

Thermodynamics

FLUID MECHANICS AND THERMAL PHYSICS

$$\rho = m/V$$

$$P = P_0 + \rho gh$$

$$F_{buoy} = \rho V g$$

$$A_1 v_1 = A_2 v_2$$

$$P + \rho gy + \frac{1}{2} \rho v^2 = \text{const.}$$

$$\Delta \ell = \alpha \ell_0 \Delta T$$

$$H = \frac{kA \Delta T}{L}$$

$$P = \frac{F}{A}$$

$$PV = nRT = Nk_B T$$

$$K_{avg} = \frac{3}{2} k_B T$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{\mu}}$$

$$W = -P \Delta V$$

$$\Delta U = Q + W$$

$$e = \left| \frac{W}{Q_H} \right|$$

$$e_c = \frac{T_H - T_C}{T_H}$$

A = area

e = efficiency

F = force

h = depth

H = rate of heat transfer

k = thermal conductivity

K_{avg} = average molecular kinetic energy

ℓ = length

L = thickness

m = mass

M = molar mass

n = number of moles

N = number of molecules

P = pressure

Q = heat transferred to a system

T = temperature

U = internal energy

V = volume

v = velocity or speed

v_{rms} = root-mean-square velocity

W = work done on a system

y = height

α = coefficient of linear expansion

μ = mass of molecule

ρ = density

$$\Delta \ell = \alpha \ell_0 \Delta T$$

$$H = \frac{kA \Delta T}{L}$$

$$PV = nRT = Nk_B T$$

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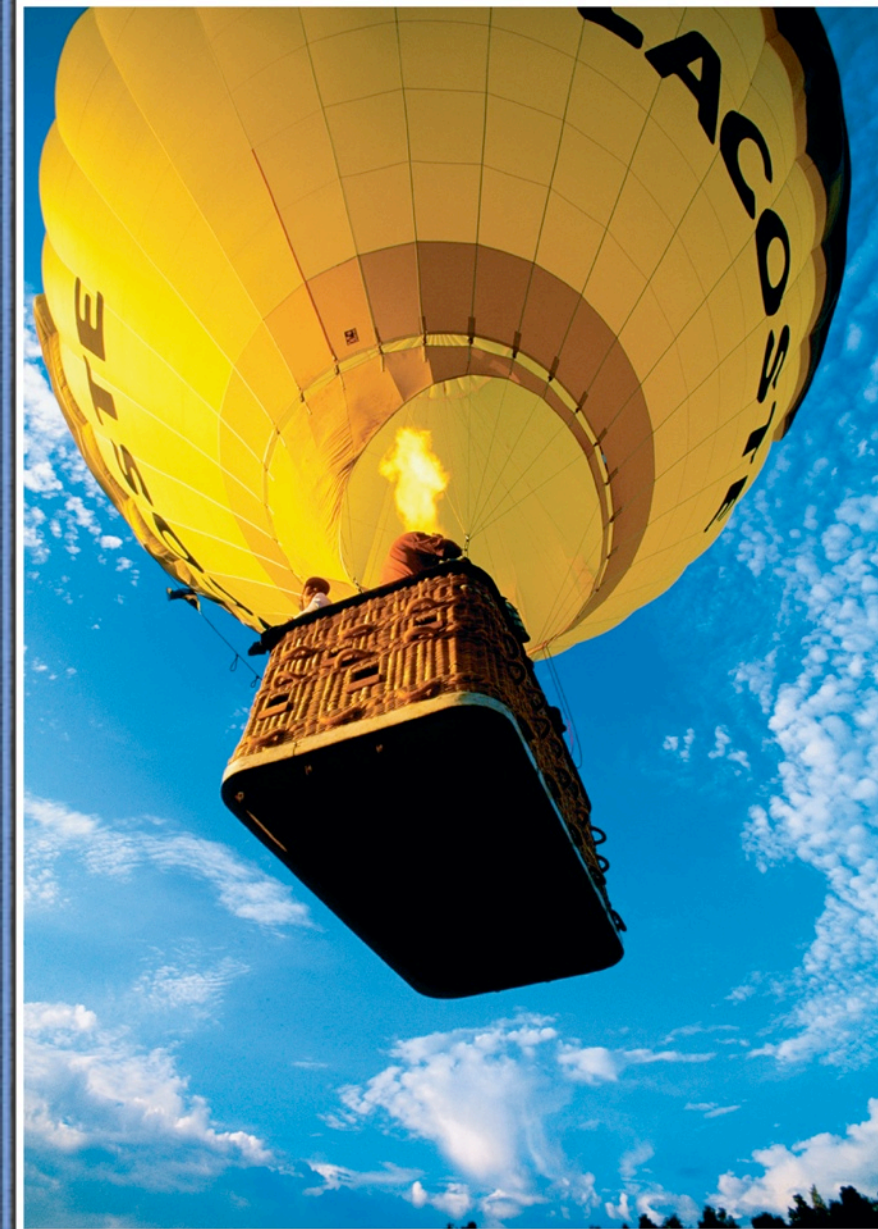
$$e_c = \frac{T_H - T_C}{T_H}$$

Temperature & Kinetic Theory

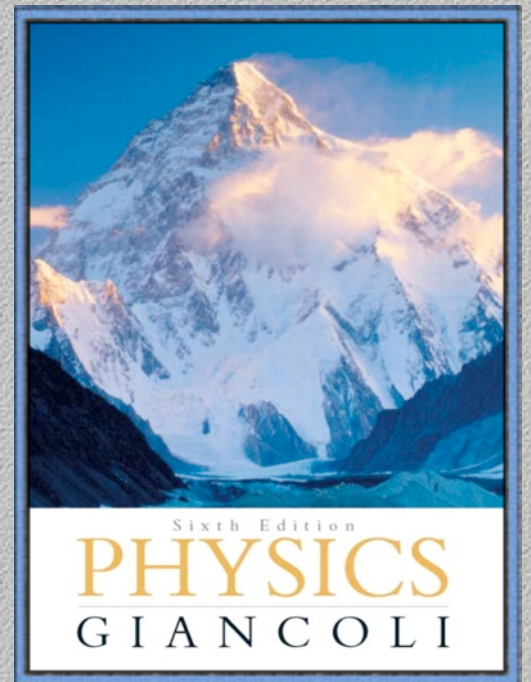
CHAPTER 13 PHYSICS: PRINCIPLES WITH APPLICATIONS 6TH EDITION GIANCOLI

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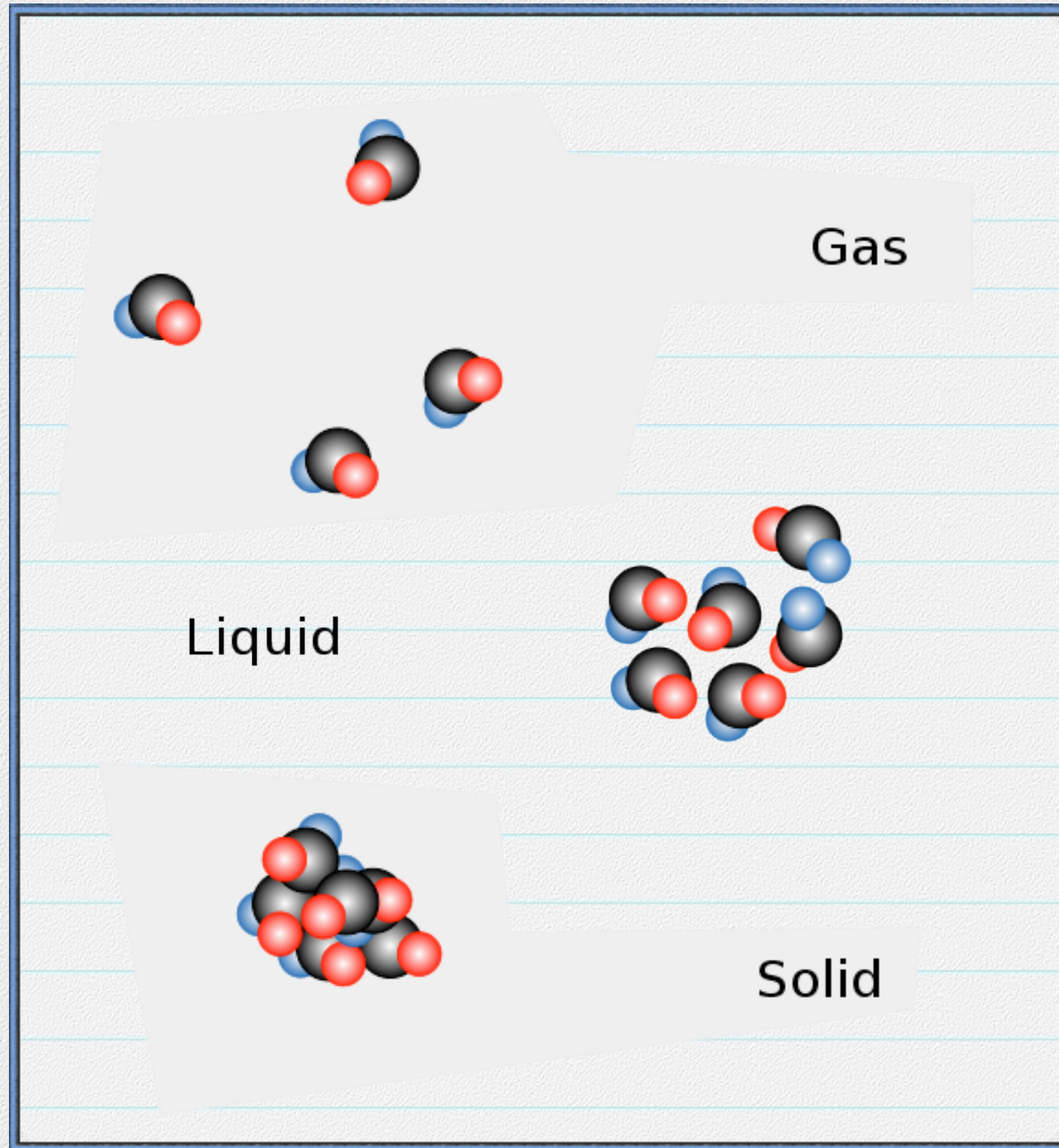
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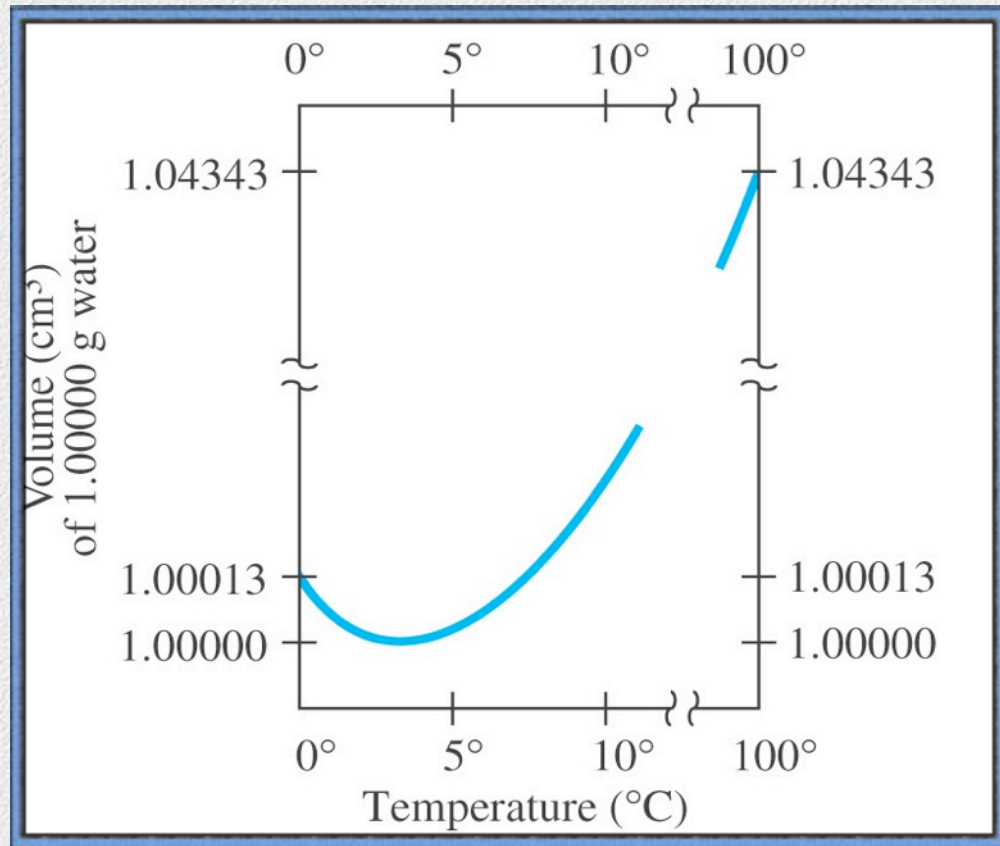
13-1 Atomic Theory of Matter



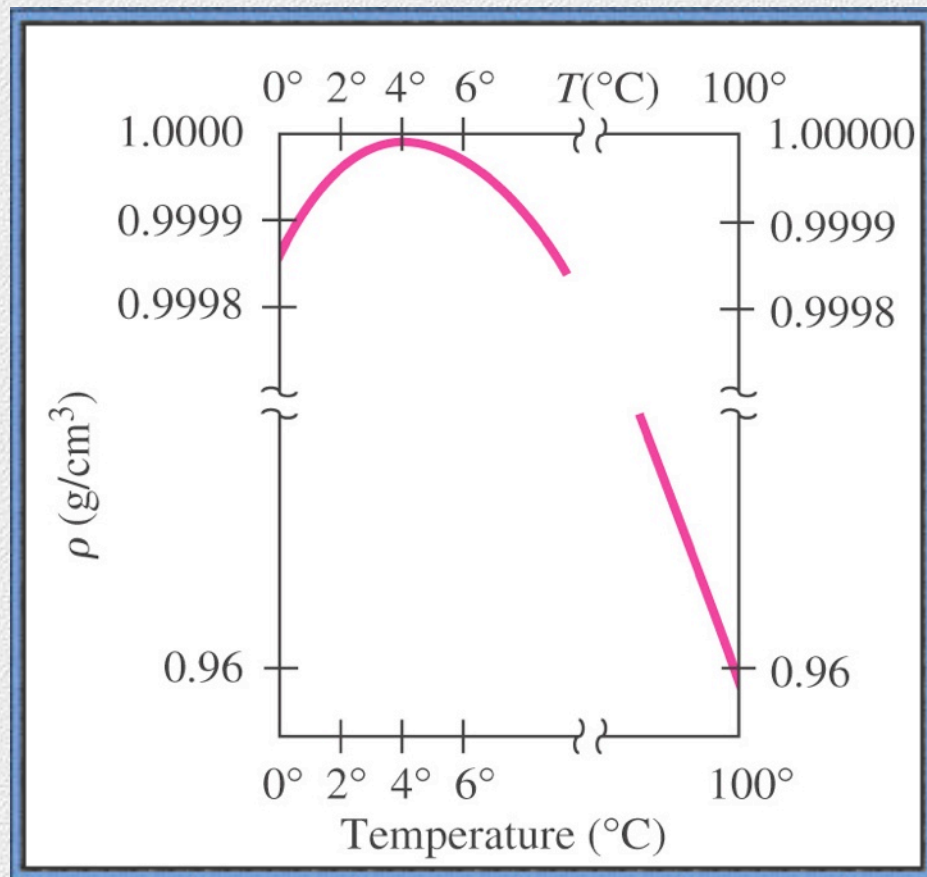
- On a microscopic scale, the arrangements of molecules in solids, liquids, and gases are quite different.

Search results for "solid liquid gas" - Wikimedia Foundation

13-4 Thermal Expansion



● Water behaves differently from most other solids; its minimum volume occurs when its temperature is 4°C.



● As it cools further, it expands, as anyone who has left a bottle in the freezer to cool and then forgets about it can testify.

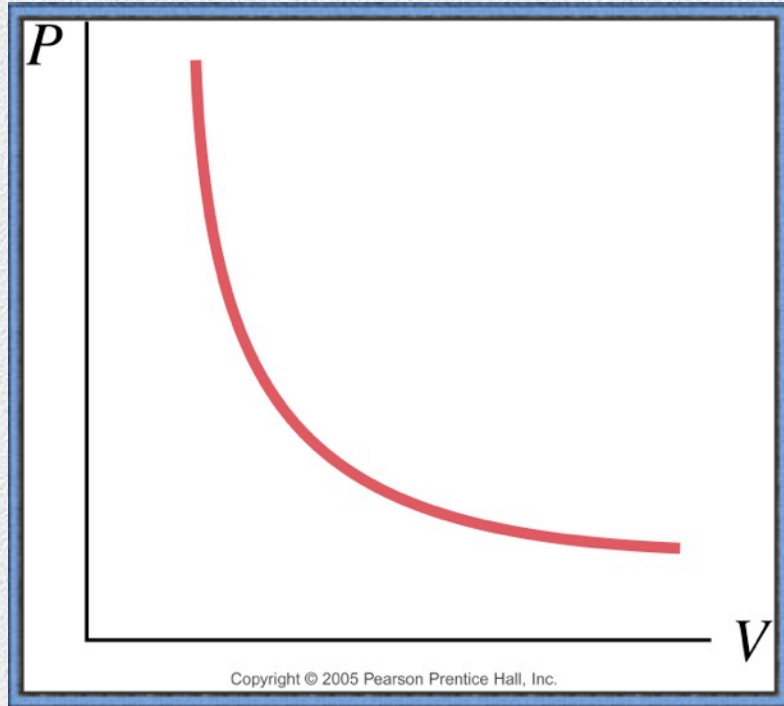
13-4 Thermal Expansion

TABLE 13-1 Coefficients of Expansion, near 20°C

Material	Coefficient of Linear Expansion, α (C°) ⁻¹	Coefficient of Volume Expansion, β (C°) ⁻¹
<i>Solids</i>		
Aluminum	25×10^{-6}	75×10^{-6}
Brass	19×10^{-6}	56×10^{-6}
Copper	17×10^{-6}	50×10^{-6}
Gold	14×10^{-6}	42×10^{-6}
Iron or steel	12×10^{-6}	35×10^{-6}
Lead	29×10^{-6}	87×10^{-6}
Glass (Pyrex®)	3×10^{-6}	9×10^{-6}
Glass (ordinary)	9×10^{-6}	27×10^{-6}
Quartz	0.4×10^{-6}	1×10^{-6}
Concrete and brick	$\approx 12 \times 10^{-6}$	$\approx 36 \times 10^{-6}$
Marble	$1.4\text{--}3.5 \times 10^{-6}$	$4\text{--}10 \times 10^{-6}$
<i>Liquids</i>		
Gasoline		950×10^{-6}
Mercury		180×10^{-6}
Ethyl alcohol		1100×10^{-6}
Glycerin		500×10^{-6}
Water		210×10^{-6}
<i>Gases</i>		
Air (and most other gases at atmospheric pressure)		3400×10^{-6}

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13-6 The Gas Laws and Absolute Temperature



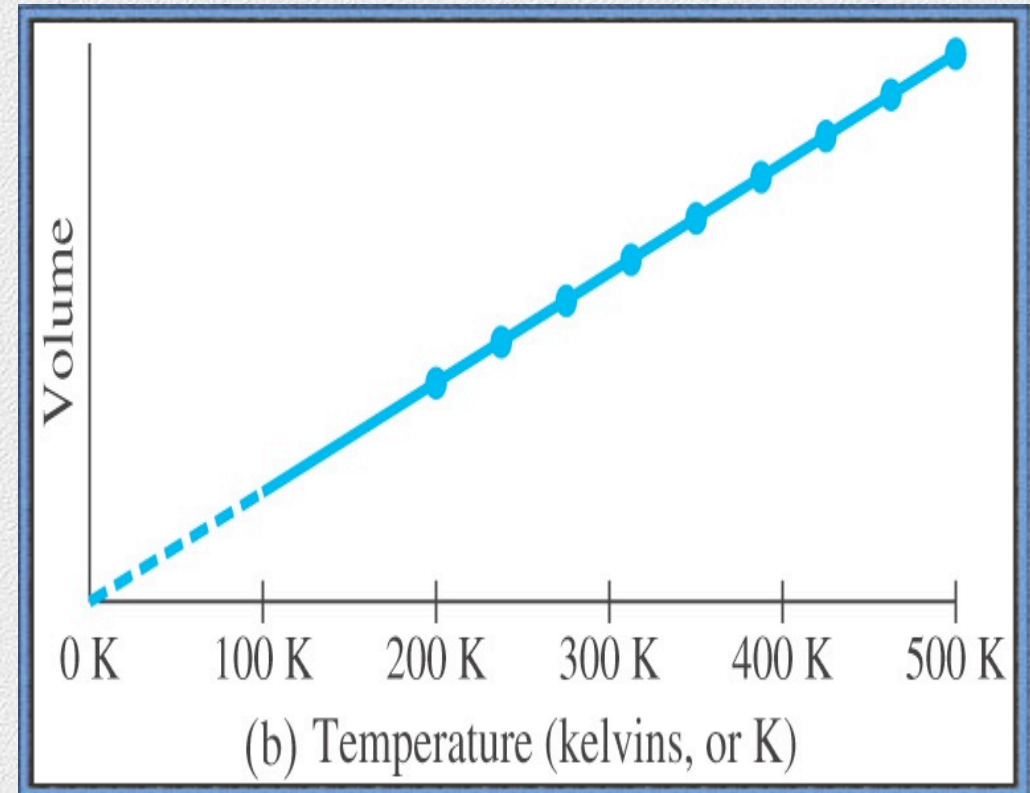
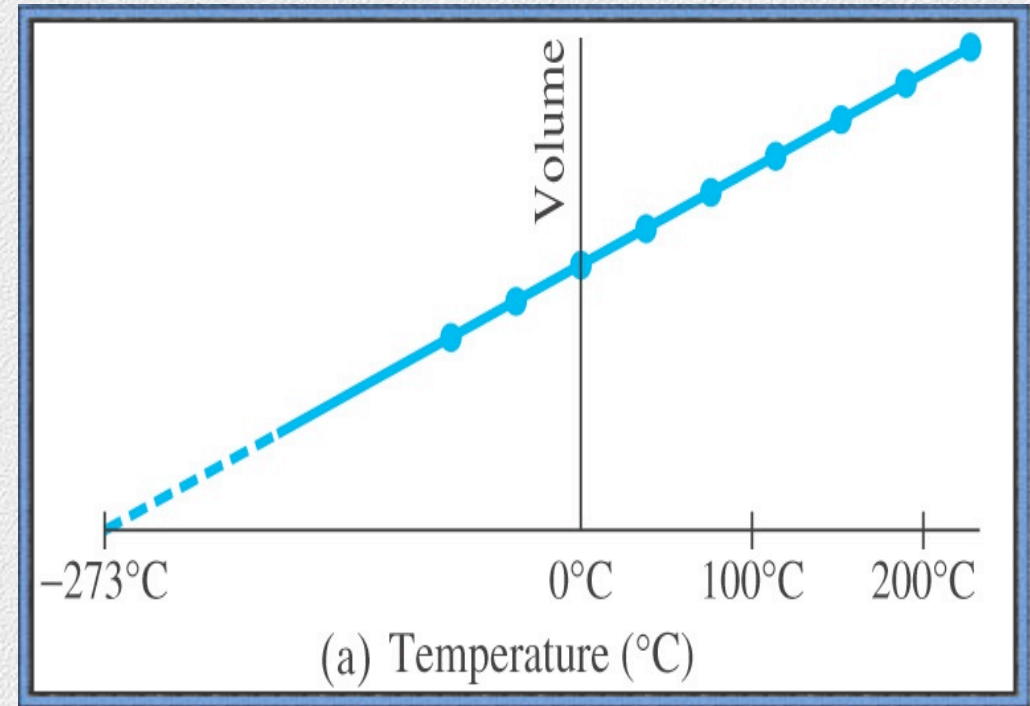
● The relationship between the volume, pressure, temperature, and mass of a gas is called an equation of state.

● We will deal here with gases that are not too dense.

● Boyle's Law: the volume of a given amount of gas is inversely proportional to the pressure as long as the temperature is constant.

13-6 The Gas Laws and Absolute Temperature

- The volume is linearly proportional to the temperature, as long as the temperature is somewhat above the condensation point and the pressure is constant.
- Extrapolating, the volume becomes zero at -273.15°C ; this temperature is called absolute zero.



13-6 The Gas Laws and Absolute Temperature

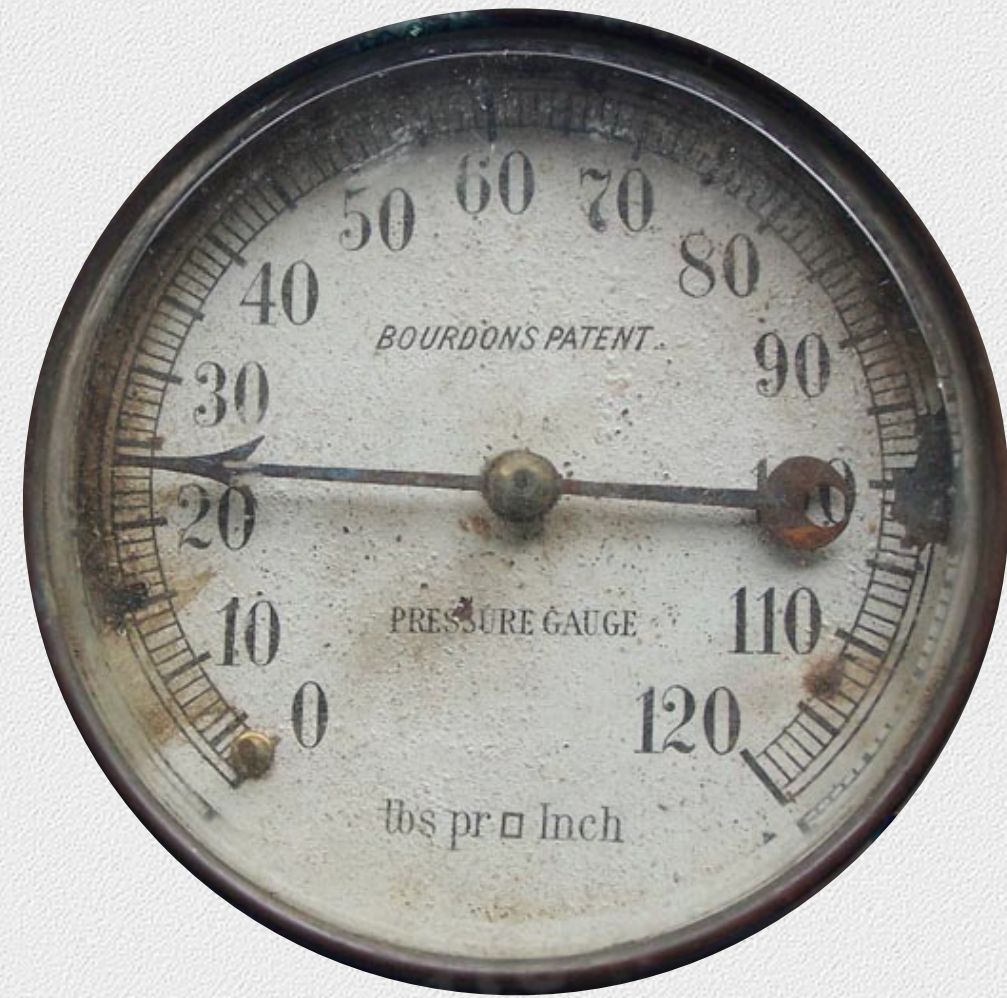
- The concept of absolute zero allows us to define a third temperature scale – the absolute, or Kelvin, scale.
- This scale starts with 0 K at absolute zero, but otherwise is the same as the Celsius scale.
- Therefore, the freezing point of water is 273.15 K, and the boiling point is 373.15 K.
- Finally, when the volume is constant, the pressure is directly proportional to the temperature:

$$p \propto T$$

13-7 The Ideal Gas Law

● We can combine the three relations just derived into a single relation:

$$P \times V \propto T$$



● What about the amount of gas present? If the temperature and pressure are constant, the volume is proportional to the amount of gas:

$$P \times V \propto mT$$

13-7 The Ideal Gas Law

- A mole (mol) is defined as the number of grams of a substance that is numerically equal to the molecular mass of the substance:
 - 1 mol H₂ has a mass of 2 g
 - 1 mol Ne has a mass of 20 g
 - 1 mol CO₂ has a mass of 44 g
- The number of moles in a certain mass of material:

$$n \text{ (mol)} = \frac{\text{mass (grams)}}{\text{molecular mass (g/mol)}}$$

13-7 The Ideal Gas Law

● We can now write the ideal gas law:

$$PV = nRT$$

● where n is the number of moles and R is the universal gas constant.

● $R = 8.315 \text{ J}/(\text{mol K})$

● $R = 0.0821 \text{ (L atm)}/(\text{mol K})$

13-8 Problem Solving with the Ideal Gas Law

- Useful facts and definitions:
- Standard temperature and pressure (STP)
 - $T = 273\text{K}$ $P = 1\text{ atm} = 101.3\text{ kPa}$
- Volume of 1 mol of an ideal gas is 22.4 L
- If the amount of gas does not change:

$$\frac{PV}{T} = \text{const}$$

- Always measure T in kelvins
- P must be the absolute pressure

13-9 Ideal Gas Law in Terms of Molecules: Avogadro's Number

● Since the gas constant is universal, the number of molecules in one mole is the same for all gases. That number is called Avogadro's number:

$$N_a = 6.02 \times 10^{23}$$

● The number of molecules in a gas is the number of moles times Avogadro's number:

$$nN_a = N$$

13-9 Ideal Gas Law in Terms of Molecules: Avogadro's Number

● Therefore we can write:

$$PV = NkT$$

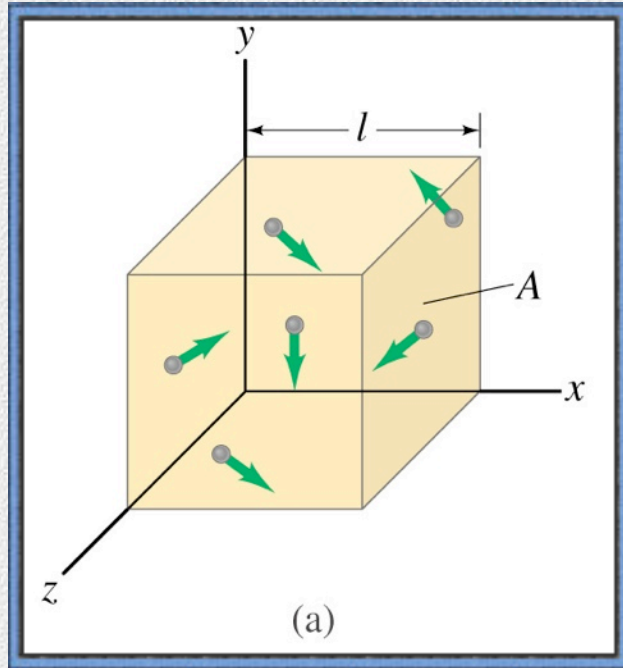
● where k is called Boltzmann's constant.

$$\frac{R}{N_a} = k = 1.38 \times 10^{-23} \text{ J/K}$$

13-10 Kinetic Theory and the Molecular Interpretation of Temperature

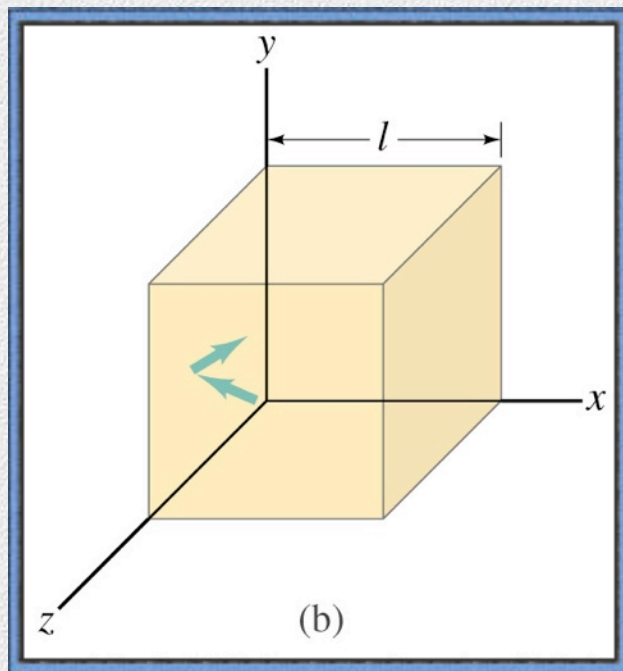
- Assumptions of kinetic theory:
 - large number of molecules, moving in random directions with a variety of speeds
 - molecules are far apart, on average
 - molecules obey laws of classical mechanics and interact only when colliding
 - collisions are perfectly elastic

13-10 Kinetic Theory and the Molecular Interpretation of Temperature



● The force exerted on the wall by the collision of one molecule is

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}$$



● Then the force due to all molecules colliding with that wall is

$$F = \frac{m}{l} N \overline{v_x^2}$$

13-10 Kinetic Theory and the Molecular Interpretation of Temperature

● The averages of the squares of the speeds in all three directions are equal:

$$F = \frac{m}{l} N \frac{\overline{v^2}}{3}$$

$$P = \frac{F}{A} = \frac{1}{3} \frac{Nm \overline{v^2}}{Al}$$

● So the pressure is:

$$= \frac{1}{3} \frac{Nm \overline{v^2}}{V}$$

13-10 Kinetic Theory & the Molecular Interpretation of Temperature

● Rewriting;

$$PV = \frac{2}{3} N \left(\frac{1}{2} m \overline{v^2} \right)$$

● meaning;

$$KE = \frac{1}{2} m v^2 = \frac{3}{2} kT$$

● The average translational kinetic energy of the molecules in an ideal gas is directly proportional to the temperature of the gas.

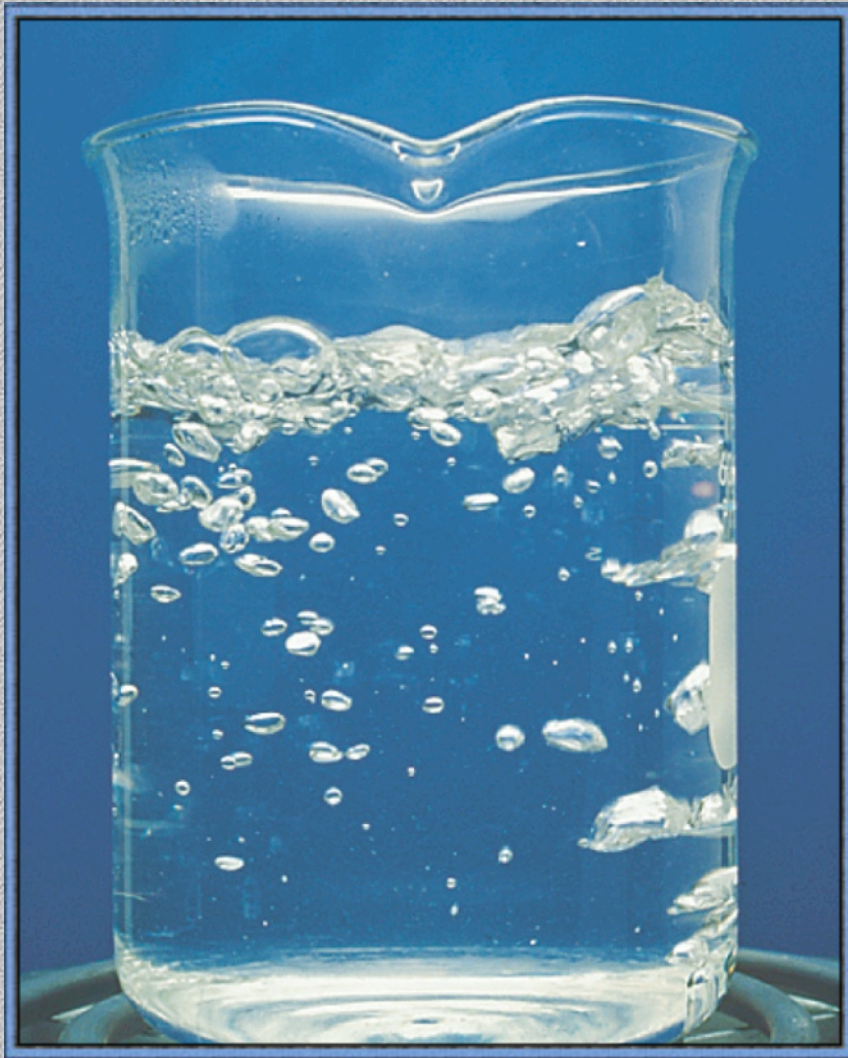
13-10 Kinetic Theory and the Molecular Interpretation of Temperature

● We can invert this to find the average speed of molecules in a gas as a function of temperature:

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

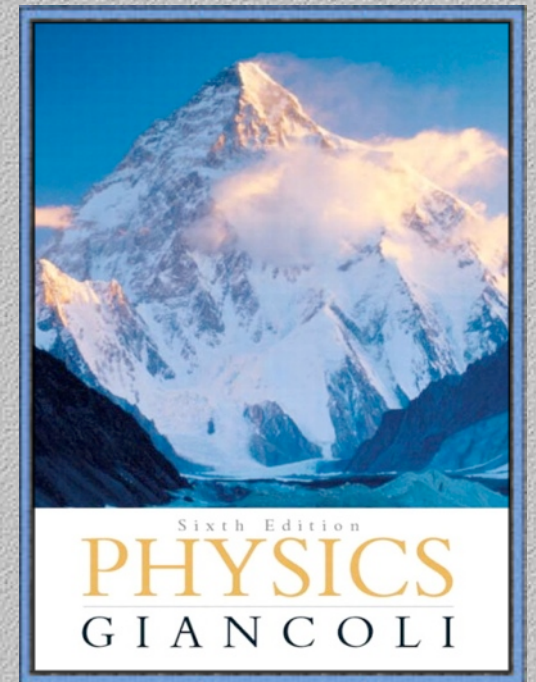
Heat

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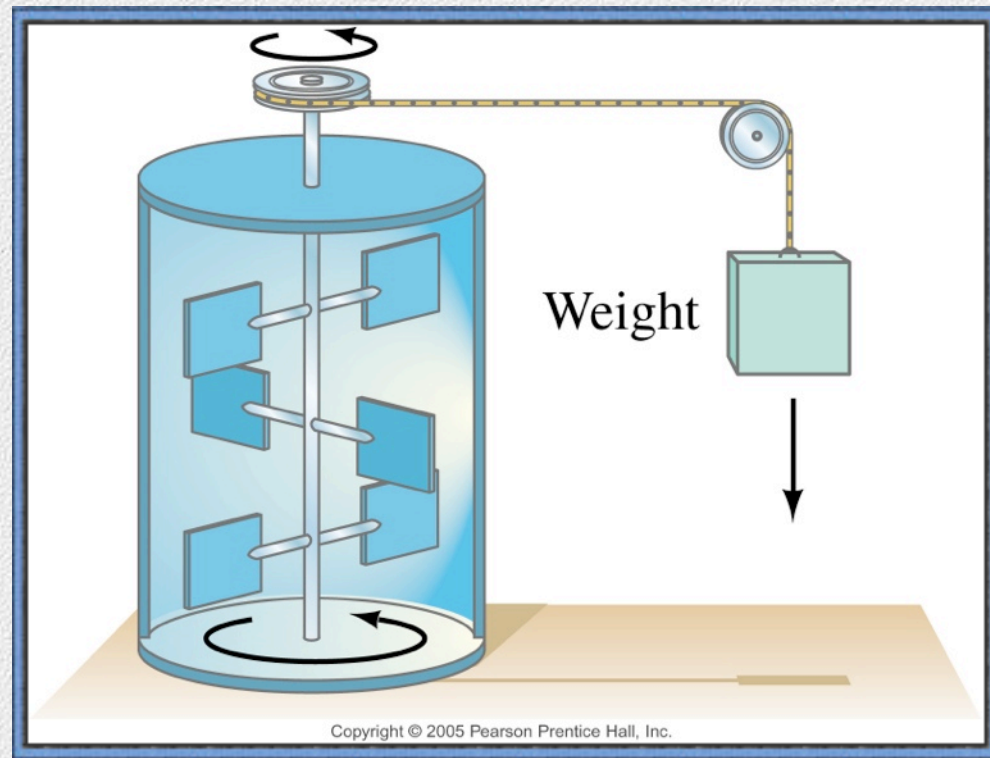


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14-1 Heat As Energy Transfer



● If heat is a form of energy, it ought to be possible to equate it to other forms.

● This experiment found the mechanical equivalent of heat by using the falling weight to heat the water.

14-2 Internal Energy

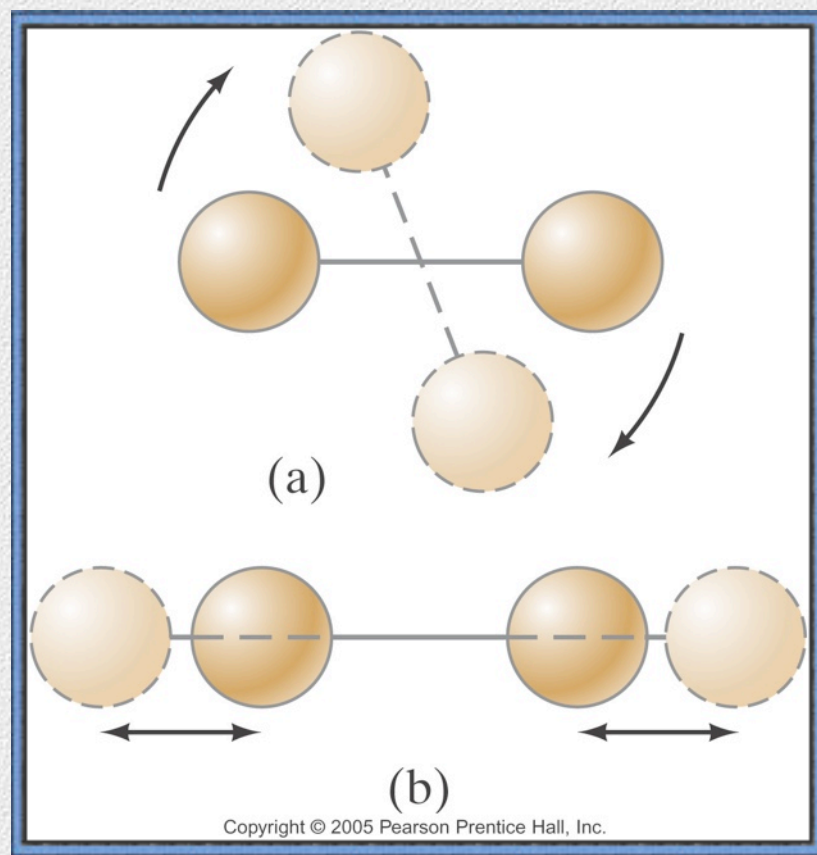
● Internal energy of an ideal (atomic) gas:

$$U = N \times \frac{1}{2}mv^2$$

● But since we know the average kinetic energy in terms of the temperature, we can write:

$$U = \frac{3}{2} nRT$$

14-2 Internal Energy



- If the gas is molecular rather than atomic, rotational and vibrational kinetic energy needs to be taken into account as well.

14-3 Specific Heat

TABLE 14–1 Specific Heats
(at 1 atm constant pressure and 20°C
unless otherwise stated)

Substance	Specific Heat, c	
	kcal/kg · C° (= cal/g · C°)	J/kg · C°
Aluminum	0.22	900
Alcohol (ethyl)	0.58	2400
Copper	0.093	390
Glass	0.20	840
Iron or steel	0.11	450
Lead	0.031	130
Marble	0.21	860
Mercury	0.033	140
Silver	0.056	230
Wood	0.4	1700
Water		
Ice (−5°C)	0.50	2100
Liquid (15°C)	1.00	4186
Steam (110°C)	0.48	2010
Human body (average)	0.83	3470
Protein	0.4	1700

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● The amount of heat required to change the temperature of a material is proportional to the mass and to the temperature change.

$$Q = mc\Delta T$$

● The specific heat, c , is characteristic of the material. Some values are listed at left.

Molar Specific Heat

● Specific heats of gases are more complicated, and are generally measured at constant pressure (c_P) or constant volume (c_V).

TABLE 14–2
Specific Heats of Gases
(kcal/kg · °C)

Gas	c_P (constant pressure)	c_V (constant volume)
Steam (100°C)	0.482	0.350
Oxygen	0.218	0.155
Helium	1.15	0.75
Carbon dioxide	0.199	0.153
Nitrogen	0.248	0.177

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Thermodynamic Laws

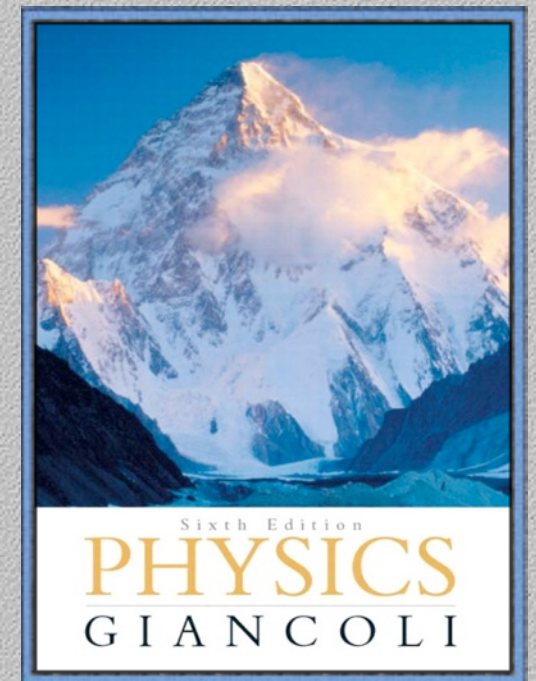


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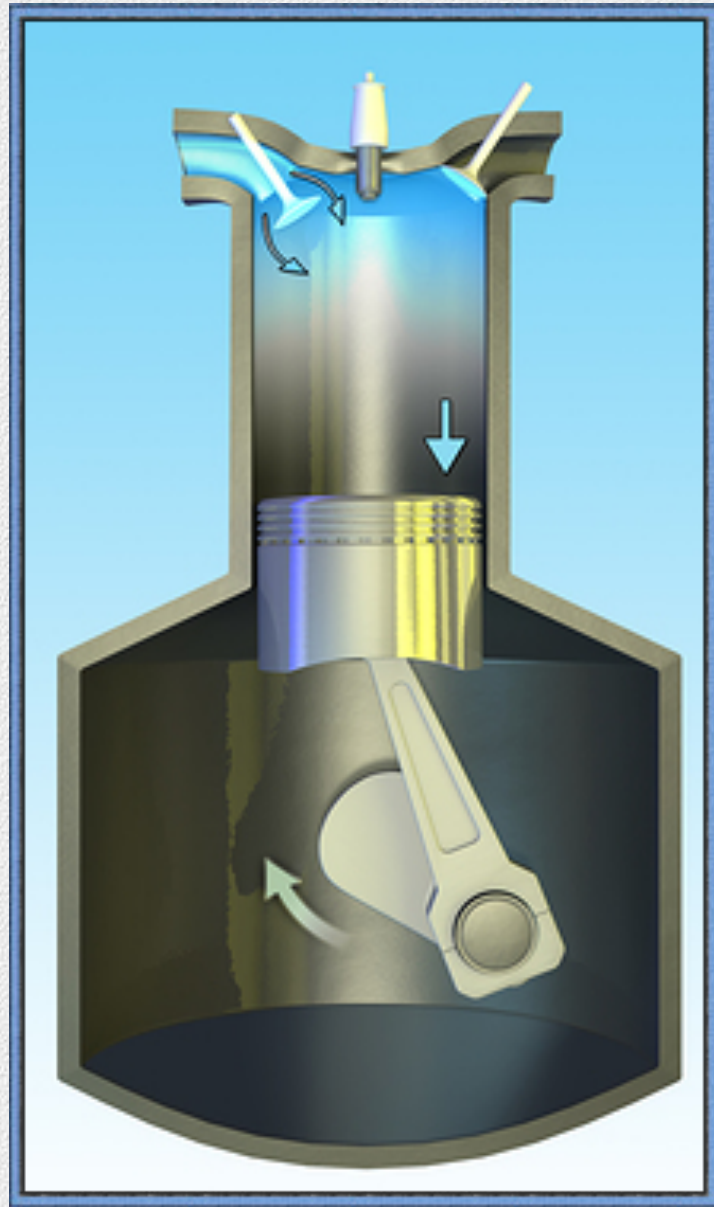
15-1 The First Law of Thermodynamics

$$\Delta U = Q + W$$

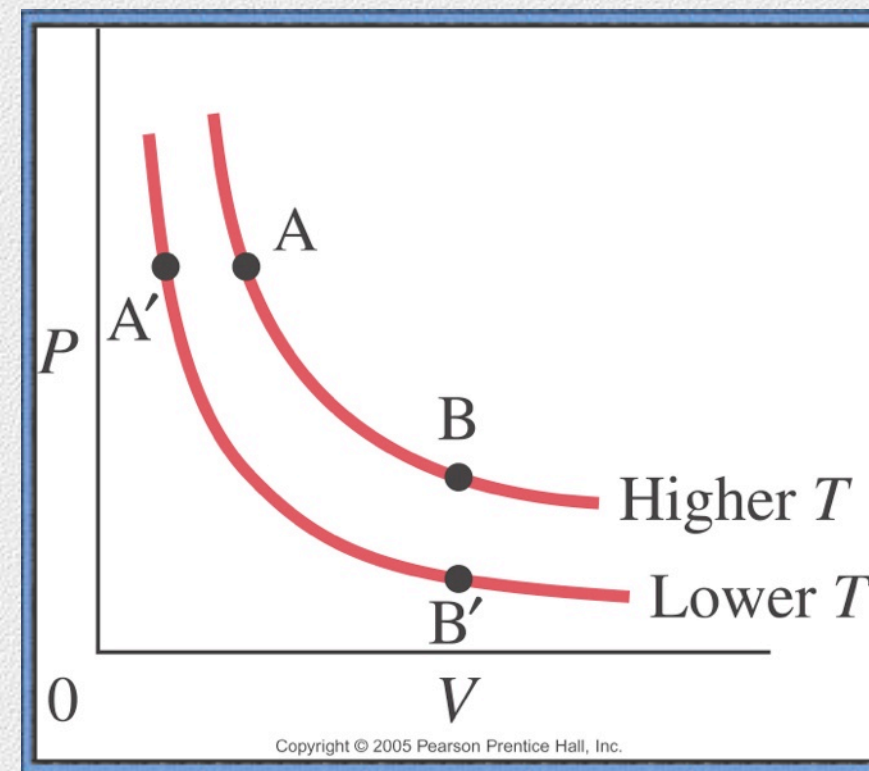
- The change in internal energy of a closed system will be equal to the energy added to the system minus the work done by the system on its surroundings.
- This is the law of conservation of energy, written in a form useful to systems involving heat transfer.

Thermodynamic Processes

15-2 Thermodynamic Processes and the First Law



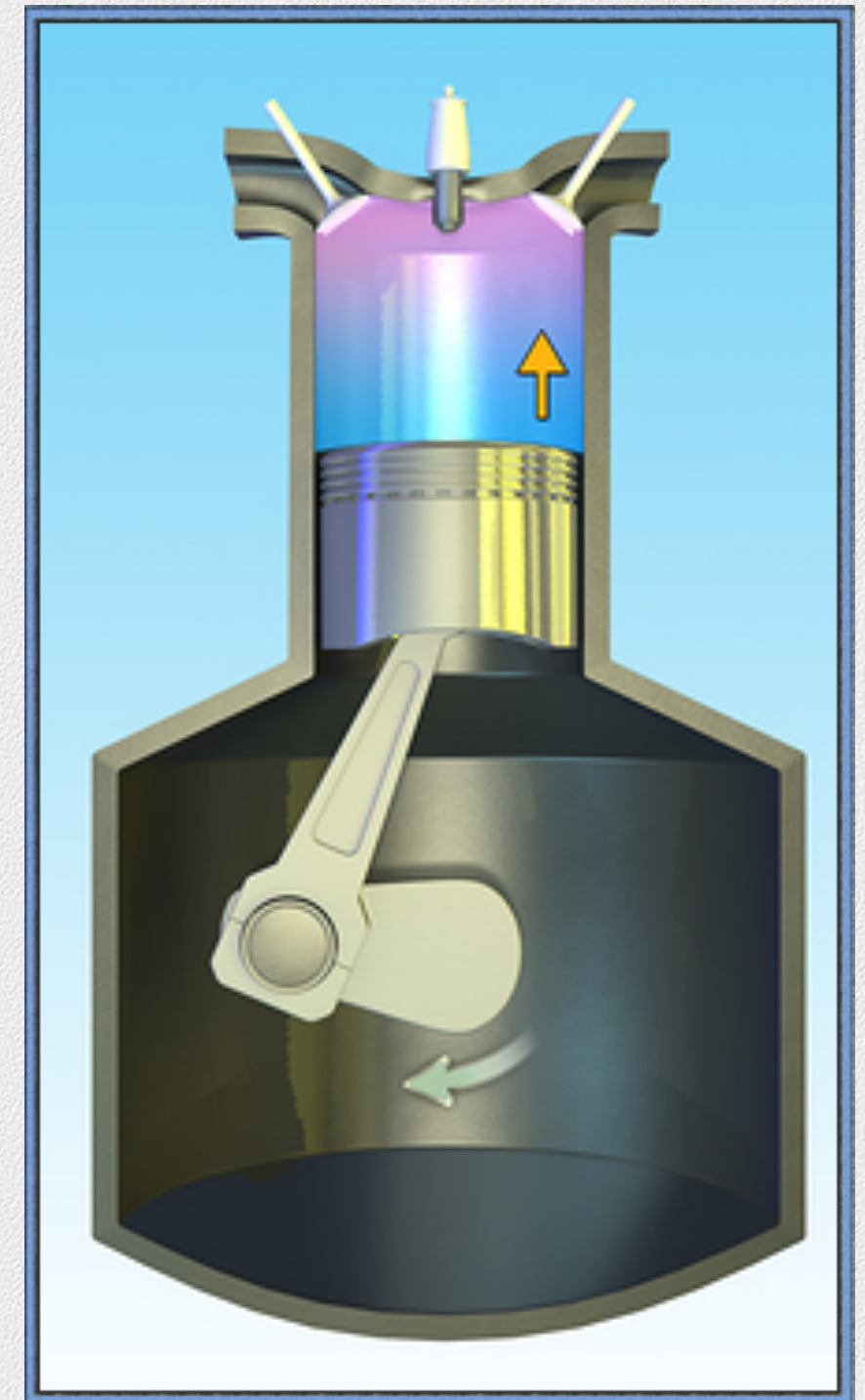
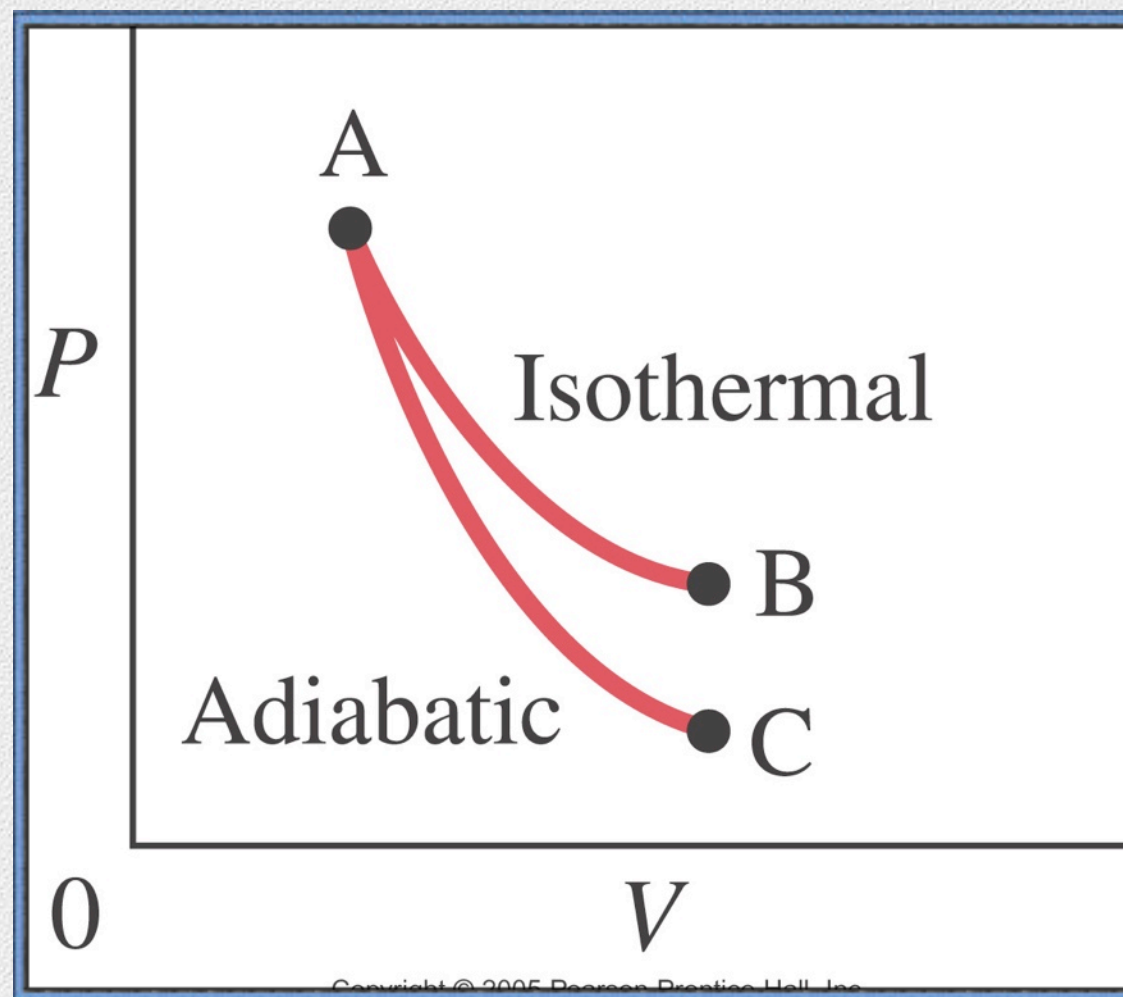
- An isothermal process is one where the temperature does not change.



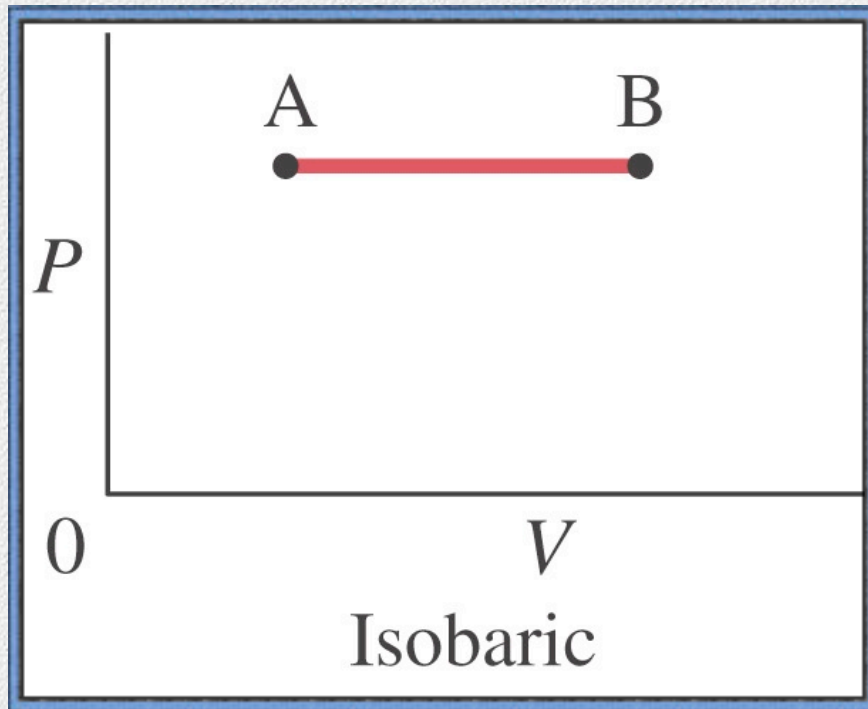
- In order for an isothermal process to take place, we assume the system is in contact with a heat reservoir.

15-2 Thermodynamic Processes and the First Law

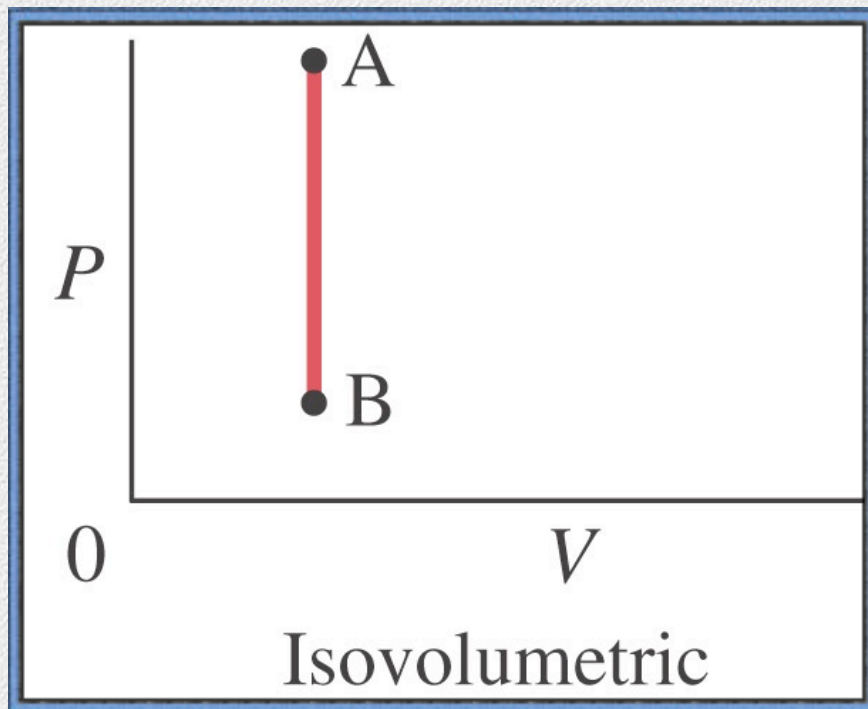
- An adiabatic process is one where there is no heat flow into or out of the system.



15-2 Thermodynamic Processes and the First Law



- An isobaric process occurs at constant pressure.



- An isochoric (isovolumetric) one occurs at constant volume.

15-2 Thermodynamic Processes and the First Law

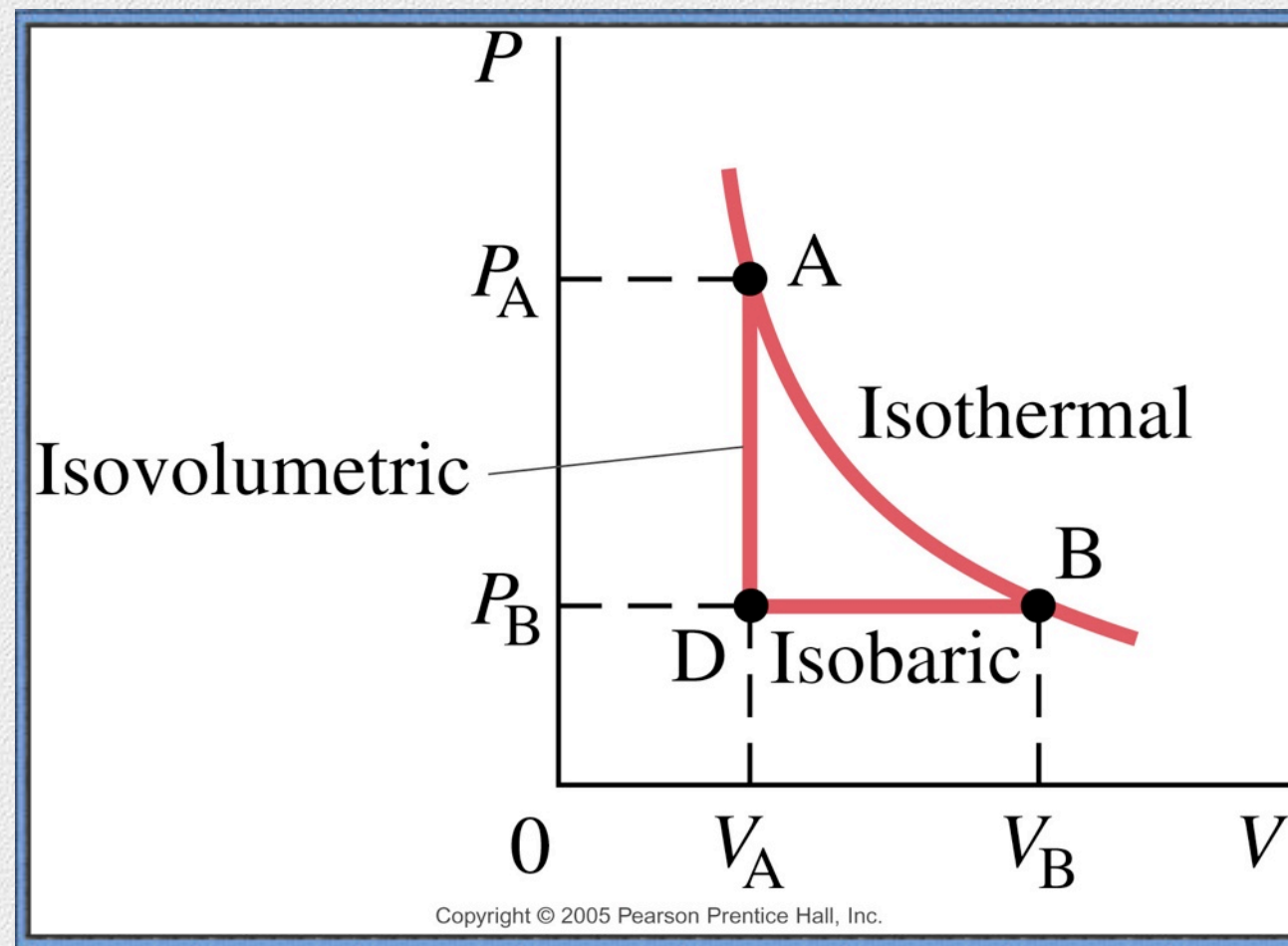
- If the pressure is constant, the work done is the pressure multiplied by the change in volume:

$$W = P\Delta V$$

- In an isometric process, the volume does not change, so the work done is zero.

15-2 Thermodynamic Processes and the First Law

- For processes where the pressure varies, the work done is the area under the P-V curve.



15-2 Thermodynamic Processes and the First Law

$$\Delta U = Q + W$$

Simple Thermodynamic Processes

Process	Constant	Predicting
Isothermal	T	$\Delta T = 0$ so $\Delta U = 0$ and $Q = W$
Isobaric	P	
Isochoric	V	$\Delta V = 0$ so $W = 0$
Adiabatic	$Q = 0$	$\Delta U = W$

15-1 The First Law of Thermodynamics

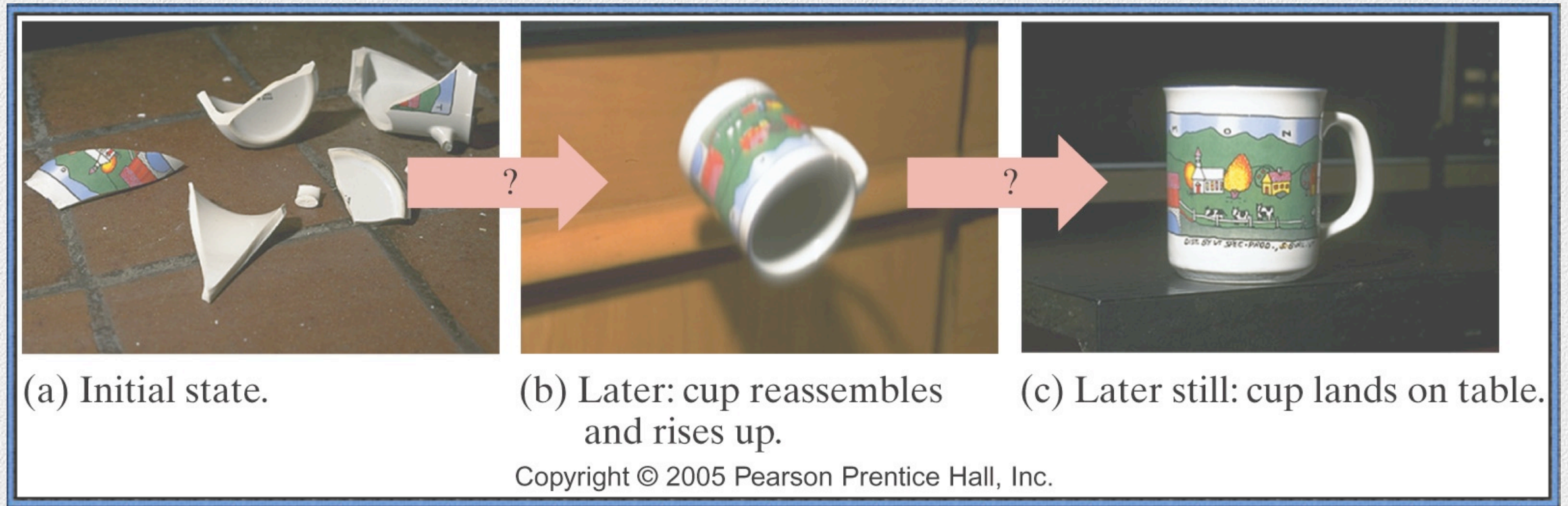
$$\Delta U = Q + W$$

- This is the law of conservation of energy, written in a form useful to systems involving heat transfer.

13-3 Thermal Equilibrium and the Zeroth Law of Thermodynamics

- Two objects placed in thermal contact will eventually come to the same temperature. When they do, we say they are in thermal equilibrium.
- The zeroth law of thermodynamics says that if two objects are each in equilibrium with a third object, they are also in thermal equilibrium with each other.

15-4 The Second Law of Thermodynamics – Introduction



- The absence of the process illustrated above indicates that conservation of energy is not the whole story. If it were, movies run backwards would look perfectly normal to us!

15-7 Entropy and the Second Law of Thermodynamics

- Definition of the change in entropy S when an amount of heat Q is added:

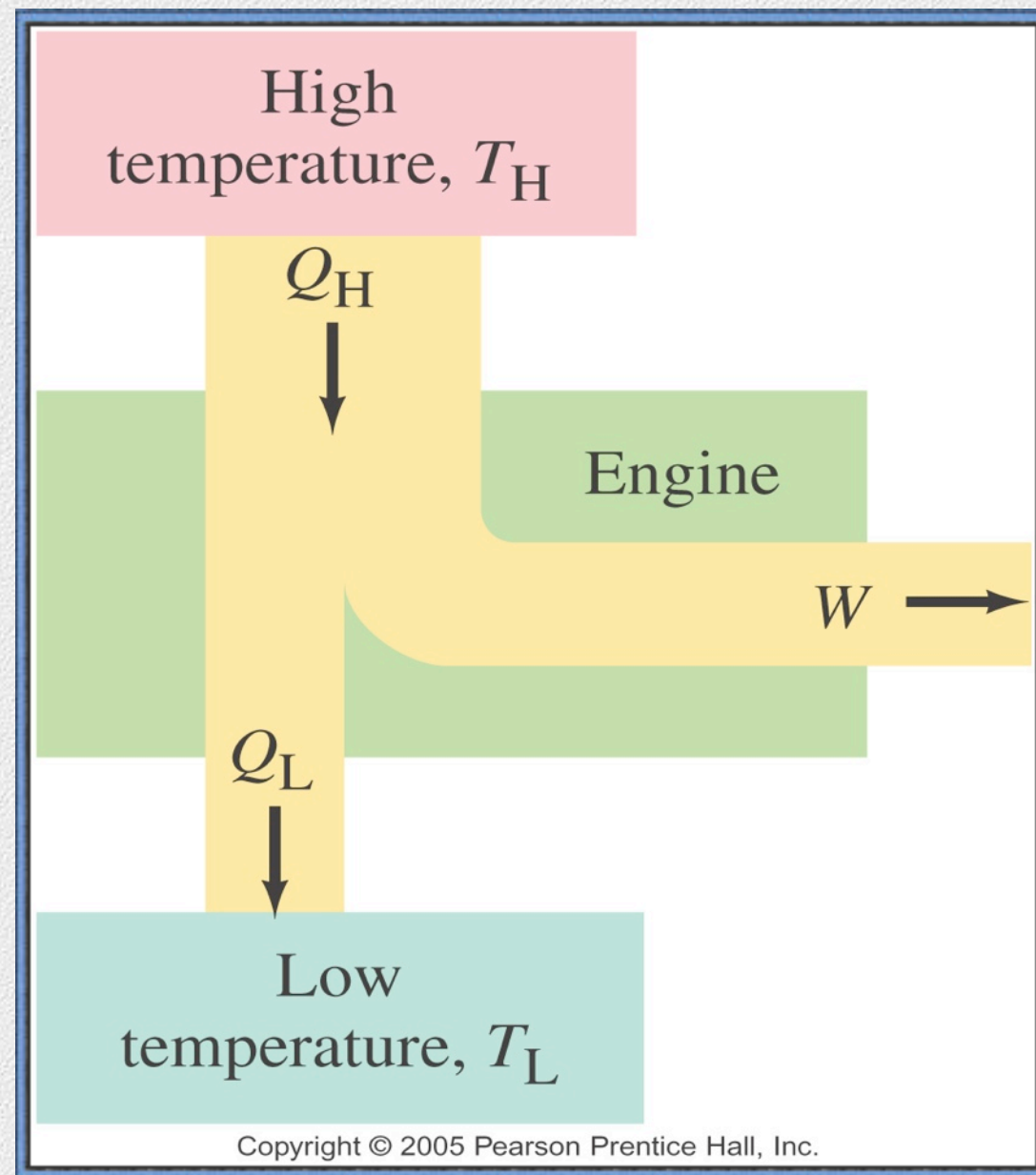
$$\Delta S = \frac{Q}{T}$$

- Another statement of the second law of thermodynamics:
- The total entropy of an isolated system never decreases.

15-5 Heat Engines

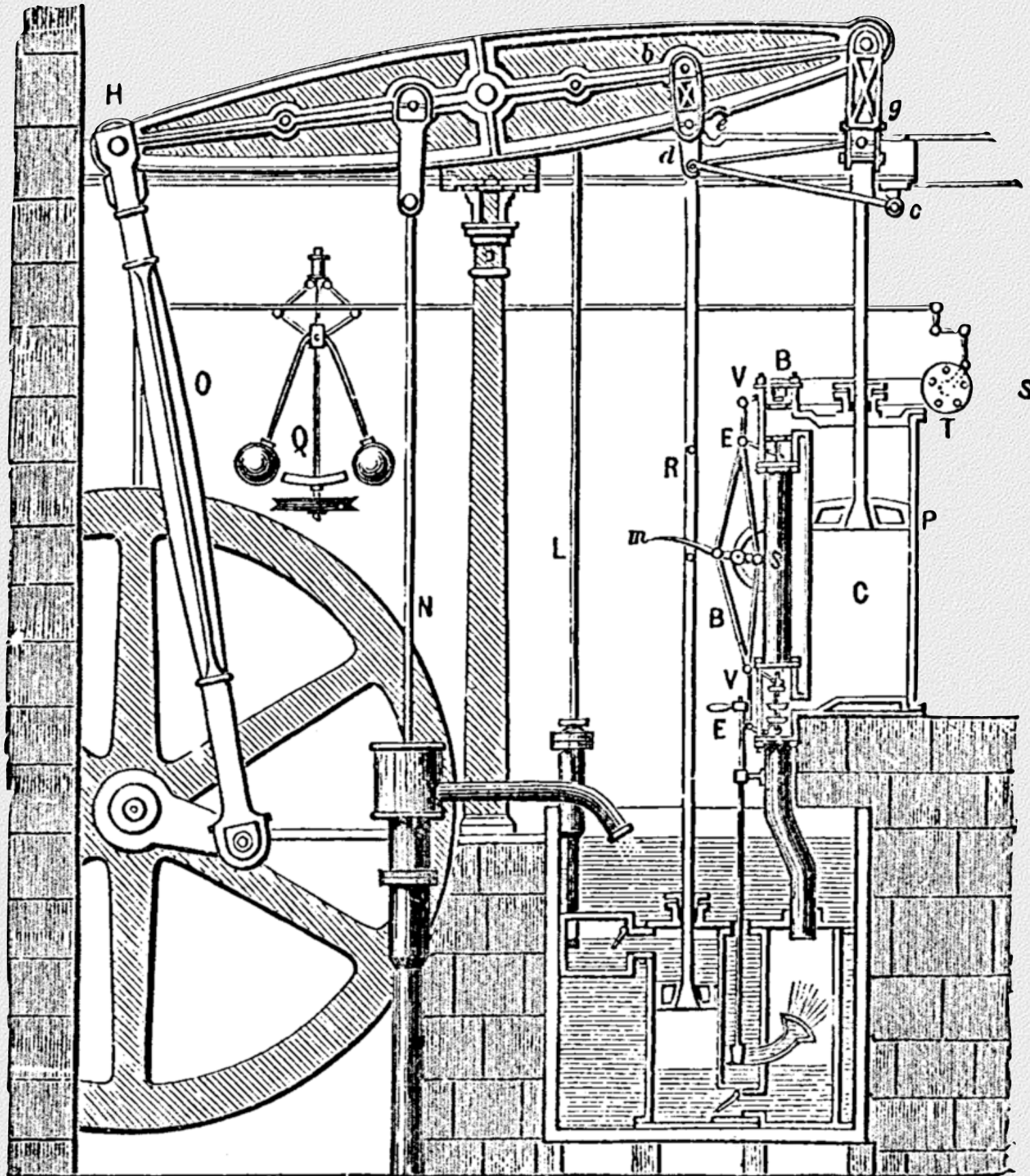
- It is easy to produce thermal energy using work, but how does one produce work using thermal energy?

This is a heat engine; mechanical energy can be obtained from thermal energy only when heat can flow from a higher temperature to a lower temperature.



15-5 Heat Engines

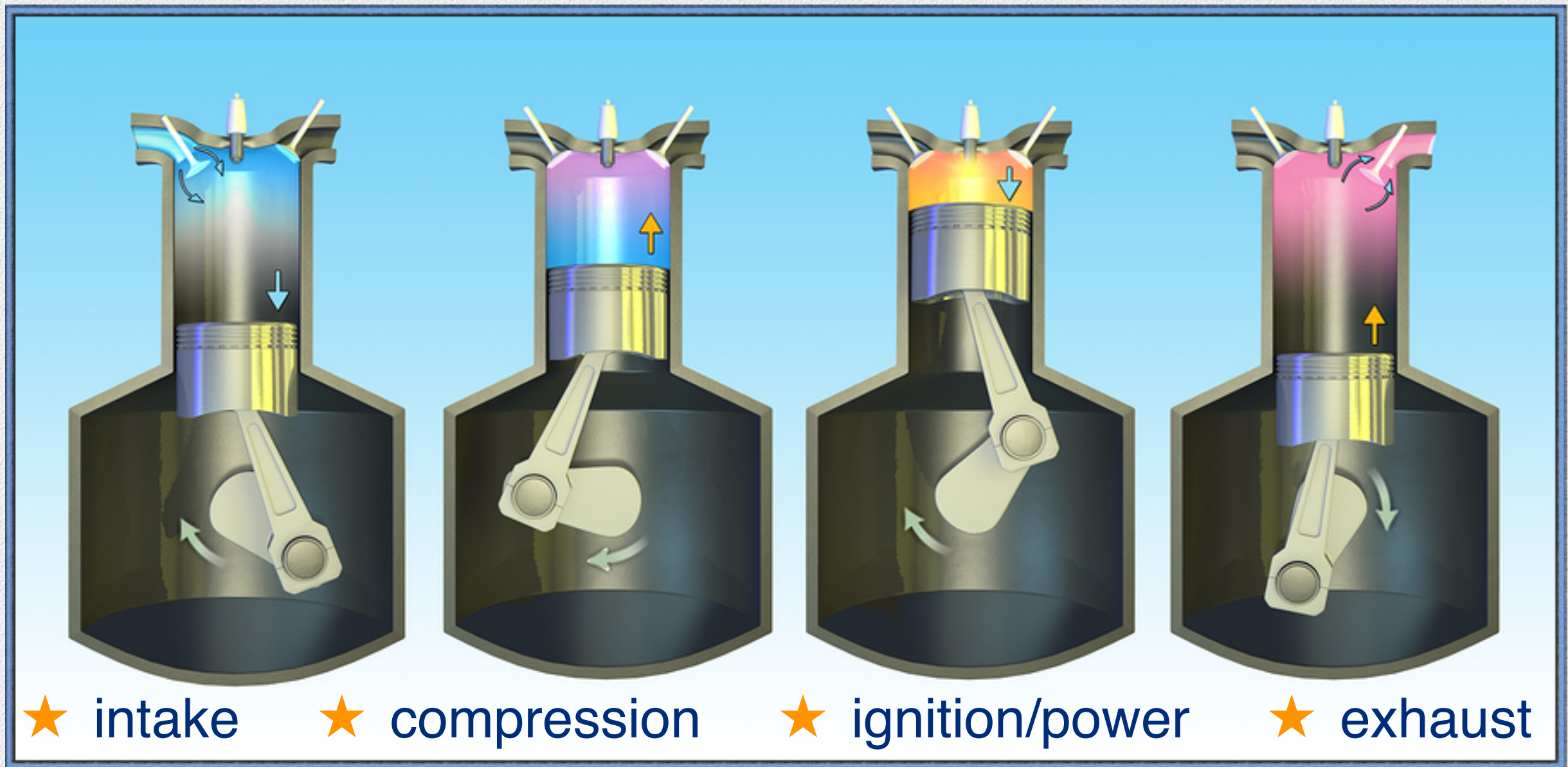
- We will discuss only engines that run in a repeating cycle; the change in internal energy over a cycle is zero, as the system returns to its initial state.
- The high temperature reservoir transfers an amount of heat Q_H to the engine, where part of it is transformed into work W and the rest, Q_L , is exhausted to the lower temperature reservoir.



File:SteamEngine Boulton&Watt 1784.png - Wikimedia Foundation

- A steam engine is one type of heat engine.

15-5 Heat Engines



- The internal combustion engine is a type of heat engine as well.

15-5 Heat Engines

- Why does a heat engine need a temperature difference?
- Otherwise the work done on the system in one part of the cycle will be equal to the work done by the system in another part, and the net work will be zero.

15-5 Heat Engines

- The efficiency of the heat engine is the ratio of the work done to the heat input:

$$e = \frac{W}{Q_H}$$

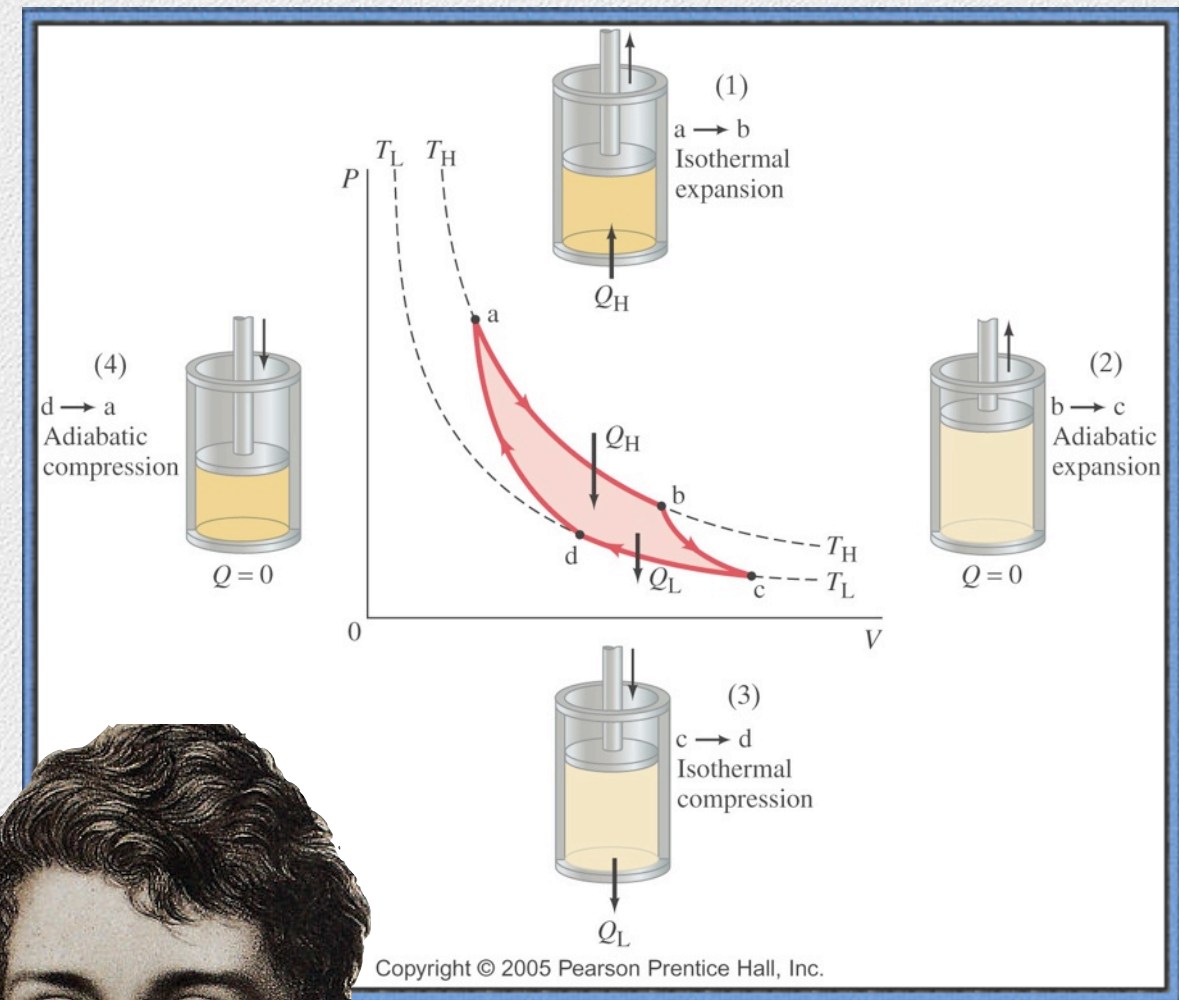
- Using conservation of energy to eliminate W , we find:

$$e = \frac{Q_H - Q_L}{Q_H}$$

$$e = 1 - \frac{Q_L}{Q_H}$$

● The Carnot engine was created to examine the efficiency of a heat engine. It is idealized, as it has no friction. Each leg of its cycle is reversible. The Carnot cycle consists of:

- Isothermal expansion
- Adiabatic expansion
- Isothermal compression
- Adiabatic compression



Nicolas Léonard Sadi Carnot
1796-1832

File:Sadi Carnot 01.jpg - Wikimedia Foundation

15-5 Heat Engines

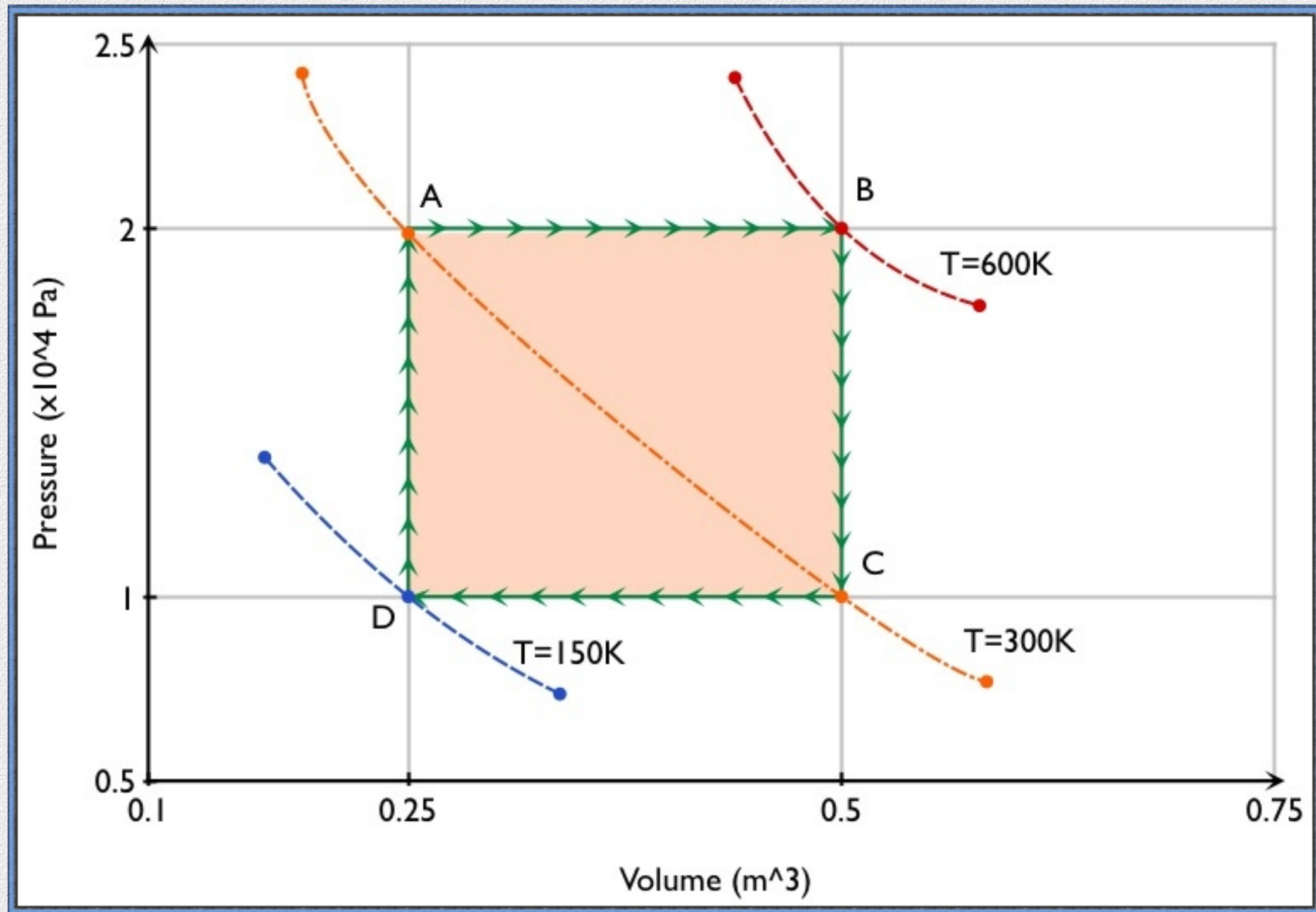
- For an ideal reversible engine, the efficiency can be written in terms of the temperature:

$$e_{ideal} = \frac{T_H - T_L}{T_H}$$

$$e_{ideal} = 1 - \frac{T_L}{T_H}$$

- From this we see that 100% efficiency can be achieved only if the cold reservoir is at absolute zero, which is impossible.
- Real engines have some frictional losses; the best achieve 60-80% of the Carnot value of efficiency.

P-V graph



Work Done In A Thermodynamic Cycle

- Applying the first law of thermodynamics. Two moles of an ideal gas are used following a thermodynamic cycle of four steps.
- $T_C = 150 \text{ K}$, $T_M = 300 \text{ K}$, $T_H = 600 \text{ K}$
- $P_a = 2.00 \times 10^4 \text{ Pa}$, $P_b = 1.00 \times 10^4 \text{ Pa}$
- $V_a = 0.250 \text{ m}^3$, $V_b = 0.500 \text{ m}^3$
- Find the work done, the heat lost or absorbed, and the internal energy of the system for the thermodynamic paths; AB, BC, CD, DA and ABCDA.

Energy Heat Work

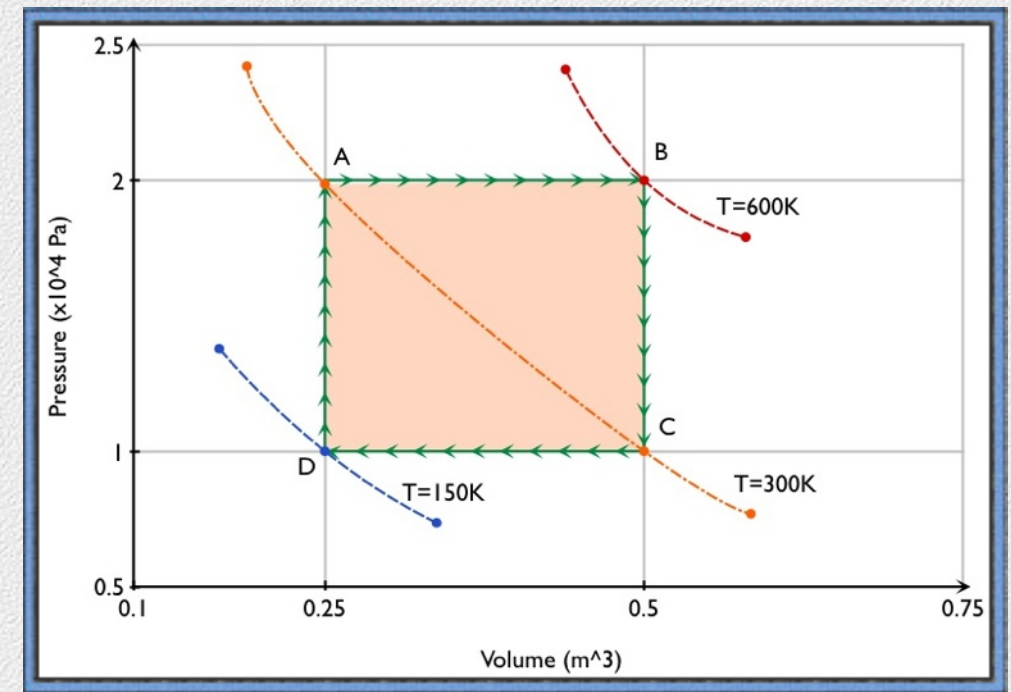
$$\Delta U = Q + W \quad Q = nC_p\Delta T \quad W = P\Delta V$$

	ΔU	Q	W
A			
B			
C			
D			
cycle			

- Work is still $F \times D$ $P = F/A$
- $Q = m c \Delta T$ was used for mass $Q = nC\Delta T$ is a molar version
- Conservation of Energy

Path A

	ΔU	Q	W
A	7,480 J	12,480 J	-5000 J



a. The work done by the expanding gas along the path AB is

$$\begin{aligned}
 W &= p\Delta V \\
 W_{AB} &= p_A(V_B - V_A) \\
 &= \left(2.00 \times 10^4 \frac{\text{N}}{\text{m}^2}\right)(0.500 \text{ m}^3 - 0.250 \text{ m}^3) \\
 &= 5.00 \times 10^3 \text{ J}
 \end{aligned}$$

The heat absorbed by the gas along path AB is

$$\begin{aligned}
 Q &= nC_p\Delta T \\
 Q_{AB} &= nC_p(T_B - T_A) \\
 &= (2 \text{ moles})\left(4.97 \frac{\text{cal}}{\text{mole K}}\right)(600 \text{ K} - 300 \text{ K}) \\
 &= (2.98 \times 10^3 \text{ cal})\left(\frac{4.185 \text{ J}}{1 \text{ cal}}\right) \\
 &= 1.25 \times 10^4 \text{ J}
 \end{aligned}$$

The change in internal energy along path AB , found from the first law equation 17.31, is

$$\begin{aligned}
 \Delta U_{AB} &= Q_{AB} - W_{AB} \\
 &= 1.25 \times 10^4 \text{ J} - 5.00 \times 10^3 \text{ J} \\
 &= 7.50 \times 10^3 \text{ J}
 \end{aligned}$$

- Work done ON the system is negative when the gas expands
- molar specific heat at a constant pressure
- $C_p = 20.8 \text{ J/ (mole K)}$
- Heat added is positive when the temperature rises

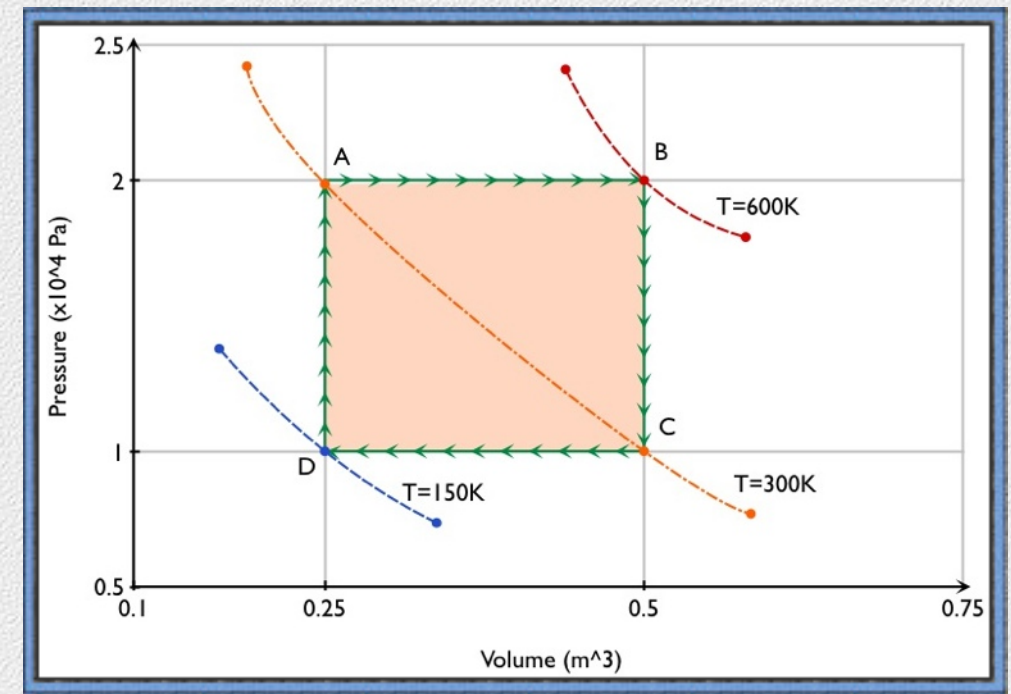
$$\Delta U = Q + W$$

$$Q = nC_p\Delta T$$

$$W = P\Delta V$$

Path B

	ΔU	Q	W
B	- 7,500 J	- 7,500 J	0 J



b. The work done along path BC is

$$W = p\Delta V$$

$$W_{BC} = p(V_B - V_B) = 0$$

$$= 0$$

The heat lost along path BC is

$$Q_{BC} = nC_V\Delta T = nC_V(T_{AC} - T_B)$$

$$= (2 \text{ moles}) \left(2.98 \frac{\text{cal}}{\text{mole K}} \right) (300 \text{ K} - 600 \text{ K})$$

$$= (-1.79 \times 10^3 \text{ cal}) \left(\frac{4.185 \text{ J}}{1 \text{ cal}} \right)$$

$$= -7.50 \times 10^3 \text{ J}$$

The loss of internal energy in dropping from 600 K at B to 300 K at C is found from the first law as

$$\Delta U_{BC} = Q_{BC} - W_{BC}$$

$$= -7.50 \times 10^3 \text{ J} - 0$$

$$= -7.50 \times 10^3 \text{ J}$$

- No work is done if the volume doesn't change
- molar specific heat at a constant volume
- $C_V = 12.5 \text{ J/ (mole K)}$
- Heat added is negative (think: heat is removed) when the temperature goes down

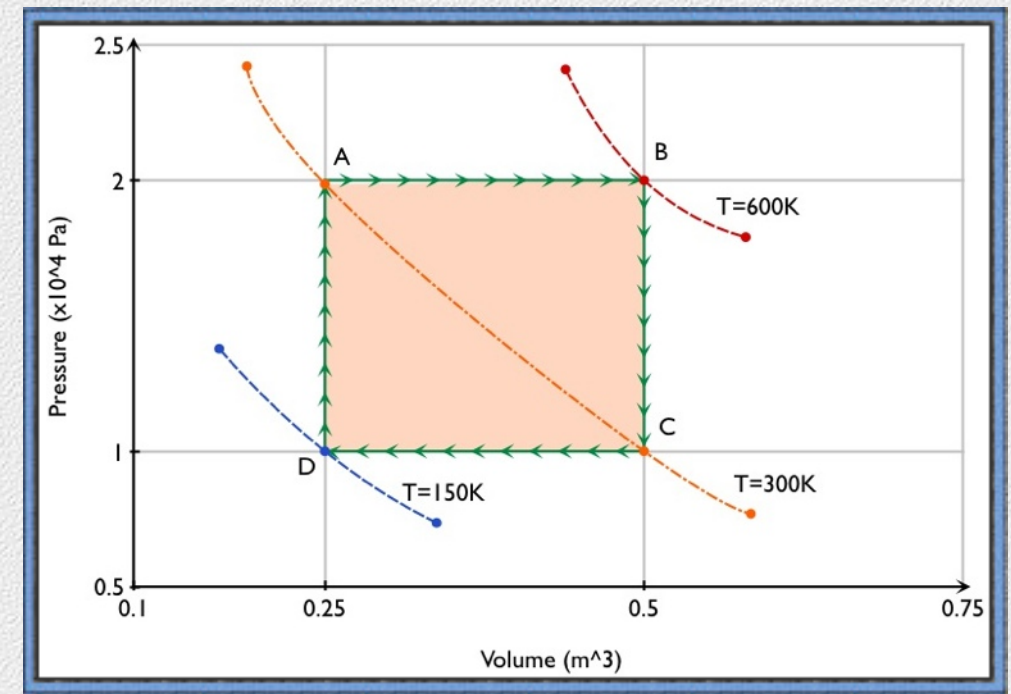
$$\Delta U = Q + W$$

$$Q = nC_p\Delta T$$

$$W = P\Delta V$$

Path C

	ΔU	Q	W
C	- 3740 J	- 6240 J	2500 J



c. The work done during the compression along the path CD is

$$\begin{aligned}
 W_{CD} &= p\Delta V = p_D(V_A - V_B) \\
 &= \left(1.00 \times 10^4 \frac{\text{N}}{\text{m}^2}\right)(0.250 \text{ m}^3 - 0.500 \text{ m}^3) \\
 &= -2.50 \times 10^3 \text{ J}
 \end{aligned}$$

The heat lost along the path CD is

$$\begin{aligned}
 Q_{CD} &= nC_p\Delta T = nC_p(T_D - T_{AC}) \\
 &= (2 \text{ moles})\left(4.97 \frac{\text{cal}}{\text{mole K}}\right)(150 \text{ K} - 300 \text{ K}) \\
 &= -6.24 \times 10^3 \text{ J}
 \end{aligned}$$

The change in internal energy along the path CD , found from the first law, is

$$\begin{aligned}
 \Delta U_{CD} &= Q_{CD} - W_{CD} \\
 &= -6.24 \times 10^3 \text{ J} - (-2.50 \times 10^3 \text{ J}) \\
 &= -3.74 \times 10^3 \text{ J}
 \end{aligned}$$

- Work done ON the system is positive when the volume decreases
- molar specific heat at a constant pressure
- $C_p = 20.8 \text{ J/ (mole K)}$
- Heat added is negative when the temperature goes down

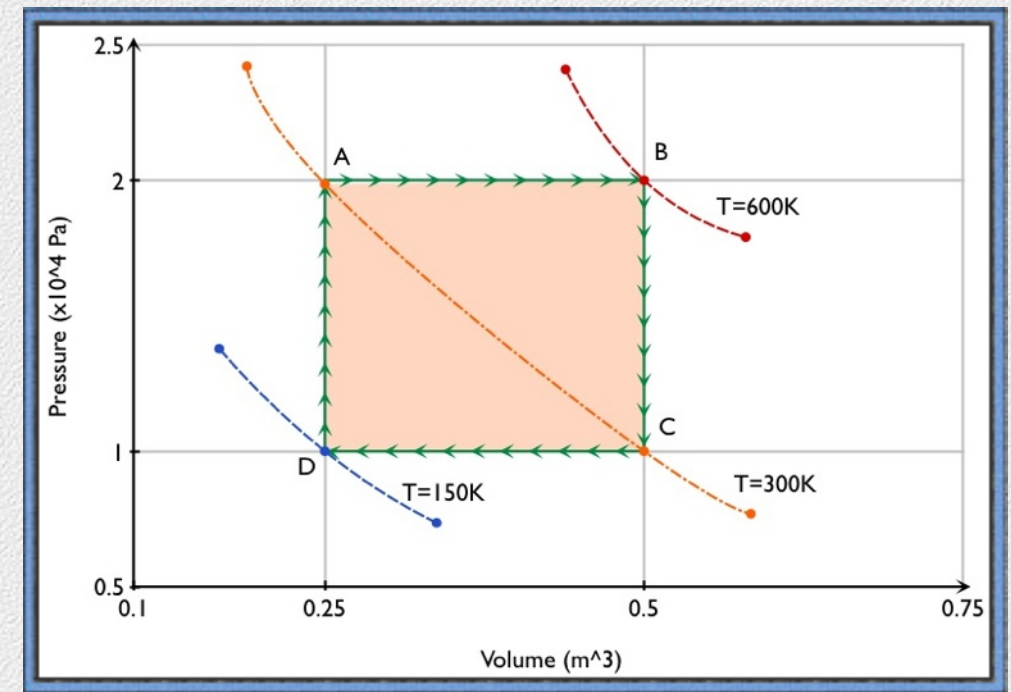
$$\Delta U = Q + W$$

$$Q = nC_p\Delta T$$

$$W = P\Delta V$$

Path D

	ΔU	Q	W
D	3,750 J	3,750 J	0 J



d. The work done along the path DA is

$$W_{DA} = p\Delta V = p(V_A - V_A) = 0$$

The heat added along the path DA is

$$\begin{aligned} Q_{DA} &= nC_v\Delta T = nC_v(T_{AC} - T_D) \\ &= (2 \text{ moles})\left(2.98 \frac{\text{cal}}{\text{mole K}}\right)(300 \text{ K} - 150 \text{ K}) \\ &= (8.94 \text{ cal})\left(4.185 \frac{\text{J}}{\text{cal}}\right) \\ &= 3.74 \times 10^3 \text{ J} \end{aligned}$$

The change in internal energy along DA is

$$\begin{aligned} \Delta U_{DA} &= Q_{DA} - W_{DA} \\ &= 3.74 \times 10^3 \text{ J} \end{aligned}$$

- No work is done if the volume doesn't change
- molar specific heat at a constant volume
- $C_v = 12.5 \text{ J/ (mole K)}$
- Heat added is positive when the temperature rises

$$\Delta U = Q + W$$

$$Q = nC_p\Delta T$$

$$W = P\Delta V$$

	ΔU	Q	W
A	7,480 J	12,480 J	-5,000 J
B	- 7,500 J	- 7,500 J	0 J
C	- 3,740 J	- 6,240 J	2,500 J
D	3,750 J	3,750 J	0 J
cycle	0 J	2,500 J	- 2,500 J

- The machine is back to its original state $\therefore \Delta U = 0$
- 2,500 Joules of work was done by the machine in this cycle.