

1. Estimate the fraction of molecular volume to the actual volume occupied by oxygen gas at STP. Take the diameter of an oxygen molecule to be 3 Å.

# Solution:

Diameter of an oxygen molecule, d = 3 Å

Radius, r = d / 2

$$r = 3 / 2 = 1.5 \text{ Å} = 1.5 \text{ x} 10^{-8} \text{ cm}$$

The actual volume occupied by 1 mole of oxygen gas at STP = 22400 cm<sup>3</sup>

The molecular volume of oxygen gas,  $V = 4 / 3 \pi r^3$ . N

Where, N is Avogadro's number = 6.023 x 10<sup>23</sup> molecules/ mole

Hence,

$$V = 4 / 3 \times 3.14 \times (1.5 \times 10^{-8})^3 \times 6.023 \times 10^{23}$$

We get,

 $V = 8.51 \text{ cm}^3$ 

Therefore, the ratio of the molecular volume to the actual volume of oxygen = 8.51/22400 = 3.8 x 10<sup>-4</sup>

2. Molar volume is the volume occupied by 1 mol of any (ideal) gas at standard temperature and pressure (STP: 1 atmospheric pressure, 0 °C). Show that it is 22.4 litres.

### Solution:

The ideal gas equation relating pressure (P), volume (V), and absolute temperature (T) is given as

PV = nRT

Where R is the universal gas constant = 8.314 J mol<sup>-1</sup>K<sup>-1</sup>

n = Number of moles = 1

T = Standard temperature = 273 K

P = Standard pressure = 1 atm = 1.013 x 10<sup>5</sup>Nm<sup>-2</sup>

Hence.

V = nRT / P

 $= 1 \times 8.314 \times 273 / 1.013 \times 10^{5}$ 

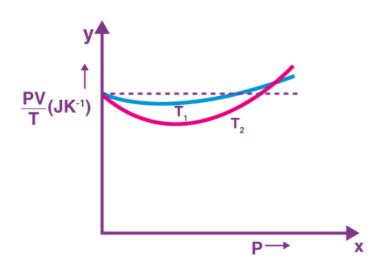
 $= 0.0224 \text{ m}^3$ 

= 22.4 litres



Therefore, the molar volume of a gas at STP is 22.4 litres.

3. Figure 13.8 shows the plot of PV/T versus P for  $1.00\times10^3$  kg of oxygen gas at two different temperatures.



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- (a) What does the dotted plot signify?
- (b) Which is true:  $T_1 > T_2$  or  $T_1 < T_2$ ?
- (c) What is the value of PV/T where the curves meet on the y-axis?
- (d) If we obtained similar plots for  $1.00\times10^{-3}$  kg of hydrogen, would we get the same value of PV/T at the point where the curves meet on the y-axis? If not, what mass of hydrogen yields the same value of PV/T (for the low-pressure, high-temperature region of the plot)? (Molecular mass of  $H_2$  = 2.02 u, of  $O_2$  = 32.0 u, R = 8.31 J mo1<sup>-1</sup> K<sup>-1</sup>.)

# Solution:

- (a) The dotted plot is parallel to X-axis, signifying that nR [PV/T = nR] is independent of P. Thus, it represents ideal gas behaviour.
- (b) The graphs at temperature  $T_1$  are closer to ideal behaviour (because they are closer to the dotted line) hence,  $T_1 > T_2$  (the higher the temperature, the ideal behaviour is higher)

$$PV/T = nR$$

Mass of the gas =  $1 \times 10^{-3} \text{ kg} = 1 \text{ g}$ 

Molecular mass of O<sub>2</sub> = 32g/ mol

Hence,



Number of mole = Given weight / Molecular weight

$$= 1/32$$

So,  $nR = 1/32 \times 8.314 = 0.26 J/K$ 

Hence,

Value of PV / T = 0.26 J/ K

(d) 1 g of H<sub>2</sub> doesn't represent the same number of mole

E.g., Molecular mass of  $H_2 = 2$  g/mol

Hence, the number of moles of H<sub>2</sub> requires is 1/32 (as per the question).

Therefore,

Mass of  $H_2$  required = No. of mole of  $H_2$  x Molecular mass of  $H_2$ 

- $= 1/32 \times 2$
- = 1 / 16 g
- = 0.0625 g
- $= 6.3 \times 10^{-5} \text{ kg}$

Hence, 6.3 x 10<sup>-5</sup> kg of H₂ would yield the same value.

4. An oxygen cylinder of volume 30 litres has an initial gauge pressure of 15 atm and a temperature of 27 °C. After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atm and its temperature drops to 17 °C. Estimate the mass of oxygen taken out of the cylinder (R = 8.31 J mol  $^{1}$  K $^{1}$ , the molecular mass of  $O_{2}$  = 32 u).

# Solution:

Volume of gas,  $V_1 = 30$  litres =  $30 \times 10^{-3} \text{ m}^3$ 

Gauge pressure,  $P_1 = 15$  atm =  $15 \times 1.013 \times 10^5$  P a

Temperature,  $T_1 = 27^{\circ} C = 300 K$ 

Universal gas constant, R = 8.314 J mol<sup>-1</sup> K<sup>-1</sup>

Let the initial number of moles of oxygen gas in the cylinder be n<sub>1</sub>

The gas equation is given as follows:

 $P_1V_1 = n_1RT_1$ 

Hence,



$$n_1 = P_1V_1 / RT_1$$

= 
$$(15.195 \times 10^5 \times 30 \times 10^{-3}) / (8.314 \times 300)$$

But 
$$n_1 = m_1 / M$$

Where,

m₁ = Initial mass of oxygen

M = Molecular mass of oxygen = 32 g

Thus,

$$m_1 = N_1M = 18.276 \times 32 = 584.84 g$$

After some oxygen is withdrawn from the cylinder, the pressure and temperature reduce.

Volume, 
$$V_2 = 30$$
 litres =  $30 \times 10^{-3} \text{ m}^3$ 

Gauge pressure,  $P_2$  = 11 atm

$$= 11 \times 1.013 \times 10^{5} Pa$$

Temperature,  $T_2 = 17^{\circ} \text{ C} = 290 \text{ K}$ 

Let n<sub>2</sub> be the number of moles of oxygen left in the cylinder.

The gas equation is given as

$$P_2V_2 = n_2RT_2$$

Hence,

$$n_2 = P_2V_2 / RT_2$$

= 
$$(11.143 \times 10^5 \times 30 \times 10^{-30}) / (8.314 \times 290)$$

= 13.86

But

$$n_2 = m_2 / M$$

Where,

m₂ is the mass of oxygen remaining in the cylinder.

Therefore,

$$m_2 = n_2 \times M = 13.86 \times 32 = 453.1 g$$



The mass of oxygen taken out of the cylinder is given by the relation,

Initial mass of oxygen in the cylinder - Final mass of oxygen in the cylinder

- $= m_1 m_2$
- = 584.84 g 453.1 g

We get,

- = 131.74 g
- = 0.131 kg

Hence, 0.131 kg of oxygen is taken out of the cylinder.

5. An air bubble of volume 1.0 cm<sup>3</sup> rises from the bottom of a lake 40 m deep at a temperature of 12 °C. To what volume does it grow when it reaches the surface, which is at a temperature of 35 °C?

#### Solution:

The volume of the air bubble,  $V_1 = 1.0 \text{ cm}^3$ 

$$= 1.0 \times 10^{-6} \,\mathrm{m}^3$$

Air bubble rises to height, d = 40 m

The temperature at a depth of 40 m,  $T_1 = 12^{\circ}$  C = 285 K

The temperature at the surface of the lake,  $T_2 = 35^{\circ}$  C = 308 K

The pressure on the surface of the lake

$$P_2 = 1$$
 atm = 1 x 1.013 x 10<sup>5</sup> Pa

The pressure at a depth of 40 m

Where,

 $\rho$  is the density of water = 10° kg / m°

g is the acceleration due to gravity = 9.8 m/s<sup>2</sup>

Hence,

$$P_1 = 1.013 \times 10^5 + 40 \times 10^3 \times 9.8$$

We get,

= 493300 Pa



We have

$$P_1V_1/T_1 = P_2V_2/T_2$$

Where, V<sub>2</sub> is the volume of the air bubble when it reaches the surface

$$V_2 = P_1 V_1 T_2 / T_1 P_2$$

$$= 493300 \times 1 \times 10^{-6} \times 308 / (285 \times 1.013 \times 10^{5})$$

We get,

Hence, when the air bubble reaches the surface, its volume becomes 5.263 cm<sup>3</sup>

6. Estimate the total number of air molecules (inclusive of oxygen, nitrogen, water vapour and other constituents) in a room of capacity 25.0 m³ at a temperature of 27 °C and 1 atm pressure.

#### Solution:

The volume of the room,  $V = 25.0 \text{ m}^3$ 

The temperature of the room,  $T = 27^{\circ} C = 300 K$ 

The pressure in the room, P = 1 atm = 1 x 1.013 x 10<sup>5</sup> Pa

The ideal gas equation relating pressure (P), Volume (V), and absolute temperature (T) can be written as

$$PV = (k_BNT)$$

Where,

 $K_B$  is Boltzmann constant = (1.38 x 10<sup>-23</sup>) m<sup>2</sup> kg s<sup>-2</sup> K<sup>-1</sup>

N is the number of air molecules in the room.

Therefore,

$$N = (PV / k_BT)$$

= 
$$(1.013 \times 10^5 \times 25) / (1.38 \times 10^{-23} \times 300)$$

We get,

= 6.11 x 10<sup>26</sup> molecules

Hence, the total number of air molecules in the given room is 6.11 x 10<sup>26</sup>

- 7. Estimate the average thermal energy of a helium atom at
- (i) room temperature (27 °C).



- (ii) the temperature on the surface of the Sun (6000 K).
- (iii) the temperature of 10 million kelvin (the typical core temperature in the case of a star).

## Solution:

(i) At room temperature, T = 27° C = 300 K

Average thermal energy = (3 / 2) kT

Where,

k is the Boltzmann constant = 1.38 x 10<sup>-23</sup> m<sup>2</sup> kg s<sup>-2</sup> K<sup>-1</sup>

Hence,

 $(3/2) kT = (3/2) x 1.38 x 10^{-23} x 300$ 

On calculation, we get

 $= 6.21 \times 10^{-21} J$ 

Therefore, the average thermal energy of a helium atom at a room temperature of 27° C is 6.21 x 10<sup>-21</sup> J

(ii) On the surface of the sun, T = 6000 K

Average thermal energy = (3 / 2) kT

 $= (3/2) \times 1.38 \times 10^{-23} \times 6000$ 

We get,

 $= 1.241 \times 10^{-19} J$ 

Therefore, the average thermal energy of a helium atom on the surface of the sun is 1.241 x 10<sup>-19</sup> J

(iii) At temperature, T = 10<sup>7</sup> K

Average thermal energy = (3 / 2) kT

 $= (3/2) \times 1.38 \times 10^{-23} \times 10^{7}$ 

We get,

 $= 2.07 \times 10^{-16} J$ 

Therefore, the average thermal energy of a helium atom at the core of a star is 2.07 x 10<sup>-16</sup> J

8. Three vessels of equal capacity have gases at the same temperature and pressure. The first vessel contains neon (monatomic), the second contains chlorine (diatomic), and the third contains uranium hexafluoride (polyatomic). Do the vessels contain an equal number of respective molecules? Is the root mean square speed of molecules the same in the three cases? If not, in which case are  $V_{\tiny rms}$  the largest?



## Solution:

All three vessels have the same capacity, they have the same volume.

So, each gas has the same pressure, volume and temperature.

According to Avogadro's law, the three vessels will contain an equal number of the respective molecules.

This number is equal to Avogadro's number, N = 6.023 x 10<sup>23</sup>

The root mean square speed (V<sub>rms</sub>) of a gas of mass m and temperature T is given by the relation

$$V_{rms} = \sqrt{3kT} / m$$

Where,

k is the Boltzmann constant.

For the given gases, k and T are constants.

Therefore,  $V_{rms}$  depends only on the mass of the atoms, i.e.,  $V_{rms} \propto (1/m)^{1/2}$ 

Hence, the root mean square speed of the molecules in the three cases is not the same.

Among neon, chlorine and uranium hexafluoride, the mass of neon is the smallest.

Therefore, neon has the largest root mean square speed among the given gases.

9. At what temperature is the root mean square speed of an atom in an argon gas cylinder equal to the rms speed of a helium gas atom at -20 °C? (atomic mass of Ar = 39.9 u, of He = 4.0 u)

# Solution:

Given

The temperature of the helium atom,  $T_{He} = -20^{\circ} \text{ C} = 253 \text{ K}$ 

The atomic mass of argon,  $M_{Ar} = 39.9 \text{ u}$ 

The atomic mass of helium,  $M_{He} = 4.0 \text{ u}$ 

Let  $(V_{rms})_{Ar}$  be the rms speed of argon and

Let  $(V_{rms})_{He}$  be the rms speed of helium

The rms speed of argon is given by

$$(V_{rms})_{Ar} = \sqrt{3RT_{Ar}} / M_{Ar} .....(i)$$

Where,

R is the universal gas constant.



T<sub>Ar</sub> is the temperature of argon gas.

The rms speed of helium is given by

$$(V_{rms})_{He} = \sqrt{3RT_{He}} / M_{He} \dots (ii)$$

Given that

$$(V_{rms})_{Ar} = (V_{rms})_{He}$$

$$\sqrt{3}RT_{Ar} / M_{Ar} = \sqrt{3}RT_{He} / M_{He}$$

$$T_{Ar} / M_{Ar} = T_{He} / M_{He}$$

$$\mathsf{T}_{\mathsf{Ar}} = \mathsf{T}_{\mathsf{He}} \: / \: \mathsf{M}_{\mathsf{He}} \: \mathsf{x} \: \mathsf{M}_{\mathsf{Ar}}$$

$$= (253 / 4) \times 39.9$$

We get

= 2523.675

$$= 2.52 \times 10^3 \text{ K}$$

Hence, the temperature of the argon atom is 2.52 x 10<sup>3</sup> K.

10. Estimate the mean free path and collision frequency of a nitrogen molecule in a cylinder containing nitrogen at 2.0 atm and temperature 17 $^{\circ}$ C. Take the radius of a nitrogen molecule to be roughly 1.0 Å. Compare the collision time with the time the molecule moves freely between two successive collisions (Molecular mass of  $N_2 = 28.0 \text{ u}$ ).

# Solution:

Mean free path =  $1.11 \times 10^{-7} \text{ m}$ 

Collision frequency = 4.58 x 10<sup>9</sup> s<sup>-1</sup>

Successive collision time  $\cong$  500 x (Collision time)

The pressure inside the cylinder containing nitrogen, P = 2.0 atm = 2.026 x 10⁵ Pa

The temperature inside the cylinder,  $T = 17^{\circ} C = 290 K$ 

The radius of a nitrogen molecule,  $r = 1.0 \text{ Å} = 1 \text{ x } 10^{10} \text{ m}$ 

Diameter,  $d = 2 \times 1 \times 10^{10} = 2 \times 10^{10} \text{ m}$ 

The molecular mass of nitrogen,  $M = 28.0 \text{ g} = 28 \text{ x} 10^3 \text{ kg}$ 

The root mean square speed of nitrogen is given by the relation

 $V_{rms} = \sqrt{3RT} / M$ 



Where,

R is the universal gas constant = 8.314 J mol<sup>-1</sup> K<sup>-1</sup>

Hence,

 $V_{rms}$ = 3 x 8.314 x 290 / 28 x 10<sup>-3</sup>

On calculation, we get

= 508.26 m/s

The mean free path (I) is given by the relation

 $I = KT / \sqrt{2} \times \pi \times d^2 \times P$ 

Where,

k is the Boltzmann constant =  $1.38 \times 10^{-23} \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-1}$ 

Hence,

 $I = (1.38 \times 10^{-23} \times 290) / (\sqrt{2} \times 3.14 \times (2 \times 10^{-10})^2 \times 2.026 \times 10^5)$ 

We get,

 $= 1.11 \times 10^{-7} \text{ m}$ 

Collision frequency = V<sub>rms</sub> / I

 $= 508.26 / 1.11 \times 10^{-7}$ 

On calculation, we get

 $= 4.58 \times 10^9 \text{ s}^{-1}$ 

The collision time is given as

 $T = d / V_{rms}$ 

 $= 2 \times 10^{-10} / 508.26$ 

On further calculation, we get

 $= 3.93 \times 10^{-13} \text{ s}$ 

Time taken between successive collisions

 $T' = I / V_{rms} = 1.11 \times 10^{-7} / 508.26$ 

We get,

 $= 2.18 \times 10^{-10}$ 



Hence,

 $T' / T = 2.18 \times 10^{-10} / 3.93 \times 10^{-13}$ 

On calculation, we get

= 500

Therefore, the time taken between successive collisions is 500 times the time taken for a collision.

11. A metre-long narrow bore held horizontally (and closed at one end) contains a 76 cm long mercury thread, which traps a 15 cm column of air. What happens if the tube is held vertically with the open end at the bottom?

#### Solution:

Length of the narrow bore, L = 1 m = 100 cm

Length of the mercury thread, I = 76 cm

Length of the air column between mercury and the closed end, la = 15 cm

Since the bore is held vertically in the air with the open end at the bottom, the mercury length that occupies the air space is

$$= 100 - (76 + 15)$$

= 9 cm

Therefore.

The total length of the air column = 15 + 9 = 24 cm

Let h cm of mercury flow out as a result of atmospheric pressure.

So,

Length of the air column in the bore = 24 + h cm

And.

Length of the mercury column = 76 - h cm

Initial pressure,  $V_1 = 15 \text{ cm}^3$ 

Final pressure,  $P_2 = 76 - (76 - h)$ 

= h cm of mercury

Final volume,  $V_2 = (24 + h) \text{ cm}^3$ 

The temperature remains constant throughout the process.



Therefore,

$$P_1V_1 = P_2V_2$$

On substituting, we get

$$76 \times 15 = h (24 + h)$$

$$h^2 + 24h - 11410 = 0$$

Solving further, we get

= 23.8 cm or -47.8 cm

Since height cannot be negative. Hence, 23.8 cm of mercury will flow out from the bore.

Length of the air column = 24 + 23.8 = 47.8 cm

12. From a certain apparatus, the diffusion rate of hydrogen has an average value of 28.7 cm<sup>3</sup> s<sup>-1</sup>. The diffusion of another gas under the same conditions is measured to have an average rate of 7.2 cm<sup>3</sup> s<sup>-1</sup>. Identify the gas.

[Hint: Use Graham's law of diffusion:  $R_1/R_2 = (M_2/M_1)^{1/2}$ , where  $R_1$ ,  $R_2$  are diffusion rates of gases 1 and 2, and  $M_1$  and  $M_2$  their respective molecular masses. The law is a simple consequence of the kinetic theory.]

## Solution:

Given

Rate of diffusion of hydrogen, R<sub>1</sub> = 28.7 cm<sup>3</sup>s<sup>-1</sup>

Rate of diffusion of another gas,  $R_2 = 7.2 \text{ cm}^3\text{s}^{-1}$ 

According to Graham's Law of diffusion,

We have

$$R_1 / R_2 = \sqrt{M_2 / M_1}$$

Where,

 $M_1$  is the molecular mass of hydrogen = 2.020g

M<sub>2</sub> is the molecular mass of the unknown gas

Hence,

$$M_2 = M_1 (R_1 / R_2)^2$$

$$= 2.02 (28.7 / 7.2)^{2}$$

We get,



= 32.09 g

32 g is the molecular mass of oxygen.

Therefore, the unknown gas is oxygen.

13. A gas in equilibrium has uniform density and pressure throughout its volume. This is strictly true only if there are no external influences. A gas column under gravity, for example, does not have a uniform density (and pressure). As you might expect, its density decreases with height. The precise dependence is given by the so-called law of the atmosphere

 $n_2 = n_1 \exp [-mg (h_2 - h_1)/k_BT]$ 

where n<sub>2</sub>, n<sub>1</sub> refer to number density at heights h<sub>2</sub> and h<sub>1</sub>

respectively. Use this relation to derive the equation for the sedimentation equilibrium of a suspension in a

liquid column:

 $n_2 = n_1 \exp [-mg N_A (\rho - \rho') (h_2 - h_1)/ (\rho RT)]$ 

where  $\rho$  is the density of the suspended particle, and  $\rho'$  that of the surrounding medium. [N<sub>A</sub> is Avogadro's number and R is the universal gas constant.] [Hint: Use Archimedes's principle to find the apparent weight of the suspended particle.]

## Ans:

Law of atmosphere

$$n_2 = n_1 \exp [-mg (h_2 - h_1)/k_BT]$$
 ———(1)

The suspended particle experiences an apparent weight because the liquid is displaced.

According to Archimedes's principle

Apparent weight = Weight of the water displaced – Weight of the suspended particle

$$= mg - m'g$$

$$= mg - V\rho'g = mg - (m/\rho)\rho'g$$

$$= mg (1 - (\rho'/\rho)) - (2)$$

ρ'= Density of the water

 $\rho$  = Density of the suspended particle

m' = Mass of the suspended particle

m = Mass of the water displaced

V = Volume of a suspended particle

Boltzmann's constant (K) =  $R/N_A$  ——(3)

Substituting equation (2) and equation (3) in equation (1)

$$n_2 = n_1 \exp [-mg (h_2 - h_1)/k_BT]$$

$$n_2 = n_1 \exp \left[ -mg \left( 1 - \rho' / \rho \right) \left( h_2 - h_1 \right) N_A / (RT) \right]$$

$$n_2 = n_1 \exp [-mg N_A (\rho - \rho') (h_2 - h_1) / (\rho RT)]$$



# 14. Given below are the densities of some solids and liquids. Give rough estimates of the size of their atoms:

Substance	Atomic Mass (u)	Density (10³
		Kg m³)
Carbon (diamond)	12.01	2.22
Gold	197.00	19.32
Nitrogen (liquid)	14.01	1.00
Lithium	6.94	0.53
Fluorine (liquid)	19.00	1.14

[Hint: Assume the atoms to be 'tightly packed' in a solid or liquid phase, and use the known value of Avogadro's number. You should, however, not take the actual numbers you obtain for various atomic sizes too literally. Because of the crudeness of the tight packing approximation, the results only indicate that atomic sizes are in the range of a few Å].

#### Ans:

If r is the radius of the atom, then the volume of each atom =  $(4/3)\pi r^3$ 

Volume of all the substance =  $(4/3)\pi r^3 x N = M/\rho$ 

M is the atomic mass of the substance.

ρ is the density of the substance.

One mole of the substance has 6.023 x 10<sup>23</sup> atoms

 $r = (3M/4\pi\rho \times 6.023 \times 10^{23})^{1/3}$ 

For carbon, M = 12. 01 x  $10^{-3}$  kg and  $\rho$  = 2.22 x  $10^{3}$  kg m<sup>-3</sup>

R =  $(3 \times 12.01 \times 10^{-3}/4 \times 3.14 \times 2.22 \times 10^{3} \times 6.023 \times 10^{23})^{1/3}$ 

=  $(36.03 \times 10^{-3} / 167.94 \times 10^{26})^{1/3}$ 

 $1.29 \times 10^{-10} \text{ m} = 1.29 \text{ Å}$ 

For gold, M = 197 x  $10^{-3}$  kg and  $\rho$  = 19. 32 x  $10^{3}$  kg m<sup>-3</sup>

R =  $(3 \times 197 \times 10^{-3}/4 \times 3.14 \times 19.32 \times 10^{3} \times 6.023 \times 10^{23})^{1/3}$ 

 $= 1.59 \times 10^{-10} \text{ m} = 1.59 \text{ Å}$ 

For lithium, M =  $6.94 \times 10^{3} \text{ kg}$  and  $\rho = 0.53 \times 10^{3} \text{ kg/m}^{3}$ 

R =  $(3 \times 6.94 \times 10^{-3}/4 \times 3.14 \times 0.53 \times 10^{3} \times 6.023 \times 10^{23})^{1/3}$ 

 $= 1.73 \times 10^{-10} \text{ m} = 1.73 \text{ Å}$ 



For nitrogen (liquid),  $M = 14.01 \times 10^3 \text{ kg}$  and  $\rho = 1.00 \times 10^3 \text{ kg/m}^3$ 

R =  $(3 \times 14.01 \times 10^{-3}/4 \times 3.14 \times 1.00 \times 10^{3} \times 6.023 \times 10^{23})^{1/3}$ 

=  $1.77 \times 10^{-10} \text{ m} = 1.77 \text{ Å}$ 

For fluorine (liquid), M = 19.00 x  $10^{-3}$  kg and  $\rho$  = 1.14 x  $10^{3}$  kg/m $^{3}$ 

R =  $(3 \times 19 \times 10^{-3}/4 \times 3.14 \times 1.14 \times 10^{3} \times 6.023 \times 10^{23})^{1/3}$ 

 $= 1.88 \times 10^{-10} \text{ m} = 1.88 \text{ Å}$ 

