Chapter 10

Thermal Physics

Thermal Physics

- Thermal physics is the study of
  - Temperature
  - Heat
  - How these affect matter

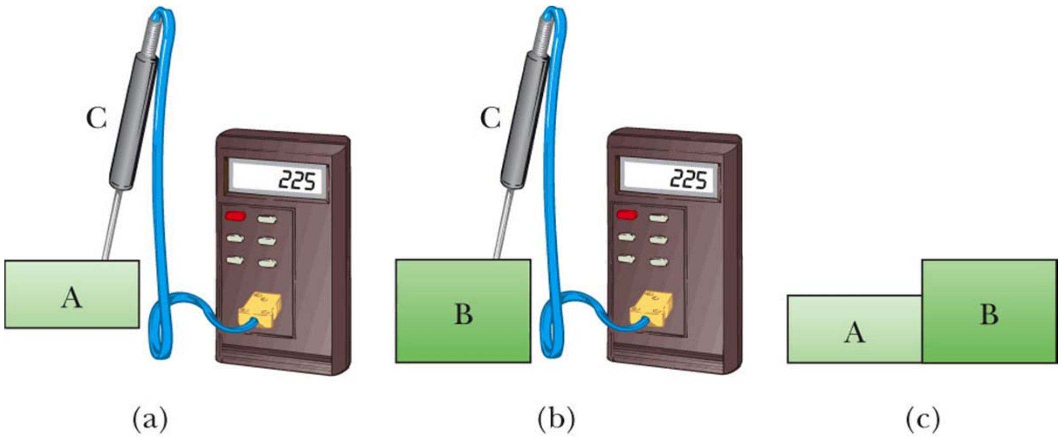
Thermal Physics, cont

- Descriptions require definitions of temperature, heat and internal energy
- Heat leads to changes in internal energy and therefore to changes in temperature
- Gases are critical in harnessing internal energy to do work

Heat

- The process by which energy is exchanged between objects because of temperature differences is called *heat*
- Objects are in *thermal contact* if energy can be exchanged between them
- *Thermal equilibrium* exists when two objects in thermal contact with each other cease to exchange energy

Zeroth Law of Thermodynamics



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- If objects A and B are separately in thermal equilibrium with a third object, C, then A and B are in thermal equilibrium with each other
  - Object C could be the thermometer
- Allows a definition of temperature

Temperature from the Zeroth Law

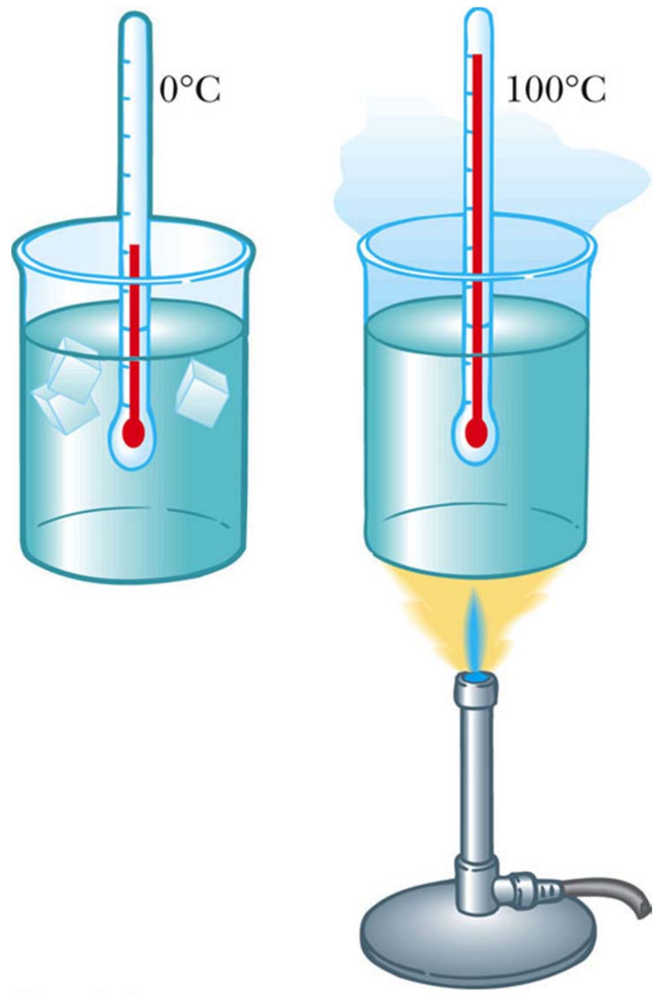
- *Temperature* is the property that determines whether or not an object is in thermal equilibrium with other objects
- Two objects in thermal equilibrium with each other are at the *same temperature*

Thermometers

- Used to measure the temperature of an object or a system
- Make use of physical properties that change with temperature
- Many physical properties can be used
  - Volume of a liquid
  - Length of a solid
  - Pressure of a gas held at constant volume
  - Volume of a gas held at constant pressure
  - Electric resistance of a conductor
  - Color of a very hot object

Thermometers, cont

- A mercury thermometer is an example of a common thermometer
- The level of the mercury rises due to thermal expansion
- Temperature can be defined by the height of the mercury column



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Temperature Scales

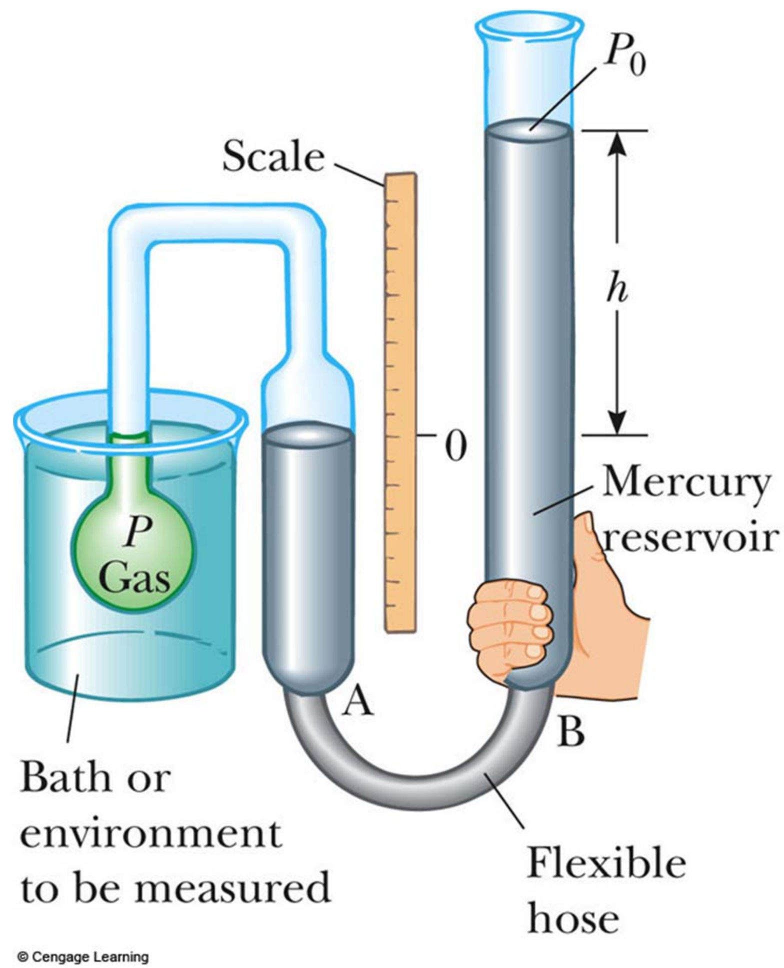
- Thermometers can be calibrated by placing them in thermal contact with an environment that remains at constant temperature
  - Environment could be mixture of ice and water in thermal equilibrium
  - Also commonly used is water and steam in thermal equilibrium

Celsius Scale

- Temperature of an ice-water mixture is defined as 0º C
  - This is the *freezing point* of water
- Temperature of a water-steam mixture is defined as 100º C
  - This is the *boiling point* of water
- Distance between these points is divided into 100 segments or degrees

Gas Thermometer

- Temperature readings are nearly independent of the gas
- Pressure varies with temperature when maintaining a constant volume

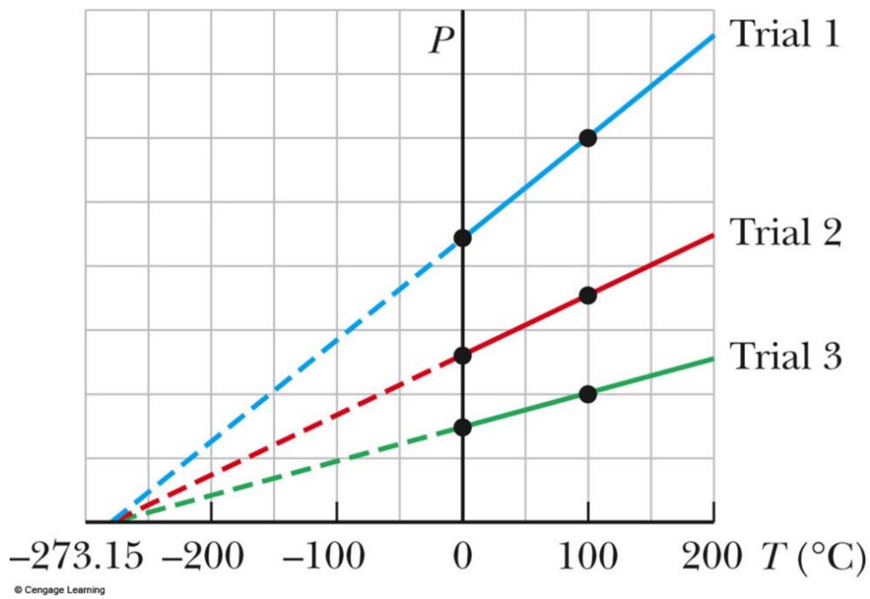


Kelvin Scale

- When the pressure of a gas goes to zero, its temperature is –273.15º C
- This temperature is called *absolute zero*
- This is the zero point of the Kelvin scale
  - –273.15º C = 0 K
- To convert: $T_C = T - 273.15$
  - The size of the degree in the Kelvin scale is the same as the size of a Celsius degree

Pressure-Temperature Graph

- All gases extrapolate to the same temperature at zero pressure
- This temperature is *absolute zero*



Modern Definition of Kelvin Scale

- Defined in terms of two points
  - Agreed upon by International Committee on Weights and Measures in 1954
- First point is absolute zero
- Second point is the *triple point* of water
  - Triple point is the single point where water can exist as solid, liquid, and gas in equilibrium
  - Single temperature and pressure
  - Occurs at 0.01º C and P = 4.58 mm Hg

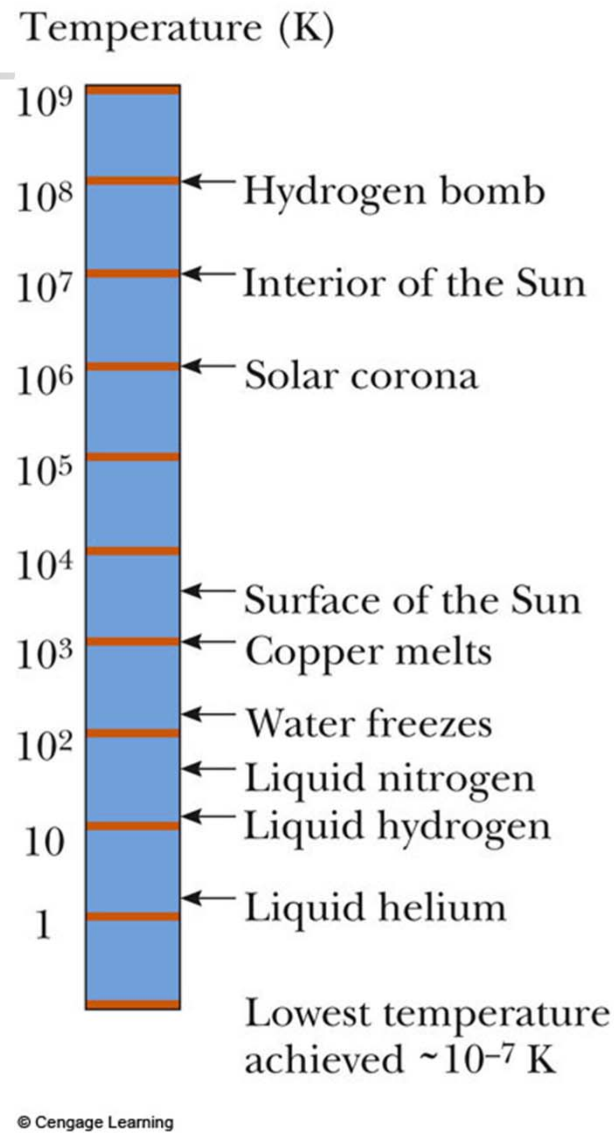
Modern Definition of Kelvin Scale, cont

- The temperature of the triple point on the Kelvin scale is 273.16 K
- Therefore, the current definition of of the Kelvin is defined as

  1/273.16 of the temperature of the triple point of water

Some Kelvin Temperatures

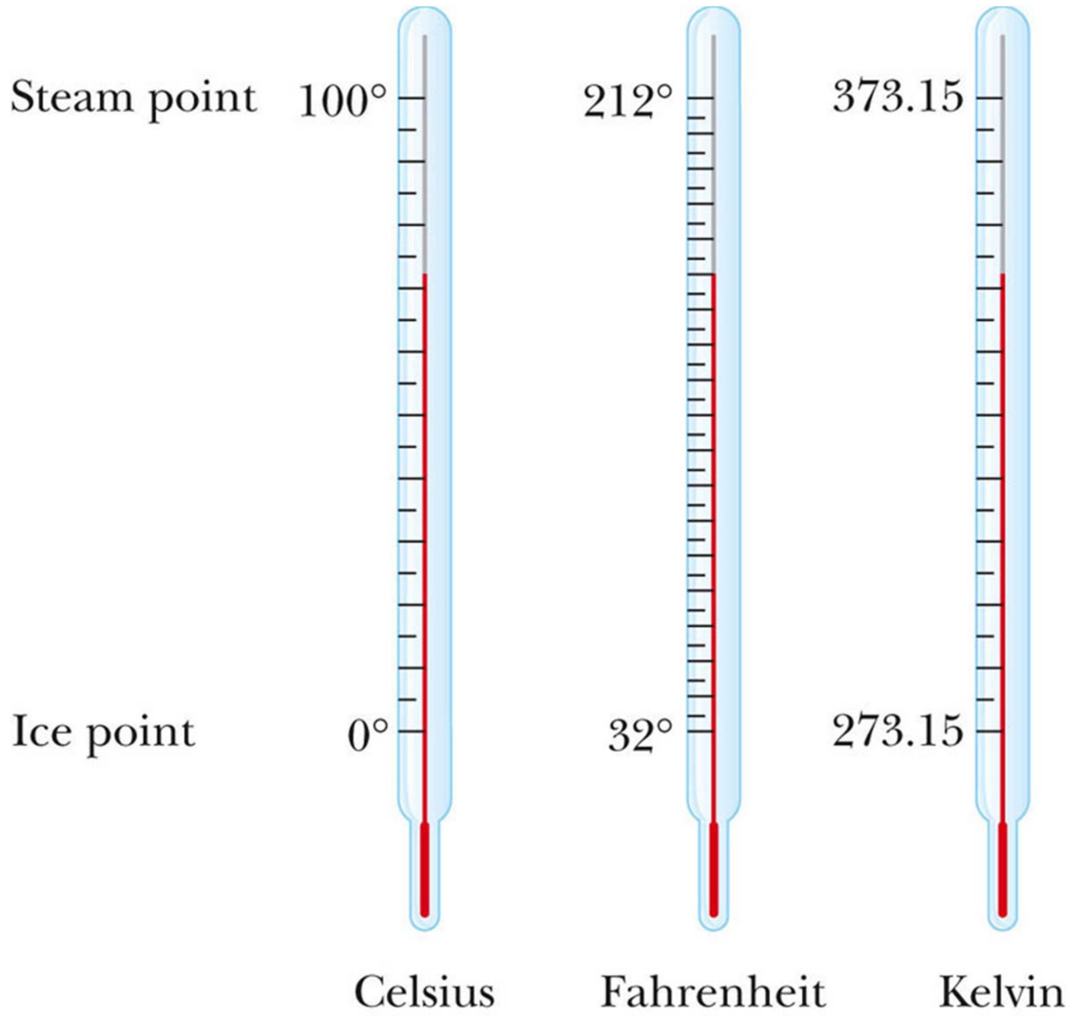
- Some representative Kelvin temperatures
- Note, this scale is logarithmic
- Absolute zero has never been reached



Fahrenheit Scales

- Most common scale used in the US
- Temperature of the freezing point is 32º
- Temperature of the boiling point is 212º
- 180 divisions between the points

Comparing Temperature Scales



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Converting Among Temperature Scales

$$T_C = T_K - 273.15$$

$$T_F = \frac{9}{5}T_C + 32$$

$$T_C = \frac{5}{9}\left(T_F - 32\right)$$

$$\Delta T_F = \frac{9}{5}\Delta T_C$$

Thermal Expansion

- The thermal expansion of an object is a consequence of the change in the average separation between its constituent atoms or molecules
- At ordinary temperatures, molecules vibrate with a small amplitude
- As temperature increases, the amplitude increases
  - This causes the overall object as a whole to expand

Linear Expansion

- For small changes in temperature

$$\Delta L = \alpha\, L_o\, \Delta T \;\; or \;\; L - L_o = \alpha\, L_o \left(T - T_o\right)$$

- α, the coefficient of linear expansion, depends on the material
  - See table 10.1
  - These are average coefficients, they can vary somewhat with temperature

Average Coefficients of Expansion for Some Materials Near Room Temperature

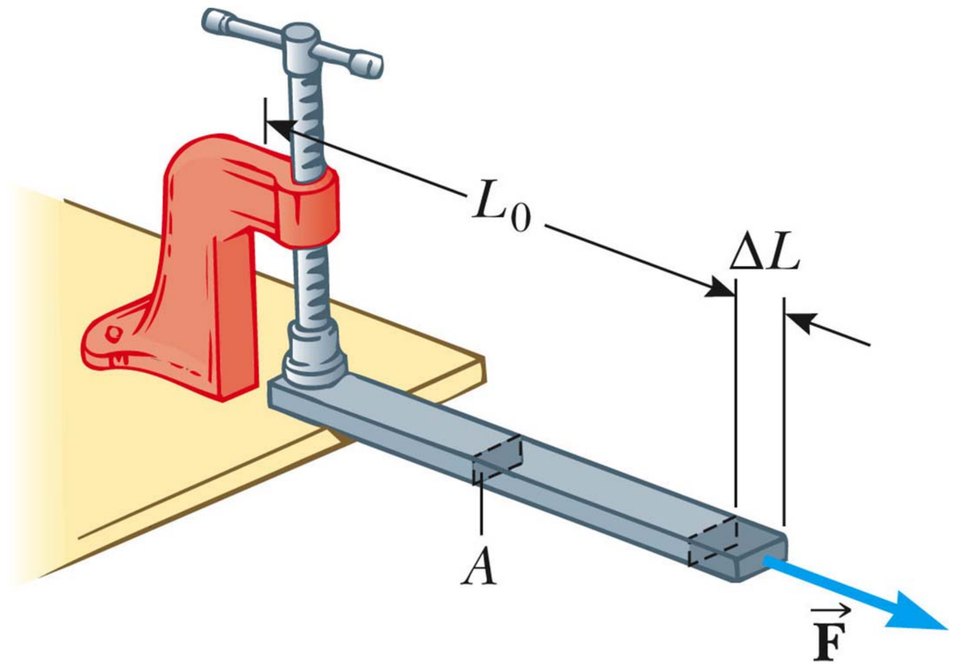
Material	Average Coefficient of Linear Expansion $[(^\circ C)^{-1}]$	Material	Average Coefficient of Volume Expansion $[(^\circ C)^{-1}]$
Aluminum	24×10^{-6}	Ethyl alcohol	1.12×10^{-4}
Brass and bronze	19×10^{-6}	Benzene	1.24×10^{-4}
Copper	17×10^{-6}	Acetone	1.5×10^{-4}
Glass (ordinary)	9×10^{-6}	Glycerin	4.85×10^{-4}
Glass (Pyrex®)	3.2×10^{-6}	Mercury	1.82×10^{-4}
Lead	29×10^{-6}	Turpentine	9.0×10^{-4}
Steel	11×10^{-6}	Gasoline	9.6×10^{-4}
Invar (Ni-Fe alloy)	0.9×10^{-6}	Air	3.67×10^{-3}
Concrete	12×10^{-6}	Helium	3.665×10^{-3}

Elastic Properties

- *Stress* is the force per unit area(σ =F/A) causing the deformation
- *Strain* is a measure of the amount of deformation ($\varepsilon = \Delta L/L$)
- The *elastic modulus Y* is the constant of proportionality between stress and strain
  - For sufficiently small stresses, the stress is directly proportional to the strain
  - The constant of proportionality depends on the material being deformed and the nature of the deformation

Young's Modulus: Elasticity in Length

- Tensile stress is the ratio of the external force to the cross-sectional area
  - Tensile is because the bar is under tension
- The elastic modulus is called *Young's modulus*



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Young's Modulus, cont.

- SI units of stress are Pascals, Pa
  - 1 Pa = 1 N/m^2
- The tensile strain is the ratio of the change in length to the original length
  - Strain is dimensionless

$$\frac{F}{A} = Y\frac{\Delta L}{L_o}$$

Elastic Modulus

Values for the Elastic Modulus

Substance	Young's Modulus (Pa)	Shear Modulus (Pa)	Bulk Modulus (Pa)
Aluminum	7.0×10^{10}	2.5×10^{10}	7.0×10^{10}
Bone	1.8×10^{10}	8.0×10^{10}	—
Brass	9.1×10^{10}	3.5×10^{10}	6.1×10^{10}
Copper	11×10^{10}	4.2×10^{10}	14×10^{10}
Steel	20×10^{10}	8.4×10^{10}	16×10^{10}
Tugsten	35×10^{10}	14×10^{10}	20×10^{10}
Glass	$6.5\text{–}7.8 \times 10^{10}$	$2.6\text{–}3.2 \times 10^{10}$	$5.0\text{–}5.5 \times 10^{10}$
Quartz	5.6×10^{10}	2.6×10^{10}	2.7×10^{10}
Rib Cartilage	1.2×10^{7}	—	—
Rubber	0.1×10^{7}	—	—
Tendon	2×10^{7}	—	—
Water	—	—	0.21×10^{10}
Mercury	—	—	2.8×10^{10}

Example 1

A 20 cm long rod with a diameter of 0.30 cm is loaded with a mass of 500 kg. If the length of the rod increases to 20.65 cm, determine the (a) stress and strain at this load, and (c) the modulus of elasticity.

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Thermal stress

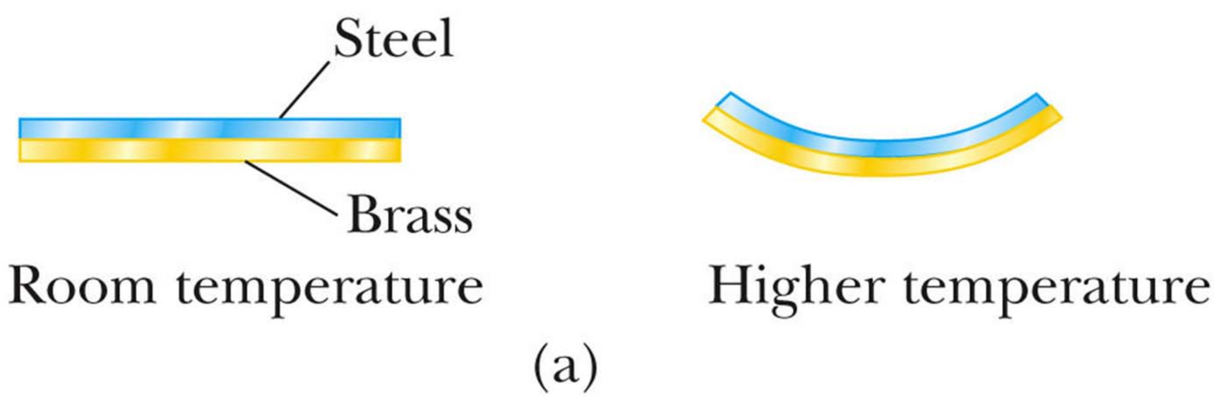
$$\sigma_{thermal} = Y\Delta L/L_0 = Y(L_o \alpha \Delta T)/L_0 = Y\,\alpha \Delta T$$

Example 2

A steel railroad track has a length of 30 km when the temperature is 0^0C. (a) What is the change is its length on a hot day when the temperature is 40.0^0C? (b) Suppose the track is nailed down so that it can't expand. What stress results in the track due to the temperature change?

$\alpha = 11x10^{-6}/^0C$, $Y = 2x10^{11}Pa$

Applications of Thermal Expansion – Bimetallic Strip



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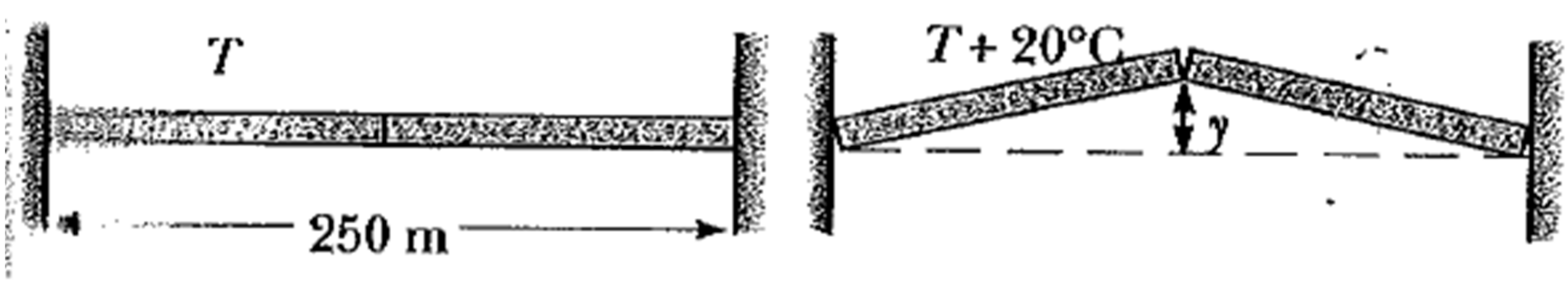
- Thermostats
  - Use a *bimetallic strip*
  - Two metals expand differently
    - Since they have different coefficients of expansion

Example 3

Two concrete spans of a 250 m long bridge are place end to end so that no room is allowed for expansion. If the temperature increases by 20ºC, what is the height y to which the spans rise when they buckle?



Area Expansion

In two dimensions :

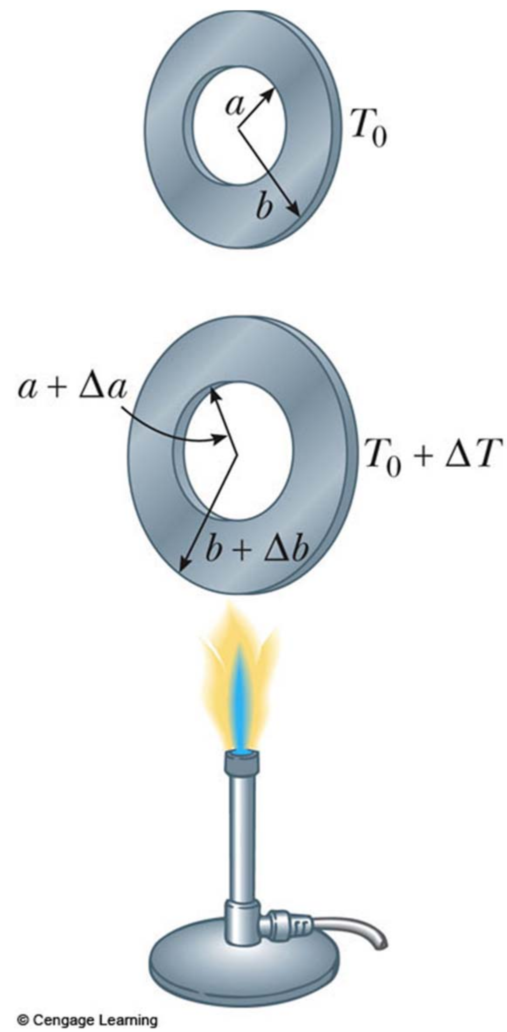
$$A = L^2 = (L_o + \alpha L_o \Delta T)^2 = A_0 + 2A_0 \alpha \Delta T$$

then

$$\Delta A = A - A_o = \gamma A_o \Delta t,$$

$$\gamma = 2\alpha$$

- γ is the coefficient of area expansion



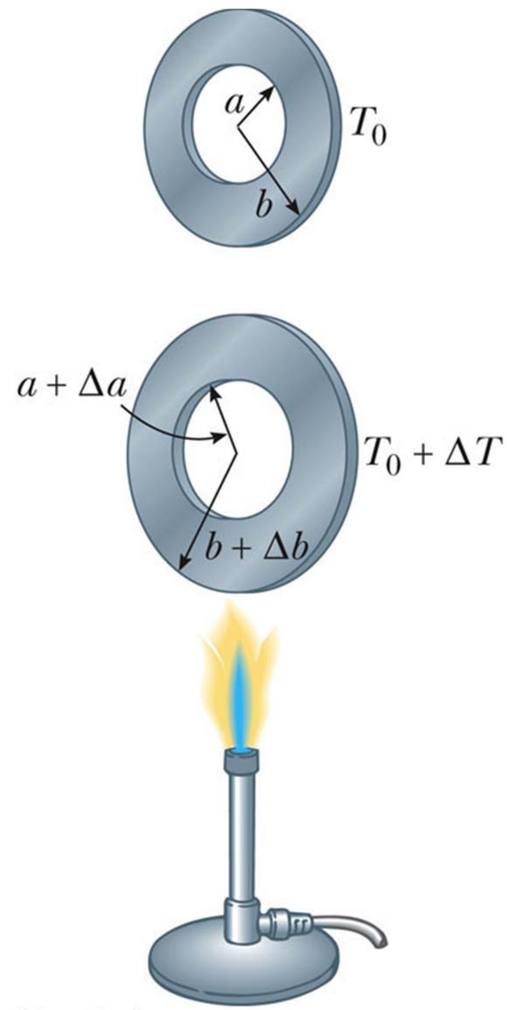
Area Expansion

- Two dimensions expand according to

$$\Delta A = A - A_o = \gamma\, A_o\, \Delta t,$$

$$\gamma = 2\alpha$$

  - γ is the coefficient of area expansion



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Example 4

In the continuous-casting process, steel sheets 2.0 m wide and 10 m long are produced at a temperature of 872^0C. What is the area of the sheet once it has cooled to 20^0? ($\alpha = 12x10^{-6}/^0C$)

Example 5

A horizontal steel-beam is rigidly connected to two vertical steel girders. If the beam was installed when the temperature was 70^0K, what stress is developed in the beam when the temperature increases to 115^0K? b. Will it fracture? The Young's modulus for the steel is 200×10^9Pa and the ultimate strength of the steel is 170×10^6 Pa, $\alpha = 12 \times 10^{-6}/^0C$

Volume Expansion

- Three dimensions expand

$$\Delta V = \beta V_o \Delta t$$

$$\text{for solids, } \beta = 3\alpha$$

  - For liquids, the coefficient of volume expansion is given in the table

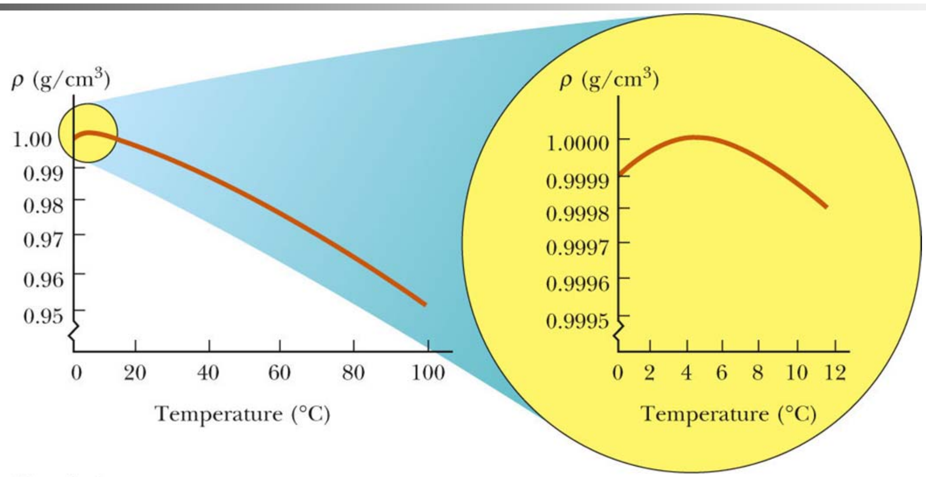
Example 6

The density of mercury is 13600 kg/m^3 at 0^0C. What would be its density at 166^0C? $\beta=0.95x10^{-3}/^0C$

More Applications of Thermal Expansion

- Pyrex Glass
  - Thermal stresses are smaller than for ordinary glass
- Sea levels
  - Warming the oceans will increase the volume of the oceans

Unusual Behavior of Water



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- As the temperature of water increases from 0ºC to 4 ºC, it contracts and its density increases
- Above 4 ºC, water exhibits the expected expansion with increasing temperature
- Maximum density of water is 1000 kg/m^3 at 4 ºC

Ideal Gas

- If a gas is placed in a container
  - It expands to fill the container uniformly
  - Its pressure will depend on the
    - Size of the container
    - The temperature
    - The amount of gas
- The pressure, volume, temperature and amount of gas are related to each other by an *equation of state*

Ideal Gas, cont

- The equation of state can be complicated
- It can be simplified if the gas is maintained at a low pressure
- Most gases at room temperature and pressure behave approximately as an ideal gas

Characteristics of an Ideal Gas

- Collection of atoms or molecules that move randomly
- Exert no long-range force on one another
- Each particle is individually point-like
  - Occupying a negligible volume

Moles

- It’s convenient to express the amount of gas in a given volume in terms of the number of moles, n

$$n = \frac{\text{mass}}{\text{molar mass}}$$

- One mole is the amount of the substance that contains as many particles as there are atoms in 12 g of carbon-12

Periodic Table of the Elements

- Metals (main-group)
- Metals (transition)
- Metals (inner transition)
- Metalloids
- Nonmetals

MAIN–GROUP ELEMENTS (IA–IIA) | TRANSITION ELEMENTS (IIIB–IIB) | MAIN–GROUP ELEMENTS (IIIA–VIIIA)

Period	IA (1)	IIA (2)	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIIIB (8)	VIIIB (9)	VIIIB (10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	VIIIA (18)
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)	112 Uub (277)	113	114 Uug (285)	115	116 Uuh (289)	117	118 Uuo

INNER TRANSITION ELEMENTS

Period															
6	Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
7	Actinides	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Source: Davis, M. and Davis, R., Fundamentals of Chemical Reaction Engineering, McGraw-Hill, 2003.

Example

A cylindrical glass of water (H_2O) has a radius of 4.5 cm and a height of 12 cm. The density of water 1 g/cm^3. How many moles of water molecules are contained in the glass? R = 8.31J/mol

Avogadro's Number

- The number of particles in a mole is called *Avogadro's Number*
  - $N_A = 6.02 \times 10^{23}$ particles / mole
  - Defined so that 12 g of carbon contains N_A atoms
- The mass of an individual atom can be calculated:

$$m_{atom} = \frac{\text{molar mass}}{N_A}$$

Avogadro's Number and Masses

- The mass in grams of one Avogadro's number of an element is numerically the same as the mass of one atom of the element, expressed in atomic mass units, u
- Carbon has a mass of 12 u
  - 12 g of carbon consists of N_A atoms of carbon
- Holds for molecules, also

Ideal Gas Law

- PV = n R T
  - R is the *Universal Gas Constant*
  - R = 8.31 J / mol·K
  - R = 0.0821 L· atm / mol·K
  - Is the equation of state for an ideal gas

Example

In the portable oxygen system the oxygen (O_2) is contained in a cylinder whose volume is 0.0028 m^3. A full cylinder has an absolute pressure of 148 $x10^5$ Pa when the temperature is 23^0C. Find the mass (in kg) of oxygen in the cylinder.

Example

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Ideal Gas Law, Alternative Version

- $P V = N k_B T$
  - k_B is *Boltzmann's Constant*
  - $k_B = R / N_A = 1.38 \times 10^{-23}$ J/ K
  - N is the total number of molecules
- $n = N / N_A$
  - n is the number of moles
  - N is the number of molecules

Kinetic Theory of Gases – Assumptions

- The number of molecules in the gas is large and the average separation between them is large compared to their dimensions
- The molecules obey Newton’s laws of motion, but as a whole they move randomly

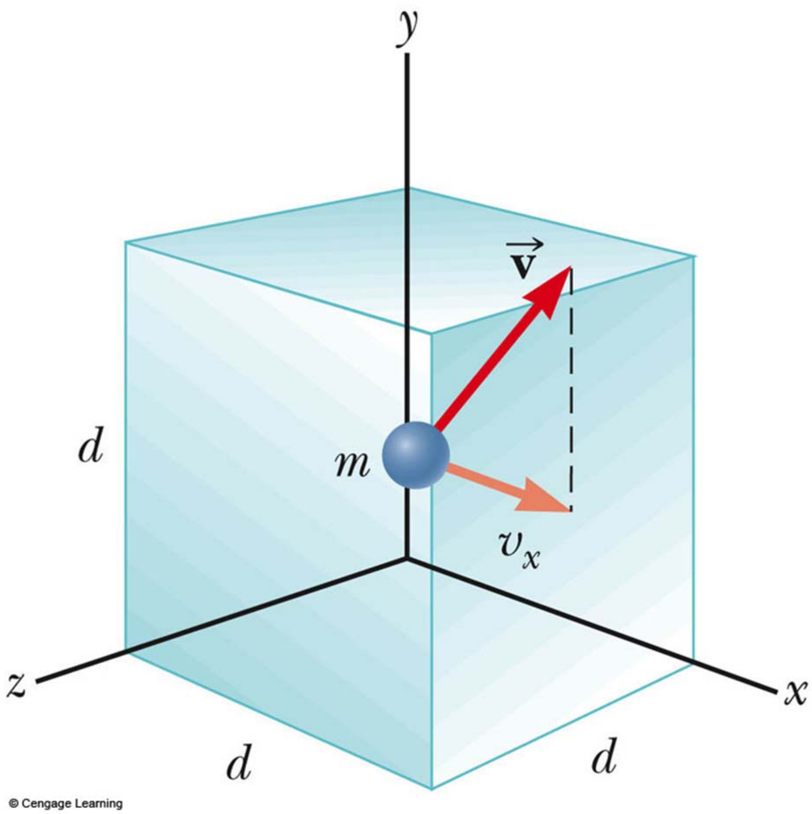
Kinetic Theory of Gases – Assumptions, cont.

- The molecules interact only by short-range forces during elastic collisions
- The molecules make elastic collisions with the walls
- The gas under consideration is a pure substance, all the molecules are identical

Pressure of an Ideal Gas

- The pressure is proportional to the number of molecules per unit volume and to the average translational kinetic energy of a molecule

$$P = \frac{3}{2}\left(\frac{N}{V}\right)\left(\frac{1}{2}mv^2\right)$$



Pressure, cont

- The pressure is proportional to the number of molecules per unit volume and to the average translational kinetic energy of the molecule
- Pressure can be increased by
  - Increasing the number of molecules per unit volume in the container
  - Increasing the average translational kinetic energy of the molecules
    - Increasing the temperature of the gas

Molecular Interpretation of Temperature

- Temperature is proportional to the average kinetic energy of the molecules

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

- The total kinetic energy is proportional to the absolute temperature

$$\mathrm{KE}_{\mathrm{total}} = \frac{3}{2}\mathrm{nRT}$$

Internal Energy

- In a monatomic gas, the KE is the only type of energy the molecules can have

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

- U is the *internal energy* of the gas
- In a polyatomic gas, additional possibilities for contributions to the internal energy are rotational and vibrational energy in the molecules

Speed of the Molecules

- Expressed as the *root-mean-square* (rms) speed

$$v_{rms} = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{3 R T}{M}}$$

- At a given temperature, lighter molecules move faster, on average, than heavier ones
  - Lighter molecules can more easily reach escape speed from the earth

Some rms Speeds

TABLE 10.2

Some rms Speeds

Gas	Molar Mass (kg/mol)	v_{rms} at 20°C (m/s)
H_2	2.02×10^{-3}	1 902
He	4.0×10^{-3}	1 352
H_2O	18×10^{-3}	637
Ne	20.2×10^{-3}	602
N_2 and CO	28.0×10^{-3}	511
NO	30.0×10^{-3}	494
O_2	32.0×10^{-3}	478
CO_2	44.0×10^{-3}	408
SO_2	64.1×10^{-3}	338

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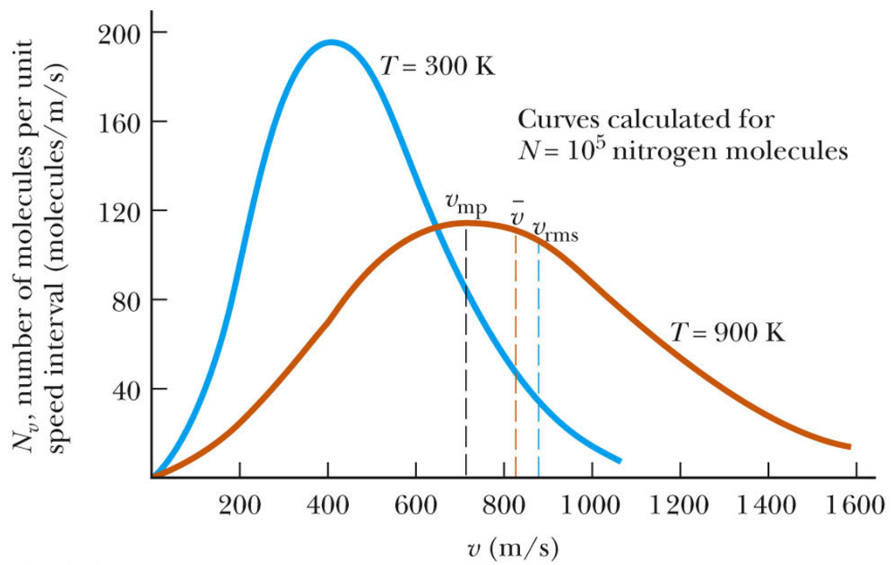
Maxwell Distribution

- A system of gas at a given temperature will exhibit a variety of speeds
- Three speeds are of interest:
  - Most probable
  - Average
  - rms



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Maxwell Distribution, cont

- For every gas, $v_{mp} < v_{av} < v_{rms}$
- As the temperature rises, these three speeds shift to the right
- The total area under the curve on the graph equals the total number of molecules