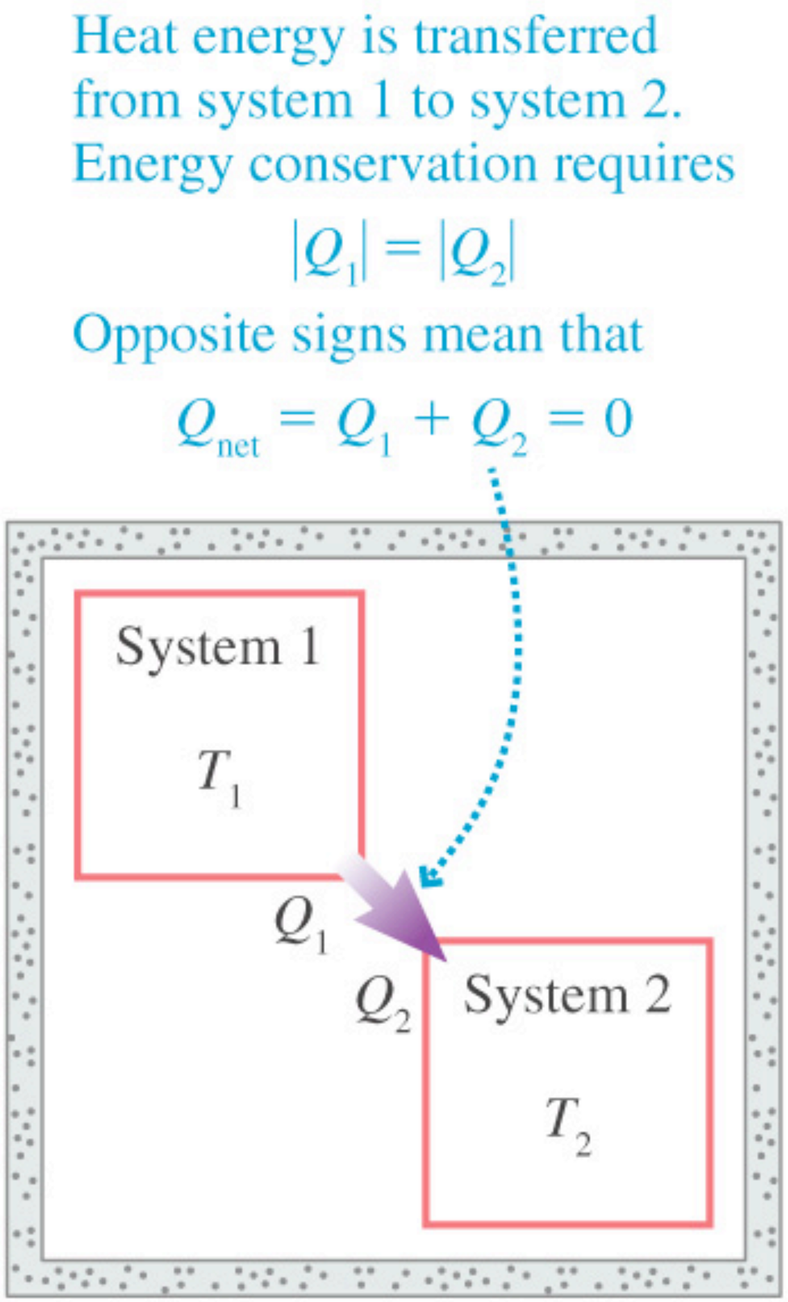
$L_{f,\,v}$: heat of fusion (solid/liquid) or vaporization (liquid/gas)

$L_v > L_f$: bonds not completely broken during melting...

Calorimetry

- 2 systems interacting thermally, but isolated from others

start at $T_1 \neq T_2$,
heat transferred till equilibrium T_f
(Q_1 is energy transferred to system 1: > 0 if energy enters...)



- Strategy for (> 2 systems)

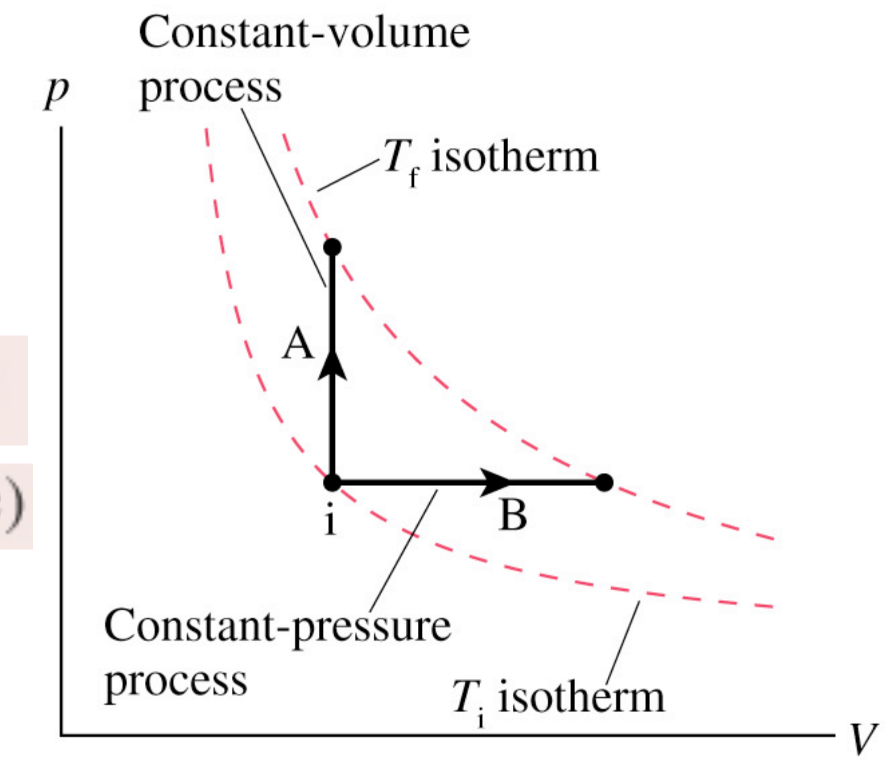
$Q_{net} = Q_1 + Q_2 + ... = 0$
Systems with temperature change:
$Q = Mc\,(T_f - T_i) \Rightarrow Q > 0$ if $T_f > T_i$
Systems with phase change:
$Q + \pm ML_{f \text{ or } v}$: for melting/freezing...
(check: T_f not higher/lower than *all* T_i)

Example

- A copper block is removed from a 300 degree Celsius oven and dropped into 1.00 L of water at 20 degree Celsius. The water quickly reaches 25.5 degree Celsius and then remains at that temperature. What is the mass of the copper block? Specific heats of copper and water are 385 J / (kg K) and 4190 J / (kg K), respectively.

Specific Heats of Gases

- same ΔT, different Q since W different...



- Two versions of molar specific heat

$Q = nC_P\Delta T$ (temperature change at constant pressure)

$Q = nC_V\Delta T$ (temperature change at constant volume)

(if p or V not constant, use $Q = W - \Delta E_{th}$)

Relation between C_P and C_V

- ΔE_{th} depends only on ΔT

$$\Delta E_{th} = Q + W \Rightarrow \text{no distinction between } Q,\, W$$

$$\text{isochoric: } (\Delta E_{th})_A = W + Q = 0 + Q_{\text{const vol}} = nC_V\Delta T$$
$$\text{isobaric: } (\Delta E_{th})_B = W + Q = -p\Delta V + Q_{\text{const vol}} = -nR\Delta T + nC_P\Delta T$$
$$(\text{using ideal gas law: } pV = nRT)$$
$$\Delta (E_{th})_A = (\Delta E_{th})_B \Rightarrow$$

$C_P = C_V + R$

$\Delta E_{th} = nC_V\Delta T$ (any ideal-gas process)

0 for isochoric, < 0 for isobaric expansion

- Q not same even if ΔT same: $Q = W - \Delta E_{th}$ ← same

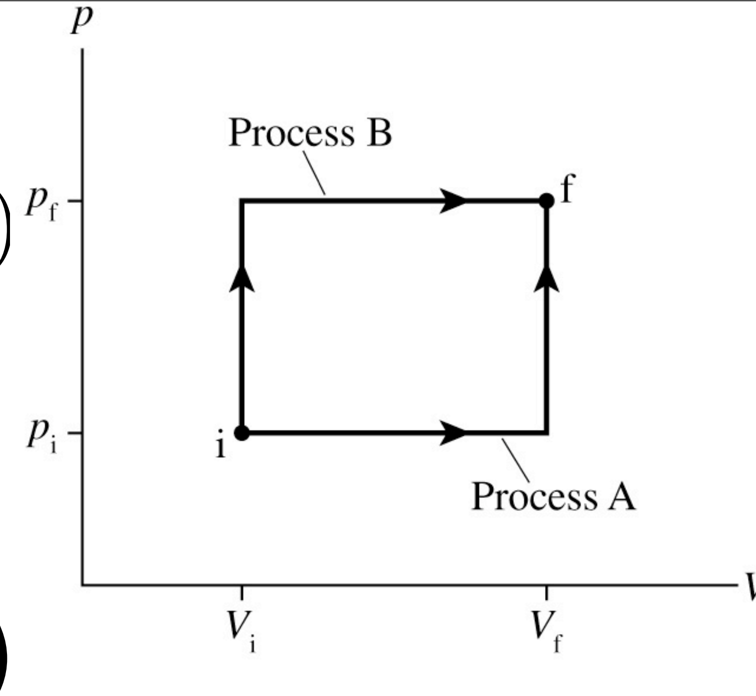
Heat depends on path

$\Delta E_{th} = E_{th\ f} - E_{th\ i}$ same (E_{th} is state variable)

$\Rightarrow W_A + Q_A = W_B + Q_B$

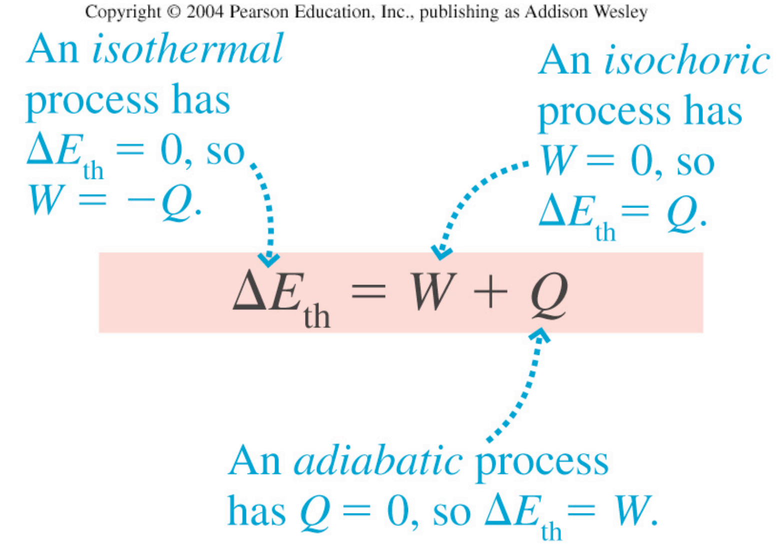
$|W_B| > |W_A|$ (area under curve); $W_{A,\ B} < 0$

$\Rightarrow Q_B > Q_A$ (Q, W are *not* state variables)



Adiabatic Process (Q=0)

- e.g. gas in thermally insulated cylinder or rapid expansion/compression (no time for heat transfer via atomic-level collisions) (can be slow enough to be quasi-static)
- $\Delta E_{th} = W \Rightarrow$ expansion lowers T...

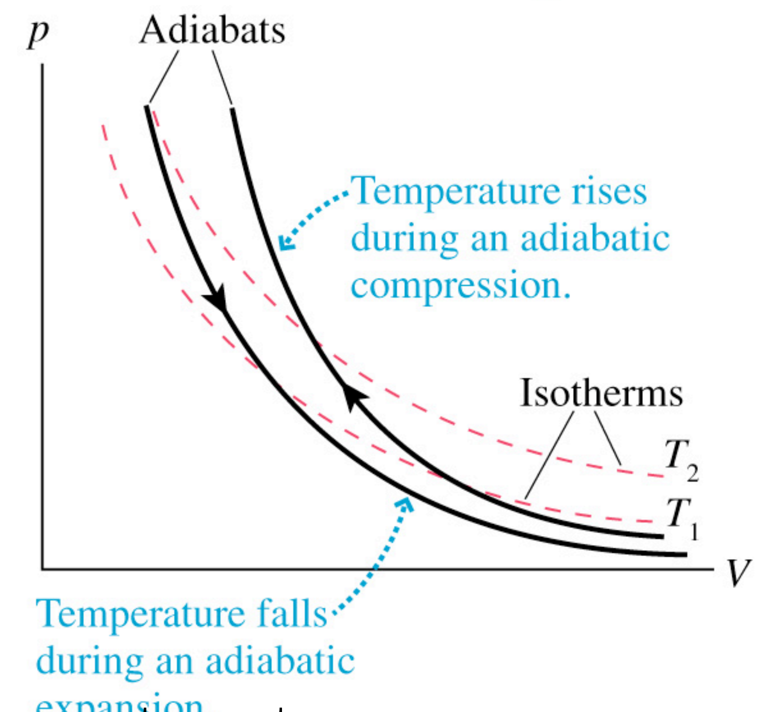


$$W = nC_V\Delta T \qquad \text{(adiabatic process)}$$

- pV diagram (adiabat: steeper than isotherm)

$$\gamma = \frac{C_P}{C_V} = \begin{matrix} 1.67 & \text{monoatomic gas} \\ 1.40 & \text{diatomic gas} \end{matrix}$$

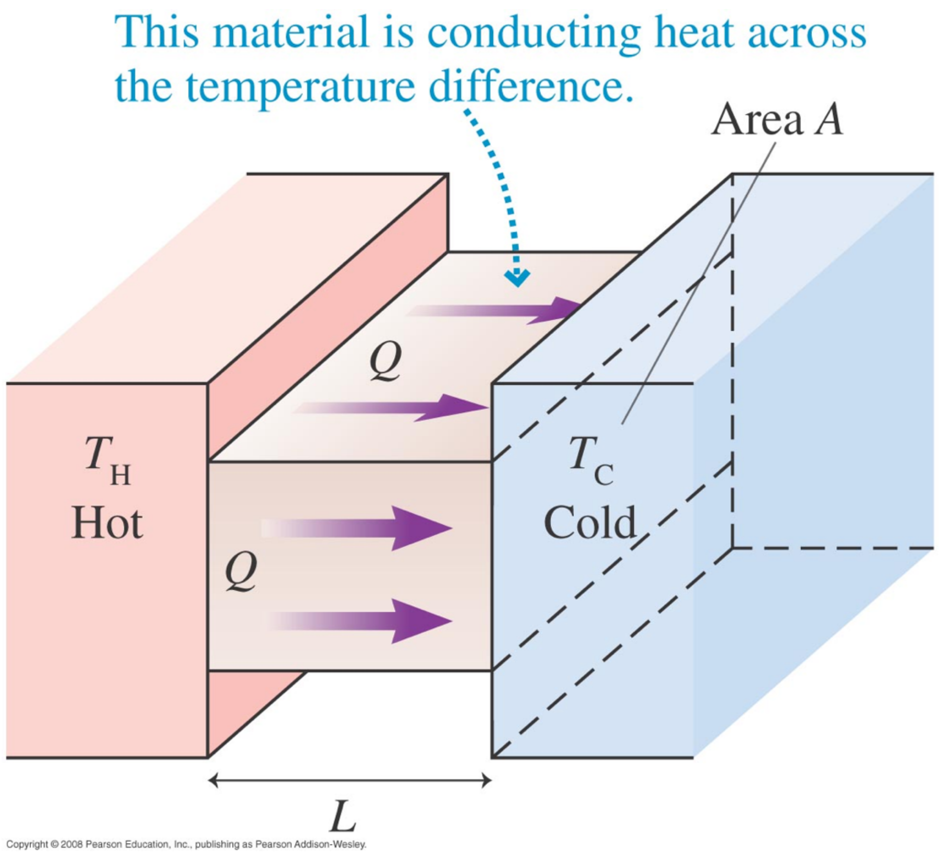
$$pV^\gamma = \text{constant} \qquad \text{or} \qquad p_f V_f^\gamma = p_i V_i^\gamma$$



Using ideal gas law $p = nRT/V$: $TV^{\gamma-1} = $ constant

Heat Transfer: I (evaporation), II, III

- Conduction: ΔT causes thermal energy transfer via object



rate of heat transfer

$$\frac{Q}{\Delta t} = k\frac{A}{L}\Delta T$$

thermal conductivity (larger for good conductor: e.g. metals/diamond...with strong bonds)

- Convection: transfer of thermal energy by motion of fluid (``heat rises"): e.g. water on stove...(cf. conduction: atoms don't move from hot to cold side)
  winds; ocean currents (more rapid in water than air)

Heat Transfer: IV

- Radiation: electromagnetic waves (generated by electric charges in atoms) transfer energy from radiating to absorbing object: e.g. sun, lightbulb...
- Radiated power: $\frac{Q}{\Delta t} = e\sigma A T^4$

  Stefan-Boltzmann constant: $5.67 \times 10^{-8}\ \mathrm{W/(m^2K^4)}$

  emissivity (0 to 1)
- Objects also absorb: $\frac{Q_{net}}{\Delta t} = e\sigma A\left(T^4 - T_0^4\right)$ ← environment
- e = 1: perfect absorber (no reflection) black body (also perfect emitter)
- climate/global warming (greenhouse effect): earth's atmosphere transparent to sunlight (visible)...cooler earth radiates infra-red (absorbed by $\mathrm{CO_2}$)...