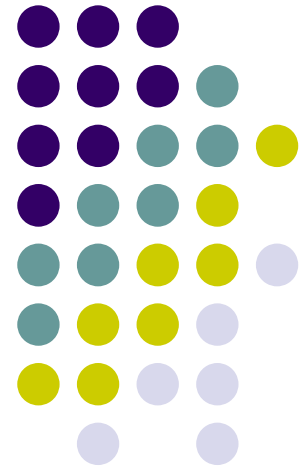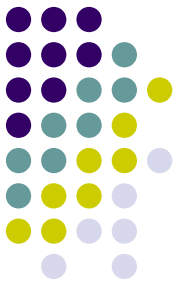# Chapter 20

The First Law of Thermodynamics

Thermodynamics – Historical Background

- Thermodynamics and mechanics were considered to be distinct branches of physics
  - Until about 1850
  - Experiments by James Joule and others showed a connection between them
- A connection was found between the transfer of energy by heat in thermal processes and the transfer of energy by work in mechanical processes
- The concept of energy was generalized to include internal energy
- The Law of Conservation of Energy emerged as a universal law of nature

Internal Energy

- **Internal energy** is all the energy of a system that is associated with its microscopic components
  - These components are its atoms and molecules
  - The system is viewed from a reference frame at rest with respect to the center of mass of the system

Internal Energy and Other Energies

- The kinetic energy due to its motion through space is not included
- Internal energy does include kinetic energies due to:
  - Random translational motion
  - Rotational motion
  - Vibrational motion
- Internal energy also includes potential energy between molecules

Heat

- **Heat** is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings
- The term heat will also be used to represent the amount of energy transferred by this method

Changing Internal Energy

- Both heat and work can change the internal energy of a system
- The internal energy can be changed even when no energy is transferred by heat, but just by work
  - Example, compressing gas with a piston
  - Energy is transferred by work

Units of Heat

- Historically, the **calorie** was the unit used for heat
  - One calorie is the amount of energy transfer necessary to raise the temperature of 1 g of water from $14.5\,^{\circ}$C to $15.5\,^{\circ}$C
    - The "Calorie" used for food is actually 1 kilocalorie
- In the US Customary system, the unit is a BTU (British Thermal Unit)
  - One BTU is the amount of energy transfer necessary to raise the temperature of 1 lb of water from $63\,^{\circ}$F to $64\,^{\circ}$F
- The standard in the text is to use Joules
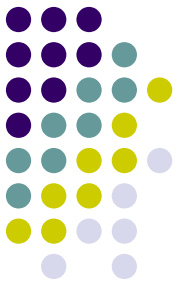
James Prescott Joule
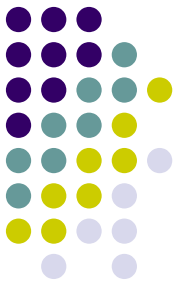
- 1818 – 1889
- British physicist
- Largely self-educated
  - Some formal education from John Dalton
- Research led to establishment of the principle of Conservation of Energy
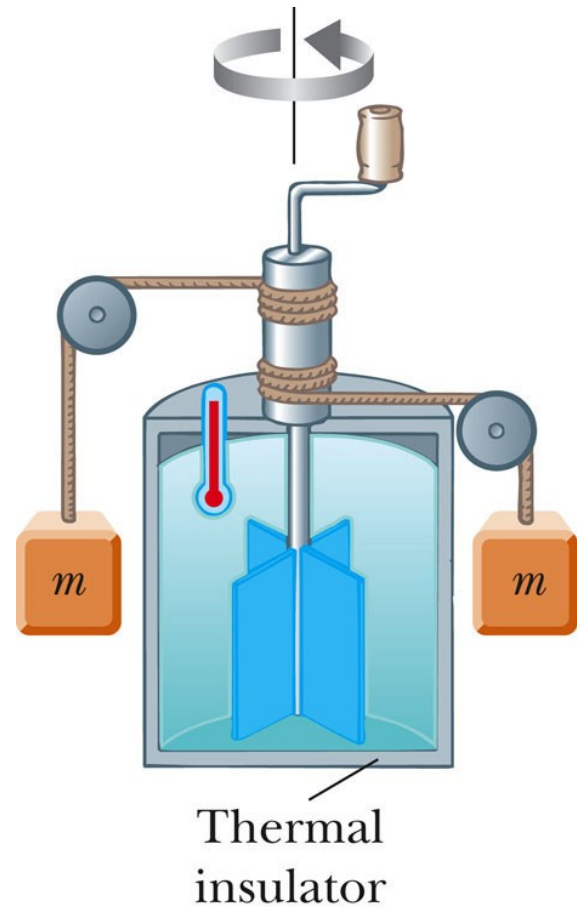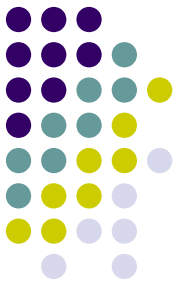- Determined the amount of work needed to produce one unit of energy

Mechanical Equivalent of Heat

- Joule established the equivalence between mechanical energy and internal energy

- His experimental setup is shown at right

- The loss in potential energy associated with the blocks equals the work done by the paddle wheel on the water

Thermal insulator

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Mechanical Equivalent of Heat, cont

- Joule found that it took approximately 4.18 J of mechanical energy to raise the water 1°C

- Later, more precise, measurements determined the amount of mechanical energy needed to raise the temperature of water from 14.5°C to 15.5°C

- 1 cal = 4.186 J
  - This is known as the **mechanical equivalent of heat**

Heat Capacity

- The **heat capacity**, C, of a particular sample is defined as the amount of energy needed to raise the temperature of that sample by $1^{\circ}C$

- If energy Q produces a change of temperature of ΔT, then

$$Q = C\,\Delta T$$

Specific Heat

- **Specific heat**, c, is the heat capacity per unit mass

- If energy Q transfers to a sample of a substance of mass m and the temperature changes by ΔT, then the specific heat is

$$c \equiv \frac{Q}{m\,\Delta T}$$

Specific Heat, cont

- The specific heat is essentially a measure of how thermally insensitive a substance is to the addition of energy

  - The greater the substance's specific heat, the more energy that must be added to cause a particular temperature change

- The equation is often written in terms of Q :

$$Q = m\,c\,\Delta T$$

Some Specific Heat Values

	Specific Heat c	
Substance	J/kg · °C	cal/g · °C
Elemental solids		
Aluminum	900	0.215
Beryllium	1 830	0.436
Cadmium	230	0.055
Copper	387	0.092 4
Germanium	322	0.077
Gold	129	0.030 8
Iron	448	0.107
Lead	128	0.030 5
Silicon	703	0.168
Silver	234	0.056

More Specific Heat Values

Substance	Specific Heat c	
	$J/kg \cdot °C$	$cal/g \cdot °C$
Other solids		
Brass	380	0.092
Glass	837	0.200
Ice ($-5°C$)	2 090	0.50
Marble	860	0.21
Wood	1 700	0.41
Liquids		
Alcohol (ethyl)	2 400	0.58
Mercury	140	0.033
Water ($15°C$)	4 186	1.00
Gas		
Steam ($100°C$)	2 010	0.48

Sign Conventions

- If the temperature increases:
  - Q and ΔT are positive
  - Energy transfers into the system
- If the temperature decreases:
  - Q and ΔT are negative
  - Energy transfers out of the system

Specific Heat Varies With Temperature
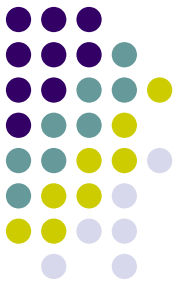
- Technically, the specific heat varies with temperature

- The corrected equation is $Q = m \int_{T_i}^{T_f} c \, dT$

- However, if the temperature intervals are not too large, the variation can be ignored and c can be treated as a constant

  - For example, for water there is only about a 1% variation between 0° and 100°C

  - These variations will be neglected unless otherwise stated

Specific Heat of Water

- Water has the highest specific heat of common materials

- This is in part responsible for many weather phenomena

  - Moderate temperatures near large bodies of water

  - Global wind systems

  - Land and sea breezes

Calorimetry

- One technique for measuring specific heat involves heating a material, adding it to a sample of water, and recording the final temperature

- This technique is known as **calorimetry**
  - A calorimeter is a device in which this energy transfer takes place

Calorimetry, cont

- The system of the sample and the water is isolated

- Conservation of energy requires that the amount of energy that leaves the sample equals the amount of energy that enters the water

  - Conservation of Energy gives a mathematical expression of this:

    $Q_{cold} = -Q_{hot}$

Calorimetry, final

- The negative sign in the equation is critical for consistency with the established sign convention

- Since each $Q = mc\Delta T$, c_{sample} can be found by:

$$c_s = \frac{m_w c_w \left(T_f - T_w\right)}{m_s \left(T_s - T_f\right)}$$

  - Technically, the mass of the container should be included, but if $m_w >> m_{container}$ it can be neglected

Calorimetry, Example

- An ingot of metal is heated and then dropped into a beaker of water. The equilibrium temperature is measured

$$c_s = \frac{m_w c_w \left(T_f - T_w\right)}{m_s \left(T_s - T_f\right)}$$

$$= \frac{(0.400\,\text{kg})(4186\,\text{J/kg} \cdot {}^{\circ}\text{C})(22.4\,{}^{\circ}\text{C} - 20.0\,{}^{\circ}\text{C})}{(0.0500\,\text{kg})(200.0\,{}^{\circ}\text{C} - 22.4\,{}^{\circ}\text{C})}$$

$$= 453 \text{ J/kg} \cdot {}^{\circ}\text{C}$$

Phase Changes

- A **phase change** is when a substance changes from one form to another
  - Two common phase changes are
    - Solid to liquid (melting)
    - Liquid to gas (boiling)
- During a phase change, there is no change in temperature of the substance
  - For example, in boiling the increase in internal energy is represented by the breaking of the bonds between molecules, giving the molecules of the gas a higher intermolecular potential energy

Latent Heat

- Different substances react differently to the energy added or removed during a phase change
  - Due to their different internal molecular arrangements
- The amount of energy also depends on the mass of the sample
- If an amount of energy Q is required to change the phase of a sample of mass m,

  $L \equiv Q / m$

Latent Heat, cont

- The quantity *L* is called the **latent heat** of the material
  - Latent means "hidden"
  - The value of *L* depends on the substance as well as the actual phase change
- The energy required to change the phase is $Q = \pm\ mL$

Latent Heat, final

- The *latent heat of fusion* is used when the phase change is from solid to liquid
- The *latent heat of vaporization* is used when the phase change is from liquid to gas
- The positive sign is used when the energy is transferred into the system
  - This will result in melting or boiling
- The negative sign is used when energy is transferred out of the system
 - This will result in freezing or condensation
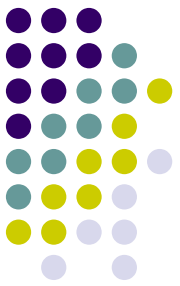
Sample Latent Heat Values

TABLE 20.2

Latent Heats of Fusion and Vaporization

| Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium	-269.65	5.23×10^3	-268.93	2.09×10^4
Nitrogen	-209.97	2.55×10^4	-195.81	2.01×10^5
Oxygen	-218.79	1.38×10^4	-182.97	2.13×10^5
Ethyl alcohol	-114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	1 750	8.70×10^5
Aluminum	660	3.97×10^5	2 450	1.14×10^7
Silver	960.80	8.82×10^4	2 193	2.33×10^6
Gold	1 063.00	6.44×10^4	2 660	1.58×10^6
Copper	1 083	1.34×10^5	1 187	5.06×10^6

Graph of Ice to Steam
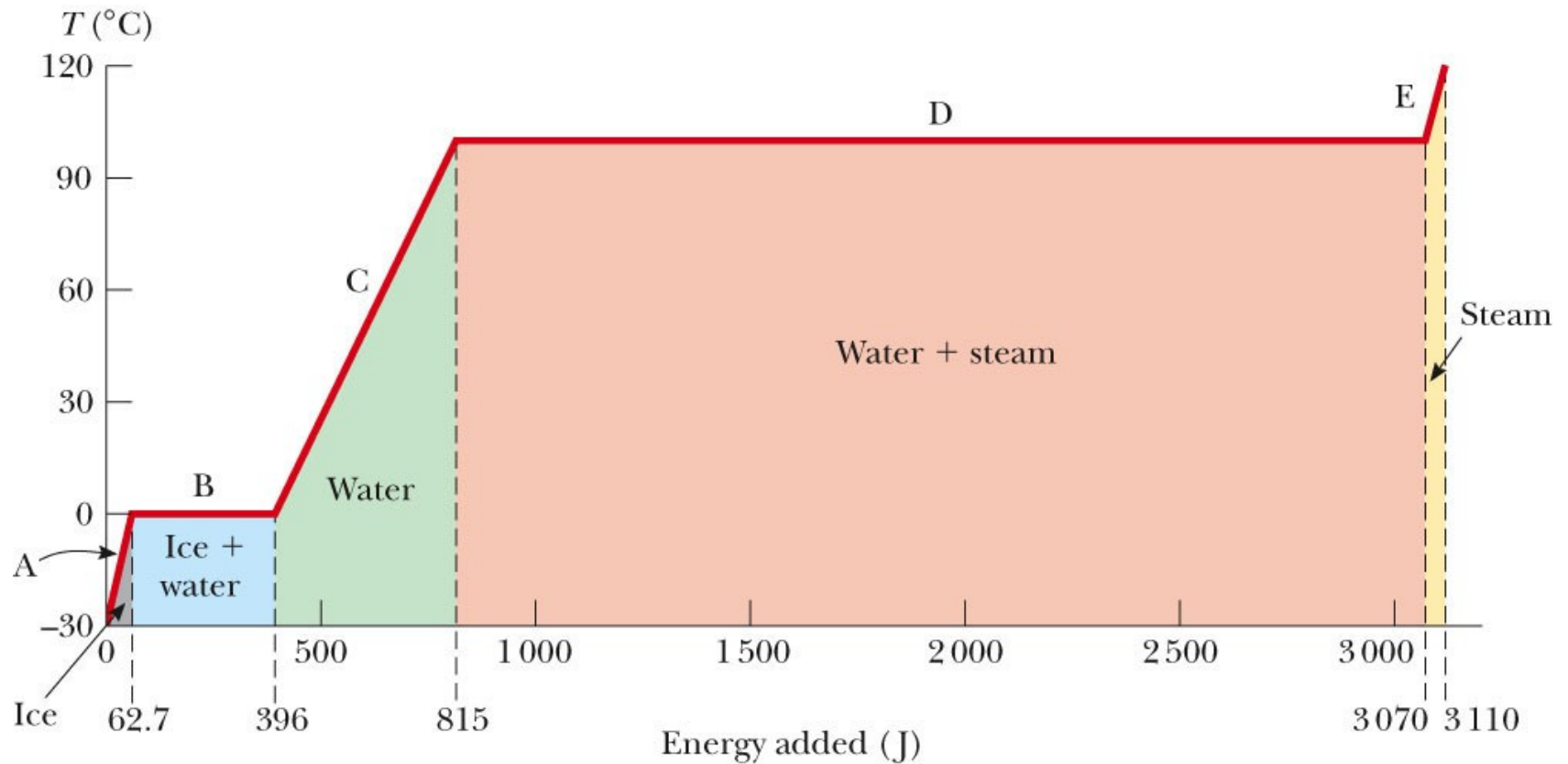
Warming Ice, Graph Part A

- Start with one gram of ice at –30.0ºC
- During phase A, the temperature of the ice changes from –30.0ºC to 0ºC
- Use $Q = m_i c_i \Delta T$
  - In this case, 62.7 J of energy are added
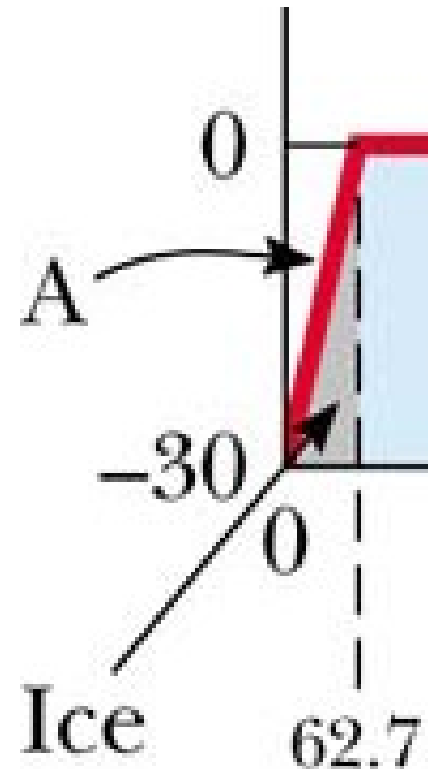
Melting Ice, Graph Part B

- Once at 0ºC, the phase change (melting) starts
- The temperature stays the same although energy is still being added
- Use $Q = m_i L_f$
  - The energy required is 333 J
  - On the graph, the values move from 62.7 J to 396 J


B

Ice + water
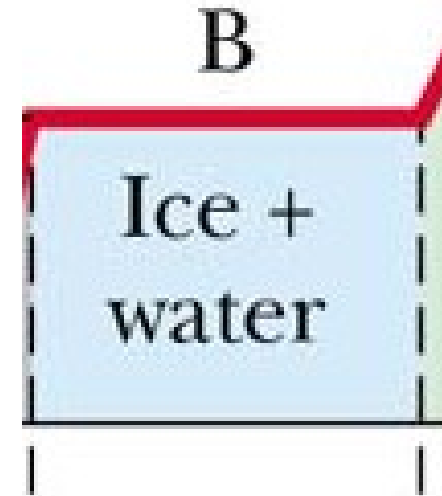
Warming Water, Graph Part C

- Between 0ºC and 100ºC, the material is liquid and no phase changes take place
- Energy added increases the temperature
- Use $Q = m_w c_w \Delta T$
  - 419 J are added
  - The total is now 815 J

C

Water

500

396   815
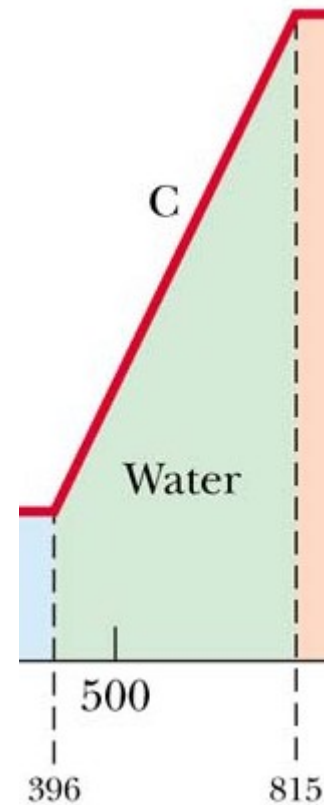
Boiling Water, Graph Part D

- At 100ºC, a phase change occurs (boiling)
- Temperature does not change
- Use $Q = m_w L_v$
  - This requires 2260 J
  - The total is now 3070 J
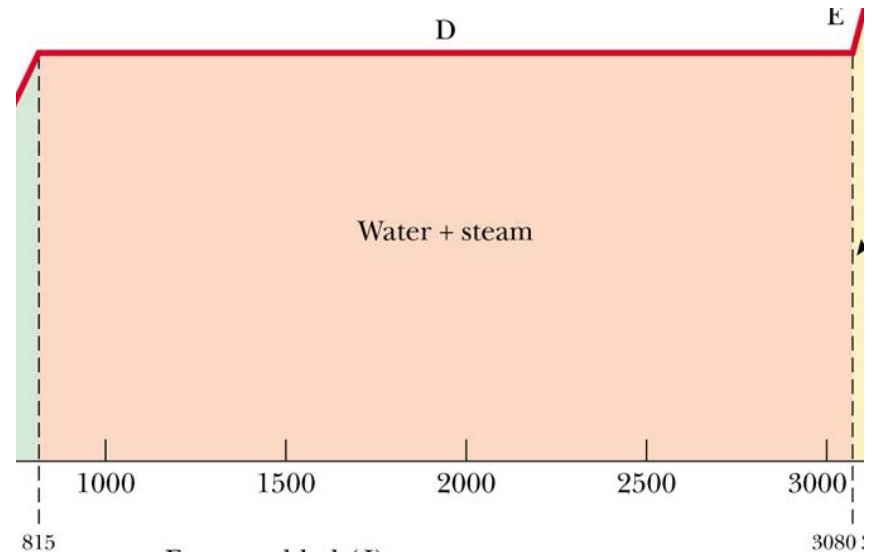
Heating Steam

- After all the water is converted to steam, the steam will heat up
- No phase change occurs
- The added energy goes to increasing the temperature
- Use $Q = m_s c_s \Delta T$
  - In this case, 40.2 J are needed
  - The temperature is going to 120° C
  - The total is now 3110 J

Supercooling

- If liquid water is held perfectly still in a very clean container, it is possible for the temperature to drop below 0° C without freezing
- This phenomena is called **supercooling**
- It arises because the water requires a disturbance of some sort for the molecules to move apart and start forming the open ice crystal structures
  - This structure makes the density of ice less than that of water
- If the supercooled water is disturbed, it immediately freezes and the energy released returns the temperature to 0° C

Superheating

- Water can rise to a temperature greater than 100° C without boiling
- This phenomena is called **superheating**
- The formation of a bubble of steam in the water requires nucleation site
  - This could be a scratch in the container or an impurity in the water
- When disturbed the superheated water can become explosive
  - The bubbles will immediately form and hot water is forced upward and out of the container

State Variables

- State variables describe the state of a system
- In the macroscopic approach to thermodynamics, variables are used to describe the state of the system
  - Pressure, temperature, volume, internal energy
  - These are examples of state variables
- The macroscopic state of an isolated system can be specified only if the system is in thermal equilibrium internally
 - For a gas in a container, this means every part of the gas must be at the same pressure and temperature

Transfer Variables

- Transfer variables are zero unless a process occurs in which energy is transferred across the boundary of a system

- Transfer variables are not associated with any given state of the system, only with changes in the state
  - Heat and work are transfer variables

Work in Thermodynamics

- Work can be done on a deformable system, such as a gas
- Consider a cylinder with a moveable piston
- A force is applied to slowly compress the gas
  - The compression is slow enough for all the system to remain essentially in thermal equilibrium
  - This is said to occur **quasi-statically**

(a)

(b)

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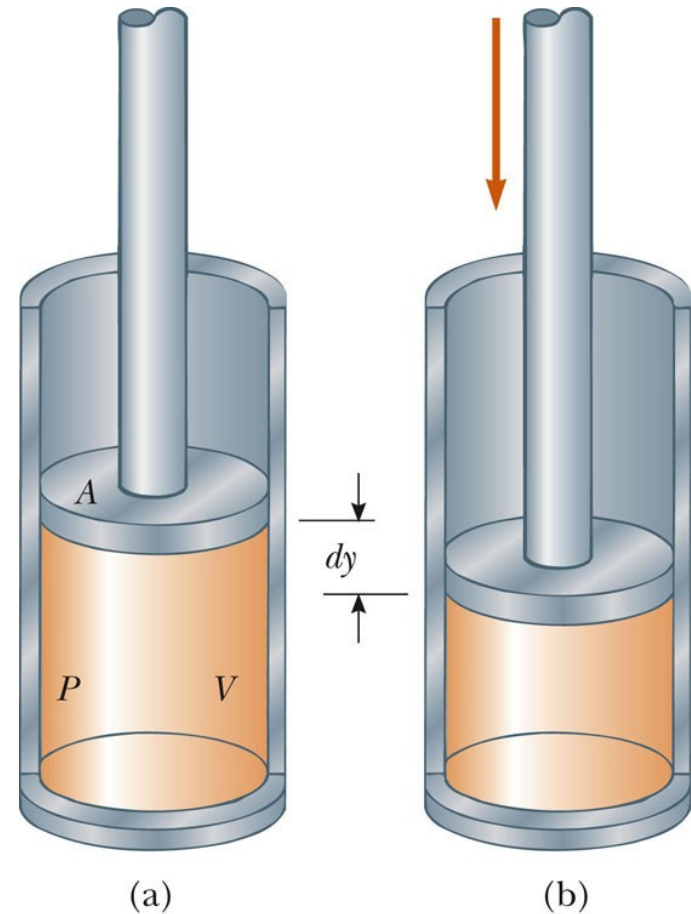
Work, 2

- The piston is pushed downward by a force through a displacement of:

$$dW = \vec{\Phi} \cdot d\vec{\rho} = -F\hat{\varphi} \cdot dy\hat{\varphi} = -Fdy = -PA\ dy$$

- $A \cdot dy$ is the change in volume of the gas, dV

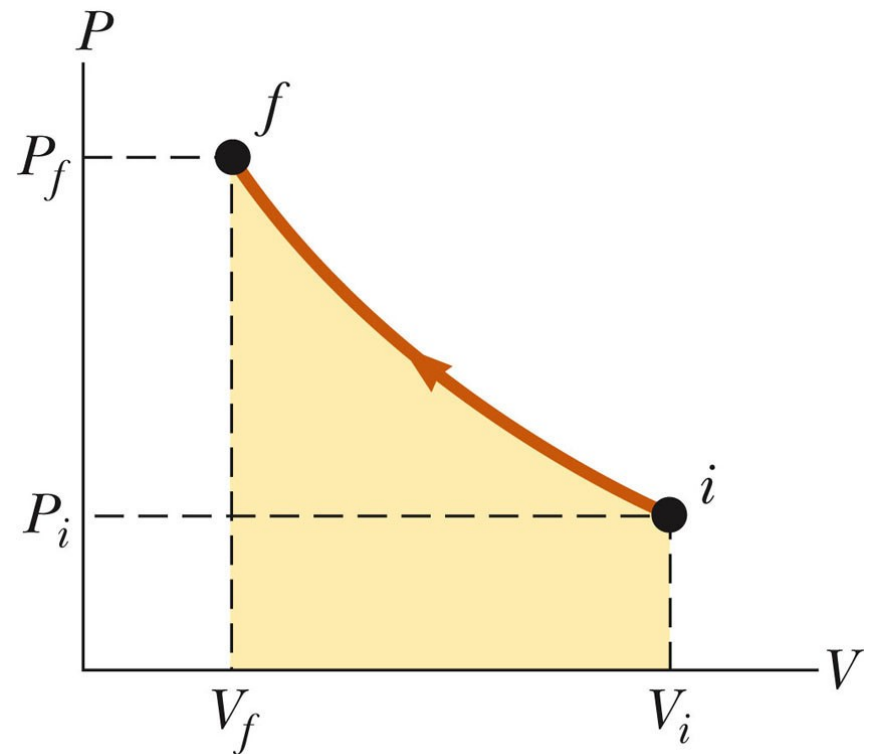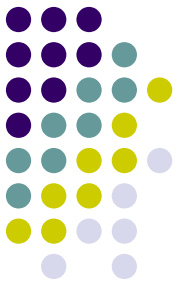- Therefore, the work done on the gas is

$dW = -P\ dV$

Work, 3

- Interpreting dW = - P dV
  - If the gas is compressed, dV is negative and the work done on the gas is positive
  - If the gas expands, dV is positive and the work done on the gas is negative
  - If the volume remains constant, the work done is zero
- The total work done is:

$$W = -\int_{V_i}^{V_f} P \, dV$$

PV Diagrams

- Used when the pressure and volume are known at each step of the process
- The state of the gas at each step can be plotted on a graph called a **PV diagram**
  - This allows us to visualize the process through which the gas is progressing
- The curve is called the *path*
- Use the active figure to compress the piston and observe the resulting path

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PV Diagrams, cont

- The work done on a gas in a quasi-static process that takes the gas from an initial state to a final state is the negative of the area under the curve on the PV diagram, evaluated between the initial and final states
  - This is true whether or not the pressure stays constant
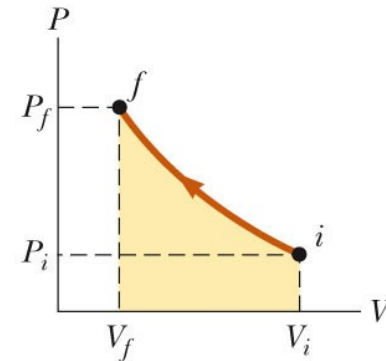 - The work done does depend on the path taken

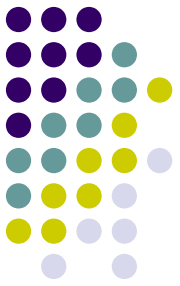# Work Done By Various Paths
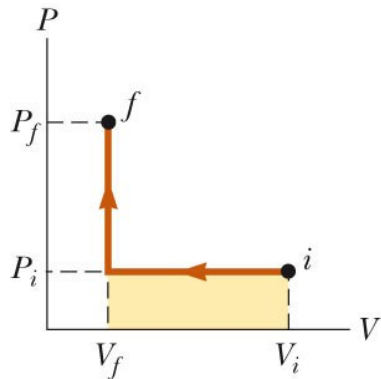
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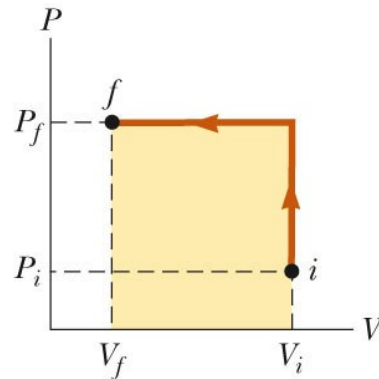
- Each of these processes has the same initial and final states
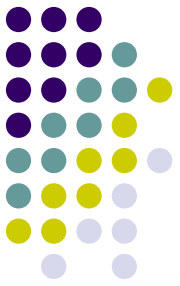- The work done differs in each process
- The work done depends on the path

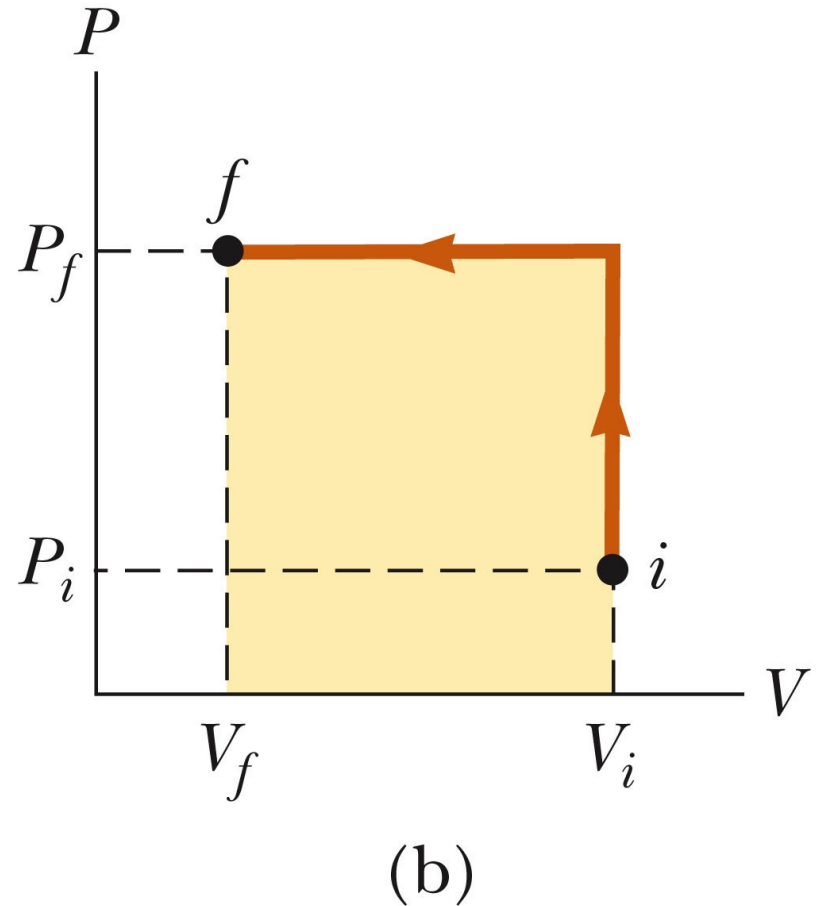# Work From a *PV* Diagram, Example 1

- The volume of the gas is first reduced from V_i to V_f at constant pressure P_i

- Next, the pressure increases from P_i to P_f by heating at constant volume V_f

- $W = -P_i(V_f - V_i)$

- Use the active figure to observe the piston and the movement of the point on the PV diagram

(a)
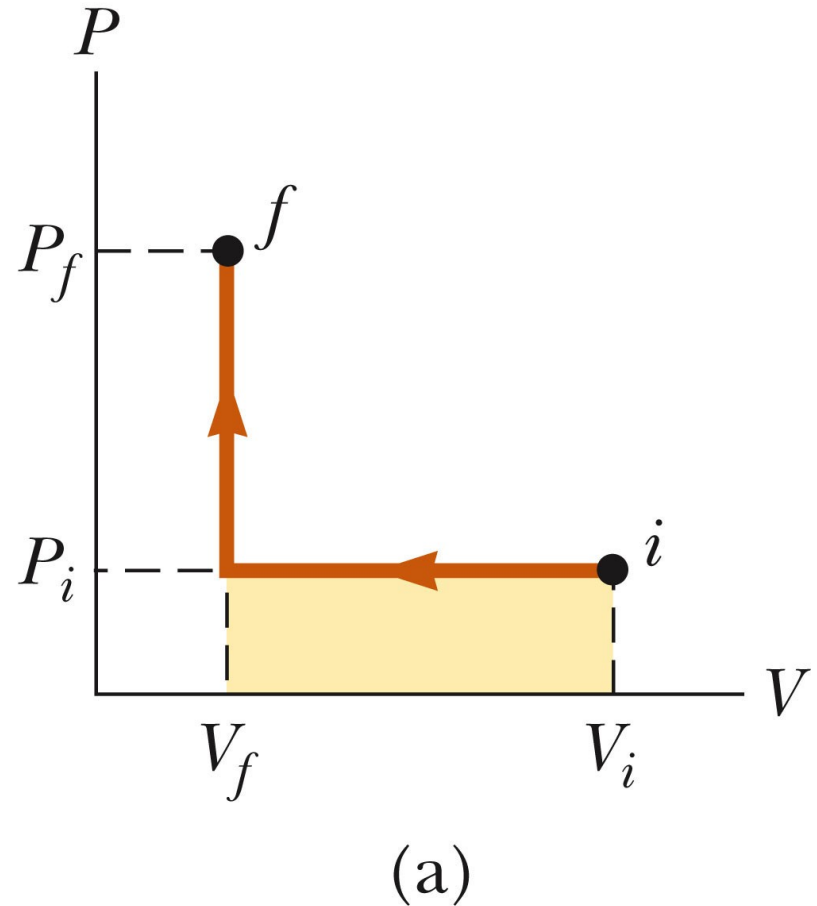
Work From a *PV* Diagram, Example 2

- The pressure of the gas is increased from P_i to P_f at a constant volume

- The volume is decreased from V_i to V_f

- $W = -P_f(V_f - V_i)$

- Use the active figure to observe the piston and the movement of the point on the PV diagram
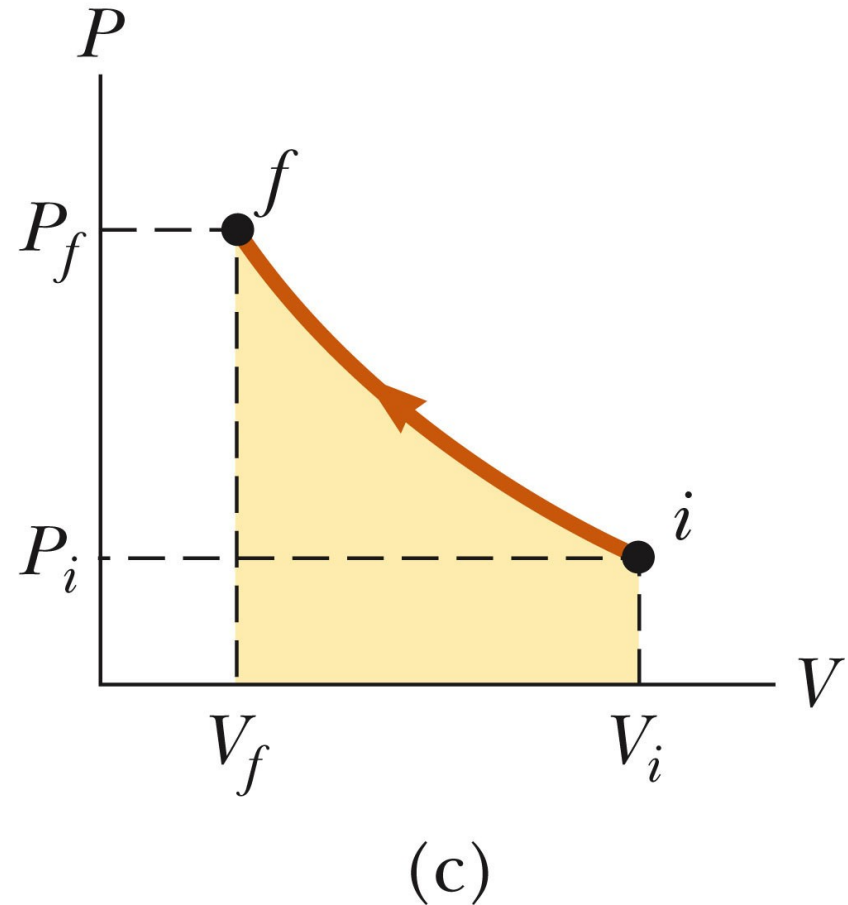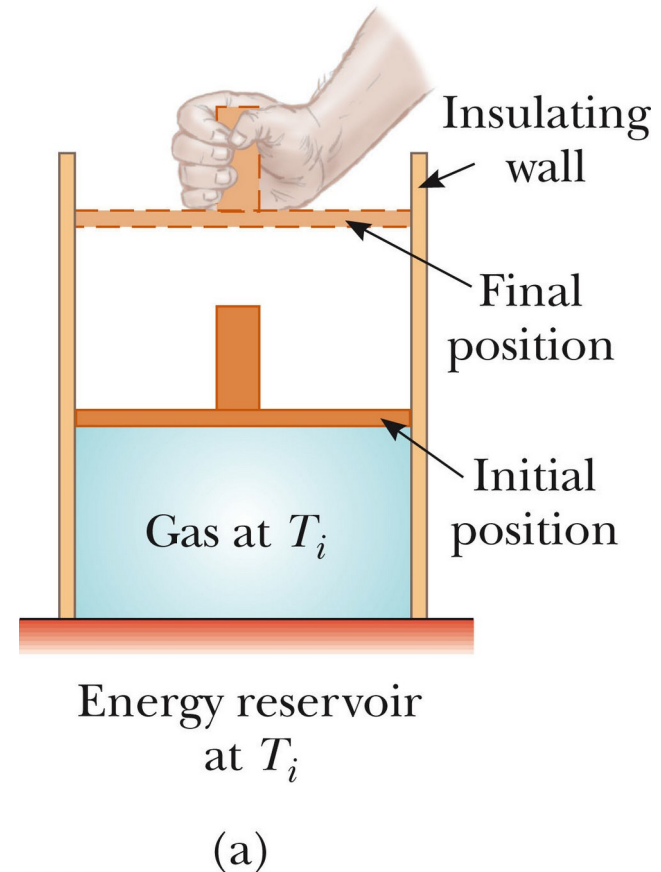

(b)

Work From a *PV* Diagram, Example 3

- The pressure and the volume continually change
- The work is some intermediate value between $-P_f(V_f - V_i)$ and $-P_i(V_f - V_i)$
- To evaluate the actual amount of work, the function $P(V)$ must be known
- Use the active figure to observe the piston and the movement of the point on the PV diagram

(c)

Heat Transfer, Example 1

- The energy transfer, Q, into or out of a system also depends on the process
- The **energy reservoir** is a source of energy that is considered to be so great that a finite transfer of energy does not change its temperature
- The piston is pushed upward, the gas is doing work on the piston

Insulating wall

Final position

Initial position

Gas at T_i

Energy reservoir at T_i

(a)

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Heat Transfer, Example 2

- This gas has the same initial volume, temperature and pressure as the previous example
- The final states are also identical
- No energy is transferred by heat through the insulating wall
- No work is done by the gas expanding into the vacuum

Insulating wall

Vacuum

Membrane

Gas at T_i

(b)

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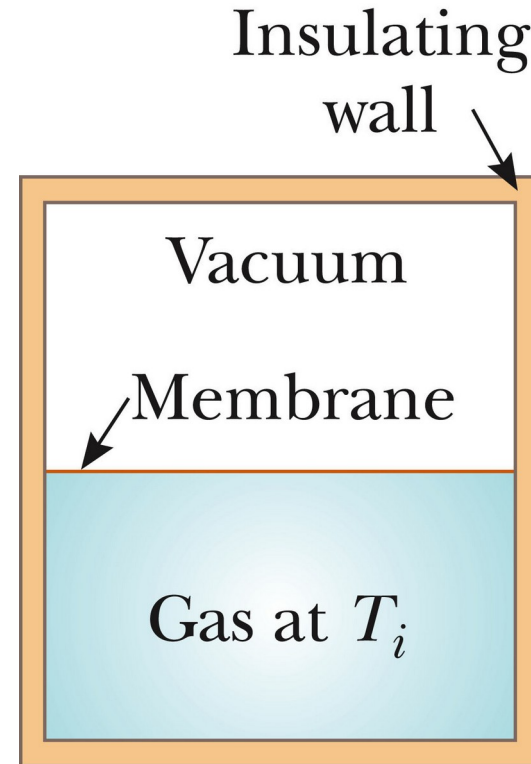
Energy Transfer, Summary

- Energy transfers by heat, like the work done, depend on the initial, final, and intermediate states of the system

- Both work and heat depend on the path taken

- Neither can be determined solely by the end points of a thermodynamic process

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

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

  - All quantities must have the same units of measure of energy

The First Law of Thermodynamics, cont

- One consequence of the first law is that there must exist some quantity known as internal energy which is 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 internal energy and the energy transfers are by heat and work

Isolated Systems

- 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 $\Delta E_{int} = 0$
- The internal energy of an isolated system remains constant

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 variable

- 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

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
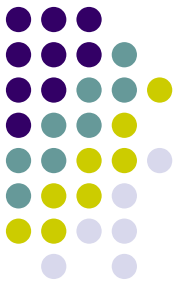

W

ΔE_{int}

Q
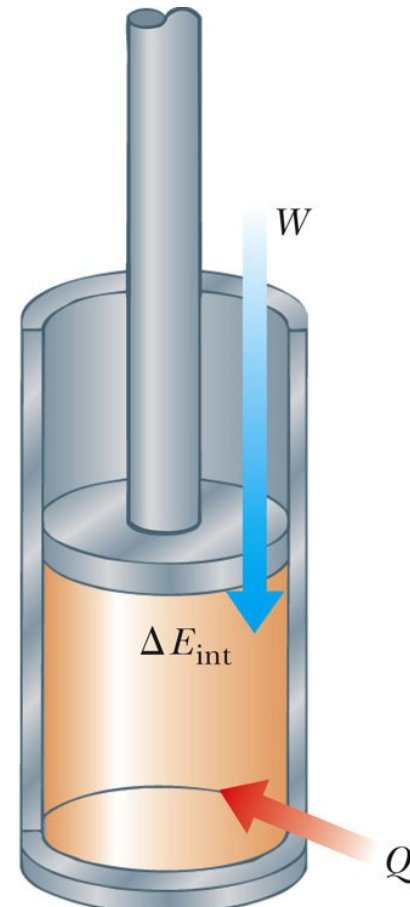
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Adiabatic Process, cont

- Since $Q = 0$, $\Delta E_{int} = W$

- If the gas is compressed adiabatically, W is positive so ΔE_{int} is positive and the temperature of the gas increases

- If the gas expands adiabatically, the temperature of the gas decreases

Adiabatic Processes, Examples

- Some important examples of 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

Adiabatic Free Expansion

- This is an example of adiabatic free expansion
- The process is adiabatic because it takes place in an insulated container
- 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

Insulating wall

Vacuum

Membrane

Gas at T_i
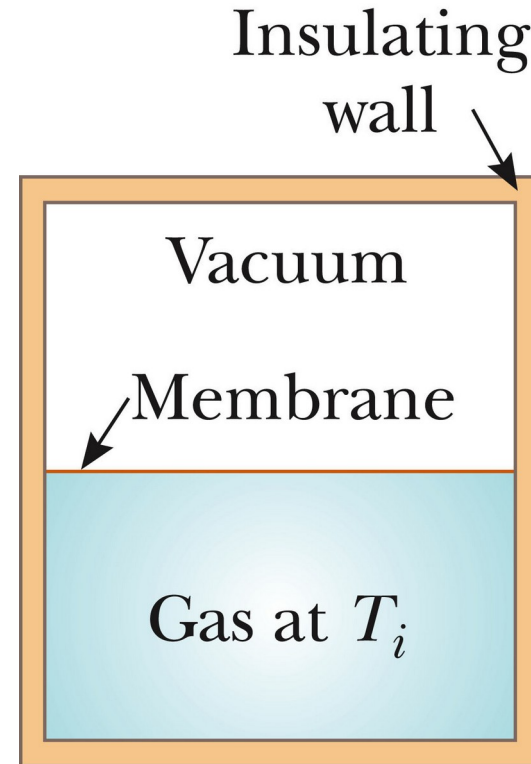
(b)

Isobaric Processes

- 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

Isovolumetric Processes

- An isovolumetric process is one in which there is no change in the volume

- Since the volume does not change, W = 0

- From the first law, $\Delta E_{int} = Q$

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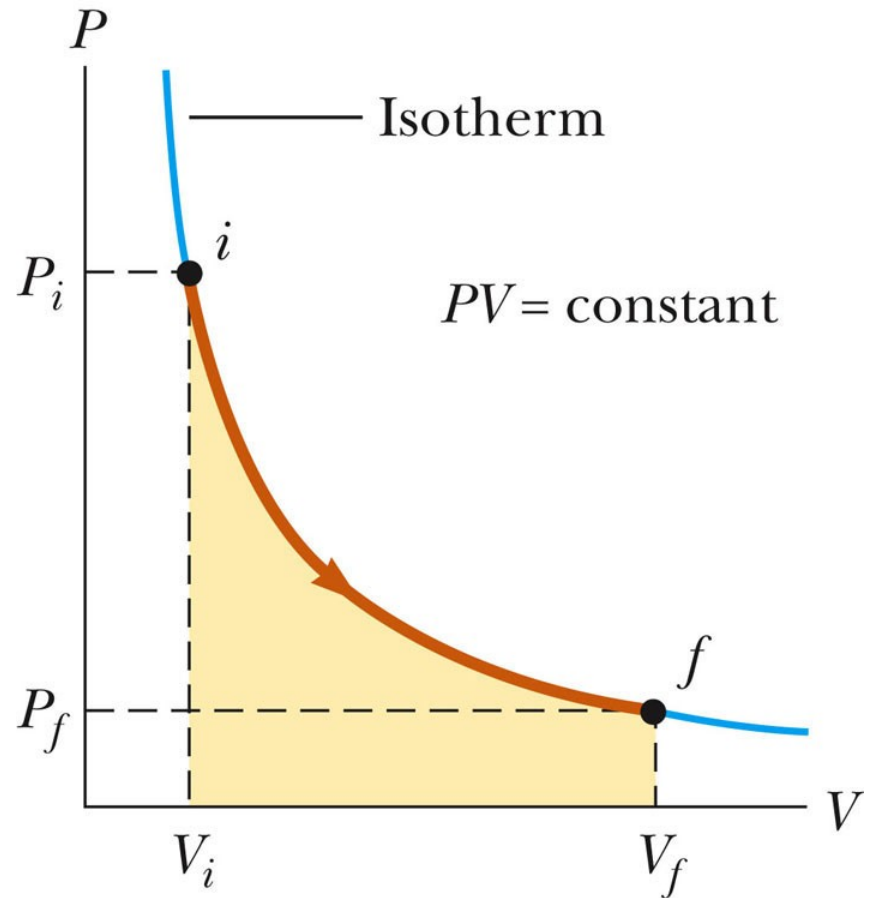
Isothermal Process

- An isothermal process is one that occurs at a constant temperature

- Since there is no change in temperature, ΔE_{int} = 0

- Therefore, Q = - W

- Any energy that enters the system by heat must leave the system by work

Isothermal Process, cont

- At right is a *PV* diagram of an isothermal expansion
- The curve is a hyperbola
- The curve is called an **isotherm**

P

Isotherm

P_i · i

$PV = $ constant

P_f · f

V_i V_f V

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Isothermal Expansion, Details

- The curve of the PV diagram indicates PV = constant

  - The equation of a hyperbola

- Because it is an ideal gas and the process is quasi-static, PV = nRT and

$$W = -\int_{V_i}^{V_f} P\,dV = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

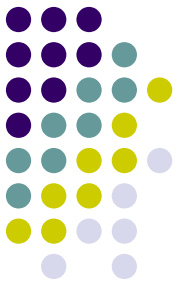$$W = nRT \ln\left(\frac{V_i}{V_f}\right)$$

Isothermal Expansion, final

- 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

Special Processes, Summary

- Adiabatic
  - No heat exchanged
  - $Q = 0$ and $\Delta E_{int} = W$
- Isobaric
  - Constant pressure
  - $W = P(V_f - V_i)$ and $\Delta E_{int} = Q + W$
- Isothermal
  - Constant temperature
  - $\Delta E_{int} = 0$ and $Q = -W$

Mechanisms of Energy Transfer by Heat

- We want to know the rate at which energy is transferred

- There are various mechanisms responsible for the transfer:
  - Conduction
  - Convection
  - Radiation

Conduction

- The transfer can be viewed on an atomic scale
  - It is an exchange of kinetic energy between microscopic particles by collisions
    - 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

Conduction, cont.

- 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 from one region to another
- Poor conductors include asbestos, paper, and gases
- Conduction can occur only if there is a difference in temperature between two parts of the conducting medium
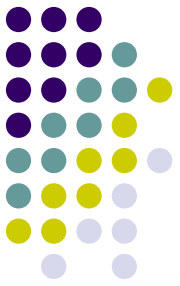
Conduction, equation

- The slab at right allows energy to transfer from the region of higher temperature to the region of lower temperature

- The rate of transfer is given by:

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

T_h

A

Energy transfer for $T_h > T_c$

T_c

Δx
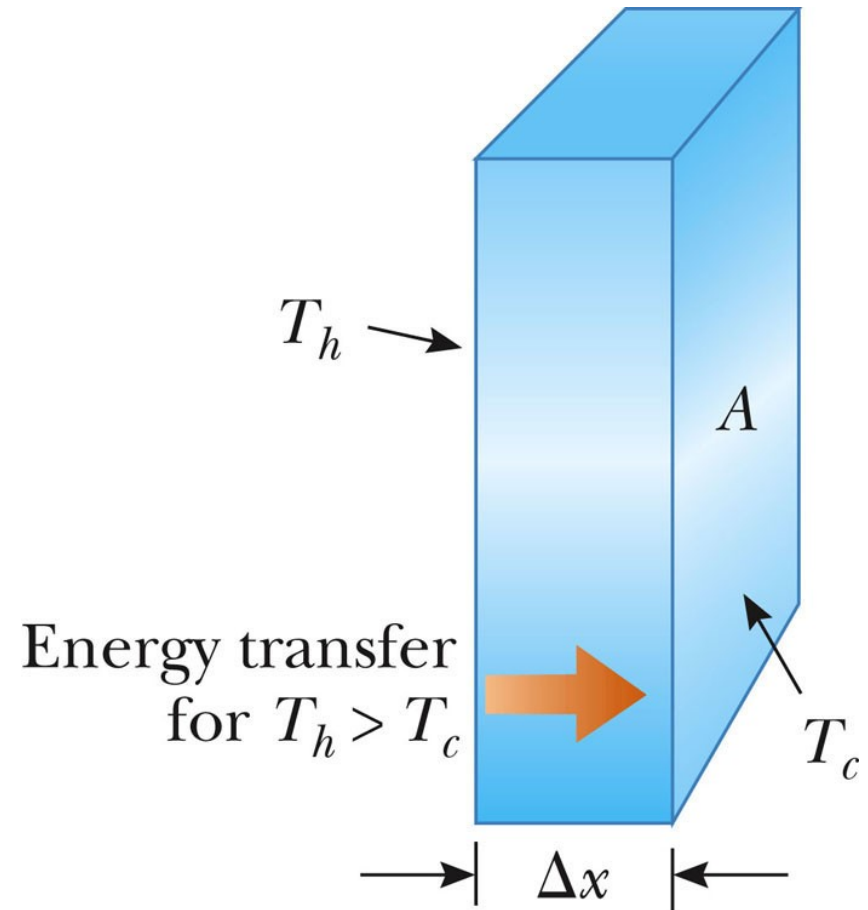
Conduction, equation explanation

- 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

Temperature Gradient

- The quantity |*dT / dx*| is called the **temperature gradient** of the material
  - It measures the rate at which temperature varies with position
- For a rod, the temperature gradient can be expressed as:

$$\left| \frac{dT}{dx} \right| = \frac{T_h - T_c}{L}$$
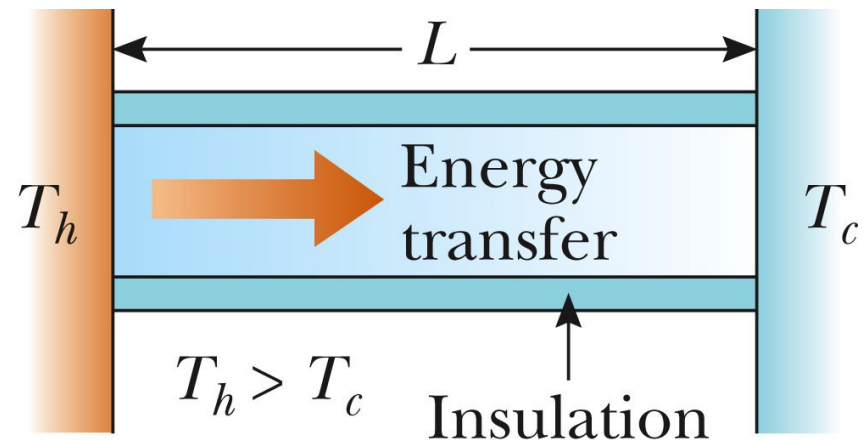
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Rate of Energy Transfer in a Rod

- Using the temperature gradient for the rod, the rate of energy transfer becomes:

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

Compound Slab

- 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:

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

Some Thermal Conductivities

TABLE 20.3

Thermal Conductivities

Substance	Thermal Conductivity (W/m · °C)
Metals (at 25°C)	
Aluminum	238
Copper	397
Gold	314
Iron	79.5
Lead	34.7
Silver	427

More Thermal Conductivities

Nonmetals (approximate values)

Asbestos	0.08
Concrete	0.8
Diamond	2 300
Glass	0.8
Ice	2
Rubber	0.2
Water	0.6
Wood	0.08

Gases (at 20°C)

Air	0.023 4
Helium	0.138
Hydrogen	0.172
Nitrogen	0.023 4
Oxygen	0.023 8

Home Insulation

- Substances are rated by their R values
  - R = L / k and the rate becomes

$$\wp = \frac{A(T_h - T_c)}{\sum_i R_i}$$

  - For multiple layers, the total R value is the sum of the R values of each layer
- Wind increases the energy loss by conduction in a home

Convection

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

Convection example

- Air directly above the radiator is warmed and expands
- The density of the air decreases, and it rises
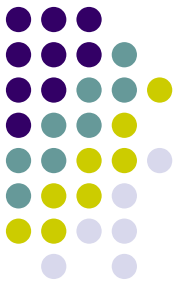- A continuous air current is established
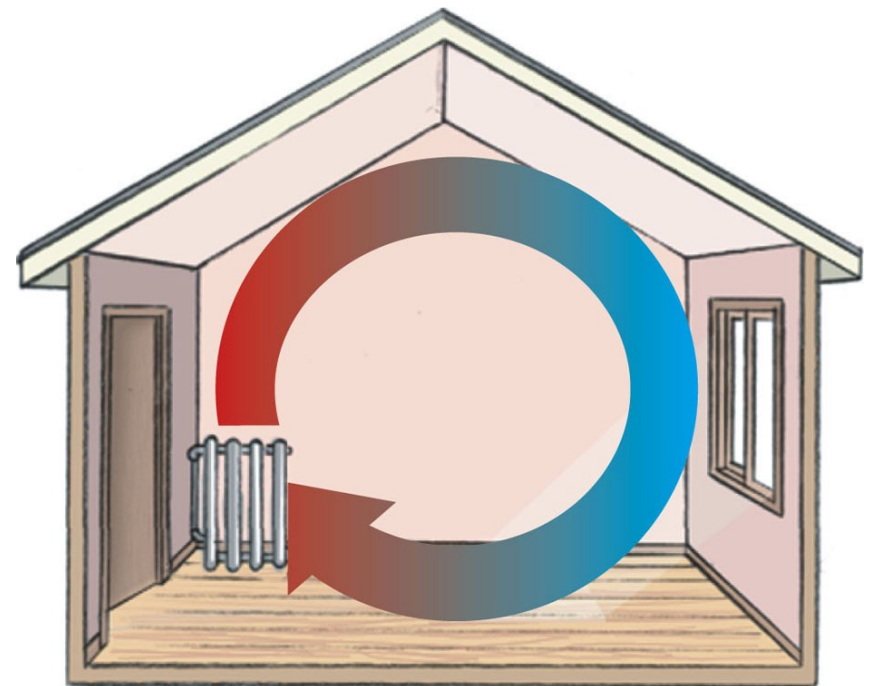
Radiation

- 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**

Stefan's Law

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

Energy Absorption and Emission by Radiation

- With its surroundings, the rate at which the object at temperature T with surroundings at T_o radiates is

  - $P_{net} = \sigma Ae (T^4 - T_o^4)$

  - When an object is in equilibrium with its surroundings, it radiates and absorbs at the same rate

    - Its temperature will not change

Ideal Absorbers

- 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

Ideal Reflector

- 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 losses by conduction, convection, and radiation
  - Invented by Sir James Dewar (1842 – 1923)
- 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

Dewar Flask, Details

- The space between the walls is a vacuum to minimize energy transfer by conduction and convection

- The silvered surface minimizes energy transfers by radiation

  - Silver is a good reflector

- The size of the neck is reduced to further minimize energy losses

Vacuum

Silvered surfaces

Hot or cold liquid

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