

Ch13: Temperature and Kinetic Theory

Matter is made up of **atoms** and they are in continuous random motion

(from Greek: atom=indivisible BUT nowadays we know it is divisible: nucleus (n,p) +electrons)

Atomic mass or **molecular mass**: relative masses of atoms and molecules

Based on assigning **12.0000 unified atomic mass units (u)** to ^{12}C

$$1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg}$$

An evidence for the atomic theory:

Brownian motion is the jittery motion of tiny flecks in water; these are the result of collisions with individual water molecules.

Experimental studies: Brown 1827

Theory: Einstein 1905 (size and mass of atoms and molecules)



Phases of Matter

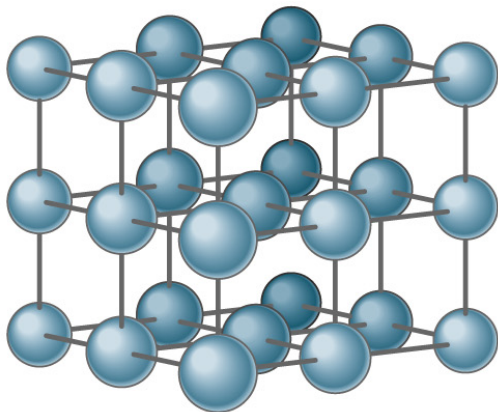
Atoms and molecules exert attractive force on each other (clear example: a solid)
But if they get too close: electric repulsion

How the phases differ from a microscopic point of view

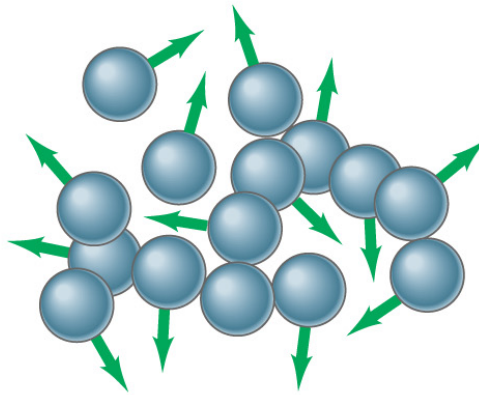
Solid: attractive forces are strong enough, atoms and molecules move slightly around fixed points (crystals)

Liquid: attractive forces are weaker, they pass over one another

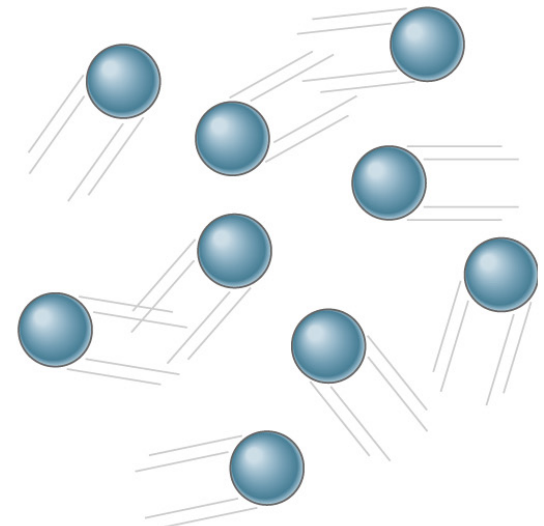
Gas: forces are very weak, molecules are not close and fill the container, speeds are high



(a)



(b)



(c)

Temperature and Thermometers



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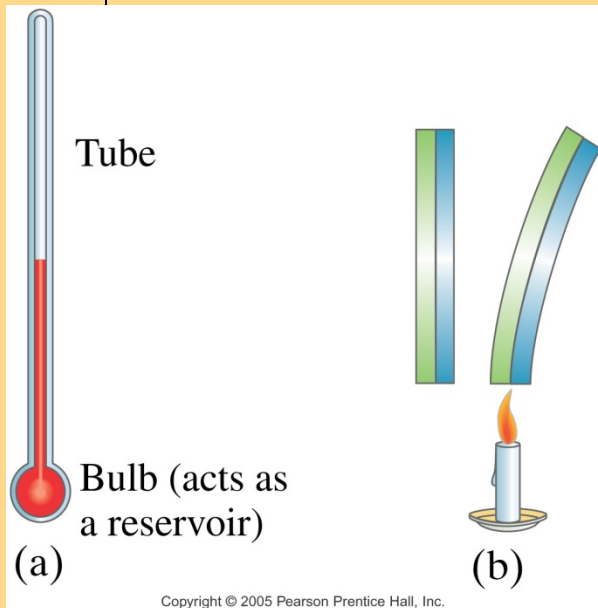
Temperature is a measure of how hot or cold something is.

Properties of matter change with temperature, such as the electrical resistance and color radiated by objects.

Most materials expand when heated -- expansion junctions.

Thermometers are instruments designed to measure temperature. To do this, they take advantage of some property of matter that changes with temperature – usually expansion

Liquid-in-glass type thermometer: liquid expands more than the glass



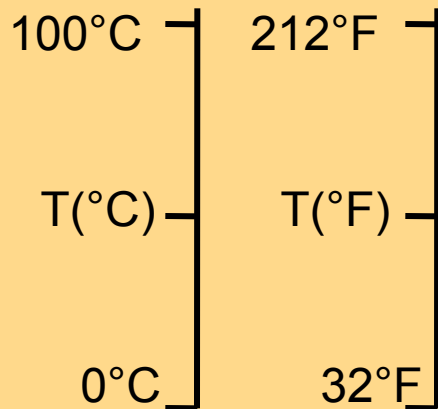
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Temperature Scale

To measure temperature some numerical scale must be defined.
Scales: Celsius (most common, Fahrenheit, Kelvin)

We need to assign arbitrary values to two reproducible temperatures
For Celsius and Fahrenheit, the two fixed points are
the freezing and boiling point of water at 1 atm.

The freezing point of water is 0°C, or 32°F;
the boiling point of water is 100°C, or 212°F.



$$\frac{T_c - 0^\circ}{100^\circ - 0^\circ} = \frac{T_F - 32^\circ}{212^\circ - 32^\circ}$$

$$T_c = \frac{100}{180} (T_F - 32^\circ) \Rightarrow T_c = \frac{5}{9} (T_F - 32^\circ)$$

Ex. 13-2 Normal body temperature is 98.6°F. What is this in the Celsius scale?
37.0°C

Thermal LINEAR Expansion

Most substances **expand** when heated and contract when cooled. But the amount of expansion or contraction varies with the material

The **change in length** of almost all solids is directly proportional to the change in **temperature**, if ΔT is not too large, and to the **original length** of the object.

$$L = L_0(1 + \alpha \Delta T)$$

α is the coefficient of linear expansion.
unit: $(C^\circ)^{-1}$

Ex. 13-3 The steel bed of a suspension bridge is 200 m long at 20°C. If the extremes of temperature to which it might be exposed are -30°C to +40°C, how much will it contract and expand?

$$\alpha_{steel} = 12 \times 10^{-6} (C^\circ)^{-1}$$

It increases 4.8 cm and decreases 12 cm

Ex. 13-5 An iron ring is to fit snugly on a cylinder iron rod. At 20°C, the diameter of the rod is 6.445 cm and the inside diameter of the ring is 6.420 cm. To slip over the rod, the ring must be slightly larger than the rod diameter by about 0.008 cm. To what temperature must the ring be brought if its hole is to be large enough so it will slip over the rod?

$$\alpha_{iron} = 12 \times 10^{-6} (C^\circ)^{-1}$$

450°C

Thermal Expansion: VOLUME

Volume expansion is similar:

$$\Delta V = \beta V_0 \Delta T$$

Here, β is the coefficient of volume expansion.

For uniform solids, $\beta \approx 3\alpha$

Ex. 13-7 The 70-L steel gas tank of a car is filled to the top with gasoline at 20°C. The car sits in the sun and the tank reaches a temperature of 40°C. How much gasoline should overflow from the tank?

Coefficient of volume expansion: *gasoline* : $950 \times 10^{-6} (C^\circ)^{-1}$

steel : $35 \times 10^{-6} (C^\circ)^{-1}$

Gasoline expands 1.3 L; tank increases in volume by 0.050 L

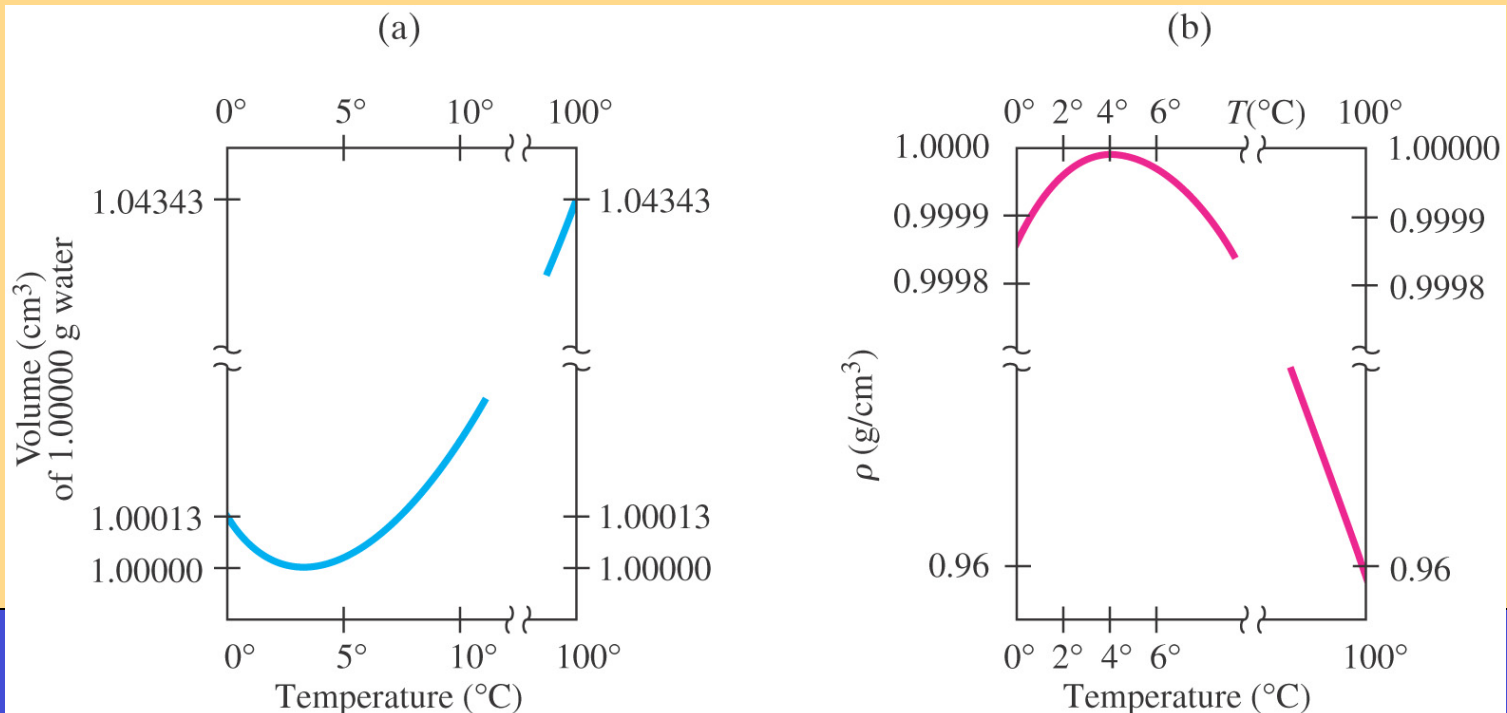
Therefore, more than a liter will overflow

Anomalous Behavior of Water

Most substances expand when temperature increases. But water at 0°C , when heated up, *DECREASES* in volume until it reaches 4°C .

At 4°C water has its highest density. Above that it behaves normally. This anomalous behavior guarantees the survival of aquatic life in winter.

Water expands as it cools from 4°C to 0°C and even more as it freezes, so the density of ice is smaller than water – ice floats

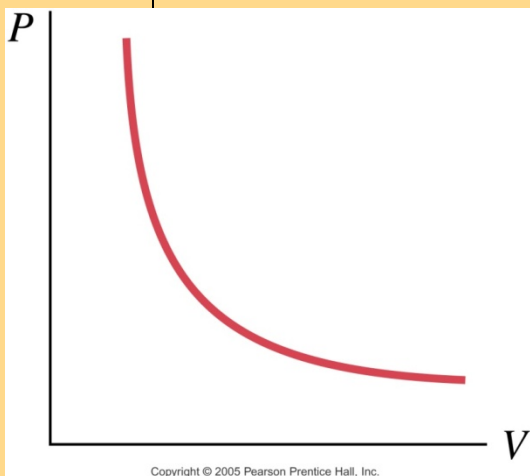


The Gas Laws

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

State = physical condition of the system, we will consider **equilibrium states**

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

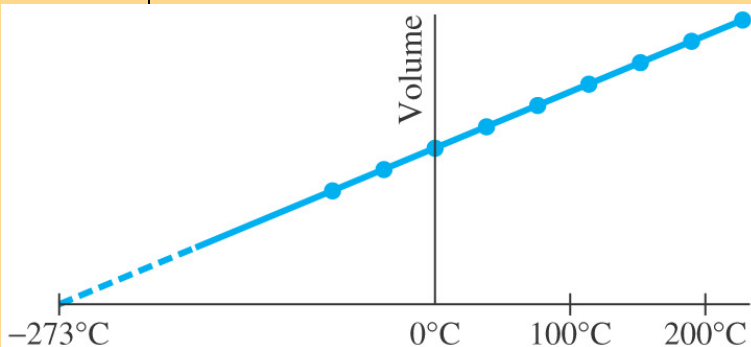


Boyle's Law: the volume of a given amount of gas is inversely proportional to the pressure as long as the temperature is constant.

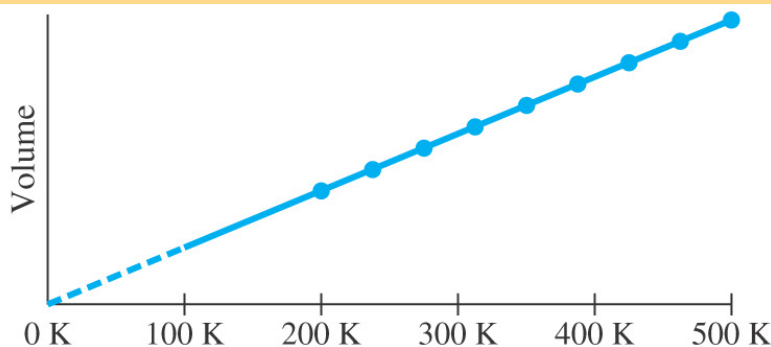
$$V \propto \frac{1}{P}$$

Charles's law: the volume is linearly proportional to the temperature, if the pressure is constant: $V \propto T$

-273.15°C is called **absolute zero**, but the gas liquefies before



(a) Temperature (°C)



(b) Temperature (kelvins, or K)

Kelvin Scale

Kelvin scale starts with 0 K at absolute zero, but otherwise is the same as the Celsius scale.

The freezing point of water is 273.15 K, and the boiling point is 373.15 K.

Gay-Lussac's law: When the volume is constant, the pressure is directly proportional to the temperature:

$$P \propto T$$

Ex. 13-9 What would happen if you would throw a closed glass jar in the fire?

It would explode, because the pressure of the air inside would increase

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

$$PV \propto T$$

Ideal Gas Law

We need to incorporate to $PV \propto T$ the amount of gas present



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$$PV \propto mT \quad (\text{m is the mass of the gas present})$$

It can be made into an equation by inserting a constant, which is different for different gases.

If instead of mass we use moles, the constant is the same for all gases

A mole (mol) = *amount of substance that contains as many molecules as there are in 12 grams of carbon 12* OR 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 CO₂ has a mass of 44 g

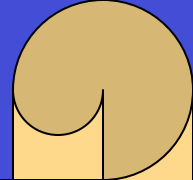
The number of moles in a certain mass of material:

1 mol Ne has a mass of 20 g

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

Example: the number of moles in 132 g of CO₂ is $n = \frac{132\text{g}}{44\text{g/mol}} = 3.0\text{mol}$

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:

$$\begin{aligned} R &= 8.315 \text{ J}/(\text{mol} \cdot \text{K}) \\ &= 0.0821 \text{ (L} \cdot \text{atm)} / (\text{mol} \cdot \text{K}) \\ &= 1.99 \text{ calories}/(\text{mol} \cdot \text{K}) \end{aligned}$$

*TEMPERATURE has to be written
in KELVINS
and
PRESSURE must be ABSOLUTE
pressure*

We often use “standard conditions” or “standard temperature and pressure” (STP)

$$T = 273 \text{ K } (0^\circ\text{C})$$

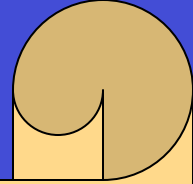
$$P = 1.00 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2 = 101.3 \text{ kPa}$$

Ex. 13-10 Determine the volume of 1.00 mol of any gas, assuming it behaves like an ideal gas at STP

22.4 L

$$1\text{L} = 1000\text{cm}^3 = 1 \times 10^{-3} \text{ m}^3$$

Exercises



Ex 13-11 A helium party balloon, assumed to be a perfect sphere, has radius of 18.0 cm. At room temperature (20°C), its internal pressure is 1.05 atm. Find the number of moles of helium in the balloon and the mass of helium needed to inflate the balloon to these values. (atomic mass of helium=4.00g/mol)

$$n=1.066 \text{ mol} \quad \text{mass}=4.26 \text{ g}$$

If the amount of gas does not change, only P, V, and T:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Ex 13-13 An automobile tire is filled to a gauge pressure of 200 kPa at 10°C. After a drive of 100 km, the temperature within the tire rises to 40°C. What is the pressure within the tire now?

$$333 \text{ kPa}$$

Avogadro's Number

Avogadro's hypothesis: equal volumes of gas at the same pressure and temperature contain equal numbers of molecules. This is consistent with R being the same for all gases.

$PV = nRT$ same number of moles, same pressure and temperature then volume is the same if R is the same.

Since 1 mol = *amount of substance that contains as many molecules as there are in 12 grams of carbon*, then the amount of molecules in 1 mole is the same for all gases. This 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:

$$N = nN_A$$

Ideal Gas in terms of molecules

$$PV = nRT = \frac{N}{N_A} RT \Rightarrow \boxed{PV = NkT},$$

where k is called Boltzmann's constant.

$$k = \frac{R}{N_A} = \frac{8.315 \text{ J/mol} \cdot \text{K}}{6.02 \times 10^{23} / \text{mol}} = 1.38 \times 10^{-23} \text{ J/K}$$

Ex. 13-14 Use Avogadro's number to determine the mass of a hydrogen atom (atomic mass = 1.008 u)

$$m = 1.67 \times 10^{-27} \text{ kg}$$

Kinetic Theory and Temperature

Kinetic Theory: the analysis of matter in terms of atoms in continuous random motion

Assumptions of kinetic theory (**ideal gas** ~ real gas at low pressure and far from liquefaction point):

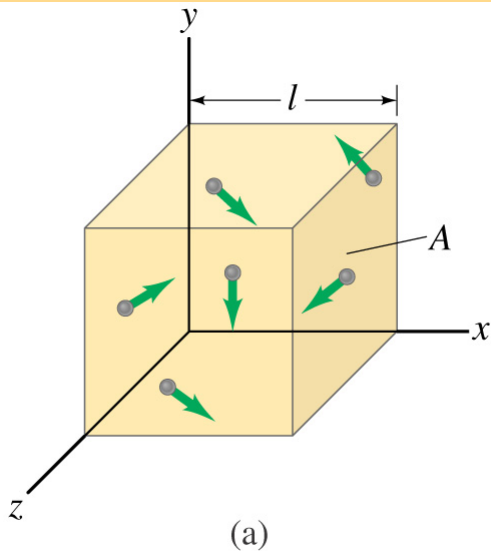
- large number of molecules, moving in random directions with a variety of speeds
- molecules are far apart, on average
- molecules obey laws of classical mechanics and interact only when colliding
- collisions are perfectly elastic

Note for Boyles' law ($PV=\text{constant}$):

Pressure on a wall is due to the bombardment of molecules

If volume is reduced, molecules are closer, more will be striking – more pressure

Kinetic Theory



We want to find the pressure a gas exerts on its container based on kinetic theory

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

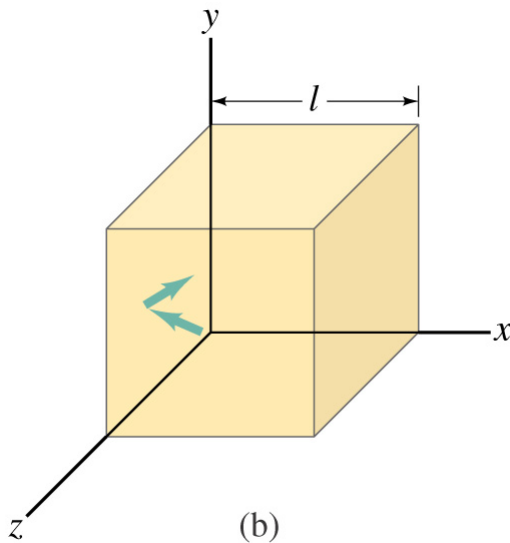
$$F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}$$

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

$$F = \frac{m}{l} (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2)$$

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2}{N}$$

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



Kinetic Theory

Taking the three directions into account: $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$

Velocities are random, there is not preference for any direction:

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

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

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

So the pressure is:

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

Interpretation of Temperature

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

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

so

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

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

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

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

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$$

Exercises

$$k = \frac{R}{N_A} = \frac{8.315 \text{ J/mol} \cdot \text{K}}{6.02 \times 10^{23} / \text{mol}} = 1.38 \times 10^{-23} \text{ J/K}$$

$$1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg}$$

Ex.13-16 What is the average translational kinetic energy of molecules in an ideal gas at 37 degrees Celsius?

$$6.42 \times 10^{-21} \text{ J}$$

Ex.13-17 What is the rms speed of air molecules (O₂ and N₂) at room temperature

(20 degrees Celsius,

O₂ – molecular mass=32 u,

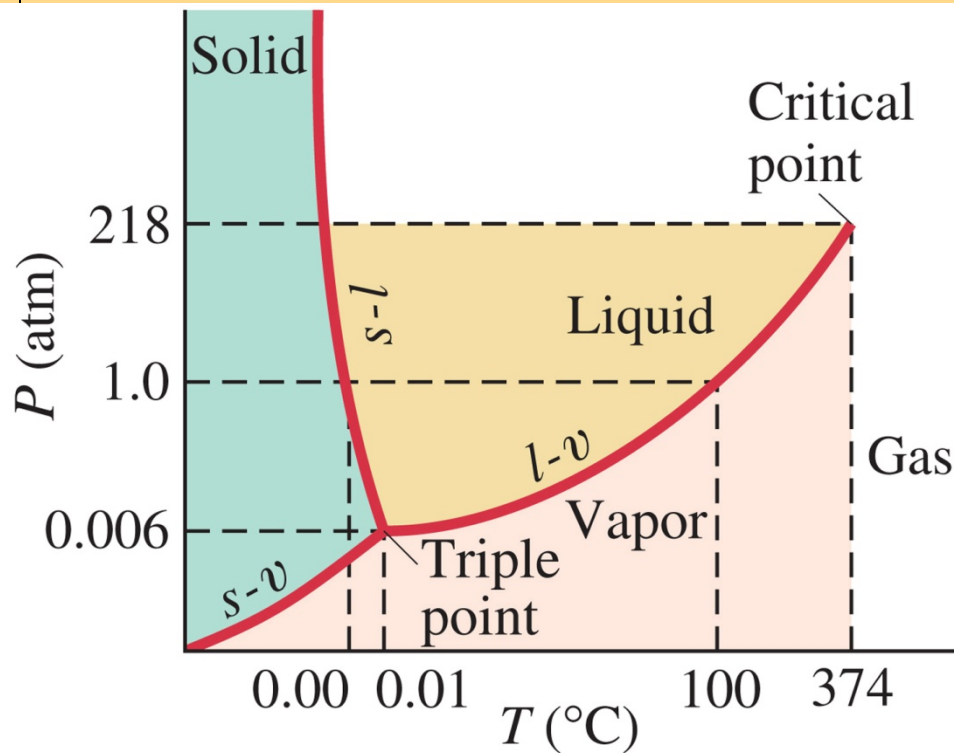
N₂ – molecular mass = 28 u)?

$$v_{\text{rms}}=480\text{m/s}$$

$$v_{\text{rms}}=510\text{m/s}$$

Real Gases and Changes of Phase

A PT diagram is called a phase diagram; it shows all three phases of matter. The solid-liquid transition is melting or freezing; the liquid-vapor one is boiling or condensing; and the solid-vapor one is sublimation.



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Phase diagram of water