THE UNIVERSITY OF
NEW SOUTH WALES

Chapter 18
Temperature

Professor Michael Burton
School of Physics, UNSW

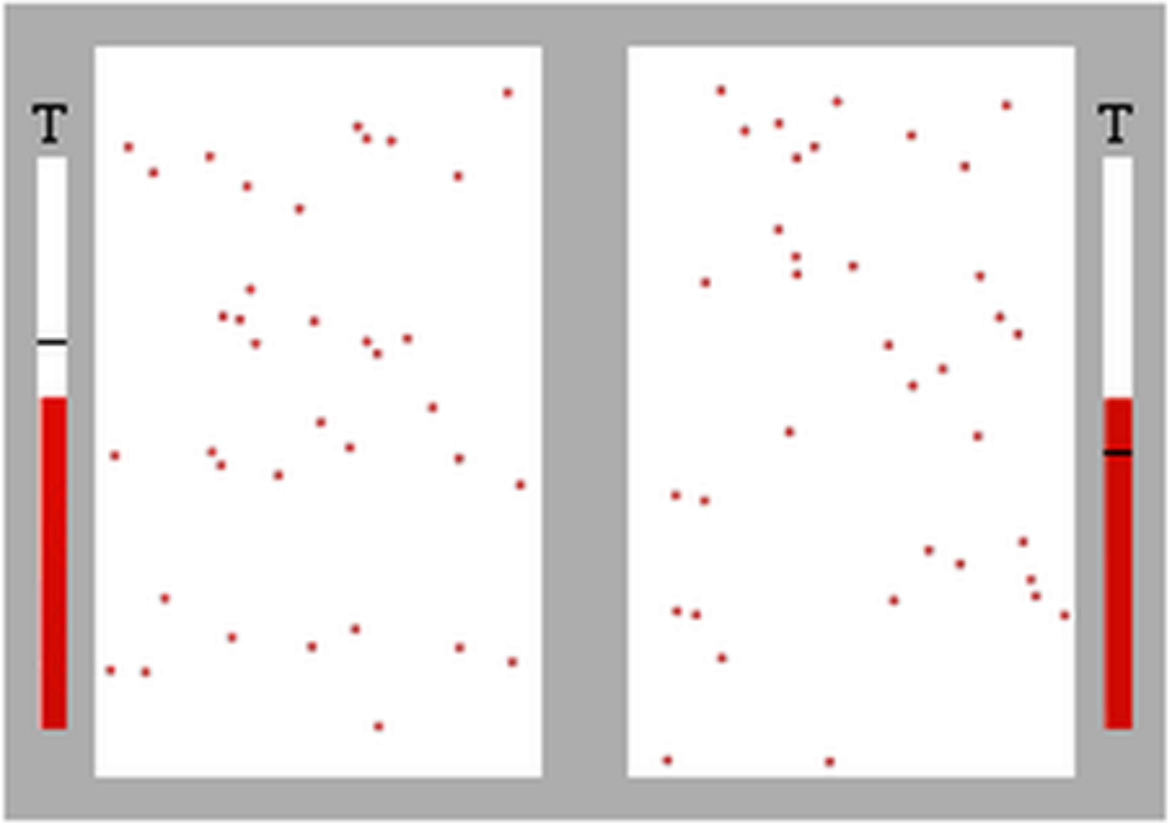
3 Phases of Water around 0°C!

Shutterstock.com/Bjorn Stefanson

Temperature

- We associate the concept of temperature with how hot or cold an objects feels
- Our senses provide us with a qualitative indication of temperature
  - Think about removing a metal ice tray and cardboard package from the freezer. Which is colder?
    - Neither! Senses unreliable.
- We need a technical definition of temperature

TDM03AN4: Thermal Contact & Thermal Equilibrium



30 seconds

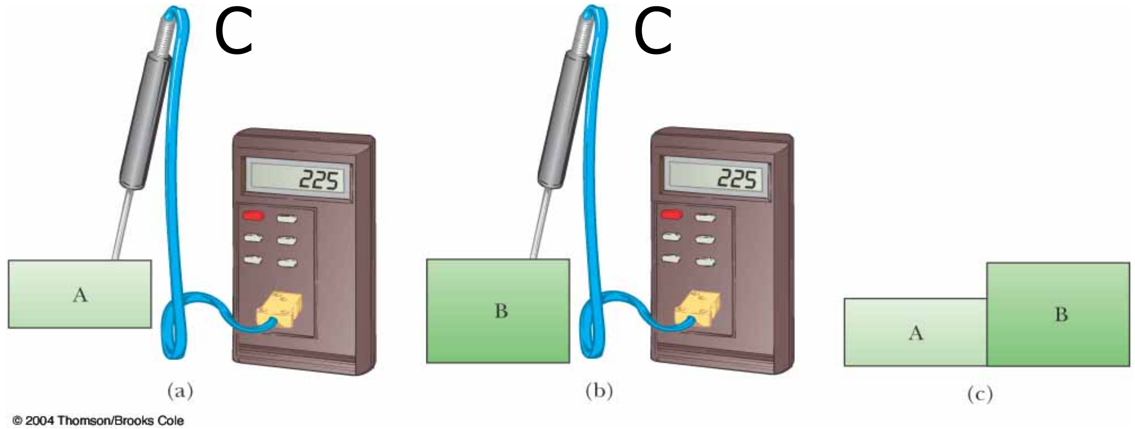
Thermal Contact

- Two objects are in **thermal contact** with each other if energy can be exchanged between them
  - in the form of heat or electromagnetic radiation
  - energy is exchanged due to a temperature difference

Thermal Equilibrium

- **Thermal equilibrium** occurs when two objects would not exchange any net energy if they were placed in thermal contact
  - Note: thermal contact does not have to also mean physical contact

Thermal Equilibrium



- Object C (thermometer) is placed in contact with A until they achieve thermal equilibrium
  - The reading on C is recorded
- Object C is then placed in contact with object B until they achieve thermal equilibrium
  - The reading on C is recorded again
- If these are the same, A and B are also in thermal equilibrium

The Zeroth Law of Thermodynamics

- 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
  - Since they are in thermal equilibrium with each other, there is no net energy exchanged between them
  - Can be used to define *Temperature*

Temperature

- **Temperature** can be thought of as the property that determines whether an object is in thermal equilibrium with other objects
- Two objects in thermal equilibrium with each other are at the same temperature
  - Conversely, if two objects have different temperatures, they are not in thermal equilibrium with each other

Quick Quiz: Two objects, with different sizes, masses, and temperatures, are placed in thermal contact. In which direction does the energy travel?

1. Energy travels from the larger object to the smaller object.

2. Energy travels from the object with more mass to the one with less mass.

3. Energy travels from the object at higher temperature to the object at lower temperature.

Thermometers

- A **thermometer** is a device that is used to measure the temperature of a system
- Thermometers are based on the principle that some physical property of a system changes as the system's temperature changes

Thermometers, cont

- These properties include:
  - The volume of a liquid
  - The dimensions of a solid
  - The pressure of a gas at a constant volume
  - The volume of a gas at a constant pressure
  - The electric resistance of a conductor
  - The colour of an object
- A temperature scale can be established on the basis of any of these physical properties

Thermometer, Liquid in Glass

- A common type of thermometer is a liquid-in-glass
- The material in the capillary tube expands as it is heated
- The liquid is usually mercury or alcohol

Calibrating a Thermometer

- A thermometer can be calibrated by placing it in contact with some natural systems that remain at constant temperature
- Common systems involve water
  - A mixture of ice and water at atmospheric pressure
    - Called the **ice point** of water
  - A mixture of water and steam in equilibrium
    - Called the **steam point** of water

Celsius Scale

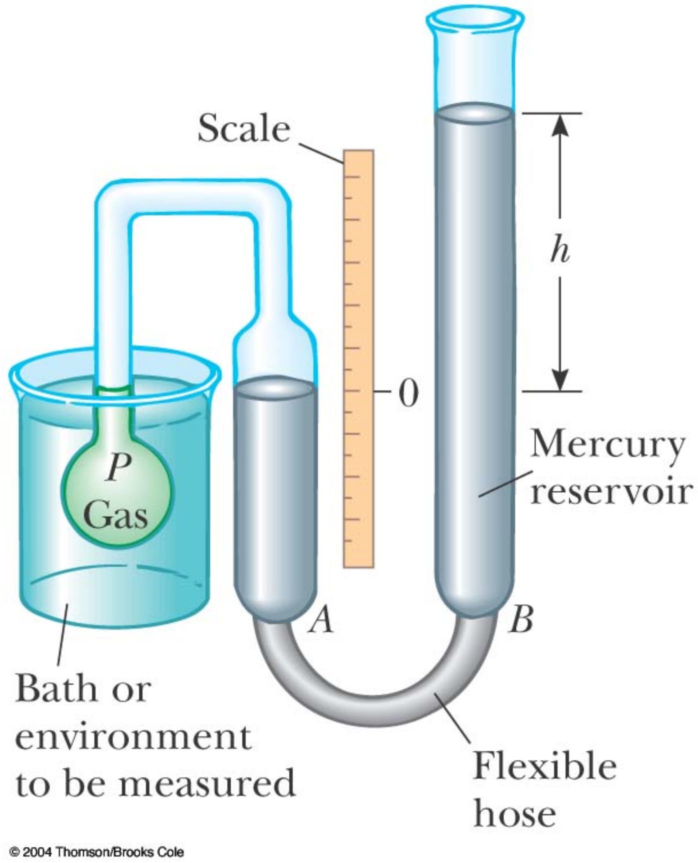
- The ice point of water is defined to be 0^{o} C
- The steam point of water is defined to be 100^{o} C
- The length of the column between these two points is divided into 100 increments, called *degrees*

Problems with Liquid-in-Glass Thermometers

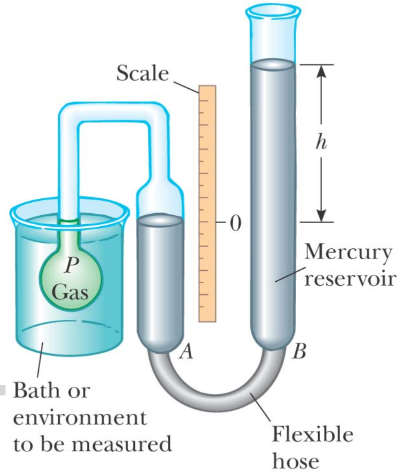
- An alcohol thermometer and a mercury thermometer may agree only at the calibration points
- The discrepancies between thermometers are especially large when the temperatures being measured are far from the calibration points
- Thermometers also have a limited range of values they can be used to measure
  - Mercury cannot be used under –30^{o} C (*why?*)
  - Alcohol cannot be used above 85^{o} C

Constant Volume Gas Thermometer

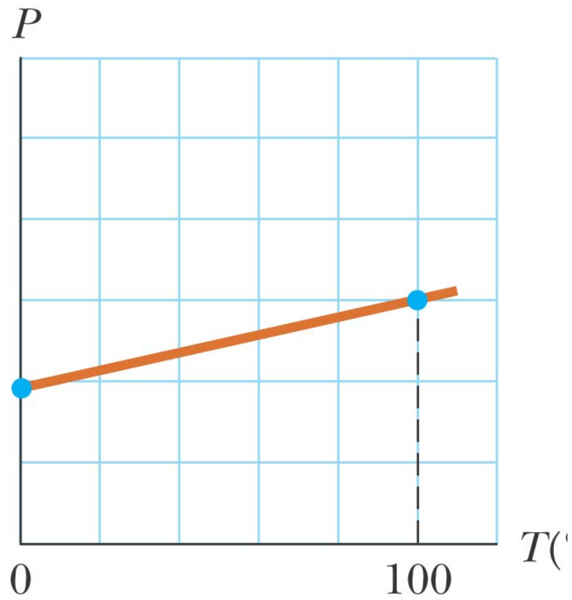
- The physical change exploited is the variation of pressure of a fixed volume gas as its temperature changes
- The volume of the gas is kept constant by raising or lowering the reservoir B to keep the mercury level at A constant



Constant Volume Gas Thermometer, cont

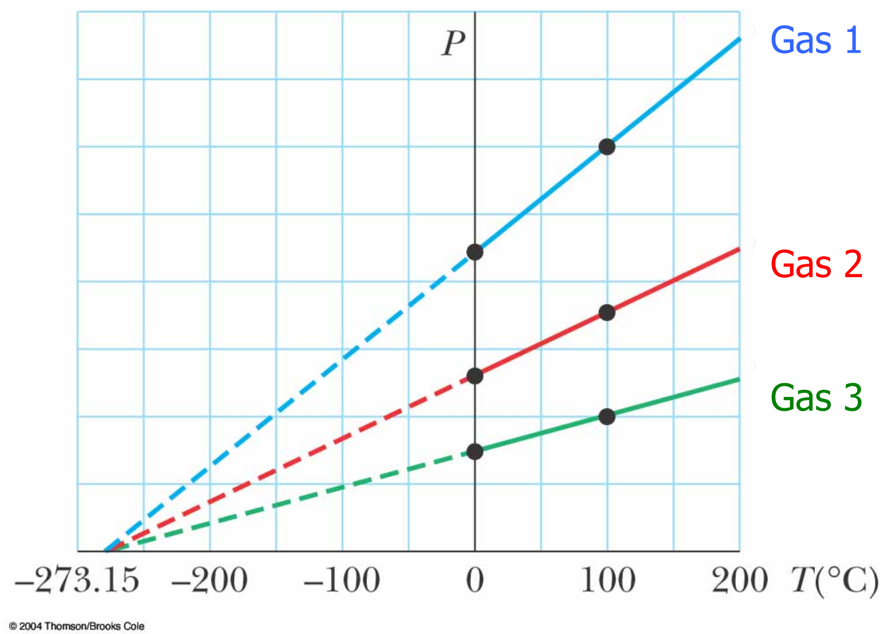


- The thermometer is calibrated by using an ice water bath and a steam water bath
- The pressures of the mercury under each situation are recorded
  - The volume is kept constant by adjusting the height *h*
- Let us consider an experiment using 3 different gases……



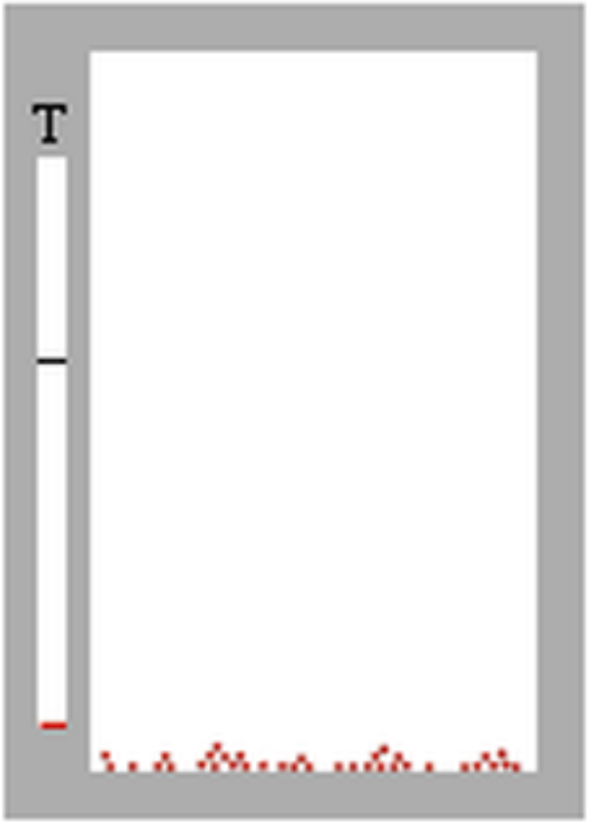
Absolute Zero

- The thermometer readings are virtually independent of the gas used
- If the lines for various gases are extended, the pressure is always zero when the temperature is –273.15° C
- This temperature is called **absolute zero**



TDM03AN7: Absolute Zero

-273°C ≡ 0K



34 seconds

Absolute Temperature Scale

- Absolute zero is used as the basis of the absolute temperature scale (in Kelvin)
  - The temperature at which a gas exerts no pressure
- The size of the degree on the absolute scale is the same as the size of the degree on the Celsius scale
- To convert:

  $T_C = T_K - 273.15$

  - Note: no degree (°) symbol for K

Comparison of Scales

- Celsius and Kelvin have the same size degrees, but different starting points

$$T_C = T_K - 273.15$$

- Celsius and Fahrenheit have different sized degrees and different starting points

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

Energy at Absolute Zero

- According to classical physics, the kinetic energy of the gas molecules would become zero at absolute zero
- The molecular motion would cease
  - Therefore, the molecules would settle out on the bottom of the container
- Quantum theory modifies this and shows some residual energy would remain
  - This energy is called the **zero-point** energy

Quick Quiz: Consider the following pairs of materials. Which pair represents two materials, one of which is twice as hot as the other?

1. boiling water at 100°C, a glass of water at 50°C
2. boiling water at 100°C, frozen methane at -50°C
3. an ice cube at -20°C, flames from a circus fire-eater at 233°C
4. none of these pairs

Hb1 & Hb2: Thermal Expansion of a Ball and Ring

- A ball will pass through a ring at room temperature but not if the ball is heated, or if the ring is cooled.

Thermal Expansion, Example

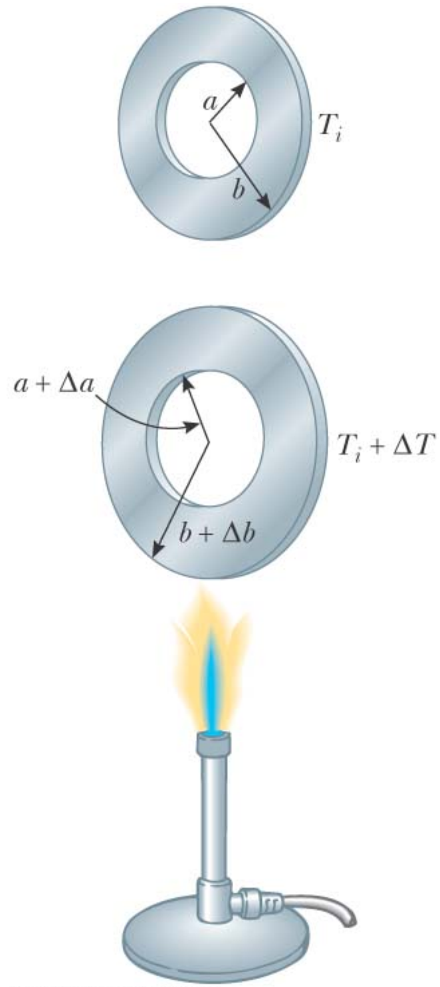
- Thermal expansion is the increase in the size of an object with an increase in its temperature
- Joints are used to allow room for “thermal expansion”
- The long, vertical joint is filled with a soft material that allows the wall to expand and contract as the temperature of the bricks changes

Thermal Expansion

- Thermal expansion is a consequence of the change in the average separation between the atoms in an object
- If the expansion is small relative to the original dimensions of the object, the change in any dimension is, to a good approximation, proportional to the first power of the change in temperature

Thermal Expansion, example

- As the washer shown at right is heated, all the dimensions will increase
  - Expansion exaggerated in this figure
- A cavity in a piece of material expands in the same way as if the cavity were filled with the material
- The expansion is linear; i.e. proportional to the change in temperature
- *See Active Figure 19.08*



Linear Expansion

- Assume object has initial length L_i
- The length increases by ΔL as the temperature changes by ΔT
- We define the **coefficient of linear expansion** as

$$\alpha = \frac{\Delta L / L_i}{\Delta T}$$

- A convenient form is $\Delta L = \alpha L_i \Delta T$
- Or, if final length L_f: $L_f - L_i = \alpha L_i (T_f - T_i)$
  - Coefficient of linear expansion, α, has units of $(^{o}C)^{-1}$

Average Expansion Coefficients for Some Materials Near Room Temperature

Material	Average Linear Expansion Coefficient $(\alpha)(°C)^{-1}$	Material	Average Volume Expansion Coefficient $(\beta)(°C)^{-1}$
Aluminum	24×10^{-6}	Alcohol, ethyl	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[a] at 0°C	3.67×10^{-3}
Concrete	12×10^{-6}	Helium[a]	3.665×10^{-3}

[a] Gases do not have a specific value for the volume expansion coefficient because the amount of expansion depends on the type of process through which the gas is taken. The values given here assume that the gas undergoes an expansion at constant pressure.

Hb4: Expansion of Metals

- The coefficient of linear expansion.
  The rod is heated, expands and moves the arrow on the scale.

Linear Expansion, final

- Some materials expand along one dimension, but contract along another as the temperature increases
- Since the linear dimensions change, it follows that the *surface area* and *volume* also change with a change in temperature

Volume Expansion

- The change in volume is proportional to the original volume and to the change in temperature
- $\Delta V = \beta V_i \, \Delta T$
  - β is the coefficient of volume expansion
  - For a solid, $\beta = 3\alpha$
    - For proof substitute the linear expansion formula for each dimension.
    - This assumes the material is isotropic, i.e. the same in all directions
    - *Exercise for the Student!*

Proof of Volume Expansion Formula

$$V_f = (L + \Delta L)^3 = \left[L_i(1 + \alpha \Delta T)\right]^3$$

$$V_f = L_i^3(1 + 3\alpha\Delta T + 3\alpha^2\Delta T^2 + \alpha^3\Delta T^3)$$

$V_f \approx V_i\ (1 + 3\alpha\Delta T)$ since ΔT is very small

Hence $\Delta V = V_f - V_i = 3\alpha V_i \Delta T$

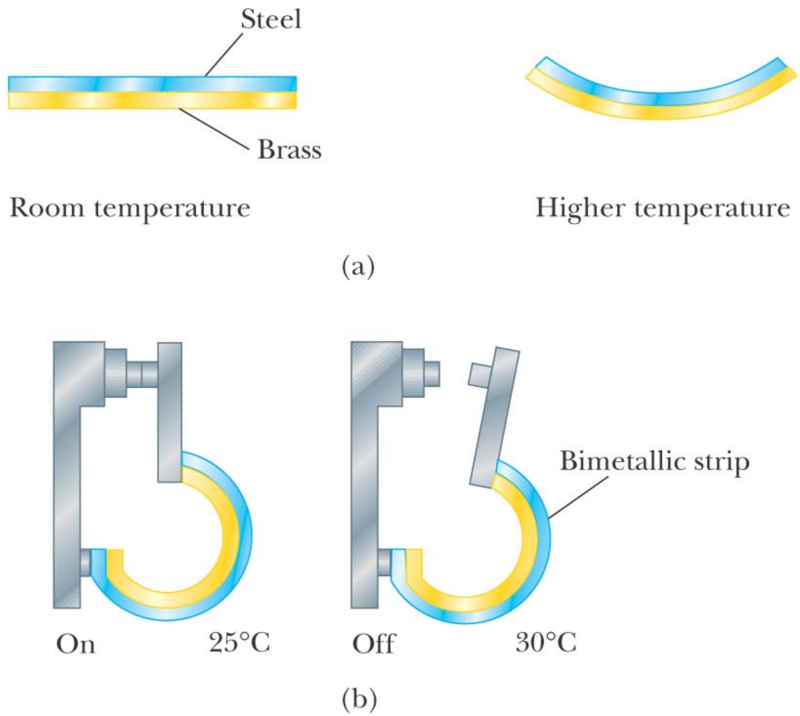
i.e. $\Delta V = \beta V_i \Delta T$ where $\beta = 3\alpha$

Area Expansion

- The change in area is proportional to the original area and to the change in temperature:
  - $\Delta A = 2\alpha A_i \Delta T$
    - *Proof similar to that for Volume expansion*

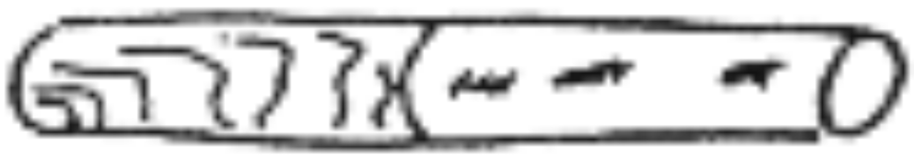
Bimetallic Strip

- Each substance has its own characteristic average coefficient of expansion
- In bimetallic strip the brass expands more than the steel for the same temperature rise
  - Strip bends
- An application is the thermostat



Hb5: Thermal Expansion – the bi-metallic strip

- The elements in simple thermostats



Copper + Steel

Quick Quiz: If you are asked to make a very sensitive glass thermometer, which of the following working liquids would you choose?

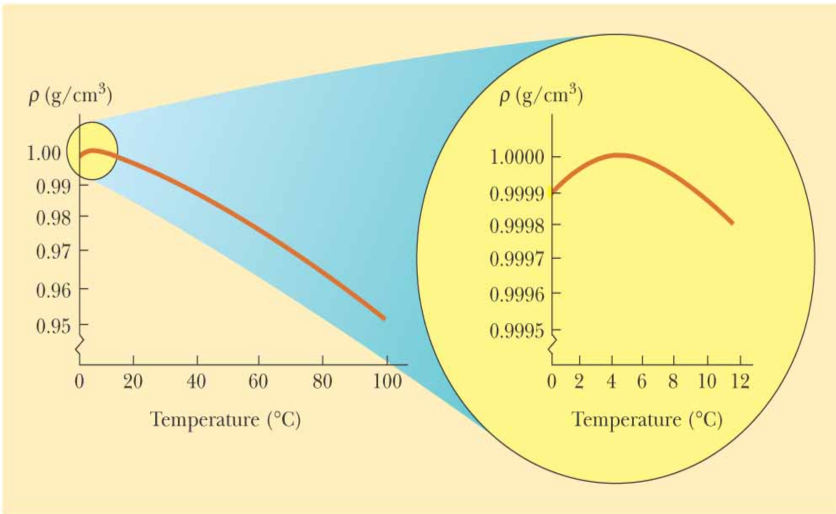
1. mercury
2. alcohol
3. gasoline (i.e. petrol)
4. glycerin

Quick Quiz: Two spheres are made of the same metal and have the same radius, but one is hollow and the other is solid. The spheres are taken through the same temperature increase. Which sphere expands more?

1. The solid sphere expands more.
2. The hollow sphere expands more.
3. They expand by the same amount.
4. There is not enough information to say.

Water's Unusual Behavior

- As the temperature increases from 0°C to 4°C, water *contracts!*
  - Its density increases
- Above 4°C, water expands with increasing temperature
  - Its density decreases
- The maximum density of water (1.000 g/cm^3) occurs at 4°C
  - Critical for the existence of marine life!



THE UNIVERSITY OF
NEW SOUTH WALES

Chapter 19
Kinetic Theory of Gases

Ideal Gases

Change in Volume for a Gas

- Volume expansion $\Delta V = \beta V_i \, \Delta T$ requires there to be an initial volume for Temperature changes
- For gases, the interatomic forces within the gas are very weak
  - We can imagine these forces to be nonexistent
- But there is no equilibrium separation for the atoms in a gas
  - Thus, no "standard" volume at a given temperature. Depends entirely on the container holding the gas.
- Thus, for gases the volume, V, is a variable
  - We consider the change in volume ΔV

Gas: Equation of State

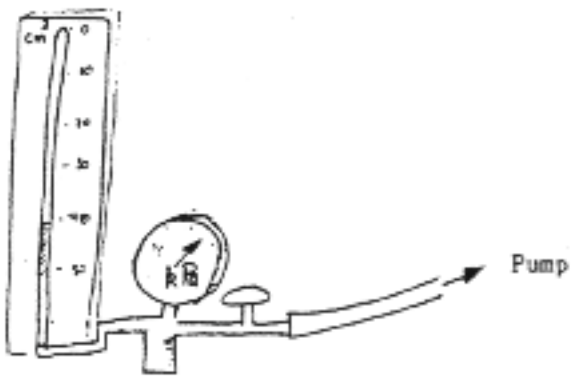
- Describes how the volume, *V*, pressure, *P*, and temperature, *T*, of a gas of mass *m* are related.
  - In general, quite complicated
  - If the gas is maintained at a low pressure, or low density, the equation of state becomes much easier
  - The **ideal gas**
    - Requires gas molecules not to interact with one another except during collisions

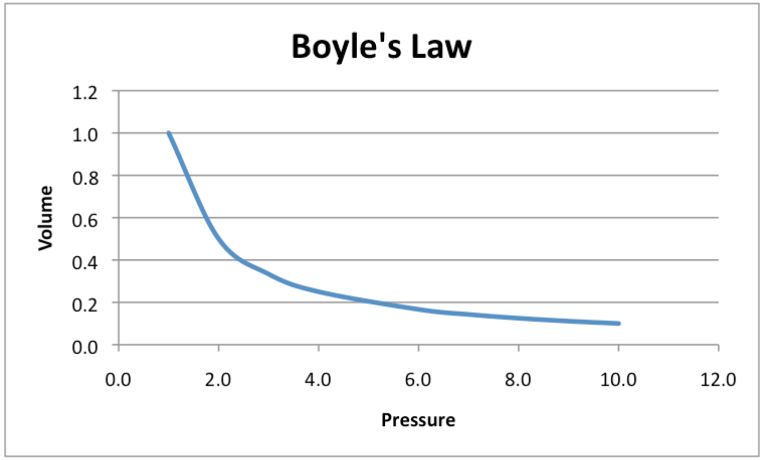
The Mole

- The amount of gas in a given volume can be expressed in terms of the number of moles
- One **mole** of any substance is that amount of the substance that contains **Avogadro's number** of constituent particles
  - Avogadro's number $N_A = 6.022 \times 10^{23}$
  - The constituent particles can be atoms or molecules
- The number of moles is $n = m / M$
  - M the molar mass of the substance (i.e. mass of 1 mole)
    - Note: often the symbol μ is used instead of M
  - m is the mass of the sample
  - n is the number of moles

Hc7 Boyle's Law

- Apparatus for the direct measurement of the relationship between volume and pressure.





YouTube Video – the Brickheads

Gas Laws

- Experiment showed that:
  - (a) When a gas is kept at a constant temperature, its pressure is inversely proportional to its volume (Boyle's law)
  - (b) When a gas is kept at a constant pressure, its volume is directly proportional to its temperature (Charles and Gay-Lussac's law)
  - *See Active Figure 19.12*
- These can be combined into a single law, the "ideal gas law"

Ideal Gas Law

- The equation of state for an ideal gas

$$PV = nRT$$

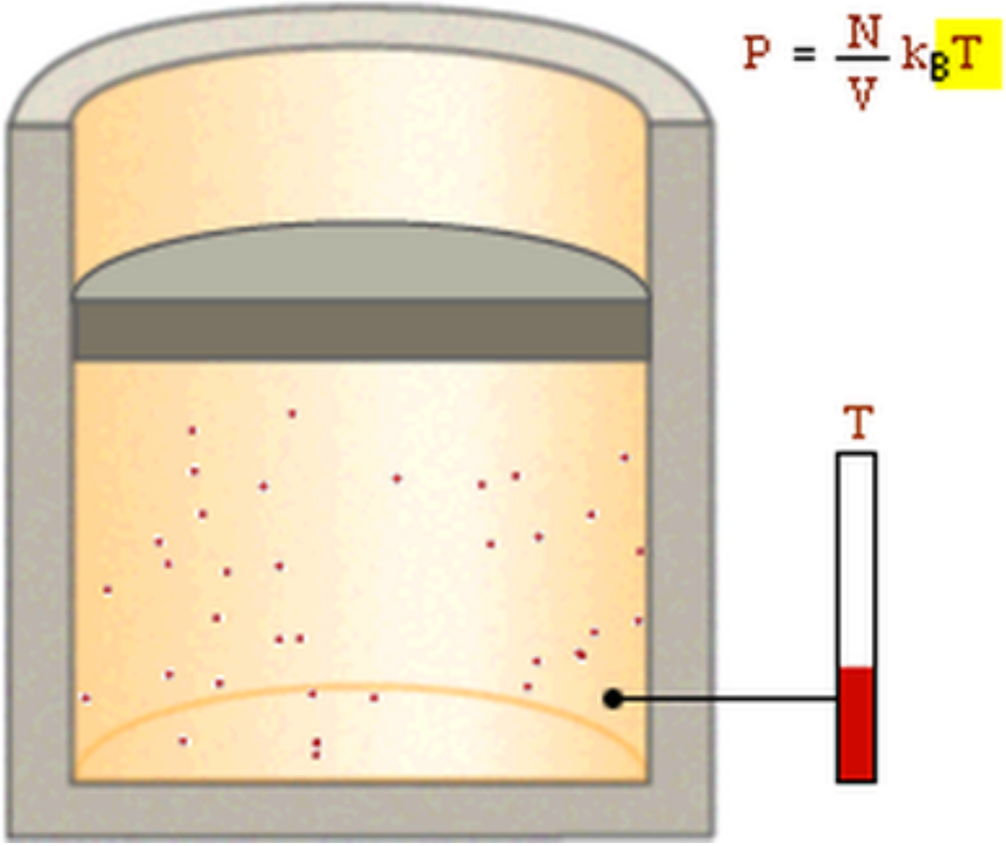
- This is known as the **ideal gas law**
- n is the number of moles of the gas
- R is a constant, called the "Universal Gas Constant"
  - $R = 8.314$ J/mol · K

Ideal Gas Law, cont

- The ideal gas law is often expressed in terms of the total number of molecules, N, present in the sample
- $PV = nRT = (N/N_A)\ RT = Nk_B T$
  - k_B is Boltzmann's constant = R/N_A
  - $k_B = 1.38 \times 10^{-23}$ J/K
    - Exercise: show this!
- It is common to call P, V, and T the **thermodynamic variables** of an ideal gas

TDA05AN1: Ideal Gas Law: Temperature & Pressure

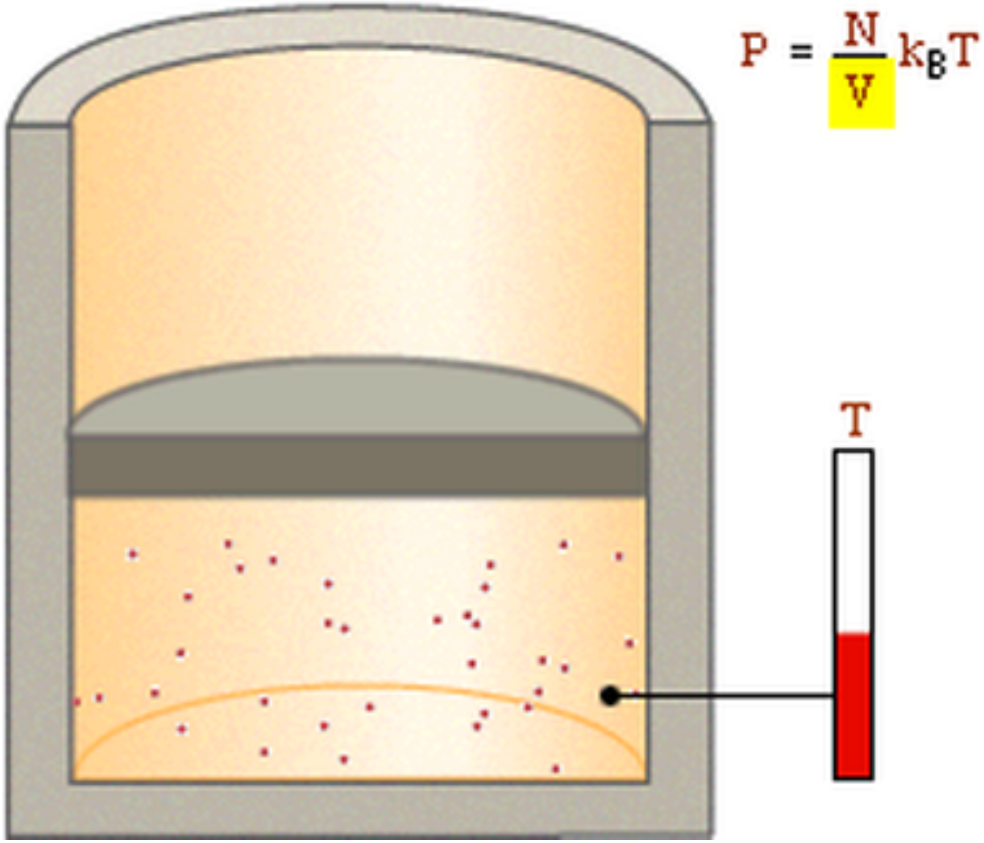
N, V fixed
$P \propto T$



17 seconds

TDA05AN2: Ideal Gas Law: Volume & Pressure

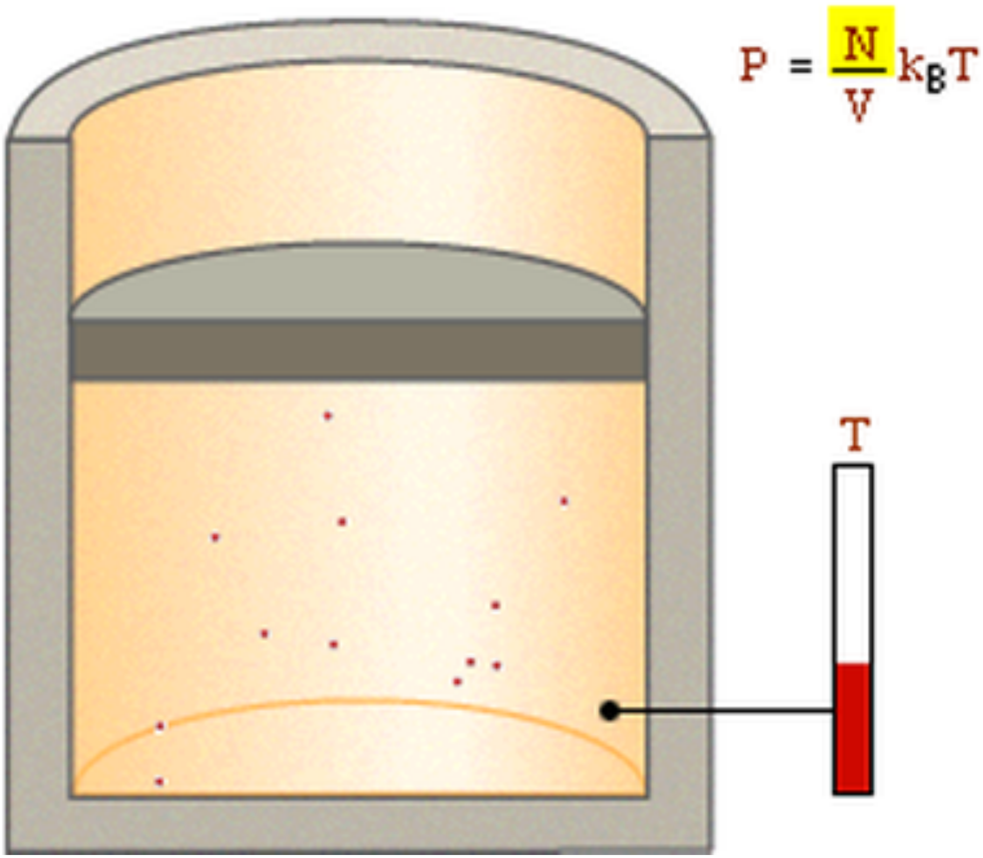
N, T fixed
Boyle's Law
$P \propto 1/V$



25 seconds

TDA05AN3: Ideal Gas Law: Number and Pressure

V, T fixed
$P \propto N$



19 seconds

Quick Quiz: A common material for cushioning objects in packages is made by trapping bubbles of air between sheets of plastic. This material is more effective at keeping the contents of the package from moving around inside the package on:

1. a hot day.
2. a cold day.
3. either hot or cold days.

Quick Quiz: On a winter day, you turn on your heating system and the temperature of the air inside your home increases. Assume your home has the normal amount of leakage between inside air and outside air. The number of moles of air in your room at the higher temperature is:

1. larger than before.
2. smaller than before.
3. the same as before.

Molecular Model of an Ideal Gas

- *See Active Figure 21.02*
- The model shows that the pressure that a gas exerts on the walls of its container is a consequence of the collisions of the gas molecules with the walls.
- This microscopic model is consistent with the macroscopic description we have seen.

Ideal Gas Assumptions: 1

1. The number of molecules in the gas is large, and the average separation between the molecules is large compared with their dimensions.
   - The molecules occupy a negligible volume within the container.
   - This is consistent with the macroscopic model where we assumed the molecules were point-like.

Ideal Gas Assumptions: 2

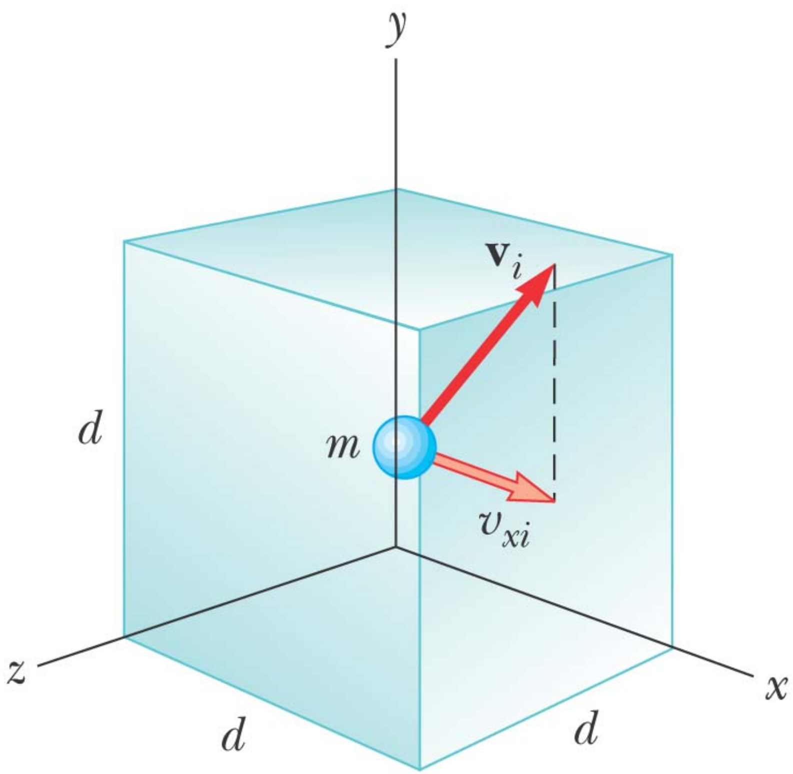
2. The molecules obey Newton's laws of motion, but as a whole they move randomly.
   - Any molecule can move in any direction with any speed
   - At any given moment, a certain percentage of molecules move at high speeds and a certain percentage move at low speeds

Ideal Gas Assumptions: 3 – 5

3. The molecules <u>interact only</u> by short-range forces <u>during elastic collisions</u>
   - Consistent with the macroscopic model, in which molecules exert no long-range forces on each other
4. Molecules make elastic collisions with the walls
5. The gas under consideration is a pure substance
   - All molecules are identical

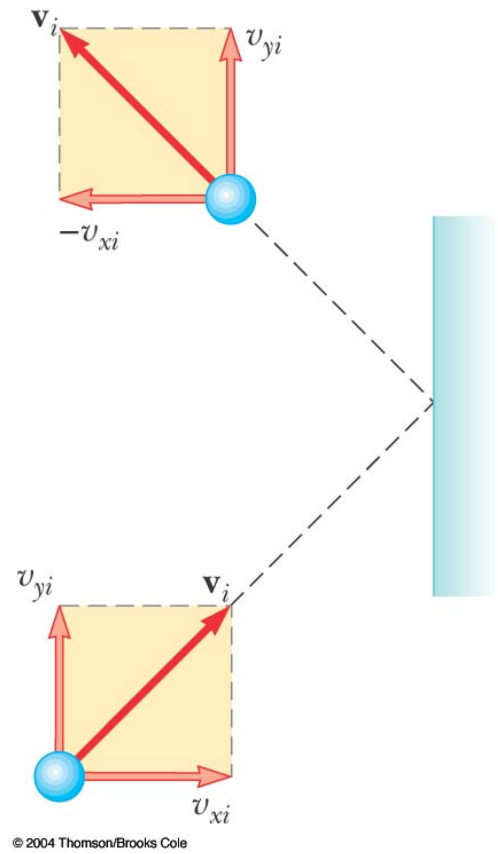
Pressure and Kinetic Energy

- Assume a container is a cube
  - Edges are length *d*
- Look at the motion of the molecule, mass m, in terms of its velocity components, v_{xi}, v_{yi}, v_{zi}
- Look at its momentum and the average force, p_i, F_i



Pressure and Kinetic Energy, 2

- Assume perfectly elastic collisions with the walls of the container
- Apply Newton's Laws to the collisions to determine the relation between the gas pressure and the molecular kinetic energy



Pressure and Kinetic Energy, 3

- The relationship we find is

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

- Interpretation: pressure is proportional to the number of molecules per unit volume (*N*/*V*) and to the average translational kinetic energy of the molecules ($\frac{1}{2}m\overline{v^2}$)
- Note: $\overline{v^2}$ is the mean value of the speed squared

Deriving the Ideal Gas Law: I

Change in Momentum $\Delta p_x = -mv_x - (mv_x) = -2mv_x$ (N2L)

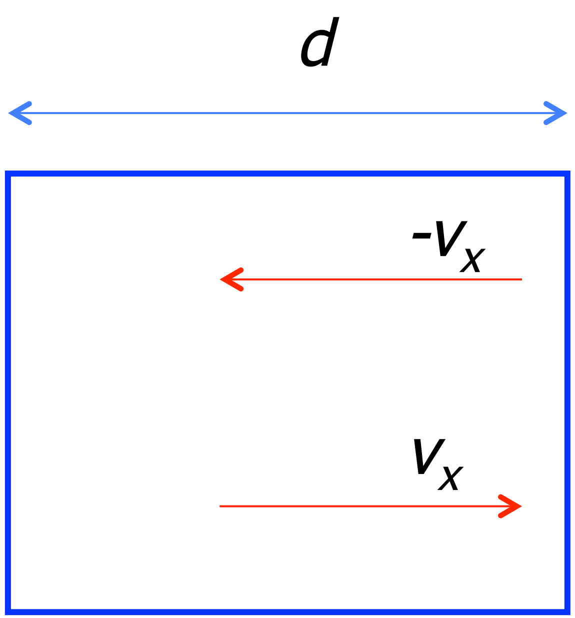
Crossing Time $\Delta t = {2d}/{v_x}$

Average Force = Rate of Change of Momentum

i.e. $\overline{F_x} = \Delta p_x / \Delta t = -2mv_x / \; [{2d}/{v_x}]$ (impulse)

So $\overline{F_x} = \dfrac{-mv_x^2}{d}$

By N3L the force on the wall is $-\overline{F_x} = \dfrac{mv_x^2}{d}$



Deriving the Ideal Gas Law: II

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$

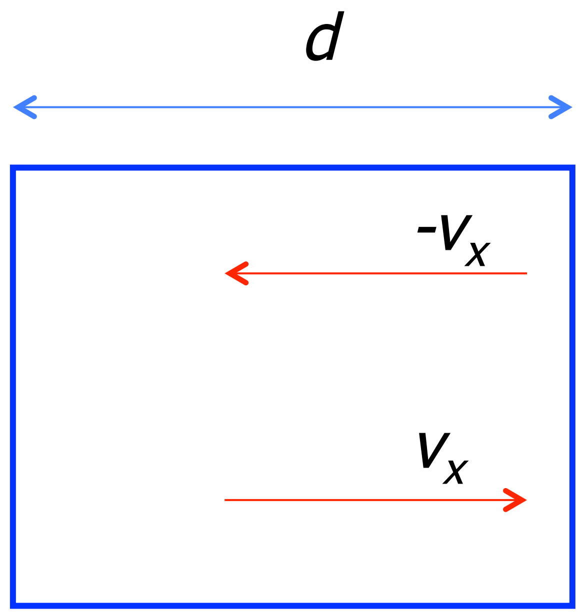
$$\text{So Force on Wall} = \frac{m\overline{v_x^2}}{d} = \frac{m\overline{v^2}}{3d}$$

Summing over N particles

$$\Rightarrow F_{wall} = \frac{N}{3}\frac{m\overline{v^2}}{d}$$

$$\text{So Pressure } P = \frac{F}{A} = \frac{1}{3}\frac{N}{V}m\overline{v^2} \text{ since } Ad = d^3 = V$$

$$\text{i.e. } P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m\overline{v^2}\right)$$



Molecular Interpretation of Temperature

- Compare the pressure as it relates to the kinetic energy to the pressure from the equation of state for an ideal gas

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

- Hence the temperature is a direct measure of the average molecular kinetic energy

Molecular Interpretation of Temperature, cont

- Simplifying the equation relating temperature and kinetic energy gives

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$$

- This can be applied to each direction,

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} k_B T$$

  with similar expressions for v_y and v_z

- i.e. each translational degree of freedom contributes an equal amount to the energy of the gas

Total Kinetic Energy of a Gas

- The total kinetic energy is just *N* times the kinetic energy of each molecule

$$K_{\text{tot trans}} = N\left(\frac{1}{2}m\overline{v^2}\right) = \frac{3}{2}Nk_{\text{B}}T = \frac{3}{2}nRT$$

  - Remember $k_B = R/N_A$, *n* is number of moles.
- If we have a gas with only translational energy, this is the internal energy of the gas (i.e. a monatomic gas)
- This tells us that the internal energy of an ideal gas depends only on the temperature

Root Mean Square Speed

- The root mean square (rms) speed is the square root of the average of the squares of the speeds
  - Square, average, take the square root
- Solving for v_{rms} we find *(exercise!)*

(monatomic gas)

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

- M is the molar mass and $M = mN_A$

Some Example v_{rms} Values

At a given temperature, lighter molecules move faster, on the average, than heavier molecules

Some rms Speeds

Gas	Molar mass (g/mol)	v_{rms} at 20°C(m/s)
H_2	2.02	1 902
He	4.00	1 352
H_2O	18.0	637
Ne	20.2	602
N_2 or CO	28.0	511
NO	30.0	494
O_2	32.0	478
CO_2	44.0	408
SO_2	64.1	338

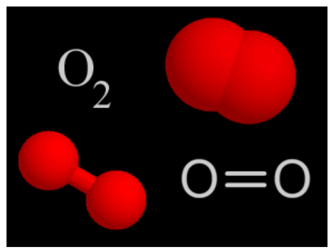
Theorem of the Equipartition of Energy

- Each degree of freedom contributes $\frac{1}{2}k_B T$ to the energy of a system
- Degrees of freedom are associated with
  - translation for atoms or molecules
  - + rotation and vibration <u>for</u> molecules (only)
- Energy associated with rotation and vibration is added to the KE to give the total internal energy of the gas
  - i.e. $E_{int}=E_{KE} + E_{rot+vib}$

Internal Energy of Diatomic Molecules

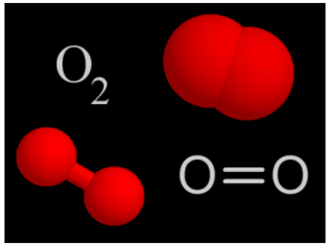
- Total Internal Energy:
  - $E_{int} = N$ x Energy of each Molecule
- For a monatomic gas (e.g. hydrogen atoms)
  - $E_{int} = 3/2nRT$ [remember $kN=nR$]

- For a diatomic gas at room temperature (e.g. air with nitrogen and oxygen molecules)
  - $E_{int} = 5/2nRT$
  - *Extra energy because the molecule can rotate about its own axis.*



Internal Energy of Diatomic Molecules

- In general the number of degrees of freedom, *f*, also depends on the temperature
- We find that $E_{int} = f/2\, nRT$, where
  - f=3 for 0K $< T <$ 100K
  - f=5 for 100K $< T <$ 1000K
  - f=7 for 1000K$< T$



Quick Quiz (i): Two containers hold an ideal gas at the same temperature and pressure. Both containers hold the same type of gas, but container B has twice the volume of container A.
What is the average translational kinetic energy per molecule in container B?

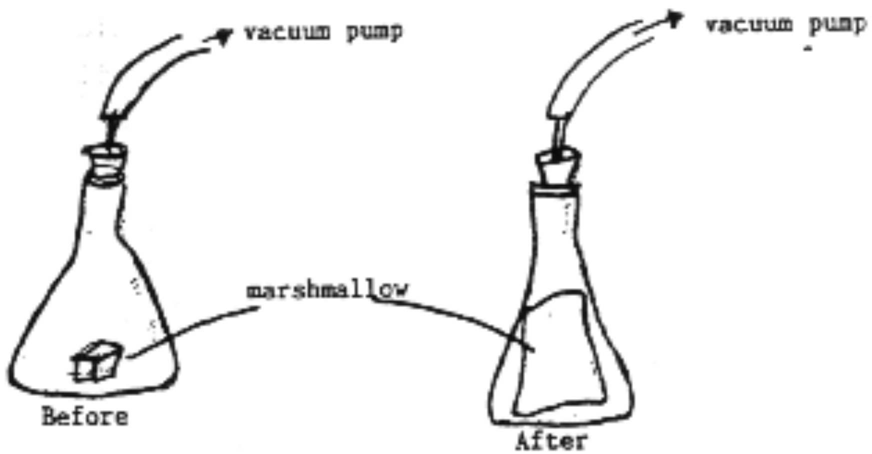
1. twice that of container A
2. the same as that of container A
3. half that of container A
4. impossible to determine

Quick Quiz (ii): Two containers hold an ideal gas at the same temperature and pressure. Both containers hold the same type of gas, but container B has twice the volume of container A.
What is the internal energy of the gas in container B?

1. twice that of container A
2. the same as that of container A
3. half that of container A
4. impossible to determine

Hc9: Gas Pressure - balloons & marshmallows in a vacuum

- Marshmallow placed in a flask, which is then evacuated of air. The marshmallow increases in size.



Water in all three phases.

At the beginning of this chapter, we asked what causes the water to take on the different forms shown in the photograph. We now know that the phase of the water depends on its temperature, which in turn depends on how much energy has been transferred into or away from the system. The water in the lake and the snow on the ground are both in thermal contact with the ground below and the air above. We know that liquid water and ice can coexist when the temperature is 0ºC. On a still winter's day, it is likely that they are close to being in thermal equilibrium with the ground, as the temperature of the ground varies quite slowly, especially when covered by layers of water or snow, as we shall see in the following chapter. The temperature of the air is also likely to be about 0ºC, but it may be slightly lower or higher depending on the time of day and the thickness of the cloud cover. If the air temperature is also 0ºC, then the whole system may be in thermal equilibrium. If the air temperature is below 0ºC, it may be in thermal equilibrium with the snow but not with the water, so that the water in the lake may cool and a layer of ice form on its surface. If the air temperature is above 0ºC, some of the snow may start to melt (without changing temperature).

So far in this chapter, we have only considered the possibility of materials existing in their gaseous form if they are heated through their boiling points. Yet we know the air can contain water vapour at much lower temperatures than 100ºC, as is evident from condensation of water out of the air onto a cold glass on a hot day or the formation of clouds at high altitudes where the temperature is very low. We shall see in the next chapter how this happens.