

## Chapter 19: Thermodynamics

Lecture covers sections 1-2, 4-11

thermodynamics = study of the thermal energy of systems, es, heat flow

Zero<sup>th</sup> Law of Thermodynamics: all bodies have a temperature  $T$ . When two bodies are in thermal equilibrium (ie, there is no heat flowing between them), they have the same temp.  $T$ .

This fundamental law was formulated in 1930s, well after 1<sup>st</sup> & 2<sup>nd</sup> Laws were discovered.

Physicists measure temperature in units of Kelvins (K):

$$T \sim 10^{39} \text{ K}$$

temperature of univers at Big Bang,  
~15 billion years ago

expansion of universe during past 15 byrs caused it to cool to  $T = 3 \text{ K}$

$T = 273.15 \text{ K} =$  temp at which water freezes

## Celsius Scale:

$$T_c = T - 273.15^\circ$$

temp in  
degrees  
Celsius

temp in  
kelvin

so  $T_c = 20^\circ \text{C}$  corresponds to

$$T = T_c + 273.15^\circ = 293 \text{ K}$$

↑  
"kelvins"

Convert to Fahrenheit scale.

$$T_F = \frac{9}{5} T_c + 32^\circ$$

for  $T_c = 20^\circ \text{C}$ ,  $T_F = 68^\circ \text{F}$

Thermal Expansion = change in size due to  
change in temperature  $\Delta T$

Raise the temperature of a rod by amount

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

The rod of length  $L$  expands by amount

$$\Delta L = L \alpha \Delta T$$

rod of length  $L$ ,  
initial temp  $T_{\text{init}}$

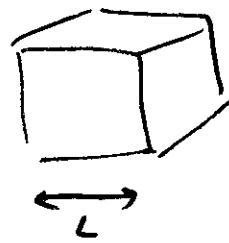
final temp  $T_{\text{final}}$

$\longleftrightarrow$   
 $\Delta L$

where  $\alpha$  = coefficient of  
linear expansion,

has units of  $K^{-1}$

examples: ice has  $\alpha = 50 \times 10^{-6} K^{-1}$  (or  $^{\circ}C^{-1}$ )  
steel has  $\alpha = 10 \times 10^{-6} K^{-1}$

Volume expansion

consider a box of volume  $V = L^3$

change its temperature by amount  $\Delta T$

its volume changes by  $\Delta V = \delta V = 3L^2 \Delta L$

$$= 3L^3 \alpha \Delta T$$

$$= 3\alpha V \Delta T$$

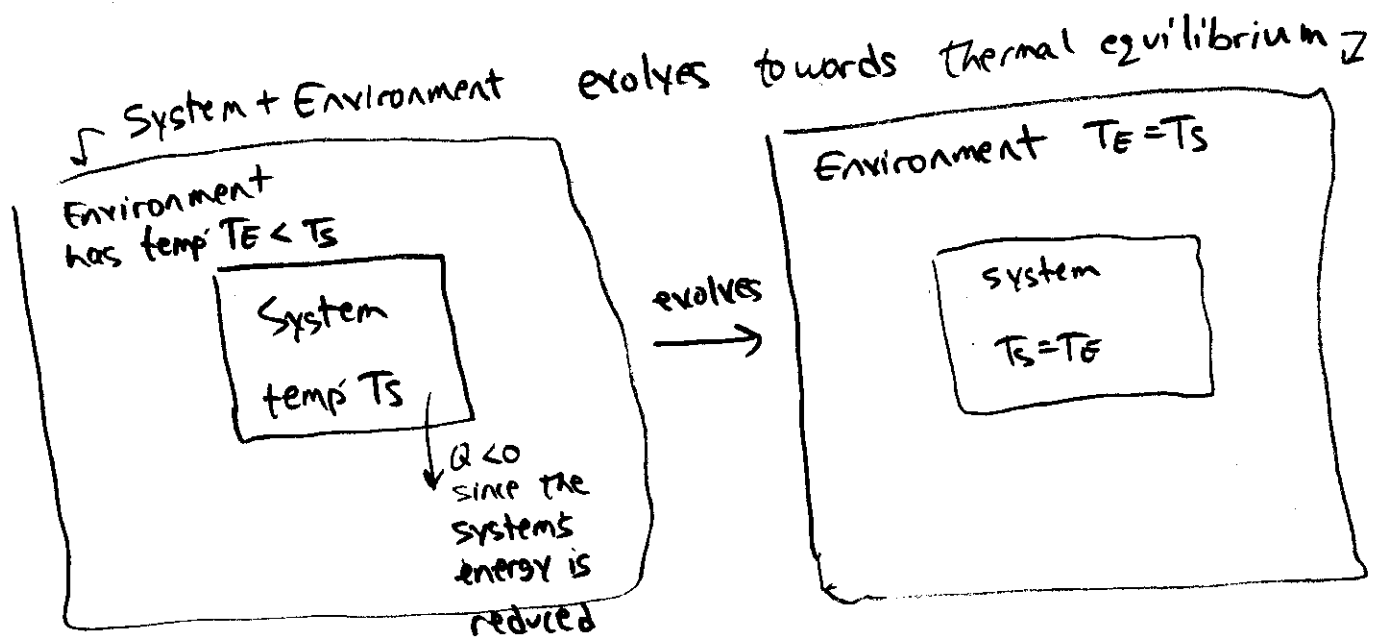
$$\equiv \beta V \Delta T$$

where  $\beta = 3\alpha =$  coefficient of volume expansion

# Temperature & Heat

Heat = energy  $Q$  transferred from one body (or system) to another due to a temperature difference between them.

Suppose some system has temp  $T_S > T_E$ , where  $T_E$  = temp of surrounding environment. Energy will be exchanged until the system is in thermodynamic equilibrium with its environment:



This cartoon could represent a hot ( $T = T_S$ ) cup of coffee cooling off to room temp ( $T = T_E$ ). Note that the coffee has  $Q < 0$ , since it lost energy.

Likewise, if  $T_S < T_E$  initially,

the system's  $Q > 0$  since it would acquire heat-energy from the environment as it warmed up. Example: a cool drink warming up to room temp.

### Heat Absorption:

changing a body's temperature  $T$  by  $\Delta T$  causes it to absorb or lose heat

$$Q = C\Delta T = C(T_{\text{final}} - T_{\text{initial}})$$

where  $C$  = body's heat capacity

since  $Q$  has units of energy,

$C$  has units of energy / temperature  
(eg, Joules/Kelvin)

However the more massive a body is, the more energy is required to raise its temperature by  $\Delta T$ .

So we usually write

$$Q = cm\Delta T$$

where  $m =$  body's mass

$c =$  body's specific heat, ie its heat capacity per unit mass  
(units =  $J/kg \cdot K$ )

Note: an alternate unit of heat-energy is the calorie ;  $1 \text{ cal} = 4.1860 \text{ J}$   
 $=$  heat required to warm 1g of water by  $\Delta T = 1^\circ C$

Note: 1 Nutritional Calorie is really a kilocal of heat energy:  $1 \text{ Cal} = 10^3 \text{ cal}$

$\Rightarrow$  water has specific heat of  $c = 1 \text{ cal/gm} \cdot C$   
not a standard SI unit

$$1 \text{ cal} = 4.186 \text{ J}$$

$$1 \text{ gm} = 10^{-3} \text{ kg}$$

$$1 C = 1 K$$

$$= 4.186 \text{ J} / 10^{-3} \text{ kg} \cdot K$$

$$= 4186 \text{ J} / \text{kg} \cdot K$$

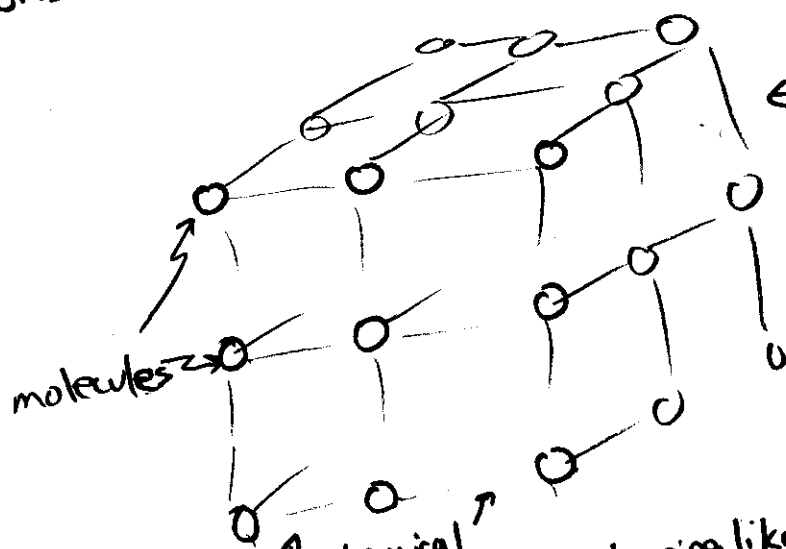
Phases of matter - the state of some material.

solid, liquid, or gas are the most common states

(other less common states include plasma, degenerate matter, Bose-Einstein condensate, ...)

a material's phase depends upon its internal energy, ie, temperature

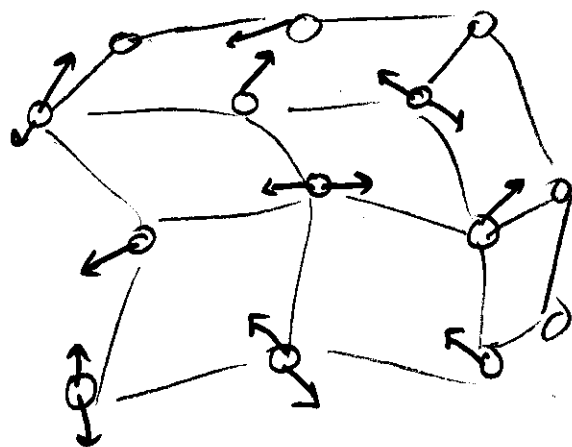
a solid is the least energetic state; its constituent molecules are locked into a rigid lattice:



chemical bonds are 'springlike', keep molecules in place

What happens to the molecules as you heat up this system, & raise its temp?

Adding heat = increasing the kinetic energy of the molecules; they start to oscillate in a very disorderly way due to their mutual spring like forces of attraction:



What happens when you raise the internal energy to the point where the bonds just start to break?

You melt the body - it is now a liquid

Breaking these bonds requires some energy:

$$Q = L_F m$$

where  $m$  = mass of body

$$L_F = \frac{\text{heat of fusion}}{\text{mass}}$$

= energy required to change from  
solid  $\leftrightarrow$  liquid state

= energy required to melt a solid body

= energy released as a liquid freezes,  
becomes a solid (works both ways)

Example: water ice has  $L_F = 333 \text{ kJ/kg}$  (Table 14.4)

for  $m = 10 \text{ kg}$  of  $T = 0^\circ\text{C}$  ice,  
 $= 273 \text{ K}$

$$Q = L_F m = 3.33 \times 10^6 \text{ J}$$

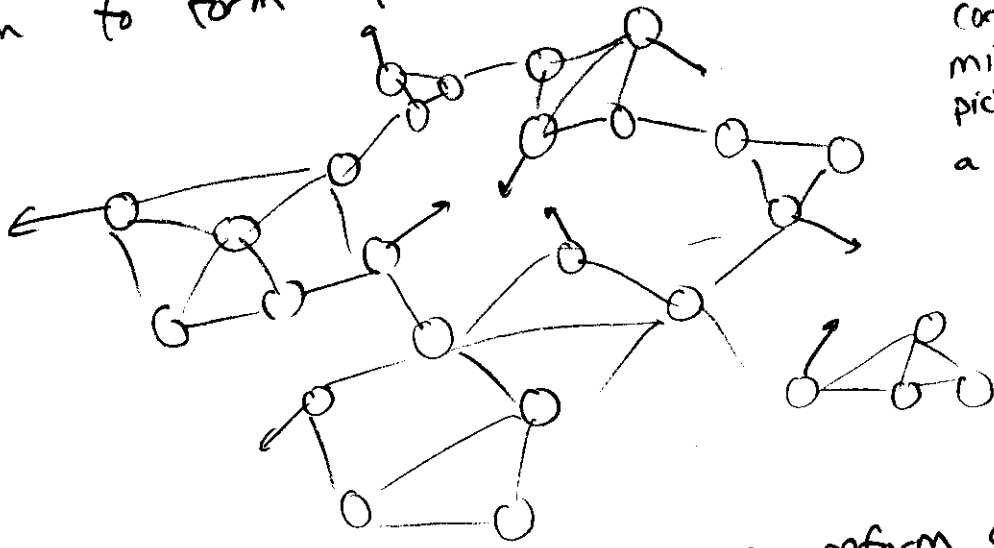
= energy required to melt  $10 \text{ kg}$  of water-ice

OR = energy released into the environment

as  $10 \text{ kg}$  of water freezes

Note that the ice/water's temp is unchanged by the melting process. Warming the water further will require additional heat energy.

Note that the molecules' mutual attractions allows them to form transient clusters

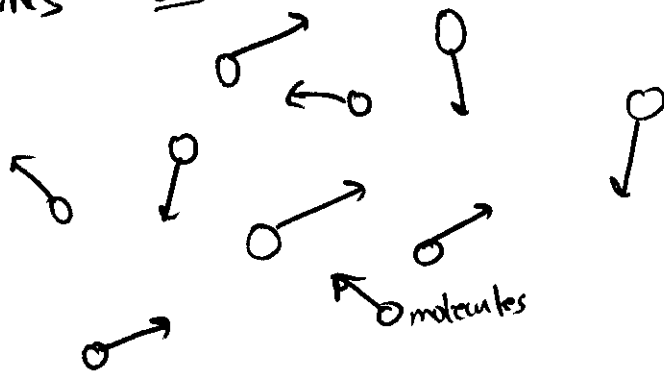


Cartoon is microscopic picture of a liquid.

however these bonds break & reform as the clusters slide about, break up, form new

what if you continue to heat this liquid?

You break all bonds, and the liquid vaporizes, becomes a gas:



## Heat of vaporization:

$$Q = L_v m$$

suppose you have  $m = 10 \text{ kg}$  of liquid water at  $T_c = 100^\circ\text{C} = 373 \text{ K}$   
 (the temperature at which water boils, ie, starts to vaporize, see table 19-4)

Since  $L_v = 2256 \text{ kJ/kg}$  (Table 19-4)

$$Q = L_v m = 2.256 \times 10^7 \text{ J}$$

= energy required to vaporize 10 kg of liquid water

OR = energy released when 10 kg of water vapor (ie, gas) condenses to liquid water.

Sample problem 19-3

a.) How much heat must be absorbed by  $m = 0.72 \text{ kg}$  of  $T = -10^\circ\text{C}$  ice to melt & raise its temp to  $T = 15^\circ\text{C}$ ?

First, raise the temp of the ice to its melting point:

$$T_{\text{init}} = -10^\circ\text{C}$$

$$T_{\text{final}} = 0^\circ\text{C} = 273\text{K}$$

= temp at which  
ice melts

(see Table 19-4 for melting & freezing points of various substances)

so  $Q_1 = c m (T_{\text{final}} - T_{\text{init}})$

$$= \left( \begin{array}{l} \text{for ice} \\ 2220 \text{ J/kg}\cdot\text{K} \\ \text{see Table 19-3} \end{array} \right) (0.72 \text{ kg}) (10 \text{ K})$$

$$= 1.6 \times 10^4 \text{ J}$$

a temp change of  $1^\circ\text{C} =$   
temp change of  $1\text{K}$ .

second, melt the ice:

$$Q_2 = L_F m = (3.33 \times 10^5 \text{ J/kg}) (0.72 \text{ kg})$$

$$= 2.4 \times 10^5 \text{ J}$$

third, raise the water's temp to  $T_{\text{final}} = 15^\circ\text{C}$ :

$$\begin{aligned}
 Q_3 &= cm (T_{\text{final}} - T_{\text{init}}) \\
 &= (4190 \text{ J/kg}\cdot\text{K}) (0.72 \text{ kg}) (15^\circ\text{C} - 0^\circ\text{C}) \\
 &= 4.5 \times 10^4 \text{ J}
 \end{aligned}$$

total heat required:

$$\underline{Q = Q_1 + Q_2 + Q_3 = 3.0 \times 10^5 \text{ J}}$$

b.) What if only  $Q = 210 \text{ kJ}$  of heat is supplied?  
 $= 2.1 \times 10^5 \text{ J}$

Note that this is not enough heat to melt the ice, which would require  $Q_1 + Q_2 = 2.56 \times 10^5 \text{ J}$ .

However  $Q > Q_1$ , so this is enough heat to raise the ice temperature to  $T = 0^\circ\text{C}$ .

The remaining amount of heat is

$$Q_{\text{rem}} = Q - Q_1 = 1.94 \times 10^5 \text{ J}$$

This residual heat will melt some, but not all the ice:

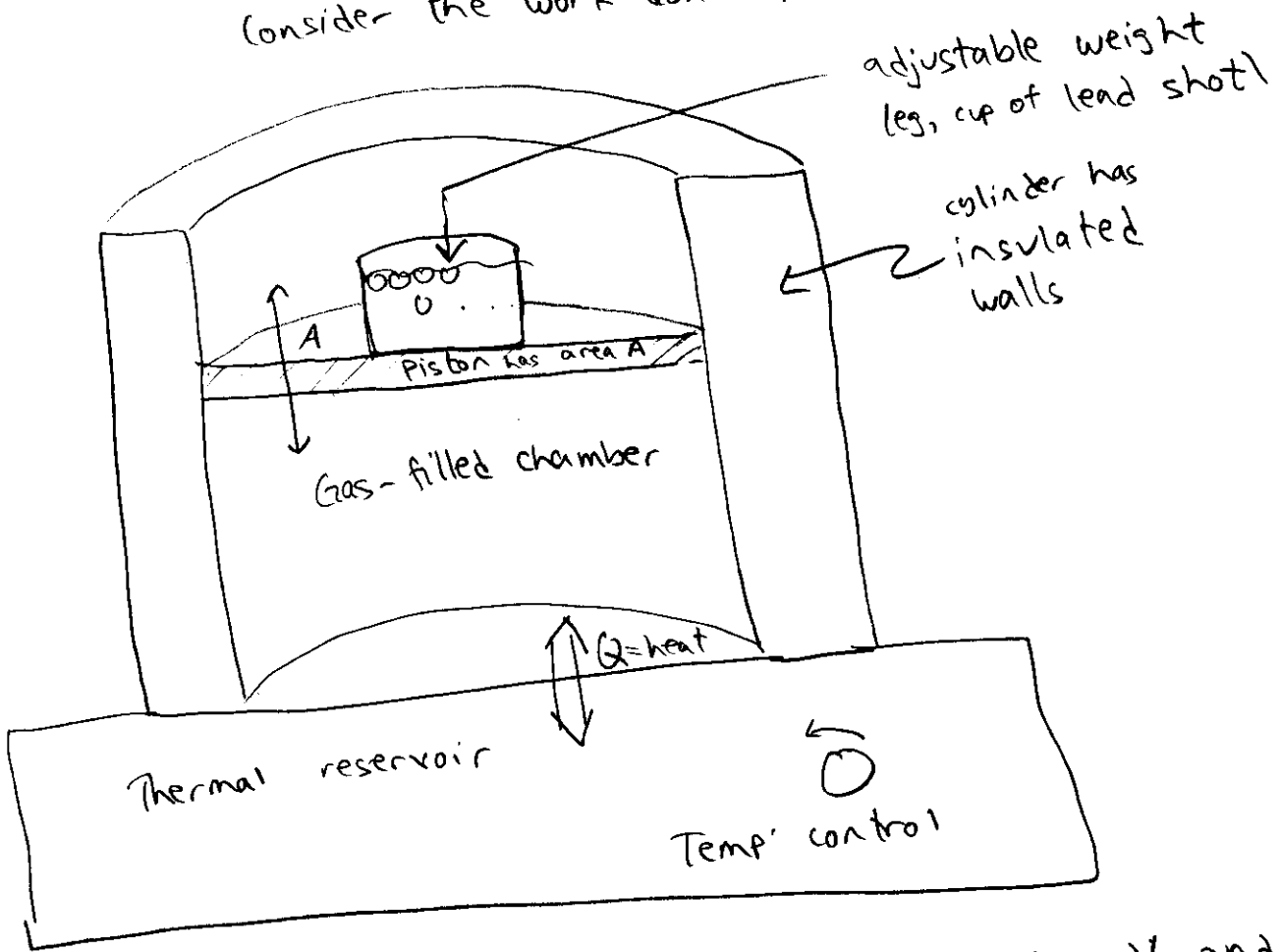
$$Q_{\text{rem}} = L_F m_{\text{melt}}$$

$$\Rightarrow m_{\text{melt}} = \frac{Q_{\text{rem}}}{L_F} = \frac{1.94 \times 10^5 \text{ J}}{3.33 \times 10^5 \text{ J/kg}} = 0.58 \text{ kg}$$

You are left with  $m_{\text{melt}} = 0.58 \text{ kg}$  of water  
 $m_{\text{ice}} = m - m_{\text{melt}} = 0.14 \text{ kg}$  ice  
all at temp  $T = 0^\circ\text{C}$

# Heat & Work

Consider the work done by the following piston:



You can adjust the gas pressure  $P$ , volume  $V$ , and temp  $T$  by adjusting the weight <sup>on the piston</sup>. Likewise, you can alter  $P, V, T$  by changing the thermal reservoir's temp (which it then adjusts the gas temp).

Let  $P_i, V_i, T_i =$  initial  $P, V, T,$

and  $P_f, V_f, T_f =$  final "

Remove some lead shot from the cup, which allows the gas to push the piston up a distance  $d\vec{s}$  with force  $\vec{F} = pA$ , so

$$dW = \vec{F} \cdot d\vec{s} = \text{differential work done by gas}$$

$$= pA ds$$

$$= p dV$$

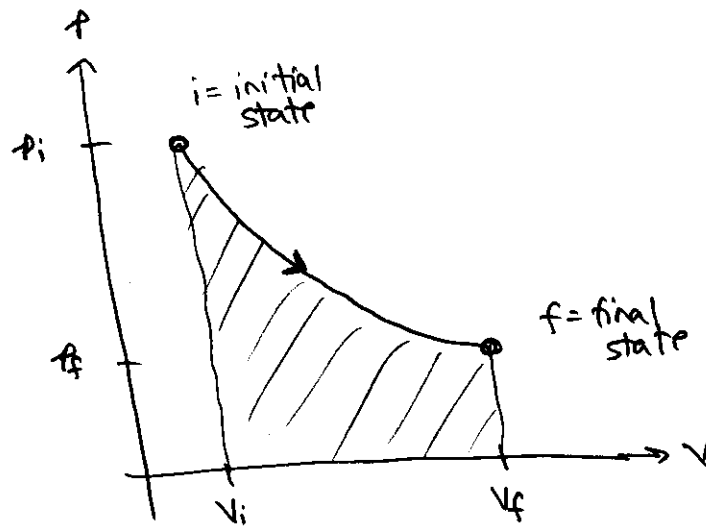
$$\text{where } dV = A ds$$

$$= \text{change in gas volume}$$

Remove more shot. The total work done by the gas as it expands from volume  $V_i \rightarrow V_f$

$$W = \int_{V_i}^{V_f} dW = \int_{V_i}^{V_f} p dV$$

Note that  $P$  decreases as  $V$  increases.  
A  $P-V$  diagram of this process is

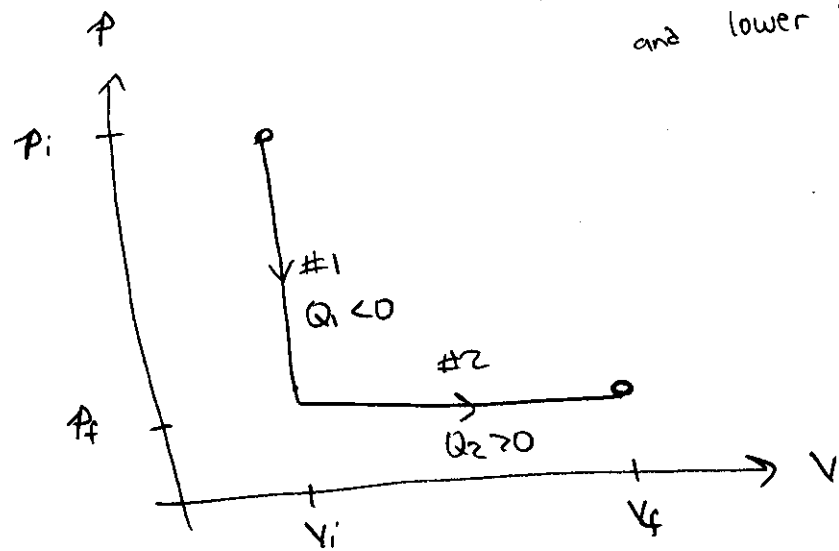


Note that work  $W = \int P dV = \text{area under curve}$

But there are other ways to drive the

19-19

"Process B" can also achieve the same endstate:



step #1: wedge piston,  $V = V_i$ ,  
and lower T so  $P \rightarrow P_f$ ,  
 $Q_1 < 0$

step #2 reduce weight on piston until balanced  
(ie, pressure-supported),  
increase T until  $V \rightarrow V_f$ ,  
so  $Q_2 > 0$

total heat exchanged  $Q_B = Q_1 + Q_2$

What is the work  $W_B$ ?

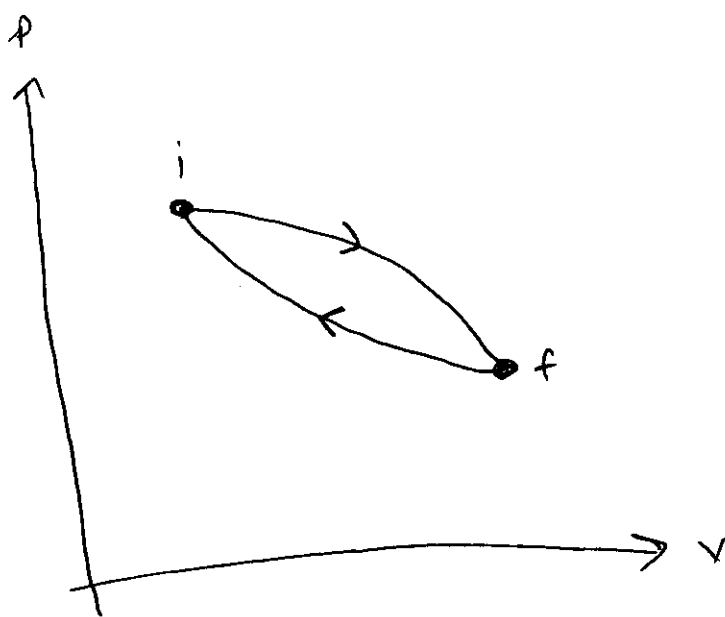
Note that  $W_A > W_B$

and  $Q_A > Q_B$

⇒ process A resulted in more work being done (by the gas on the environment) than that done by process B.

However, that extra work had a higher cost - it absorbed more heat ( $Q_A > Q_B$ ) from the environment.

Thermodynamic cycle



What is the work done by this cycle?  
Is  $w > 0$ ?

# First Law of Thermodynamics

The change in a system's internal energy  $\Delta E_{int}$

(where  $\Delta E_{int} = E_f - E_i$ ) is

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

= heat exchanged with environment - work done

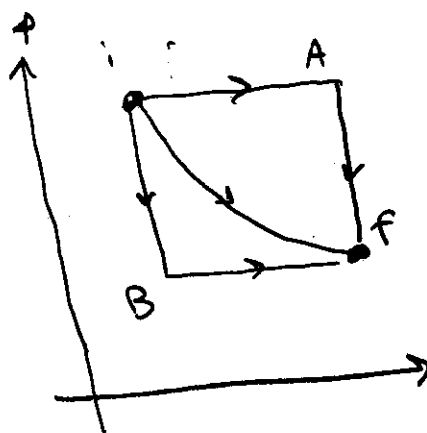
We often write this in a differential form for small changes in  $E_{int}$ ,  $Q$ ,  $W$ :

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

This Law follows from the fact that as the system evolves from state  $i \rightarrow f$ , the difference  $Q - W$  is the same, regardless of the process used to drive the system (ie, regardless of the path in a  $p$ - $V$  diagram)

Recall that  $Q$  &  $W$  differed for process A & B.

But experiments show that  $Q - W = \Delta E_{int} = \text{same}$  for all processes.



recall that  
 $W_A > W_B$   
 &  $Q_A > Q_B$ ,  
 but  $Q_A - W_A$   
 $= Q_B - W_B$   
 $= \Delta E_{int}$

## Thermodynamic Processes

In general,  $\Delta E_{int} = Q - W$

1st Law of Thermo

Let's consider 4 particular processes that often occur in nature:

1. Adiabatic process - a change in the system results in no heat transfer. Occurs when the system is well-insulated

$$Q = 0 \quad (\text{no heat transfer})$$

$$\text{so } \Delta E_{int} = -W$$

if the system does work, i.e.  $W > 0$ ,

then  $\Delta E_{int} < 0 \Leftarrow$  the system loses energy

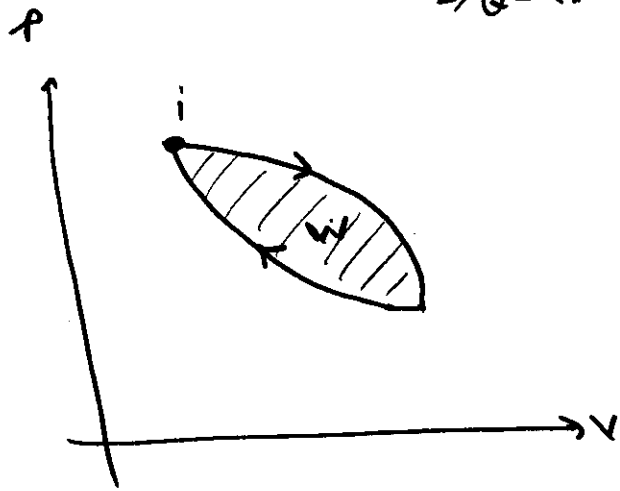
2. Constant-volume process

example: heating the gas with the piston wedged.

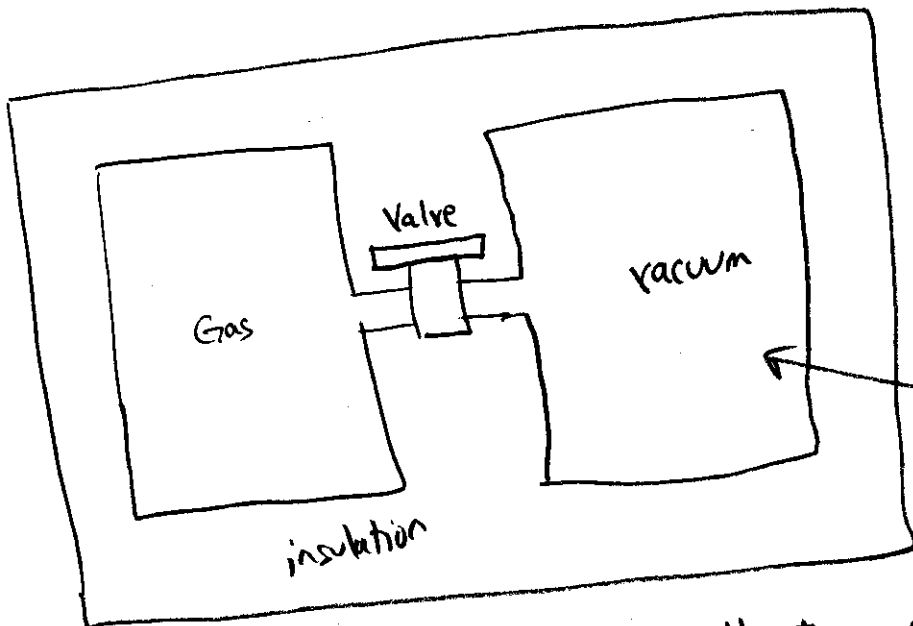
Since  $W = \int P dV$  where  $dV = 0$

$W = 0 \Leftarrow$  the system can't do work if the piston is stuck.

3. cyclic process - restores the system to its initial state; so  $\Delta E_{int} = 0$   
 $\Rightarrow Q = W$



4. free expansion: this is an adiabatic process in which no heat is exchanged with the environment and no work is done, so  $Q = W = 0$  and  $\Delta E_{int} = 0$



opening valve lets gas fill the evacuated chamber. No work is done by gas on the "environment," because the environment is a pressureless void

### Sample problem 19-5

Convert  $m=1\text{kg}$  of water at  $T=100^\circ\text{C}$  to steam by boiling at a pressure of  $p=1\text{atm}=1.01\times 10^5\text{Pa}$  ( $1\text{Pa}=1\text{Pascal}=1\text{N/m}^2$ ). The water's initial volume was  $V_i=1.0\times 10^{-3}\text{m}^3$ , and the steam's final volume is  $V_f=1.671\text{m}^3$

a.) How much work is done by this process?

$$W = \int_{V_i}^{V_f} p \, dV = p(V_f - V_i) = (1.01 \times 10^5 \text{ N/m}^2)(1.67 \text{ m}^3)$$

$$= 1.7 \times 10^5 \frac{\text{N} \cdot \text{m}}{\text{J}} = \text{energy required to push back the atmosphere}$$

b.) How much heat is required to boil off this water?

$$Q = L_v m \quad \text{where} \quad L_v = 2256 \text{ kJ/kg} = \text{water's heat of vaporization}$$

$$\text{so } Q = 2.3 \times 10^6 \text{ J} = \text{energy required to separate H}_2\text{O molecules}$$

c.) What is the change in the systems internal energy?

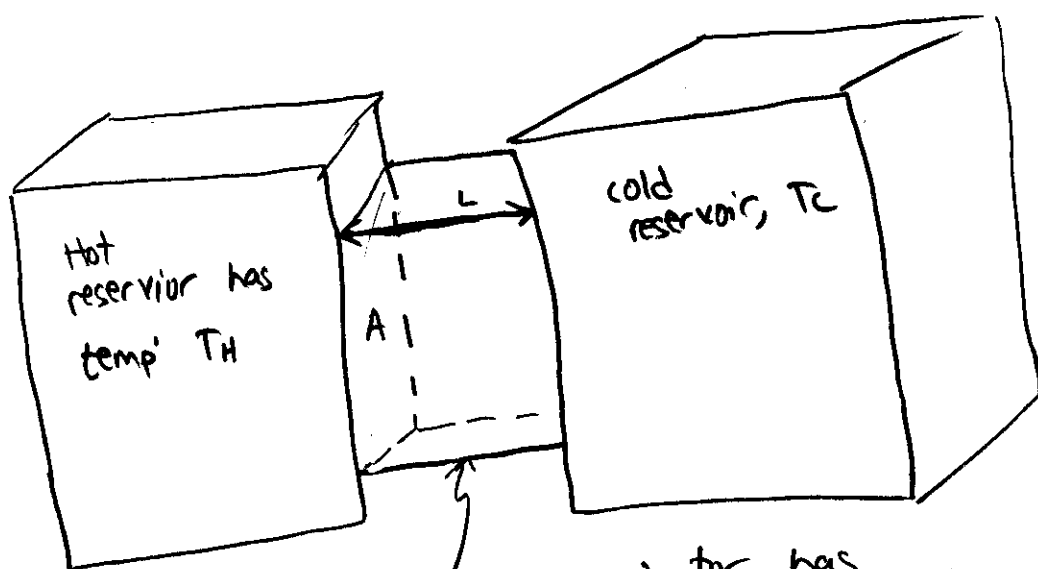
$$\Delta E = Q - W = 2.1 \times 10^6 \text{ J}$$

Heat Transfer - how heat moves between the system & the environment.

3 transfer mechanisms:

1. conduction - put a metal poker in a fire, and its handle gets hot.

recall that heat = vibrations of atoms and electrons. Heating one end of the poker causes those hot atoms to jiggle their neighbors, allowing heat to propagate along the poker.



thermal conductor has area  $A$  facing each reservoir, width  $L$ , and thermal conductivity  $k$

The rate at which heat is conducted from hot  $\rightarrow$  cold reservoir is

$$\text{power } P_{\text{cond}} = \frac{\text{energy } Q}{\text{time } t} = \frac{kA}{L} (T_H - T_C)$$

For example, you would build a radiator that maximizes any heat conduction, so choose a conductor that:

has high conductivity  $k$  (Table 19-6),

large area

narrow, i.e., small  $L$ ,

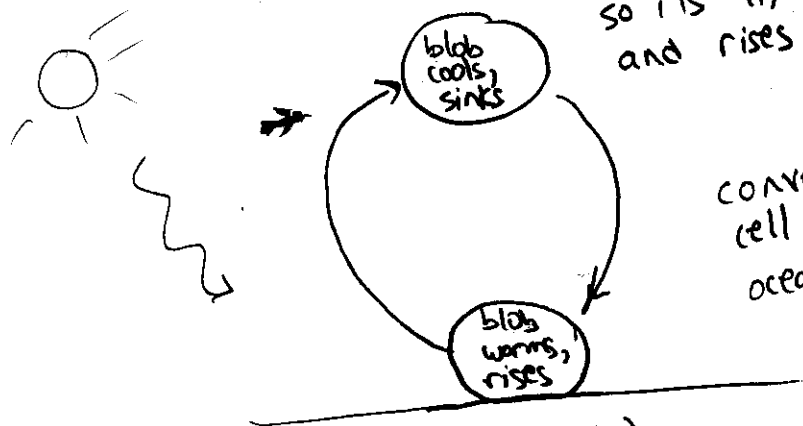
placed between a large thermal gradient (i.e., large  $\Delta T = T_H - T_C$ )

do the reverse to minimize heat losses due to conductivity, to thermally isolate an object (eg, electronics)

2. convection -

heating a fluid causes it to expand, which reduces its density, so it's lighter than the cooler fluid, and rises as cooler air sinks

convection cell - occurs in atmospheres, oceans, stars, etc.



The Sun warms the ground, which heats surface air

3. radiation - all bodies emit electromagnetic radiation, usually called thermal radiation, at the rate

$$P_{\text{rad}} = \sigma \epsilon A T^4$$

where

$T$  = temp

$A$  = body's surface area

$\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$  = Stefan-Boltzmann constant

$\epsilon$  = emissivity ← depends on the body's surface property, usually  $\sim 1$

You are constantly losing internal energy due to your thermal radiation. But so is everything else in your environment, some of which you intercept & absorb, which prevents you from cooling off too fast.

What is the Sun's thermal output?

The sun has

radius  $R_{\odot} = 7 \times 10^8 \text{ m}$

$A = 4\pi R_{\odot}^2 = 6.2 \times 10^{18} \text{ m}^2$

$T = 5800 \text{ K}$  at surface

so  $P_{\text{rad}} = 4 \times 10^{26} \text{ J/sec} = L_{\odot}$

= solar luminosity