Work and Heat

- Both W and Q measure **energy** transferred to/from the system, that is a connection was found between the transfer of energy by heat in thermal processes and the transfer of energy by work in mechanical processes
- Although Q and W each are dependent on the path, $Q + W$ is independent of the path. Neither can be determined solely by the end points of a thermo-dynamic process
- The concept of energy was generalized to include the internal energy
- The *Law of Conservation of Energy* emerged as a universal law of nature (**1st law of thermodynamics**)

The First Law of Thermodynamics

- The **First Law of Thermodynamics** is a special case of the **Law of Conservation of Energy**
  - It takes into account changes in internal energy and energy transfers by heat and work
- The First Law of Thermodynamics states that

$$\Delta E_{int} = Q + W$$

- One consequence of the first law is that there must exist some quantity known as **internal energy** which is completely determined by the state of the system

- For infinitesimal changes in a system

$$dE_{int} = dQ + dW$$

- The first law is an energy conservation statement specifying that the only type of energy that changes in a system is the internal energy
- An **isolated system** is one that does not interact with its surroundings
  - No energy transfer by heat takes place
  - The work done on the system is zero
  - $Q = W = 0$, so that $\Delta E_{int} = 0$
- The internal energy of an isolated system remains constant

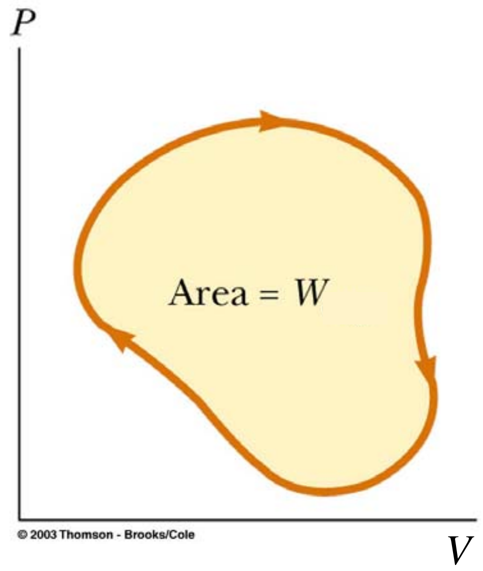
- Changing the state in different ways

$$(P_1, V_1, T_1) \rightarrow (P_2, V_2, T_2)$$

- ΔE_{int} depends only on the endpoints (independent of the path), i.e. it is a *state function*
- **Cyclic process**: starts and ends in the same state, $dE_{int} = 0$
- **Adiabatic process:** no energy enters or leaves the system by heat $\rightarrow$ $Q = 0$
- **Isobaric process:** occurs at a constant pressure, $dP = 0$
- **Isovolumetric process:** no change in the volume, $dV = 0$
- **Isothermal process:** is one that occurs at a constant temperature, $dT = 0$

Cyclic Processes

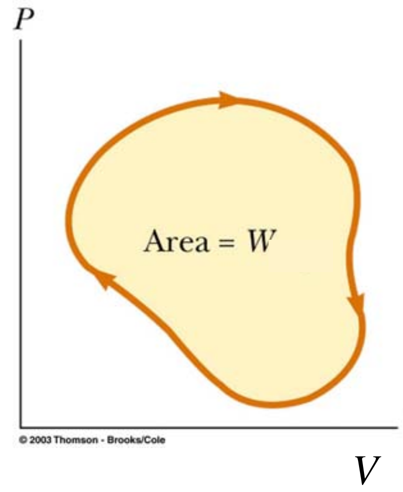
- A **cyclic process** is one that starts and ends in the same state
  - This process would not be isolated
  - On a *PV* diagram, a cyclic process appears as a closed curve



- The internal energy must be zero since it is a state function
- If $\Delta E_{int} = 0$, $Q = -W$
- In a cyclic process, the net work done on the system per cycle equals the area enclosed by the path representing the process on a *PV* diagram

- For a cyclic process we have

$$\Delta E_{int} = \oint dE_{int} = \oint dW + \oint dQ$$



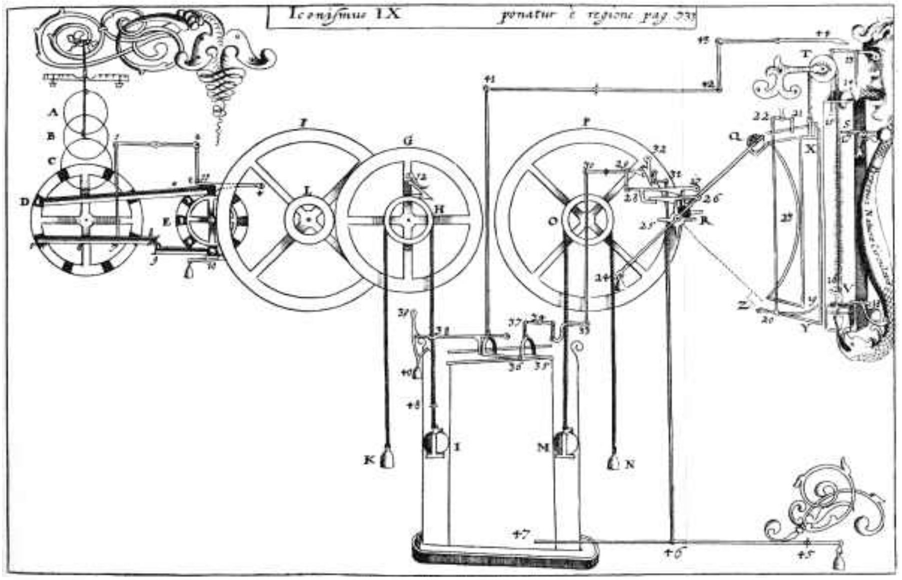
- Since $\Delta E_{\text{int}} = 0$ we have $\oint dW = -\oint dQ$

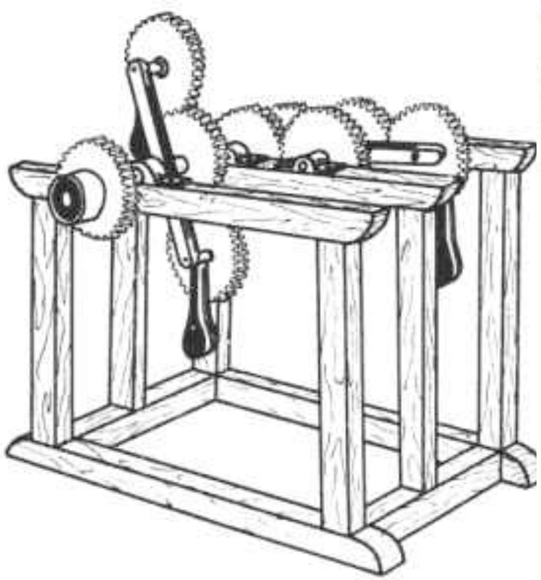
- A **perpetuum mobile of the first kind** is a machine which produces constant work in a cyclic process without adding energy (for example heat). This means

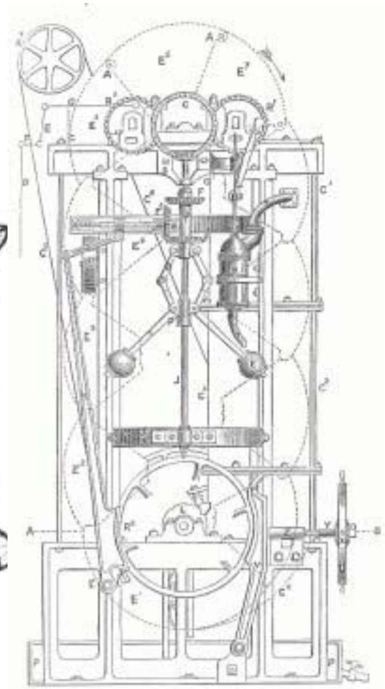
$$\Delta E_{\text{int}} = 0, \quad \oint dW > 0 \quad \text{and} \quad \oint dQ = 0$$

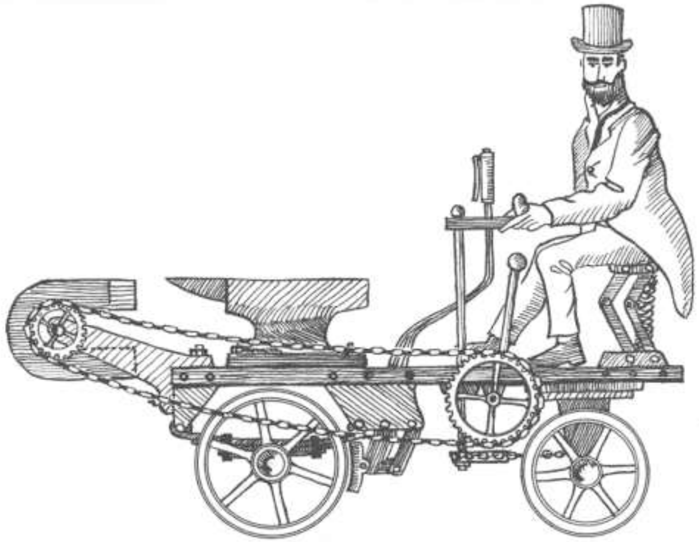
➡ **This violates the first law of thermodynamics**

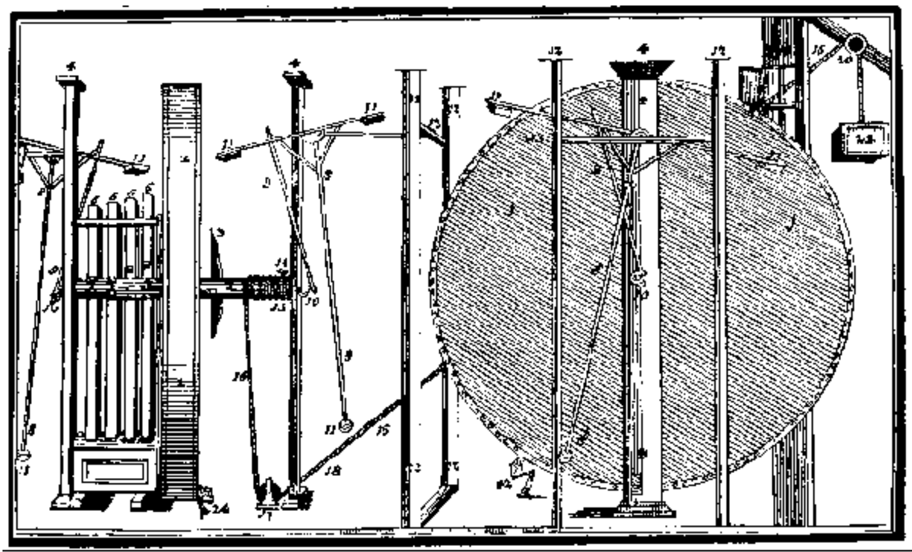
- People tried since more than 2000 years to build these perpetuum mobile





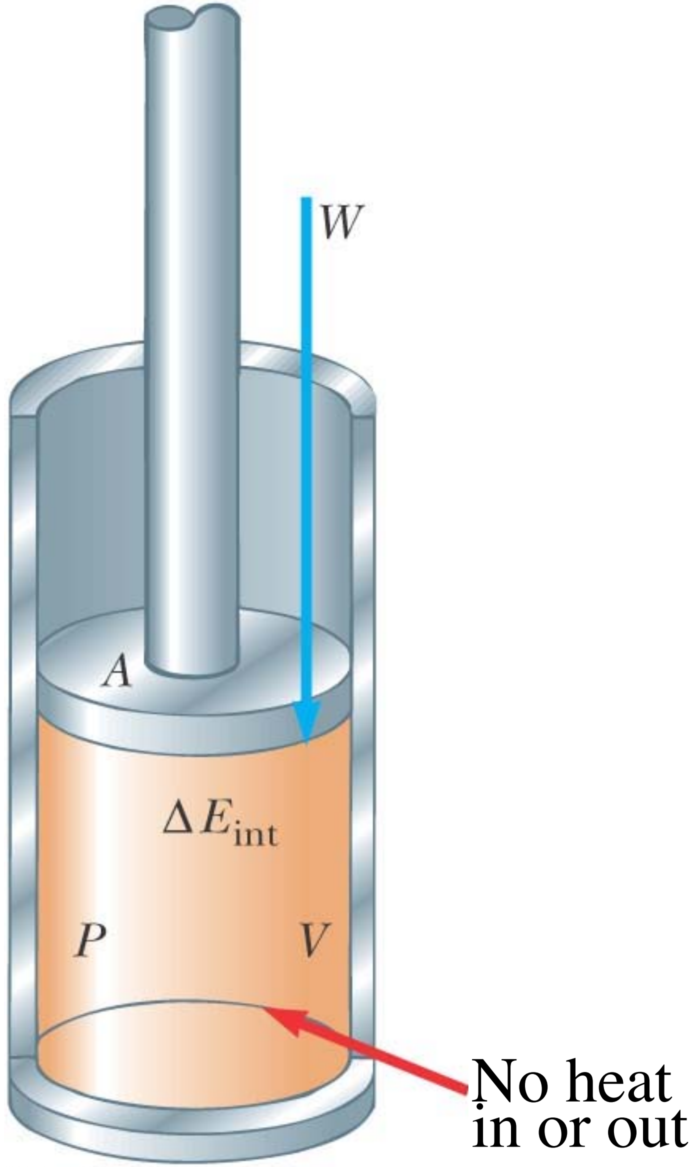






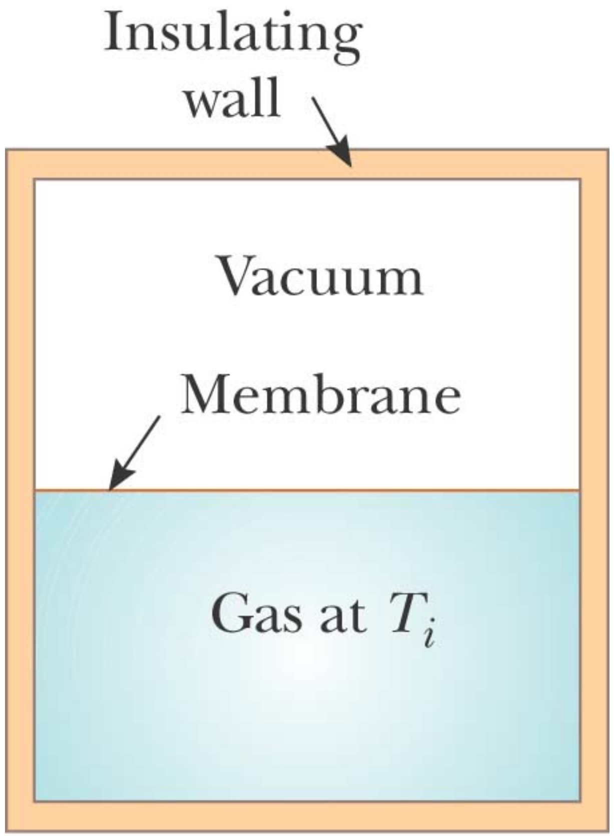
Adiabatic Process

- An **adiabatic process** is one during which no energy enters or leaves the system by heat
  - $Q = 0$
  - This is achieved by:
    - Thermally insulating the walls of the system
    - Having the process proceed so quickly that no heat can be exchanged



- Since $Q = 0$, $\Delta E_{int} = W$
- If the gas is compressed adiabatically, W is positive (remember $\Delta W = -P\Delta V = -P(V_f - V_i)$) so ΔE_{int} is positive and the temperature of the gas increases
- If the gas expands adiabatically, the temperature of the gas decreases
- Some important examples of (almost ideal) adiabatic processes related to engineering are:
  - The expansion of hot gases in an internal combustion engine
  - The liquefaction of gases in a cooling system
  - The compression stroke in a diesel engine

- This is an example of adiabatic free expansion
- The process is adiabatic because it takes place in an insulated container ($Q = 0$)
- Because the gas expands into a vacuum, it does not apply a force on a piston and $W = 0$
- Since $Q = 0$ and $W = 0$, $\Delta E_{int} = 0$ and the initial and final states are the same
  - No change in temperature is expected



Isobaric Process

- An **isobaric process** is one that occurs at a constant pressure
- The values of the heat and the work are generally both nonzero
- The work done is $W = -P\,(V_f - V_i)$ where P is the constant pressure
- The **total differential** for $E_{int}=f(V,T)$

$$dE_{int} = dQ + dW = CdT - PdV = \left(\frac{\partial E_{int}}{\partial T}\right)_{P,V} dT + \left(\frac{\partial E_{int}}{\partial V}\right)_{P,T} dV$$

- The **heat capacity**: $C = \frac{\partial E_{int}}{\partial T}$

Isovolumetric Process

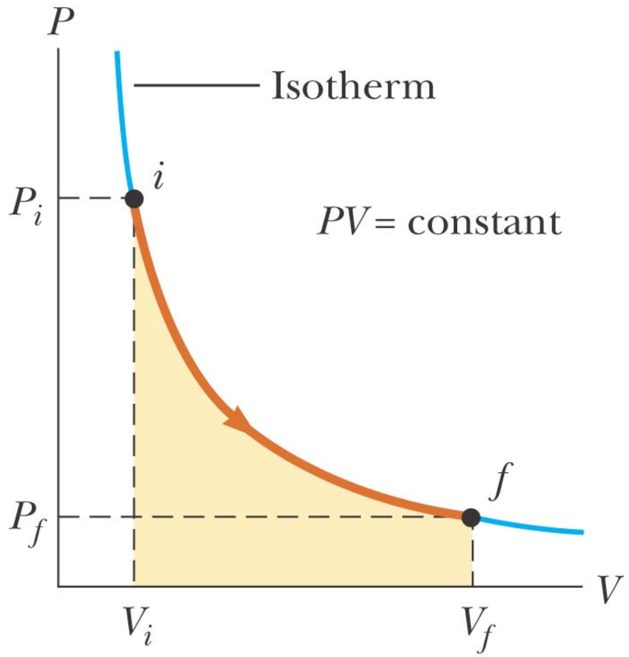
- An **isovolumetric process** (also called isochoric process in older literature) is one in which there is no change in the volume
- Since the volume does not change, $W = 0$
- From the first law, $\Delta E_{int} = Q$ or $dE_{int} = C_V dT$

The **heat capacity at constant volume**: $C_V = \left(\frac{\partial E_{int}}{\partial T}\right)_V$

- If energy is added in form of heat to a system kept at constant volume, all of the transferred energy remains in the system as an increase in its internal energy

Isothermal Process

- An **isothermal process** is one that occurs at a constant temperature
- Since there is no change in temperature, $\Delta E_{int} = 0$
- Therefore, $Q = -W$
- Any energy that enters the system by heat must leave the system by work
- At right is a *PV* diagram of an **isothermal gas expansion**
- The curve is a *hyperbola*
- The curve is called an **isotherm**



- The curve of the PV diagram indicates PV = constant
  - The equation of a hyperbola (y=c/x or P=c/V)
- Because it is an ideal gas and the process is quasi-static, $\boldsymbol{PV = nRT}$ and (T=const. $\Rightarrow$ PV=const.)

$$W = -\int_{V_i}^{V_f} P\,dV = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT\int_{V_i}^{V_f} \frac{1}{V}\,dV = nRT\,ln\left(V_i / V_f\right)$$

- Numerically, the work equals the area under the PV curve (the shaded area in the diagram)
- If the gas expands, $V_f > V_i$ and the work done on the gas is negative
- If the gas is compressed, $V_f < V_i$ and the work done on the gas is positive

Example 1: Cyclic Process $A \rightarrow B \rightarrow C \rightarrow A$

Work done (area)

$W_{AB} = -P\Delta V = -300$ Pa 0.4 m^3 $= -120$ J

(gas expands W <0)

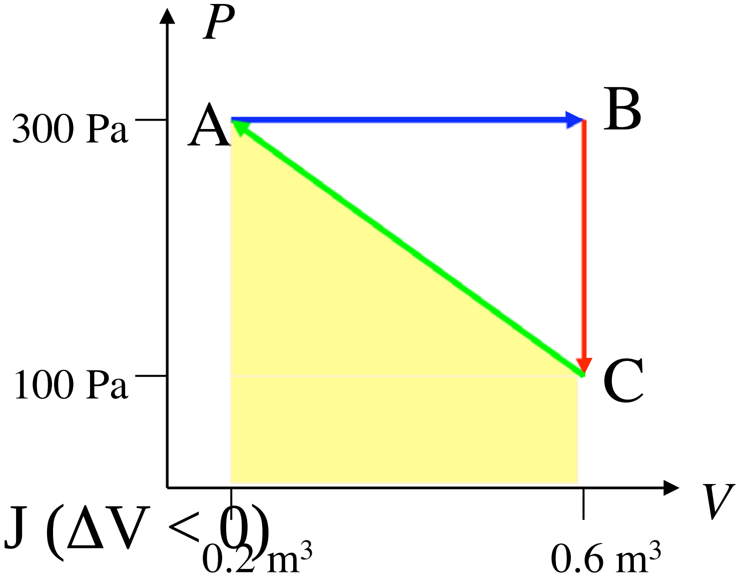
$W_{BC} = 0$ (zero area, ΔV=0 no expansion)

$W_{CA} = -\ 1/2 \times 200$ Pa $(-0.4$ m$^3)$

$-\ 100$ Pa $(-0.4$ m$^3) = +80$ J $(\Delta V < 0)$

(area of trapezium)

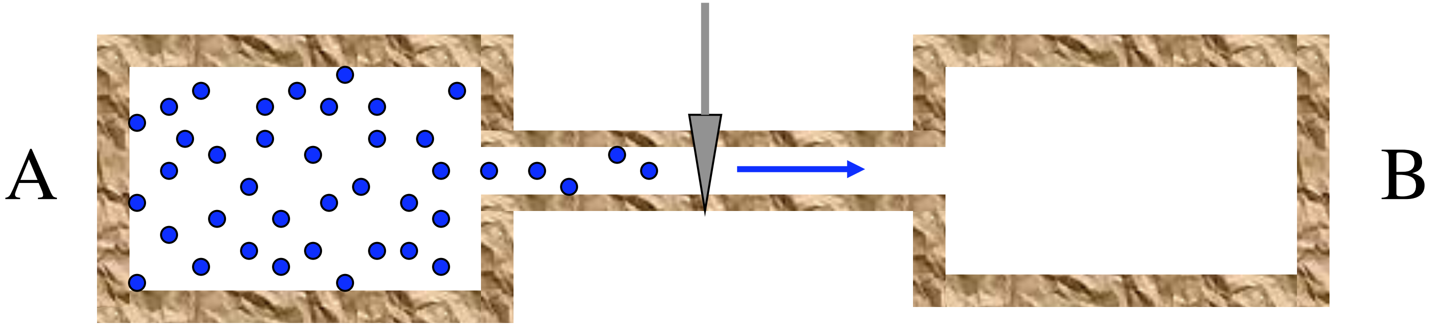
(volume decreases, W > 0)



Complete Cycle $W = W_{AC} + W_{CB} + W_{BA} = -40$ J

(Reverse cycle $A \rightarrow C \rightarrow B \rightarrow A$: W = +40 J)

<u>Example 2:</u> Sudden expansion of a gas



- This is an **irreversible process** (system is not in equilibrium)
- In contrast to the adiabatic free expansion, gas cools (*Joule-Thomson effect*)
- Gas does not flow back into one container (A or B), hence the process is not reversible
- The pressure varies greatly between different areas
- As a consequence, the (p,V) diagrams cannot be used to describe such processes

The Maxwellian demon

- The demon opens the gate only for gas molecules coming from the left.
- Eventually the left gas chamber will be empty.
- The first law does not disallow this machine.
- This is called a **perpetuum mobile of the second kind**.
- The second law of thermodynamic forbids this process.

Heat Transfer

- We want to know the rate at which energy is transferred between systems
- There are various mechanisms responsible for the transfer:
  - (1) **Conduction** (vibrating atoms transfer energy to adjacent atoms)
  - (2) **Convection** (bulk fluid/gas motion)
  - (3) **Radiation** (electromagnetic waves, photons)
- Usually (1) > (2) > (3) when all 3 modes are applicable

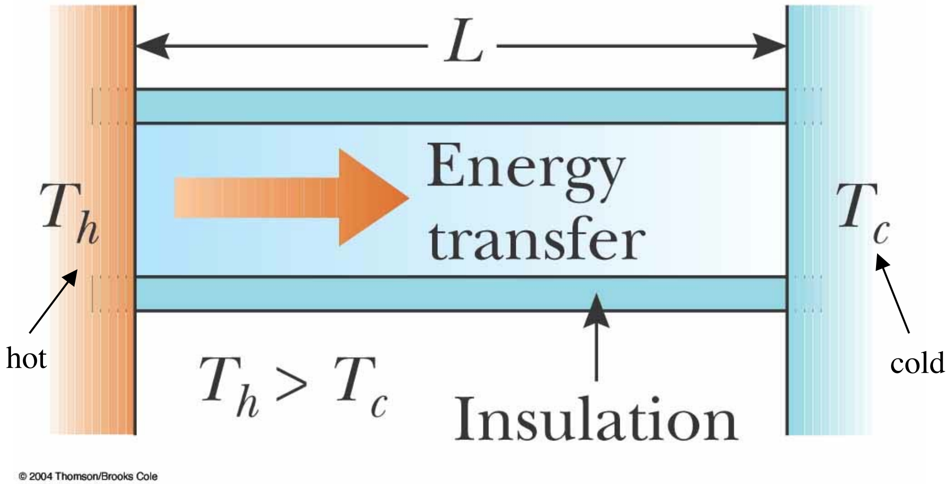
Conduction

- The transfer can be viewed on an atomic scale
  - It is an exchange of energy between microscopic particles by collision. The microscopic particles can be atoms, molecules or free electrons
  - Less energetic particles gain energy during collisions with more energetic particles
- Rate of conduction depends upon the characteristics of the substance
- Particles near the heat source

  move with larger amplitudes.

  These collide adjacent with molecules and transfer some energy. Eventually, the energy travels entirely through the pan.

- In general, metals are good thermal conductors
  - They contain large numbers of electrons that are relatively free to move through the metal
  - They can transport energy fast from one region to another
- Poor conductors include asbestos, paper, and gases
- Conduction occurs only if there is a difference in temperature between two parts of the conducting medium
- Heat transfer through a conducting rod



Temperature gradient

$$\left|\frac{dT}{dx}\right| = \frac{T_h - T_c}{L}$$

- The slab at right allows energy to transfer from the region of higher temperature to the region of lower temperature
- The <u>rate</u> of heat transfer is given by:

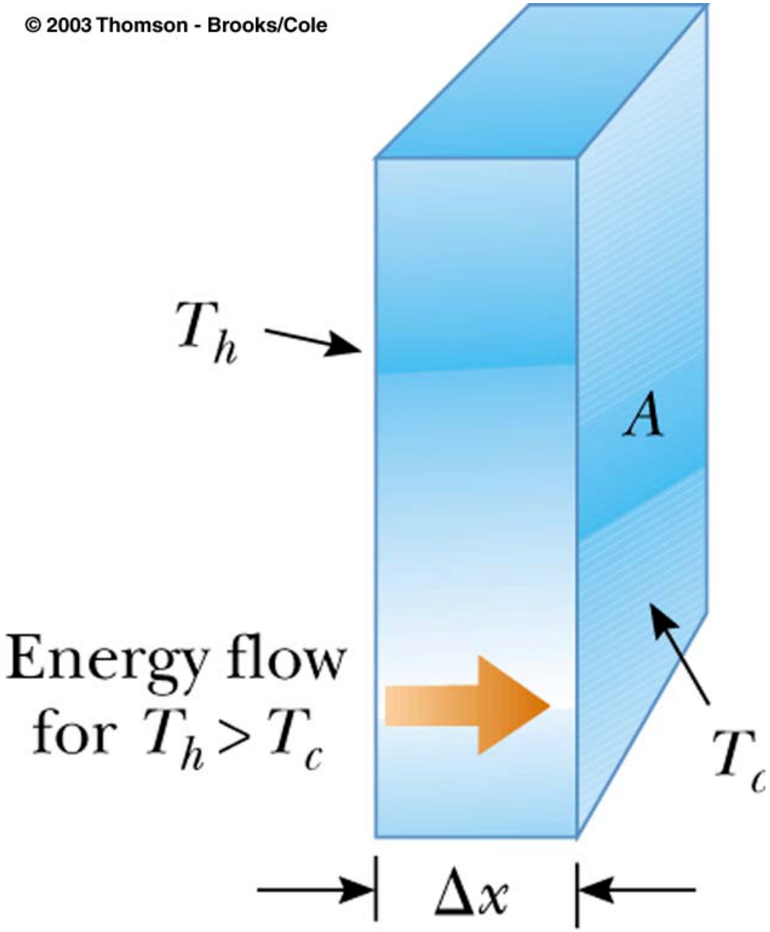
$$\wp = \frac{Q}{\Delta t}$$

- Since $\wp \propto A$ and $\wp \propto dT / dx$

we have

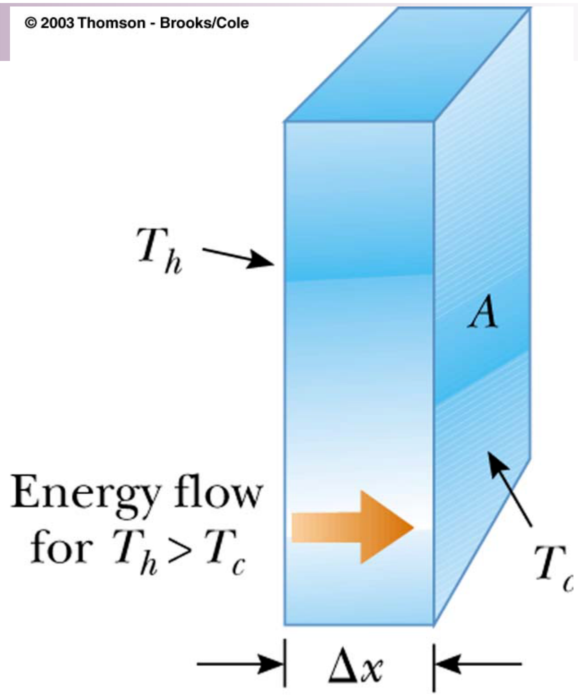
$$\wp = \frac{Q}{\Delta t} = kA\left|\frac{dT}{dx}\right|$$

k: thermal conductivity (J s^{-1} $m^{-1}K^{-1}$ = W $m^{-1}K^{-1}$)



- *A* is the cross-sectional area
- Δx is the thickness of the slab
  - or the length of a rod
- $\wp$ is in Watts when *Q* is in Joules and *t* is in seconds
- *k* is the **thermal conductivity** of the material
  - Good conductors have high *k* values and good insulators have low *k* values
- Using the temperature gradient for the rod, the rate of energy transfer becomes:

$$\wp = kA\left(\frac{T_h - T_c}{L}\right)$$



- For a compound slab containing several materials of various thicknesses (L_1, L_2, …) and various thermal conductivities (k_1, k_2, …) the rate of energy transfer depends on the materials and the temperatures at the outer edges:

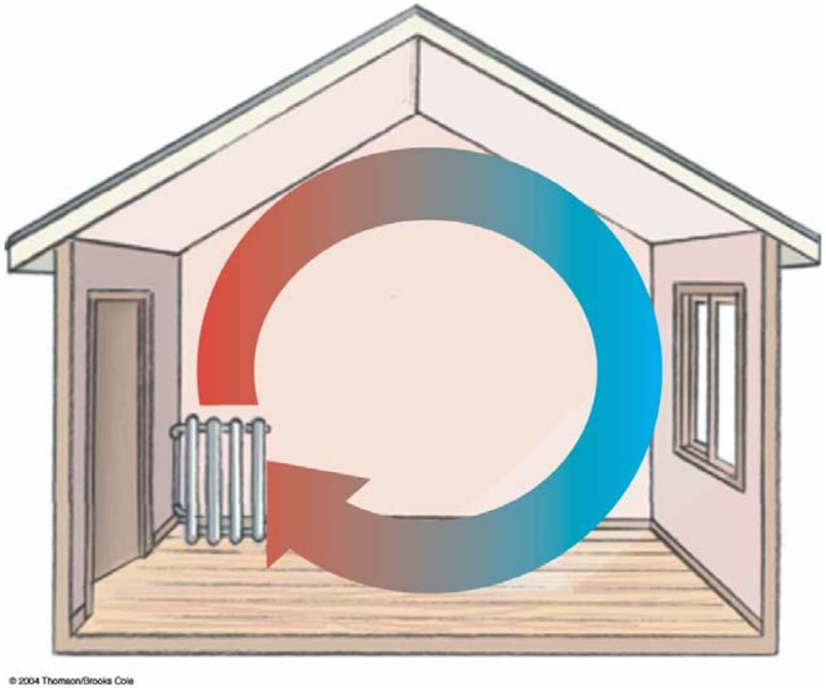
$$\wp = \frac{A\left(T_h - T_c\right)}{\sum_i \left(L_i / k_i\right)}$$

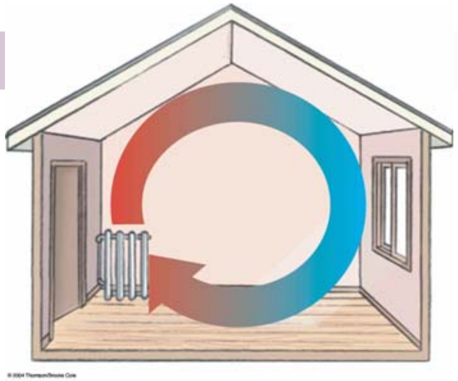
- Home Insulation: substances are rated by their *R values* (good insulator $\longrightarrow$ large *R* value)
  - $R = L / k$ and the rate becomes $\wp = \dfrac{A\left(T_h - T_c\right)}{\sum_i R_i}$
  - For multiple layers, the total *R* value is the sum of the *R* values of each layer

Substance	**Thermal Conductivity in W/m °C**	**Substance**	**Thermal Conductivity in W/m °C**
Metals (*at* 25°C)		*Nonmetals (approximate values)*	
Aluminium	238		
Copper	397	Asbestos	0.08
Gold	314	Concrete	0.8
Iron	79.5	Diamond	2300
Lead	34.7	Glass	0.8
Siver	427	Ice	2
Gases (*at* 20°C)		Rubber	0.2
Air	0.0234	Water	0.6
Helium	0.138	Wood	0.08
Hydrogen	0.172		
Nitrogen	0.0234		
Oxygen	0.0238		

Convection

- Energy transferred by the movement of a substance
  - When the movement results from differences in density, it is called *natural convection* (diffusion)
  - When the movement is forced by a fan or a pump, it is called *forced convection*





- Air directly above the radiator is warmed and expands
- The density of the air decreases, and it rises
- A continuous air current is established
- The rate of energy transfer through an area *A* by natural convection becomes:

$$\wp = hA\Delta T$$

- *h* is called the **convection coefficient**
- Improve efficiency by forced convection or by increasing the area *A*

Radiation

- Radiation does not require physical contact
- All objects radiate energy continuously in the form of electromagnetic waves due to thermal vibrations of their molecules
- Rate of radiation is given by **Stefan's law**

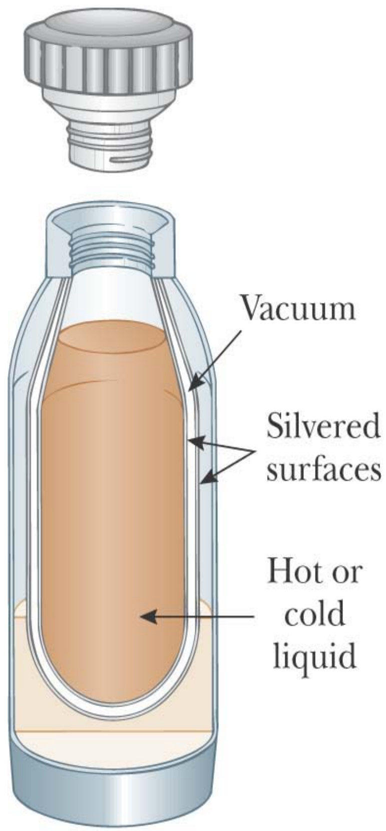
$$\wp = \sigma A e T^4$$

  - $\wp$ is the rate of energy transfer, in Watts
  - $\sigma = 5.6696 \times 10^{-8}$ W m^{-2} K^{-4} (Stefan-Boltzmann constant)
  - *A* is the surface area of the object, *T* is the temperature in K
  - *e* is a constant called the **emissivity (***e* varies from 0 to 1)
    - The emissivity is also equal to the **absorptivity**

- With its surroundings, the rate at which the object at temperature T with surroundings at T_0 radiates is
  - $\wp_{net} = \sigma A e\left(T^4 - T_0^4\right)$
  - When an object is in equilibrium with its surroundings, it radiates and absorbs at the same rate (its temperature will not change)
- An **ideal absorber** is defined as an object that absorbs all of the energy incident on it: $e = 1$
  - This type of object is called a **black body**
  - An ideal absorber is also an ideal radiator of energy
- An ideal reflector absorbs none of the energy incident on it: $e = 0$

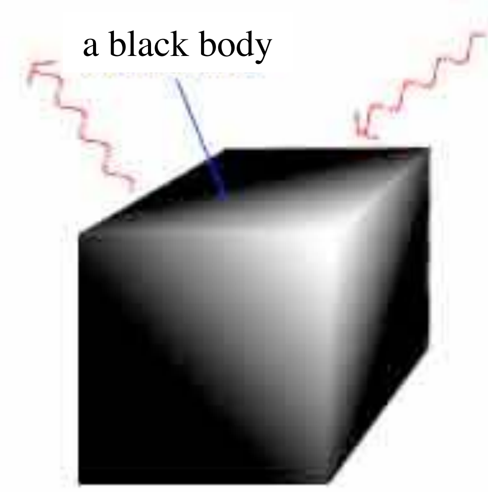
The Dewar Flask

- A Dewar flask is a container designed to minimize the energy loss by conduction, convection, or radiation
- It is used to store either cold or hot liquids for long periods of time
  - A thermos bottle is a common household equivalent of a Dewar flask
- The space between the walls is a vacuum to minimize energy transfer by conduction and convection. The silvered surface minimizes energy transfer by radiation
- The size of the neck is reduced to further minimize energy losses



Black Body Radiation

- All material can emit and absorb light at specific wavelengths.
- An idealized case is the so-called **black body**, which can absorb or emit light equally well.



- The sun λ_{max} =500 nm corresponding to yellow light and to a surface temperature of around T = 5,800 K. In comparison, our earth emits light with λ_{max} =10 μm corresponding to a surface temperature of 288 K.

$$E = h\nu = h\frac{c}{\lambda}$$