Chapter 12

The Laws of Thermodynamics

First Law of Thermodynamics

- The First Law of Thermodynamics tells us that the internal energy of a system can be increased by
  - Adding energy to the system
  - Doing work on the system
- There are many processes through which these could be accomplished
  - As long as energy is conserved

Second Law of Thermodynamics

- Second Law: If two systems are in thermal contact, net thermal energy transfers spontaneously by heat from the hotter system to the colder system
  - The heat transfer occurs without work being done
- Heat engines are an important application

Second Law of Thermodynamics

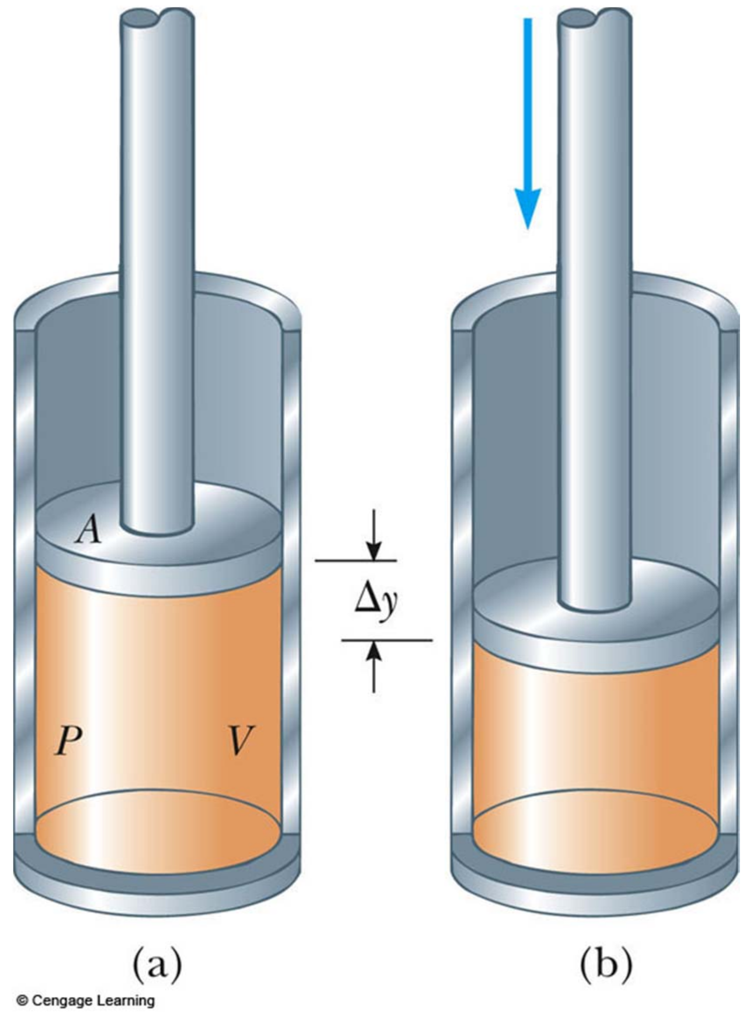
- Constrains the First Law
- Establishes which processes actually occur
- Heat engines are an important application

Work in Thermodynamic Processes – Assumptions

- Dealing with a gas
- Assumed to be in thermodynamic equilibrium
  - Every part of the gas is at the same temperature
  - Every part of the gas is at the same pressure
- Ideal gas law applies

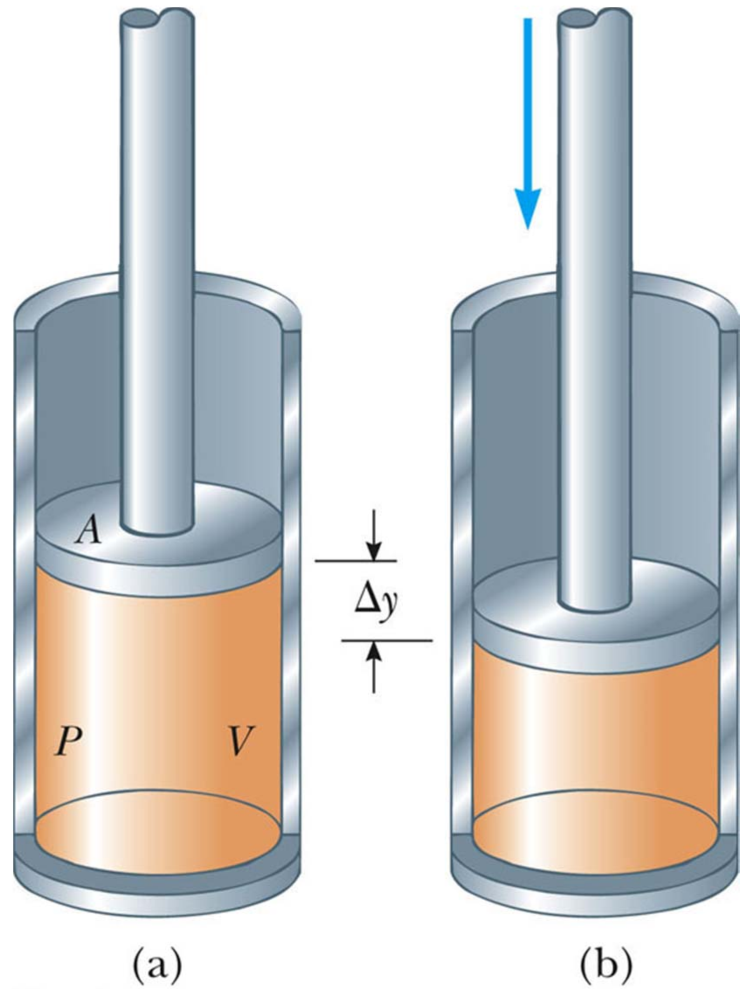
Work in a Gas Cylinder

- The gas is contained in a cylinder with a moveable piston
- The gas occupies a volume V and exerts pressure P on the walls of the cylinder and on the piston



Work in a Gas Cylinder, cont.

- A force is applied to slowly compress the gas
  - The compression is slow enough for all the system to remain essentially in thermal equilibrium
- $W = - P \Delta V$
  - This is the work done *on* the gas where P is the pressure throughout the gas



More about Work on a Gas Cylinder

- When the gas is compressed
  - ΔV is negative
  - The work done on the gas is positive
- When the gas is allowed to expand
  - ΔV is positive
  - The work done on the gas is negative
- When the volume remains constant
  - No work is done on the gas

Example 1

The gas in the cylinder is at a pressure equal to 1.01 $\times 10^5$ Pa and the piston has an area of 0.1 m^2. As energy is slowly added to the gas by heat, the piston is pushed up a distance of 4 cm. Calculate the work done by expanding gas on the surroundings assuming the pressure remains constant.

Example 2

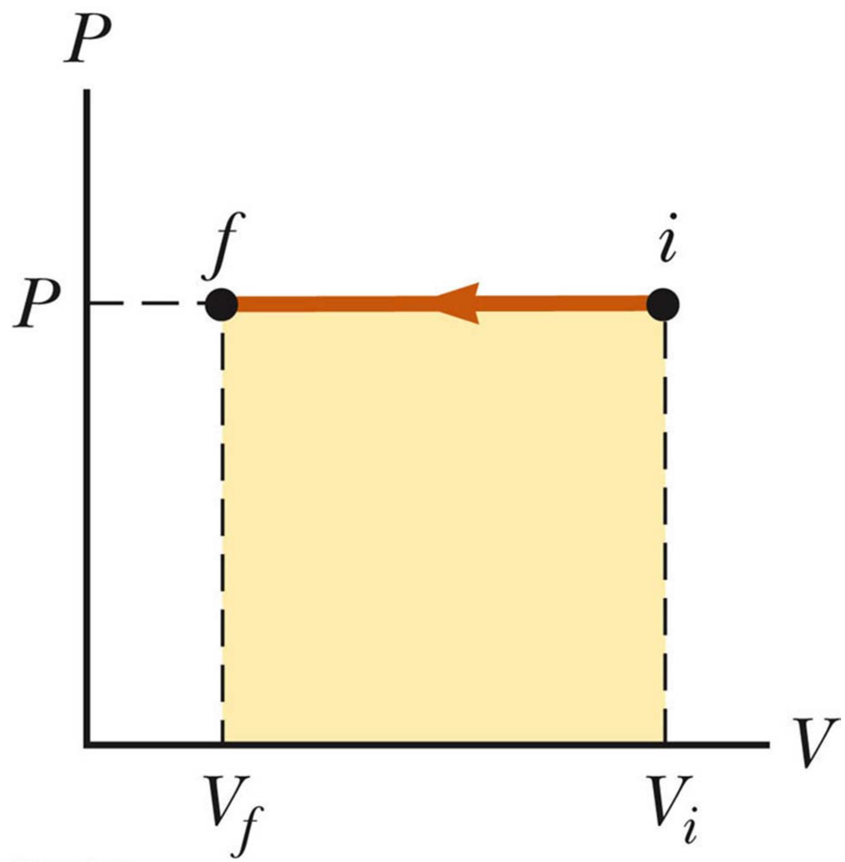
An ideal gas is compressed at constant pressure to one-third its initial volume. If the pressure of the gas is 150 kPa and 1760 J of work is done on it, find the initial volume of the gas.

Notes about the Work Equation

- The pressure remains constant during the expansion or compression
  - This is called an *isobaric* process
- The previous work equation can be used only for an isobaric process

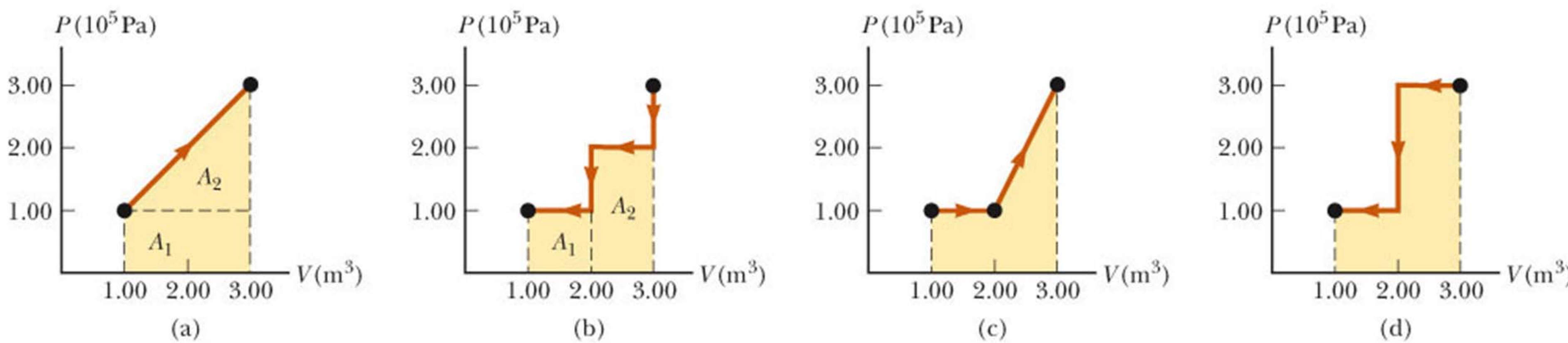
PV Diagrams

- Used when the pressure and volume are known at each step of the process
- The work done on a gas that takes it from some initial state to some final state is equal in magnitude to the area under the curve on the PV diagram
  - This is true whether or not the pressure stays constant



PV Diagrams, cont.

- The curve on the diagram is called the *path* taken between the initial and final states
- The work done depends on the particular path
  - Same initial and final states, but different amounts of work are done



First Law of Thermodynamics

- Energy conservation law
- Relates changes in internal energy to energy transfers due to heat and work
- Applicable to all types of processes
- Provides a connection between microscopic and macroscopic worlds

First Law, cont.

- Energy transfers occur due to
  - By doing work
    - Requires a macroscopic displacement of an object through the application of a force
  - By heat
    - Occurs through the random molecular collisions
- Both result in a change in the internal energy, ΔU, of the system

First Law, Equation

- If a system undergoes a change from an initial state to a final state, then $\Delta U = U_f - U_i = Q + W$
  - Q is the energy transferred to the system by heat
  - W is the work done on the system
  - ΔU is the change in internal energy

First Law – Signs

- Signs of the terms in the equation
  - Q
    - Positive if energy is transferred *to* the system by heat
    - Negative if energy is transferred *out of* the system by heat
  - W
    - Positive if work is done *on* the system
    - Negative if work is done *by* the system
  - ΔU
    - Positive if the temperature increases
    - Negative if the temperature decreases

Results of ΔU

- Changes in the internal energy result in changes in the measurable macroscopic variables of the system
  - These include
    - Pressure
    - Temperature
    - Volume

Notes About Work

- Positive work increases the internal energy of the system
- Negative work decreases the internal energy of the system
- This is consistent with the definition of mechanical work

Example 3

An ideal gas aborbs 5000 J of energy while doing 2000 J of work on the environment during a constant pressure process. (a) Calculate the change in the internal energy of the gas. (b) If the internal energy drops by 4500 J and 7500 J is expelled from the system, find the change in volume , assuming a constant pressure of 1.01×10^5 Pa

Molar Specific Heat

- The molar specific heat at constant volume for a monatomic ideal gas
  - $C_v = 3/2\ R$
- The change in internal energy can be expressed as $\Delta U = n\ C_v\ \Delta T$
  - For an ideal gas, this expression is always valid, even if not at a constant volume

Molar Specific Heat, cont

- A gas with a large molar specific heat requires more energy for a given temperature change
- The value depends on the structure of the gas molecule
- The value also depends on the ways the molecule can store energy

Degrees of Freedom

- Each way a gas can store energy is called a *degree of freedom*
- Each degree of freedom contributes ½ R to the molar specific heat
- See table 12.1 for some C_v values

TABLE 12.1

Molar Specific Heats of Various Gases

Gas	Molar Specific Heat (J/mol·K)[a]			
	C_p	C_v	$C_p - C_v$	$\gamma = C_p/C_v$
Monatomic Gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic Gases				
H_2	28.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic Gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31

[a] All values except that for water were obtained at 300 K.

Types of Thermal Processes

- *Isobaric*
  - Pressure stays constant
  - Horizontal line on the PV diagram
- *Isovolumetric*
  - Volume stays constant
  - Vertical line on the PV diagram
- *Isothermal*
  - Temperature stays the same
- *Adiabatic*
  - No heat is exchanged with the surroundings

Isobaric Processes

- The work done by an expanding gas in an isobaric process is at the expense of the internal energy of the gas
- $Q = 5/2\ n\ R\ \Delta T = n\ C_P\ \Delta T$
  - C_p is the molar heat capacity at constant pressure
  - $C_P = C_v + T$

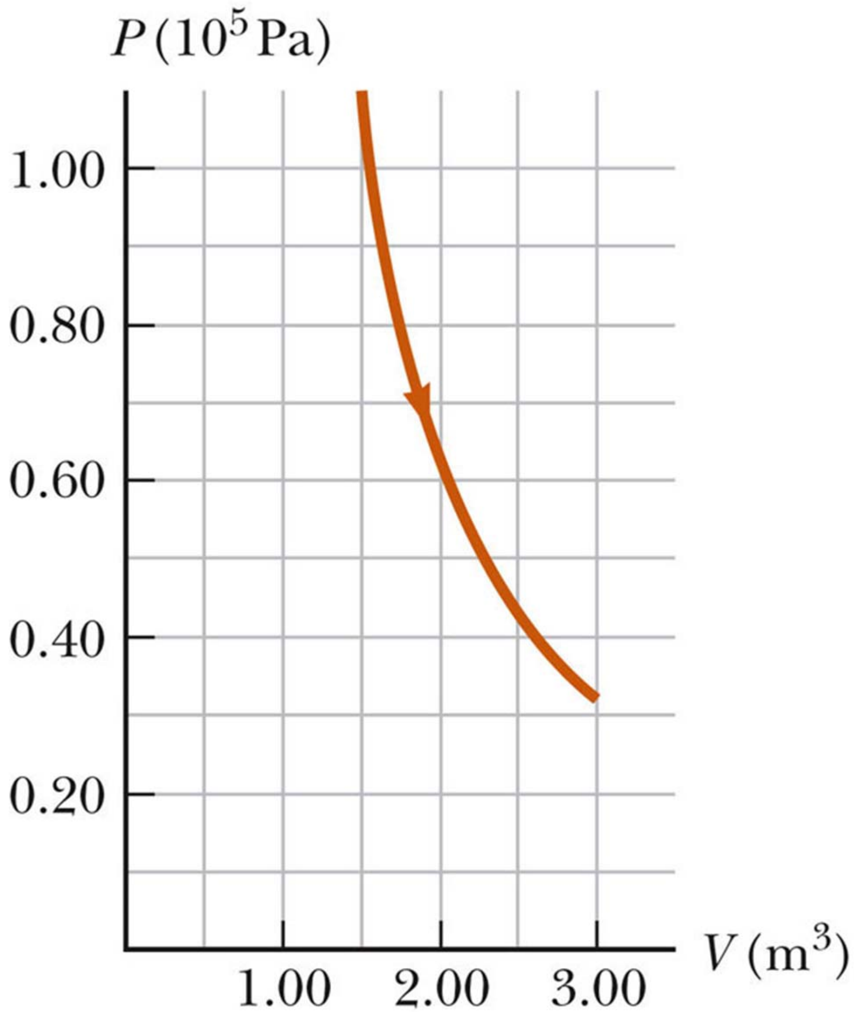
Adiabatic Processes

- For an adiabatic process, Q = 0
- First Law becomes $\Delta U = W$
- For an ideal gas undergoing an adiabatic process

$$PV^{\gamma} = constant \quad where \quad \gamma = \frac{C_P}{C_v}$$

  - γ is called the *adiabatic index* of the gas

Adiabatic Expansion, Diagram



Isovolumetric Process

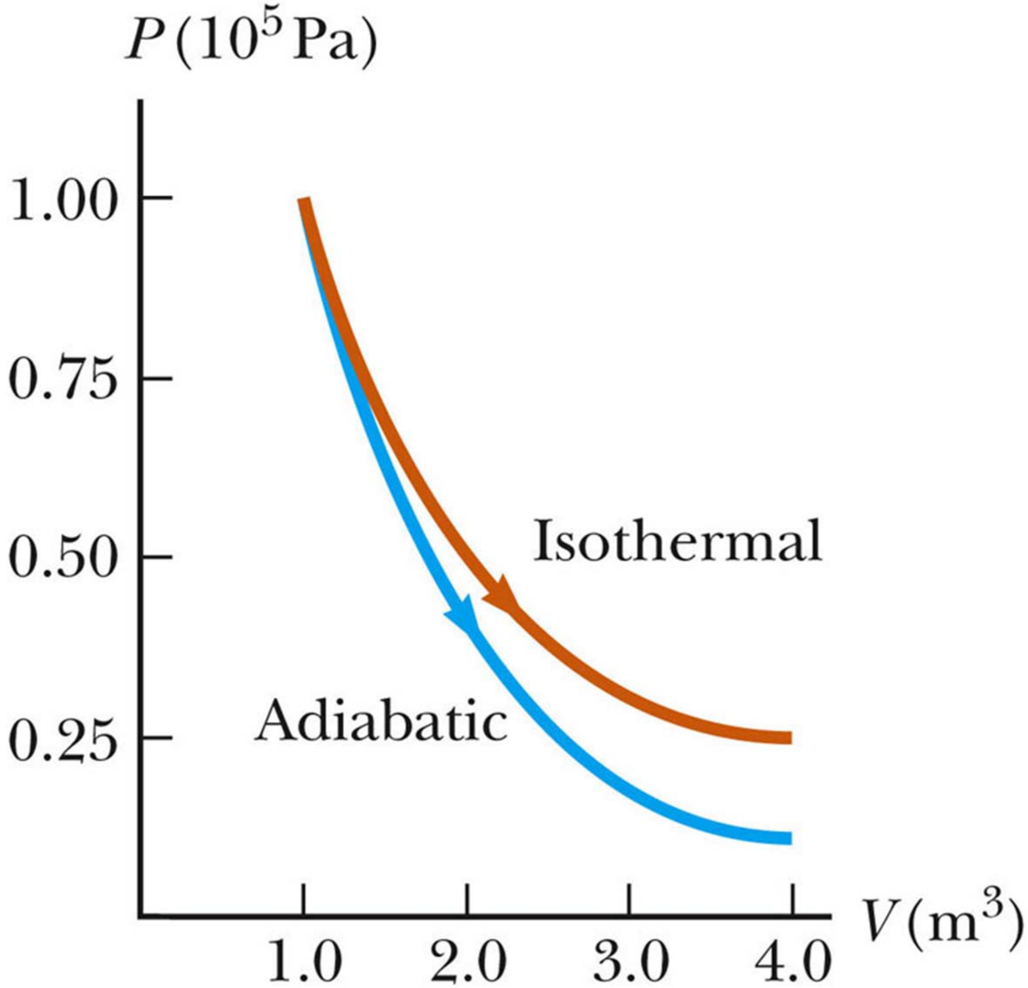
- Also called *isochoric* process
- Constant volume
  - Vertical line on PV diagram
- $W = 0$ (since $\Delta V = 0$)
- First Law becomes $\Delta U = Q$
  - The change in internal energy equals the energy transferred to the system by heat
- $Q = n C_v \Delta T$

Isothermal Process

- The temperature doesn't change
  - In an ideal gas, since Δ T = 0, the ΔU = 0
- First Law becomes W = - Q and

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

Isothermal Process, Diagram



General Case

- Can still use the First Law to get information about the processes
- Work can be computed from the PV diagram
- If the temperatures at the endpoints can be found, ΔU can be found

Cyclic Processes

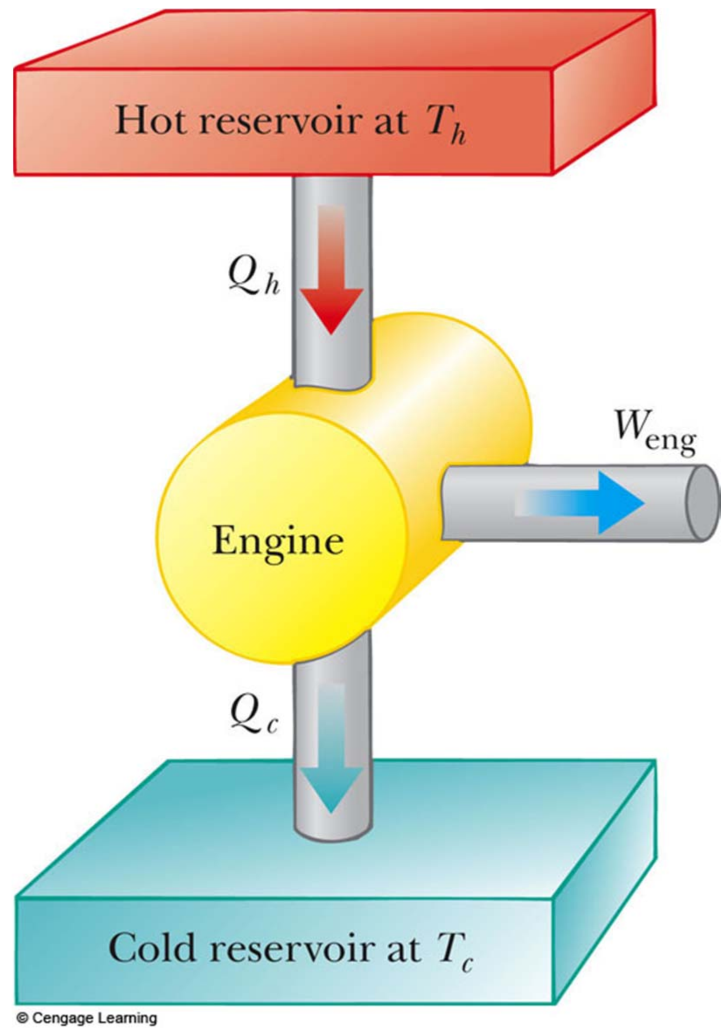
- A cyclic process is one in which the process originates and ends at the same state
  - $U_f = U_i$ and $Q = -W$
- The net work done per cycle by the gas is equal to the area enclosed by the path representing the process on a PV diagram

Heat Engine

- A heat engine takes in energy by heat and partially converts it to other forms
- In general, a heat engine carries some working substance through a cyclic process

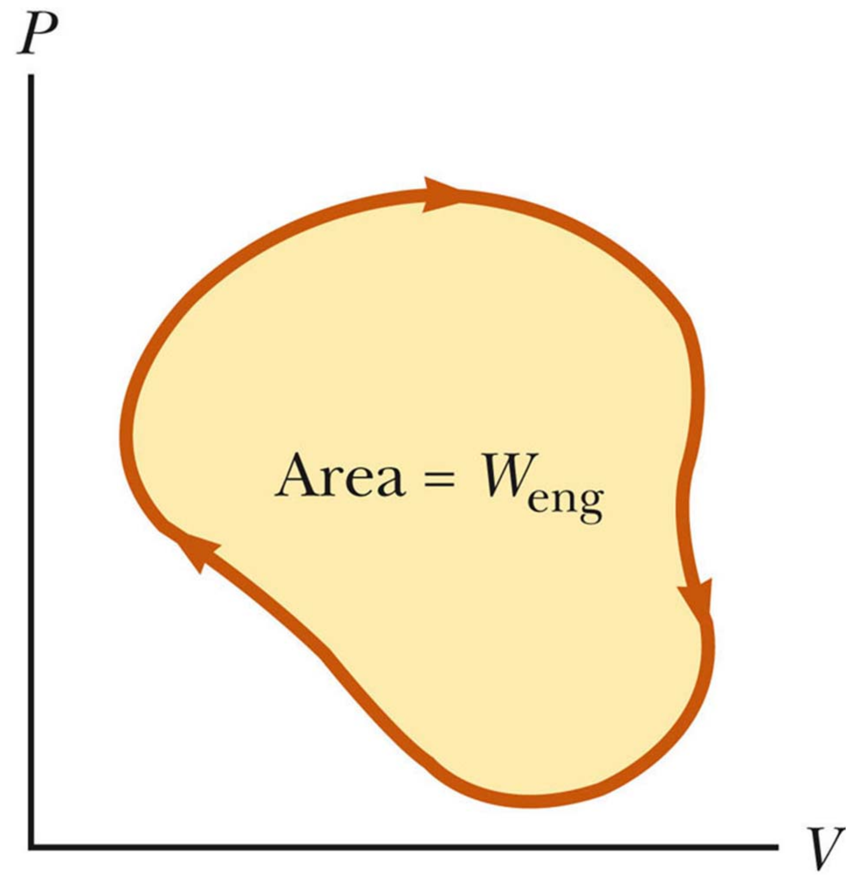
Heat Engine, cont.

- Energy is transferred from a source at a high temperature (Q_h)
- Work is done by the engine (W_{eng})
- Energy is expelled to a source at a lower temperature (Q_c)



Heat Engine, cont.

- Since it is a cyclical process, $\Delta U = 0$
  - Its initial and final internal energies are the same
- Therefore, $Q_{net} = W_{eng}$
- The work done by the engine equals the net energy absorbed by the engine
- The work is equal to the area enclosed by the curve of the PV diagram



Thermal Efficiency of a Heat Engine

- Thermal efficiency is defined as the ratio of the work done by the engine to the energy absorbed at the higher temperature

$$e \equiv \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

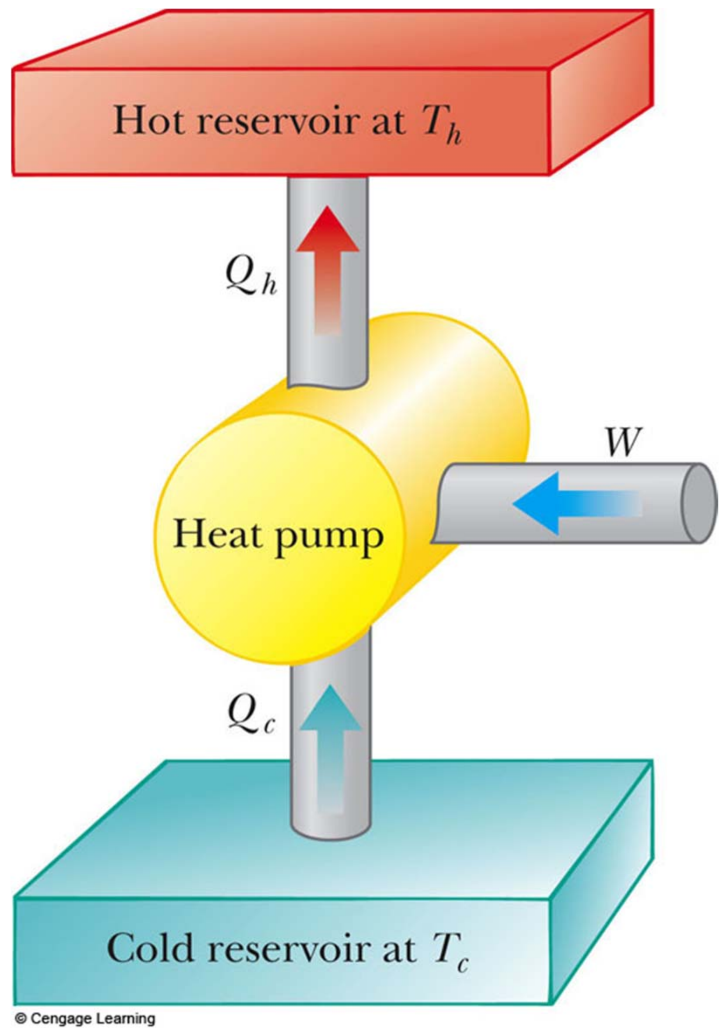
- e = 1 (100% efficiency) only if $Q_c = 0$
  - No energy expelled to cold reservoir

Heat Pumps and Refrigerators

- Heat engines can run in reverse
  - Energy is injected
  - Energy is extracted from the cold reservoir
  - Energy is transferred to the hot reservoir
- This process means the heat engine is running as a heat pump
  - A refrigerator is a common type of heat pump
  - An air conditioner is another example of a heat pump

Heat Pump, cont

- The work is what you pay for
- The Q_c is the desired benefit
- The coefficient of performance (COP) measures the performance of the heat pump running in cooling mode



Heat Pump, COP

- In cooling mode, $COP = \frac{|Q_c|}{W}$
- The higher the number, the better
- A good refrigerator or air conditioner typically has a COP of 5 or 6

Heat Pump, COP

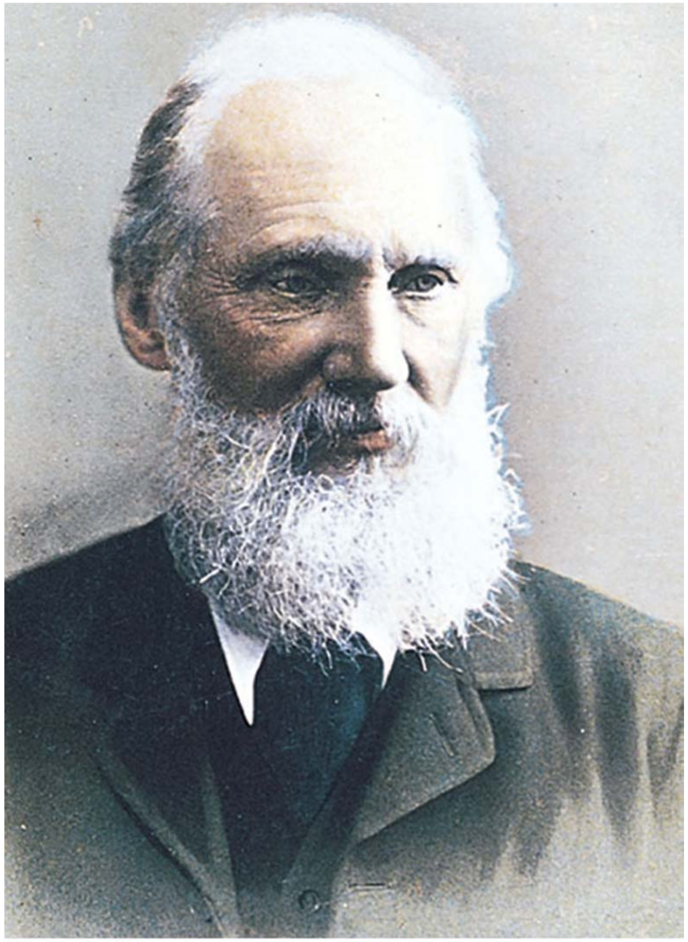
- In heating mode, $COP = \frac{|Q_H|}{W}$
- The heat pump warms the inside of the house by extracting heat from the colder outside air
- Typical values are greater than one

Second Law of Thermodynamics

- No heat engine operating in a cycle can absorb energy from a reservoir and use it entirely for the performance of an equal amount of work
  - Kelvin – Planck statement
  - Means that Q_c cannot equal 0
    - Some Q_c must be expelled to the environment
  - Means that e must be less than 100%

William Thomson, Lord Kelvin

- 1824 – 1907
- British physicist
- First to propose the use of an absolute temperature scale
- Formulated a version of the Second Law



Summary of the First and Second Laws

- First Law
  - We cannot get a greater amount of energy out of a cyclic process than we put in
- Second Law
  - We can’t break even

Second Law, Alternative Statement

- If two systems are in thermal contact, net thermal energy transfers spontaneously by heat from the hotter system to the colder system
  - The heat transfer occurs without work being done

Reversible and Irreversible Processes

- A *reversible* process is one in which every state along some path is an equilibrium state
  - And one for which the system can be returned to its initial state along the same path
- An *irreversible* process does not meet these requirements
  - Most natural processes are irreversible
- Reversible process are an idealization, but some real processes are good approximations

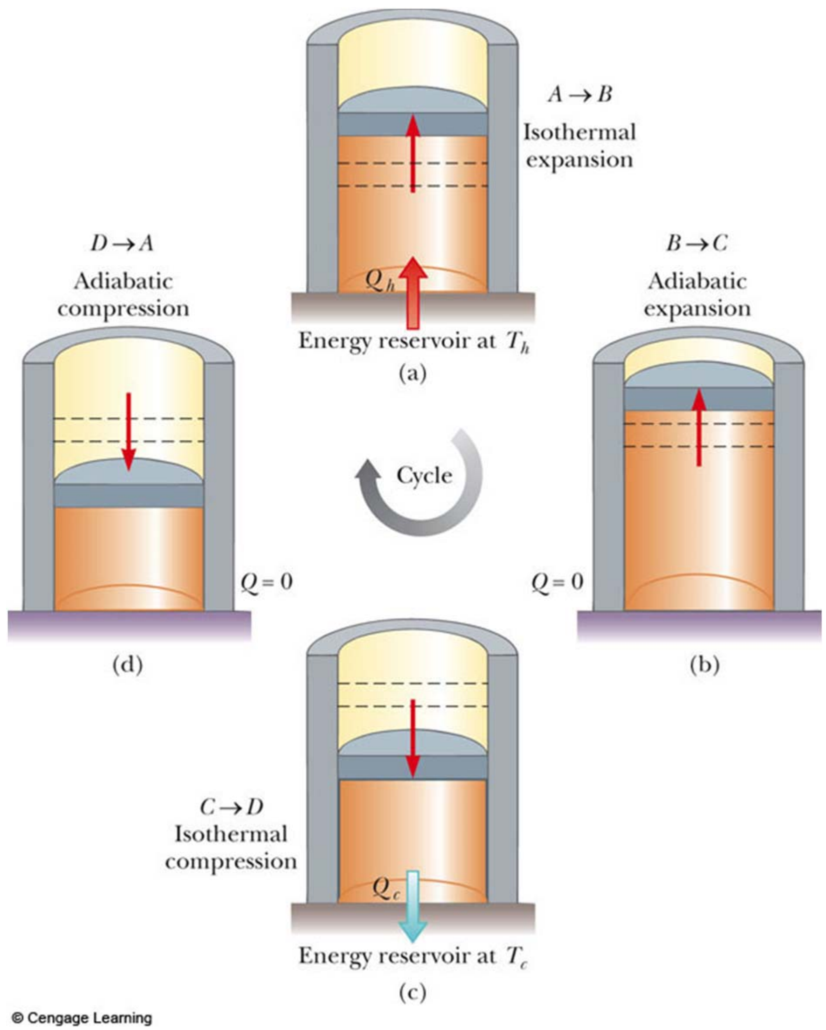
Sadi Carnot

- 1796 – 1832
- French Engineer
- Founder of the science of thermodynamics
- First to recognize the relationship between work and heat

Carnot Engine

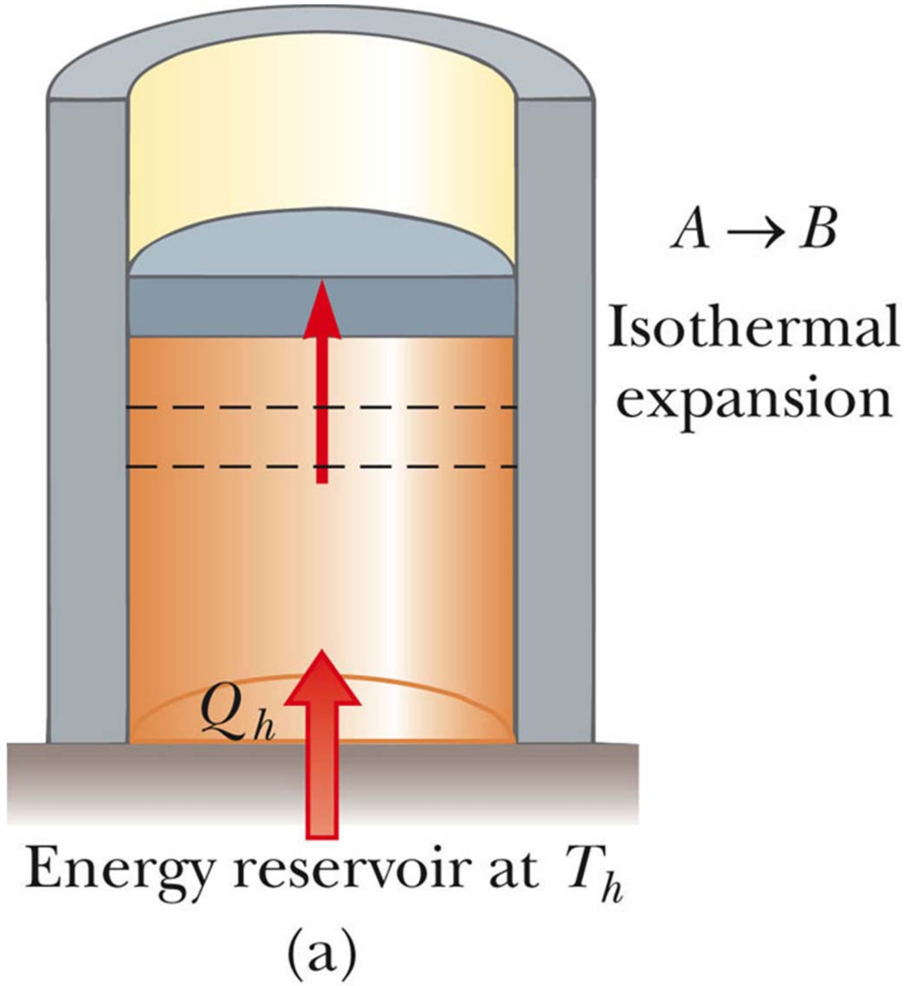
- A theoretical engine developed by Sadi Carnot
- A heat engine operating in an ideal, reversible cycle (now called a *Carnot Cycle*) between two reservoirs is the most efficient engine possible
- *Carnot's Theorem*: No real engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs

Carnot Cycle



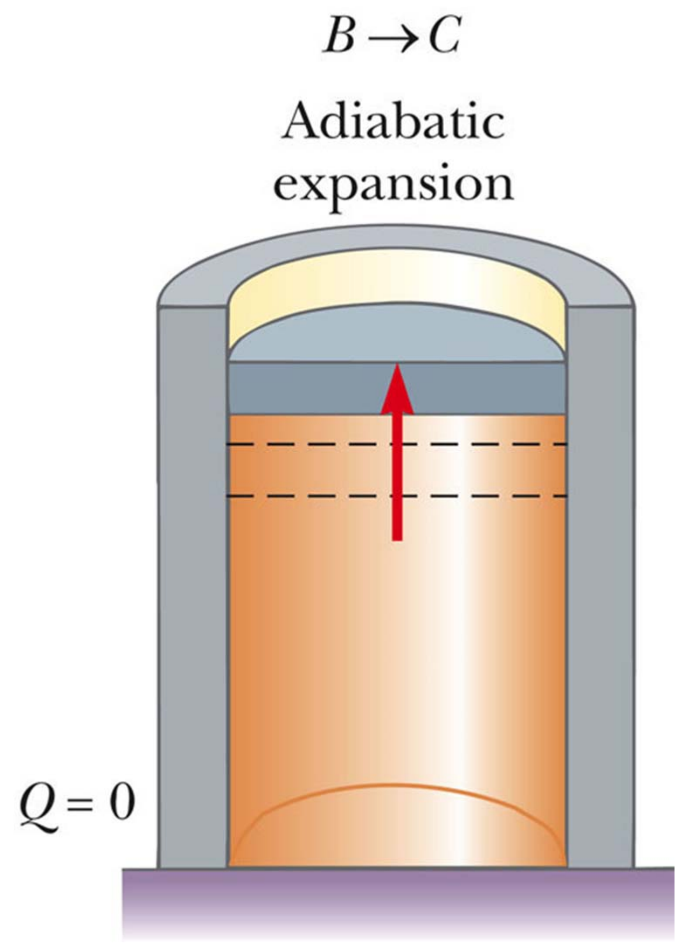
Carnot Cycle, A to B

- A to B is an isothermal expansion at temperature T_h
- The gas is placed in contact with the high temperature reservoir
- The gas absorbs heat Q_h
- The gas does work W_{AB} in raising the piston



Carnot Cycle, B to C

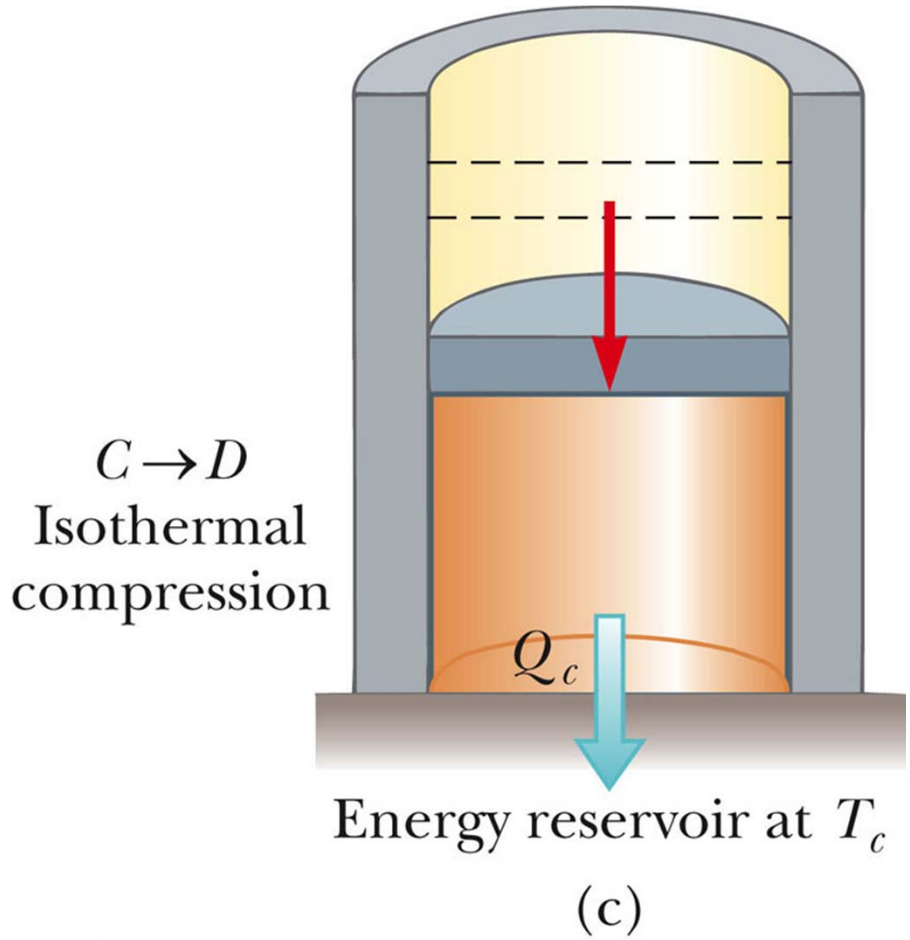
- B to C is an adiabatic expansion
- The base of the cylinder is replaced by a thermally nonconducting wall
- No heat enters or leaves the system
- The temperature falls from T_h to T_c
- The gas does work W_{BC}



(b)

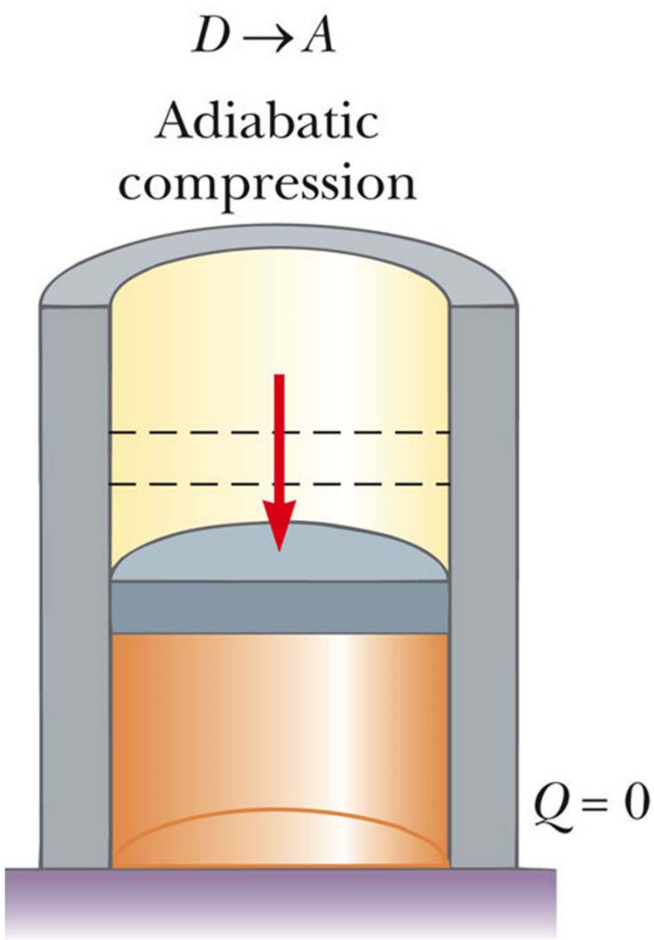
Carnot Cycle, C to D

- The gas is placed in contact with the cold temperature reservoir at temperature T_c
- C to D is an isothermal compression
- The gas expels energy Q_C
- Work W_{CD} is done on the gas



Carnot Cycle, D to A

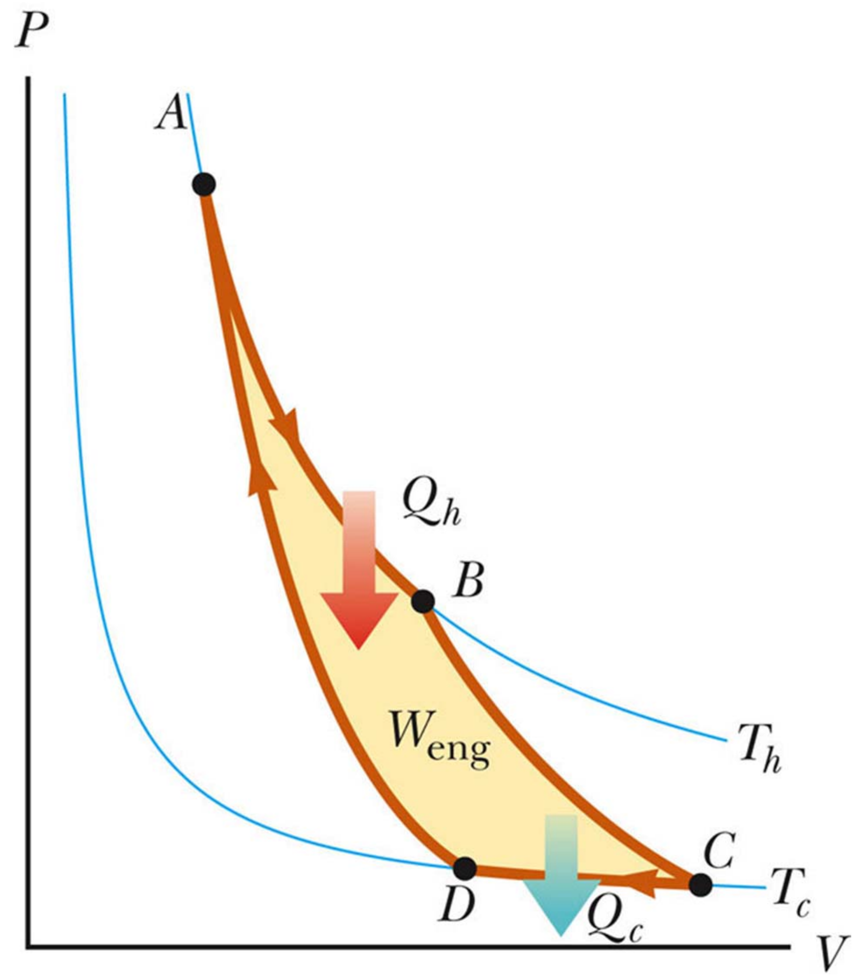
- D to A is an adiabatic compression
- The gas is again placed against a thermally nonconducting wall
  - So no heat is exchanged with the surroundings
- The temperature of the gas increases from T_C to T_h
- The work done on the gas is W_{CD}



(d)

Carnot Cycle, PV Diagram

- The work done by the engine is shown by the area enclosed by the curve
- The net work is equal to Q_h - Q_c



Efficiency of a Carnot Engine

- Carnot showed that the efficiency of the engine depends on the temperatures of the reservoirs

$$e_c = 1 - \frac{T_C}{T_h}$$

- Temperatures must be in Kelvins
- All Carnot engines operating reversibly between the same two temperatures will have the same efficiency

Example 5

At a coal –burning power plant a steam turbine is operated with power output of 650 MW. The thermal efficiency of the power plant is 30%. A. At what rate must heat be supplied to the power plant by burning coal? B. At what rate is heat discarded to the environment by this power plant.

Example 6

During one cycle, an engine extracts 2000 J of energy from hot reservoir and transfers 1500 J to a cold reservoir. (a) Find the thermal efficiency of the engine. (b) How much work does this engine do in one cycle? © How much power does the engine generate if it goes through four cycles in 2.5 s?

Notes About Carnot Efficiency

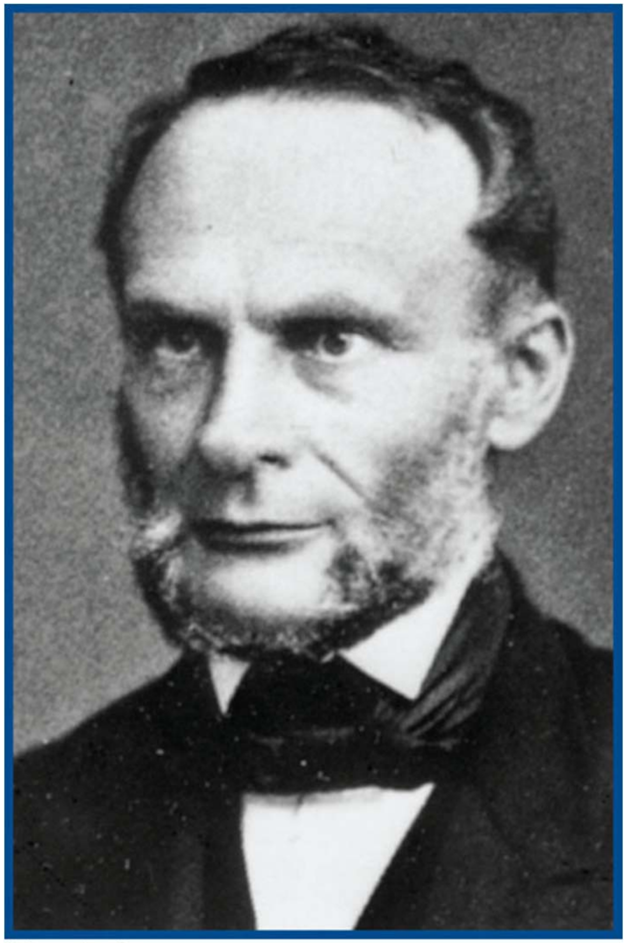
- Efficiency is 0 if $T_h = T_c$
- Efficiency is 100% only if $T_c = 0$ K
  - Such reservoirs are not available
- The efficiency increases as T_c is lowered and as T_h is raised
- In most practical cases, T_c is near room temperature, 300 K
  - So generally T_h is raised to increase efficiency

Real Engines Compared to Carnot Engines

- All real engines are less efficient than the Carnot engine
  - Real engines are irreversible because of friction
  - Real engines are irreversible because they complete cycles in short amounts of time

Rudolf Clausius

- 1822 – 1888
- German physicist
- Ideas of entropy



Entropy

- A state variable related to the Second Law of Thermodynamics, the entropy
- Let Q_r be the energy absorbed or expelled during a reversible, constant temperature process between two equilibrium states
  - Then the change in entropy during any constant temperature process connecting the two equilibrium states can be defined as the ratio of the energy to the temperature

Entropy, cont.

- Mathematically, $\Delta S = \frac{Q_r}{T}$
- This applies only to the reversible path, even if the system actually follows an irreversible path
  - To calculate the entropy for an irreversible process, model it as a reversible process
- When energy is absorbed, Q is positive and entropy increases
- When energy is expelled, Q is negative and entropy decreases

More About Entropy

- Note, the equation defines the *change in entropy*
- The entropy of the Universe increases in all natural processes
  - This is another way of expressing the Second Law of Thermodynamics
- There are processes in which the entropy of a system decreases
  - If the entropy of one system, A, decreases it will be accompanied by the increase of entropy of another system, B.
  - The change in entropy in system B will be greater than that of system A.

Perpetual Motion Machines

- A perpetual motion machine would operate continuously without input of energy and without any net increase in entropy
- Perpetual motion machines of the first type would violate the First Law, giving out more energy than was put into the machine
- Perpetual motion machines of the second type would violate the Second Law, possibly by no exhaust
- Perpetual motion machines will never be invented

Entropy and Disorder

- Entropy can be described in terms of disorder
- A disorderly arrangement is much more probable than an orderly one if the laws of nature are allowed to act without interference
  - This comes from a statistical mechanics development

Entropy and Disorder, cont.

- Isolated systems tend toward greater disorder, and entropy is a measure of that disorder
  - $S = k_B \ln W$
    - k_B is Boltzmann's constant
    - W is a number proportional to the probability that the system has a particular configuration
- This gives the Second Law as a statement of what is most probable rather than what must be
- The Second Law also defines the direction of time of all events as the direction in which the entropy of the universe increases

Grades of Energy

- The tendency of nature to move toward a state of disorder affects a system's ability to do work
- Various forms of energy can be converted into internal energy, but the reverse transformation is never complete
- If two kinds of energy, A and B, can be completely interconverted, they are of the *same grade*

Grades of Energy, cont.

- If form A can be completely converted to form B, but the reverse is never complete, A is a *higher grade* of energy than B
- When a high-grade energy is converted to internal energy, it can never be fully recovered as high-grade energy
- *Degradation of energy* is the conversion of high-grade energy to internal energy
- In all real processes, the energy available for doing work decreases

Heat Death of the Universe

- The entropy of the Universe always increases
- The entropy of the Universe should ultimately reach a maximum
  - At this time, the Universe will be at a state of uniform temperature and density
  - This state of perfect disorder implies no energy will be available for doing work
- This state is called the *heat death* of the Universe

The First Law and Human Metabolism

- The First Law can be applied to living organisms
- The internal energy stored in humans goes into other forms needed by the organs and into work and heat
- The *metabolic rate* ($\Delta U / \Delta t$) is directly proportional to the rate of oxygen consumption by volume

Measuring Metabolic Rate

- The metabolic rate is related to oxygen consumption by

$$\frac{\Delta U}{\Delta t} = 4.8\frac{\Delta V_{O_2}}{\Delta t}$$

- About 80 W is the basal metabolic rate, just to maintain and run different body organs

Various Metabolic Rates

TABLE 12.4

Oxygen Consumption and Metabolic Rates for Various Activities for a 65-kg Male[a]

Activity	O_2 Use Rate (mL/min · kg)	Metabolic Rate (kcal/h)	Metabolic Rate (W)
Sleeping	3.5	70	80
Light activity (dressing, walking slowly, desk work)	10	200	230
Moderate activity (walking briskly)	20	400	465
Heavy activity (basketball, swimming a fast breaststroke)	30	600	700
Extreme activity (bicycle racing)	70	1 400	1 600

Aerobic Fitness

- One way to measure a person's physical fitness is their maximum capacity to use or consume oxygen

TABLE 12.5

Physical Fitness and Maximum Oxygen Consumption Rate[a]

Fitness Level	**Maximum Oxygen Consumption Rate (mL/min · kg)**
Very poor	28
Poor	34
Fair	42
Good	52
Excellent	70

Efficiency of the Human Body

TABLE 12.6

Metabolic Rate, Power Output, and Efficiency for Different Activities[a]

Activity	Metabolic Rate $\frac{\Delta U}{\Delta t}$ (watts)	Power Output $\frac{W}{\Delta t}$ (watts)	Efficiency e
Cycling	505	96	0.19
Pushing loaded coal cars in a mine	525	90	0.17
Shoveling	570	17.5	0.03

- Efficiency is the ratio of the mechanical power supplied to the metabolic rate or total power input