# CHEM1011 LECTURE 5

Dr Shannan Maisey

# ANSWERS TO HOMEWORK (LECTURE 4)

1. $2H^+(aq) + CO_3^{2-}(aq) \rightarrow CO_2(g) + H_2O(l)$
2. $2H^+(aq) + Mg(s) \rightarrow H_2\,(g) + Mg^{2+}(aq)$
3. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
4. $2H^+(aq) + Zn(s) \rightarrow H_2\,(g) + Zn^{2+}(aq)$

# TODAY'S LEARNING OUTCOMES

- Describe the properties which distinguish gases from other states of matter
- Understand the gas laws:
  - Boyle's Law
  - Charles' Law
  - Avogadro's Law
- Use the above gas laws (the Combined Gas Law) to derive the Ideal Gas Law and do calculations involving gases

# BRANCHES OF CHEMISTRY

Chemistry often split into 4 branches:

| | | | |
|---|---|---|---|
| **Physical chemistry** | **Analytical chemistry** | **Inorganic chemistry** | **Organic chemistry** |

- Boundaries blurred, much overlap
- Categorization not essential
- Gases topics usually put in the physical chemistry basket
- ➢ So what is physical chemistry about?

# WHAT IS PHYSICAL CHEMISTRY?

A simple definition for this diverse topic is not available

“Physical chemistry is the explanation of the properties and reactions of matter in terms of the fundamental forces of nature” (Colleague)

“Physical chemistry is the study of the underlying physical principles that govern the properties and behavior of chemical systems.” (Levine)

More than the other branches of chemistry, physical chemistry is about **WHY** things happen at the molecular level

# GASES – WHAT WOULD WE LIKE TO KNOW?

- Why do gases behave the way they do?

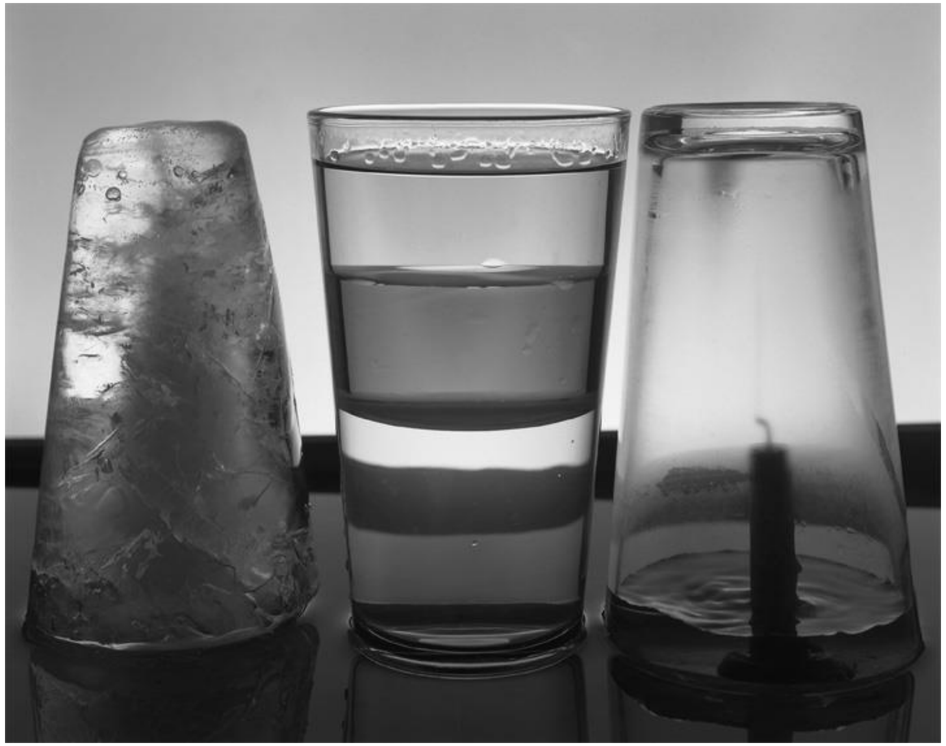
- How can the properties of gases be predicted?

  (*e.g.*, pressure, volume, density, diffusion rates)

- Relate bulk properties such as pressure and temperature to the behaviour of gases at the molecular level – the kinetic theory of gases
  - later in first year

# WHAT IS A GAS? HOW DO YOU DISTINGUISH IT FROM OTHER STATES OF MATTER?

Discuss with the people around you



# PROPERTIES OF GASES

Gas volume changes greatly with pressure *and* temperature;

- Occupy shape of container quickly – *fill space available.*
- Compressible

Gases have relatively low viscosity; (viscosity is a measure of resistance to flow)

Most gases have relatively low densities under normal conditions;

Gases are miscible, *i.e*., they mix with one another in any proportions.

**Solids**

Dense

Non-compressible

**Liquids**

Medium density

Not very compressible

Flow

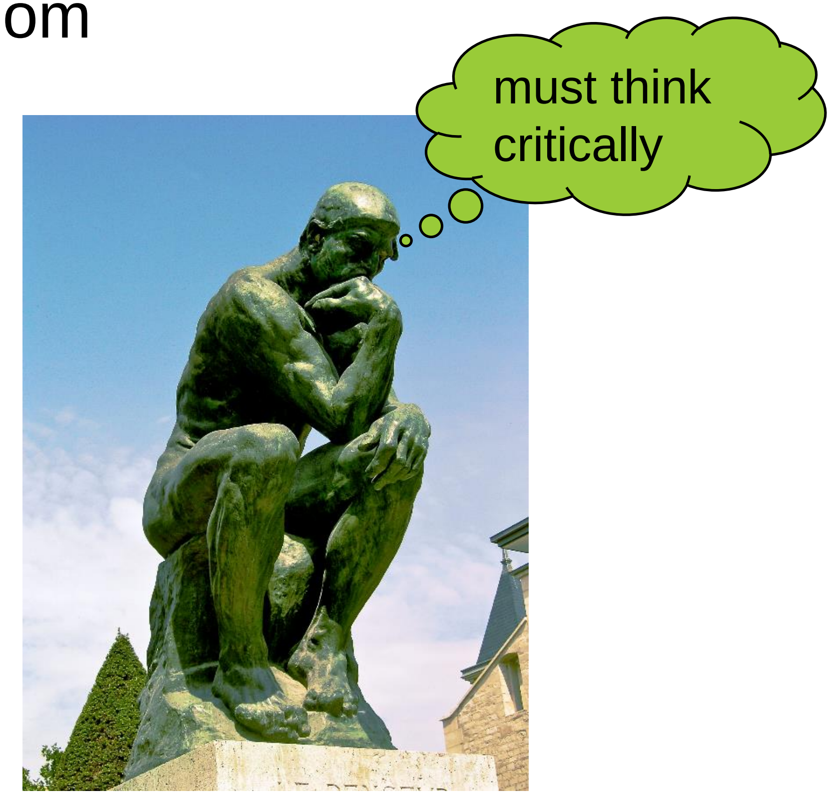
Occupy shape of container

https://acidcow.com/pics/8924-installations-of-caleb-charland-33-pics.html

# THINK!

Q: Oxygen ($O_2$) and hydrogen ($H_2$) are both gases at room temperature (298 K) but water ($H_2O$) is a liquid at room temperature.

WHY??

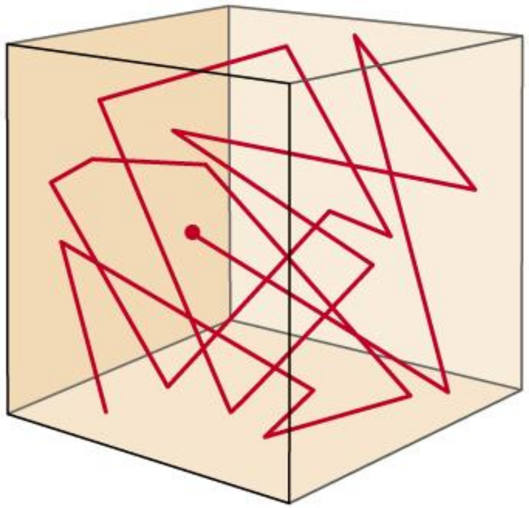


# DESCRIBING GASES (BLACKMAN 6.2)

Gases fill all the available space in a container (i.e. they have **volume**) – why? What properties allow them to do this?

- Individual atoms/molecules **free to move**
  - **Kinetic energy of gases greater** than solids or liquids
- **Forces between** these atoms and molecules **weak**

*(More later)*



As a consequence gases have **pressure** (exert a force against container walls)

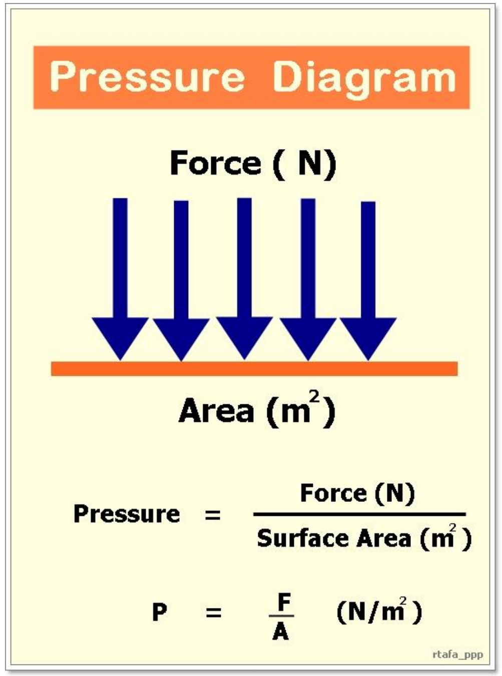
# DESCRIBING GASES (BLACKMAN 6.2)

The defining characteristic of gases is the pressure they exert.

The pressure (p) exerted by a gas is dependent on:

- The amount of gas present  (n – number of moles)
- The volume in which it is contained (V)
- Temperature (T)

# GAS PRESSURE AND MEASUREMENT




Pressure is defined as force exerted per unit area:

$$\boxed{\text{Pressure} = \frac{\text{force}}{\text{area}}}$$

SI unit of force is **newton** (**N**)

1 N = 1 kg m s$^{-2}$,

and of pressure is **pascal** (**Pa**),

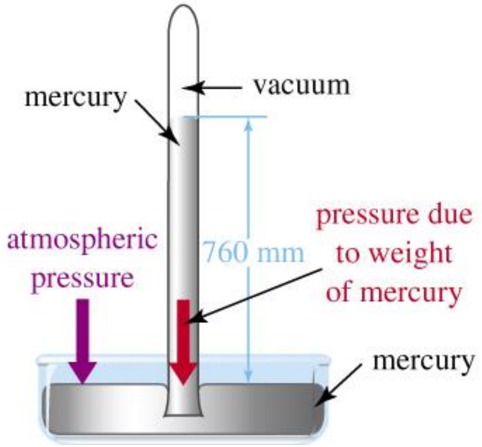
1 Pa = 1 N m$^{-2}$

1 bar = 1 $\times$ 10$^5$ Pa

# MEASURING PRESSURE

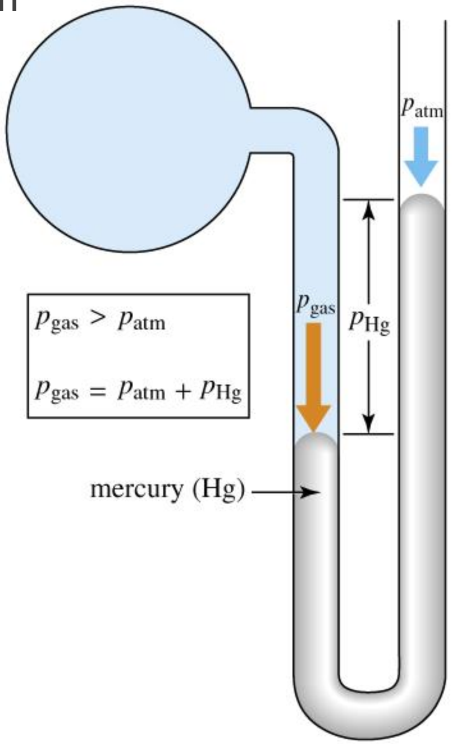
## Barometer

- Measures pressure of atmosphere
- Competition between atmospheric pressure and gravity

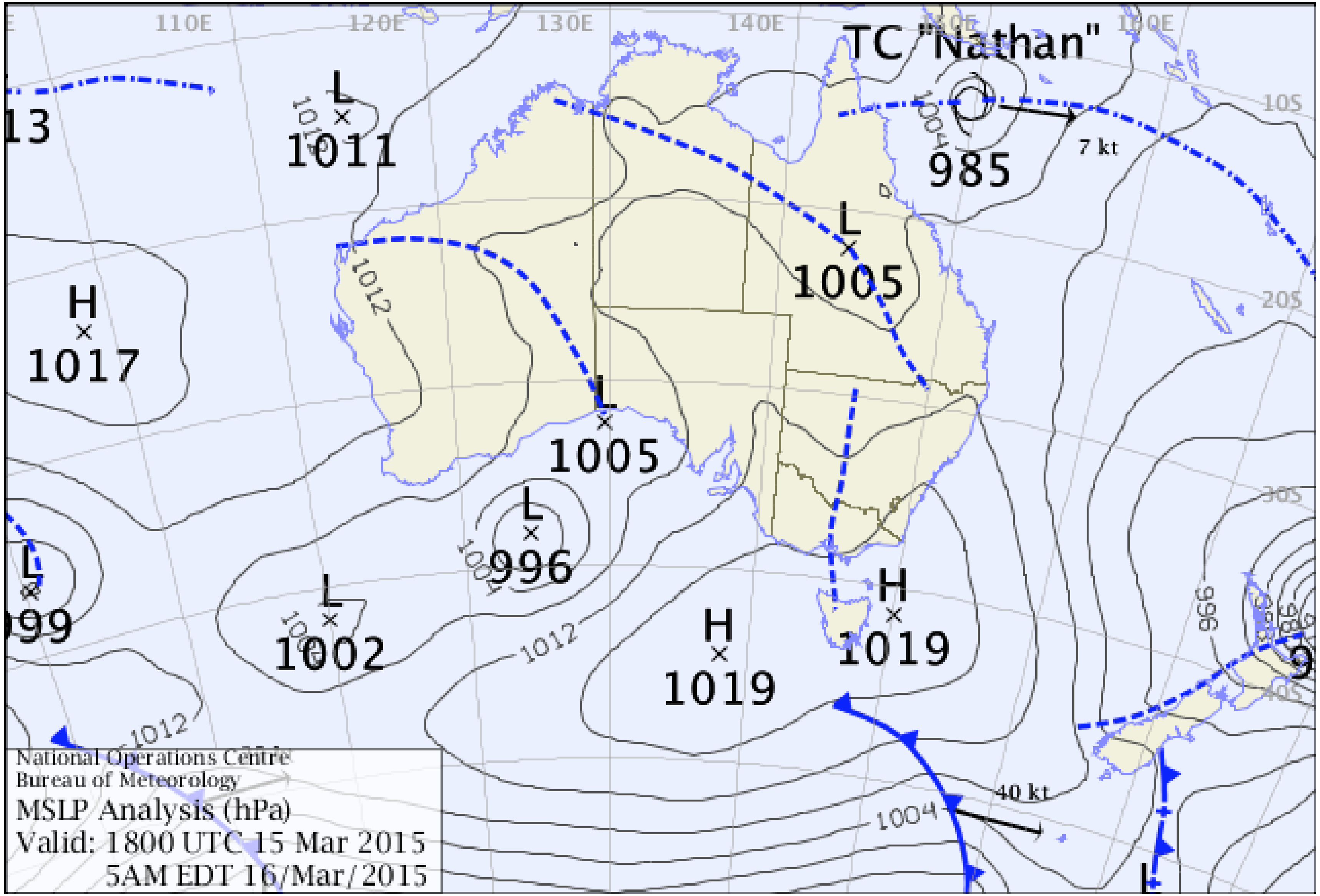



## Manometer

- Measures difference in pressures exerted from two gases
- This is where the popular unit mmHg comes from



| | | |
|---|---|---|
| 1 atm | = | 760 mm Hg |
| | = | 760 Torr |
| | = | 14.7 psi |
| | = | 101 325 Pa |
| | = | 1.01325 bar |




1 atm = 101325 Pa = 1013.25 hPa (hectopascals)

# GAS LAWS

Four variables define the physical behaviour of a sample of gas: pressure (*P*), volume (*V*), temperature (*T*), amount / no. of moles of gas (*n*);

**Variables are interdependent**: any one of them can be determined by measuring the other three;

Three key relationships exist among the 4 gas variables: Boyle's, Charles's and Avogadro's laws

– laws are special cases of the **Ideal Gas Law**.

# BOYLE'S LAW RELATIONSHIP BETWEEN *V* AND *P*

*At constant temperature, the volume of a fixed amount of gas is inversely proportional to the applied (external) pressure*;

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

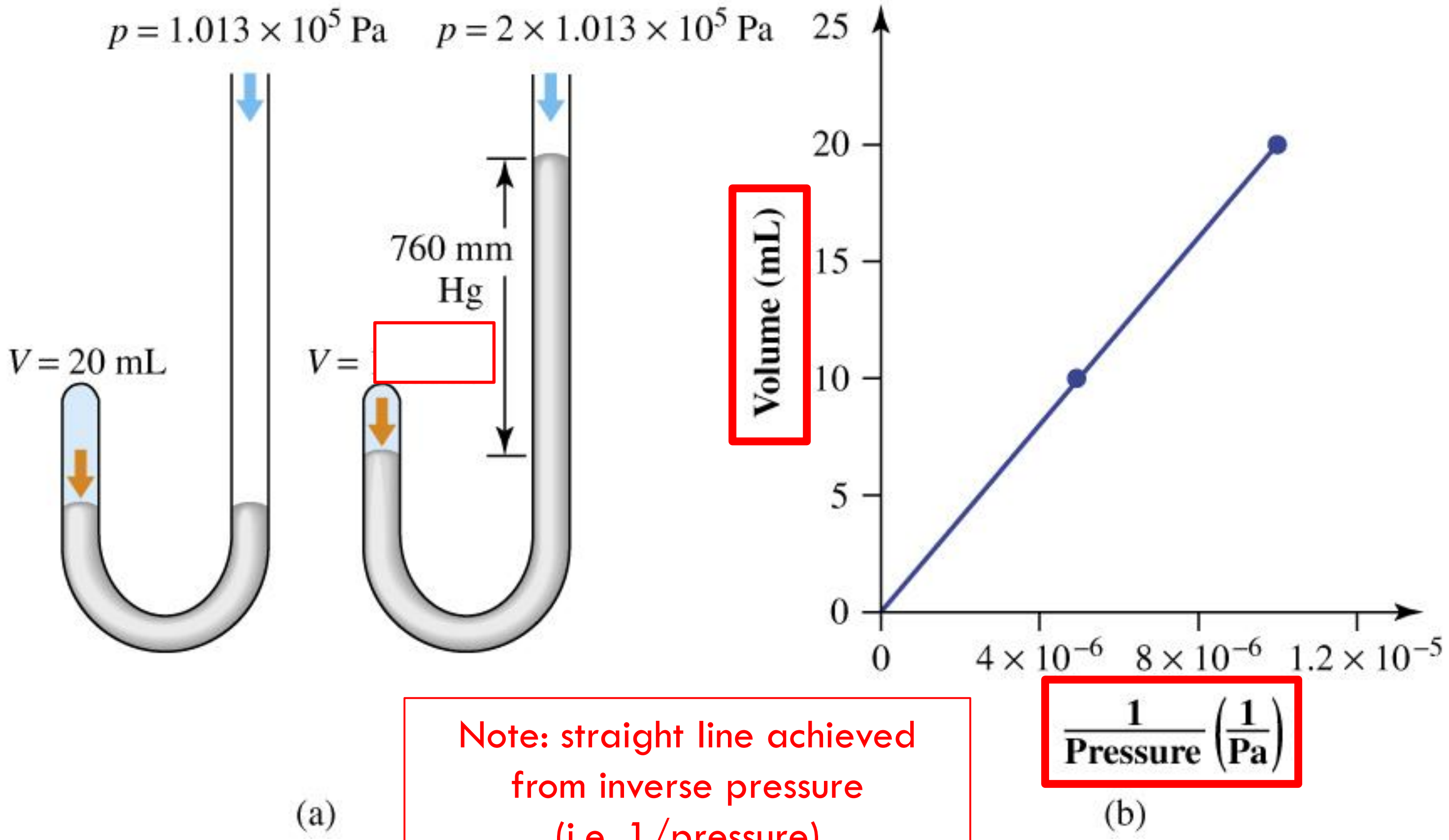
or $PV$ = constant (note $T$ and $n$ are fixed)

The constant is the same for the great majority of gases. $P_1V_1 = P_2V_2$

*Robert Boyle (1627-1691)*
*Irish natural philosopher*

# BOYLE'S LAW

What happens to the volume of the gas?

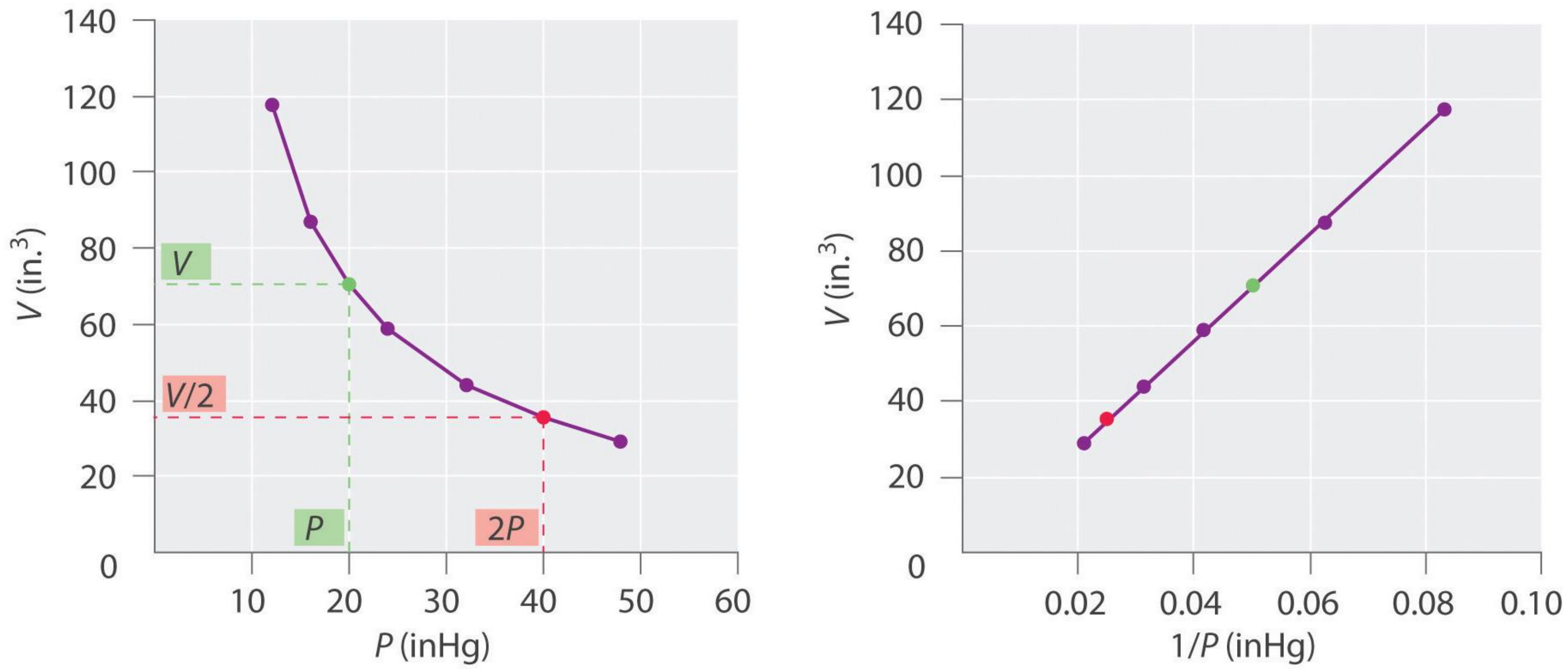



Note: straight line achieved from inverse pressure (i.e. 1/pressure)

# BOYLE'S LAW

$P_1V_1 = P_2V_2$

A different example – from pressure to 1/pressure:




(b) Volume vs. pressure

(c) Volume vs. 1/pressure

Worked Example 6.1-6.2

You try: Tute Set 1, Q 8a

# WORKED EXAMPLE

At constant temperature a sample of a gas at 124 kPa occupies a volume of 12.0 L.

If the pressure is increased to 200 kPa, what volume would the gas occupy?

$P_1V_1 = P_2V_2$

124 kPa x 12.0 L = 200 kPa x $V_2$

$V_2$ = 7.44 L (3 sig. fig)

# CHARLES'S LAW RELATIONSHIP BETWEEN $V$ AND $T$

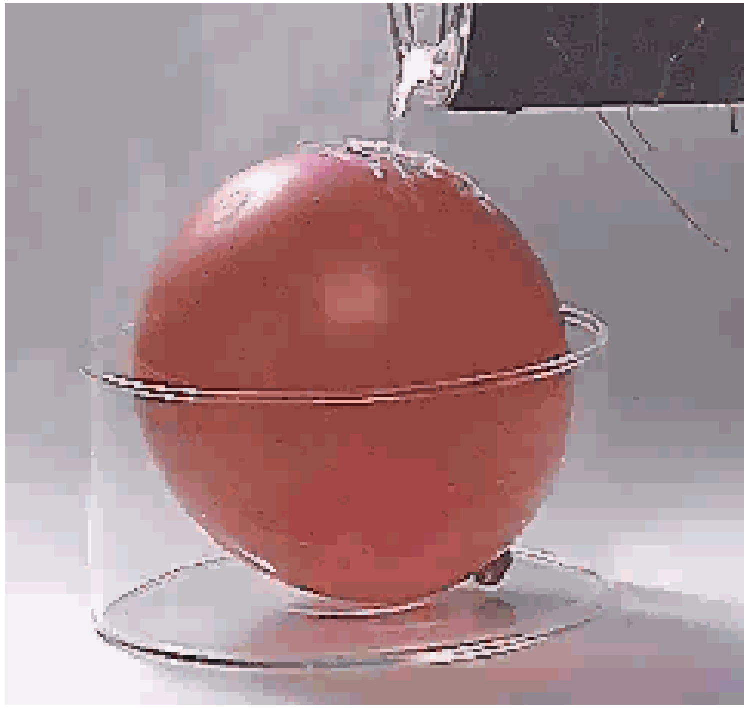
J. Charles & J.L. Gay–Lussac: 18th/19th century French scientists.

*At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature*:

$$\boxed{V \propto T \;\; [P \text{ and } n \text{ fixed}) \;\; \text{or} \;\; \frac{V}{T} = \text{constant}}$$

If T increases, V increases, and vice versa.

*Kelvin scale* needs to be used in gas calculations.



Source: http://www.chem.uiuc.edu

# CELSIUS TO KELVIN

0 °C =273.15 K

So to covert from °C to K : °C + 273.15 = K

*For example 25 ° C = 298.15 K*

*Note: sometimes chemists are a bit lazy and drop the .15 use 273K instead*

# CHARLES' LAW EXAMPLE

At a fixed pressure, a fixed amount of gas occupies 3.5 L at 110 °C.

What is the volume if the temperature is decreased to 40 °C?

110 $^{o}$C = 273 + 110 K = 383 K
40 $^{o}$C = 273 + 40 K = 313 K

From Charles' Law:

$V_2 = (V_1 \times T_2) / T_1$

= (3.5 L x 313 K) / 383 K

= 2.86 L

= 2.9 L (2 sig. fig)

# AVOGADRO'S LAW RELATIONSHIP BETWEEN VOLUME AND AMOUNT

*At fixed temperature and pressure, the volume of a gas is directly proportional to the amount (mol) of gas*:

$$\boxed{V \propto n \quad (P \text{ and } T \text{ fixed}) \Rightarrow \frac{V}{n} = \text{constant}}$$

At fixed $T$ and $P$, equal volumes of **any ideal gas** contain equal numbers of particles (or amounts in mol);

The constant is the same for all gases at fixed $T$ and $P$.

Note: Not to be confused with Avocado’s law which says that too much smashed avo on toast at a young age will preclude you from ever affording a house (Millennial specific).


# AVOGADRO'S LAW RELATIONSHIP BETWEEN VOLUME AND AMOUNT

*At fixed temperature and pressure, the volume of a gas is directly proportional to the amount (mol) of gas*:

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At fixed *T* and *P*, equal volumes of **any ideal gas** contain equal numbers of particles (or amounts in mol);

The constant is the same for all gases at fixed *T* and *P*.

# THE IDEAL GAS LAW

| | | |
|---|---|---|
| Boyle's Law: | $V \propto 1 / P$ | (fixed $n$, $T$) |
| Charles's Law: | $V \propto T$ | (fixed $n$, $P$) |
| Avogadro's Law: | $V \propto n$ | (fixed $P$, $T$) |

**Ideal Gas Law**:

$$V \propto \frac{nT}{P} \quad \text{or} \quad PV \propto nT \quad \text{or} \quad \frac{PV}{nT} = R$$

$$\boxed{\text{or } PV = nRT}$$

$R$ is a proportionality constant known as the **universal gas constant** = 8.314 J $K^{-1}$ $mol^{-1}$

# THE IDEAL GAS LAW

*The gas equation becomes one of the individual gas laws when two of the four variables are kept constant:*

*e.g.*, when initial conditions (subscript 1) change to final conditions  (subscript 2)

$$P_1V_1 = n_1RT_1 \quad \text{and} \quad P_2V_2 = n_2RT_2$$

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

Dont forget – always use temperatures in Kelvin!

When *P* and *T* are constant, equation is:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

# WORKED EXAMPLE 6.1

$$pV = nRT$$

A $1.000 \times 10^3$ L steel storage tank contains 88.5 kg of methane gas, $CH_4$. If the temperature is 25°C, what is the pressure inside the tank?

*Need to convert mass to moles and Celcius to Kelvin to use $R = 8.314$ L kPa $K^{-1}$ $mol^{-1}$.*

$M(CH_4) = 16.04$ g $mol^{-1}$

$n = m / M$

$n = 88.5 \times 10^3 / 16.04$

$n = \underline{5.52 \times 10^3 \text{ mol of methane}}$

$T = 25 + 273.15 = \underline{298.15 \text{ K}}$

$V = 1.000 \times 10^3 \text{ L} = 1000\text{L}$

Putting all values into universal gas law:

$P = nRT / V$

$= (5.52 \times 10^3 \text{ mol} \times 8.314 \text{ L kPa K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}) / 1000 \text{ L}$

$= \underline{1.36 \times 10^4 \text{ kPa or } 13.6 \text{ MPa}}$

# REAL GASES

## How much space do gas atoms occupy?

## How 'empty' is a 3 L balloon filled with helium gas at 1 atm?

One He atom has an atomic **radius of 31 $\times$ $10^{-12}$ m**) and therefore a "**volume" of 1.25 $\times$ $10^{-31}$ $m^3$**.

$$PV = nRT$$

1 atm $\times$ 3 L = n $\times$ 0.08206 L atm $K^{-1}$ $mol^{-1}$ $\times$ 298 K

$\therefore$ **n = 0.123 moles** of He

$\therefore$ 0.123 $\times$ $N_A$ = ***7.39* $\times$ $10^{22}$ atoms** of He in the balloon

*So the total "volume" of He atoms in the balloon is:*

(7.39 $\times$ $10^{22}$) atoms $\times$ (1.25 x $10^{-31}$) $m^3$ = 9.23 $\times$ $10^{-9}$ $m^3$.

*How does that compare with the balloon volume?*

(9.23 $\times$ $10^{-9}$ $m^3$) / (3 x $10^{-3}$ $m^3$) $\times$ 100% = 0.00032 %

**… the balloon is 99.9997% "empty"**

# OTHER UNITS OF PRESSURE

- The SI unit for pressure is pascal (Pa)
- 1 Pa = 1 N $m^{-2}$
- A number of non-SI units are used:
  - 1 atm is the pressure that will support a column of mercury 760 mm in height
  - 1 atm = 1.01325 x $10^5$ Pa
  - 1 torr is the pressure exerted by a column of mercury 1 mm in height
  - 1 atm = 760 torr
  - 1 bar = $10^5$ Pa

# A WORD ABOUT UNITS AND THE VALUE OF R...

SI units:

- P is in Pascals, Pa
- V is in cubic metres, $m^3$
- IF V in $m^3$ and P in Pa, R = 8.314 J $mol^{-1}$ $K^{-1}$

"Commonly used units"

- P is in atmospheres, atm
- V is in litres, L or $dm^3$
- IF V in L and P in atm, R = 0.08206 atm L $mol^{-1}$ $K^{-1}$
- **CONVERT TO ONE PAIR OF UNITS OR THE OTHER**

| Values of $R$ [1] | Units ($V P T^{-1} n^{-1}$) |
|---|---|
| 8.314 4598(48) | $kg\ m^2\ s^{-2}\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) | $J\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) × $10^{-3}$ | $kJ\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) × $10^{7}$ | $erg\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) × $10^{-3}$ | $amu\ (km/s)^2\ K^{-1}$ |
| 8.314 4598(48) | $m^3\ Pa\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) × $10^{6}$ | $cm^3\ Pa\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) | $L\ kPa\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) × $10^{3}$ | $cm^3\ kPa\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) × $10^{-6}$ | $m^3\ MPa\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) | $cm^3\ MPa\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) × $10^{-5}$ | $m^3\ bar\ K^{-1}\ mol^{-1}$ |
| 8.314 4598(48) × $10^{-2}$ | $L\ bar\ K^{-1}\ mol^{-1}$ |
| 83.144 598(48) | $cm^3\ bar\ K^{-1}\ mol^{-1}$ |
| 62.363 577(36) | $L\ Torr\ K^{-1}\ mol^{-1}$ |
| 1.987 2036(11) × $10^{-3}$ | $kcal\ K^{-1}\ mol^{-1}$ |
| 8.205 7338(47) × $10^{-5}$ | $m^3\ atm\ K^{-1}\ mol^{-1}$ |
| 0.082 057 338(47) | $L\ atm\ K^{-1}\ mol^{-1}$ |
| 82.057 338(47) | $cm^3\ atm\ K^{-1}\ mol^{-1}$ |

https://en.wikipedia.org/wiki/Gas_constant



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# GAS BEHAVIOUR AT STANDARD CONDITIONS

Chosen set of *standard conditions* called **standard temperature and pressure (STP)**:

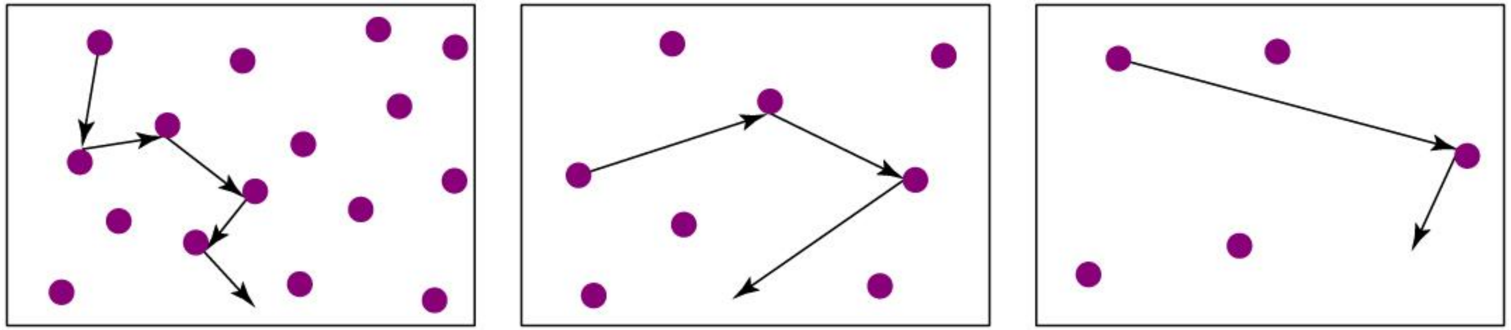
STP: 0 $^{o}$C (273.15 K) & 1 atm (760 Torr)

Volume of 1 mol of an ideal gas at STP is called ***standard molar volume*** (22.414 L)

At room temperature, ~25 $^{o}$C or ~298 K,

1 mole of gas occupies about 25 L.

# GAS DENSITY



Think about the interactions between molecules of gases with different densities:

**More dense:** collisions occur more frequently, travel short distances between collisions

**Less dense:** molecules move greater distances between collisions

$$\boxed{\rho = \frac{MP}{RT}}$$

*Note: Capital p is used for pressure just to distinguish it from density*

*This is the symbol for density*

Density = mass / volume

$$\rho = \frac{m}{V}$$

(Molar mass)

*Where m = n×M*

Rearrange Ideal gas equation to substitute $n = pV/RT$

*Cancel out V:*

$$\rho = \frac{\boldsymbol{M\,P\,V}}{\boldsymbol{V\,R\,T}}$$

<u>Note</u>: Density of a gas is: directly proportional to its molar mass *and* inversely proportional to its temperature (in *K*).

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# GAS DENSITY

$$\rho = \frac{MP}{RT}$$

The density of a given gas ________ linearly with increasing **pressure** (at fixed temperature)?

- A Increases ✓
- B Decreases
- C Has no relationship
- D Don't know

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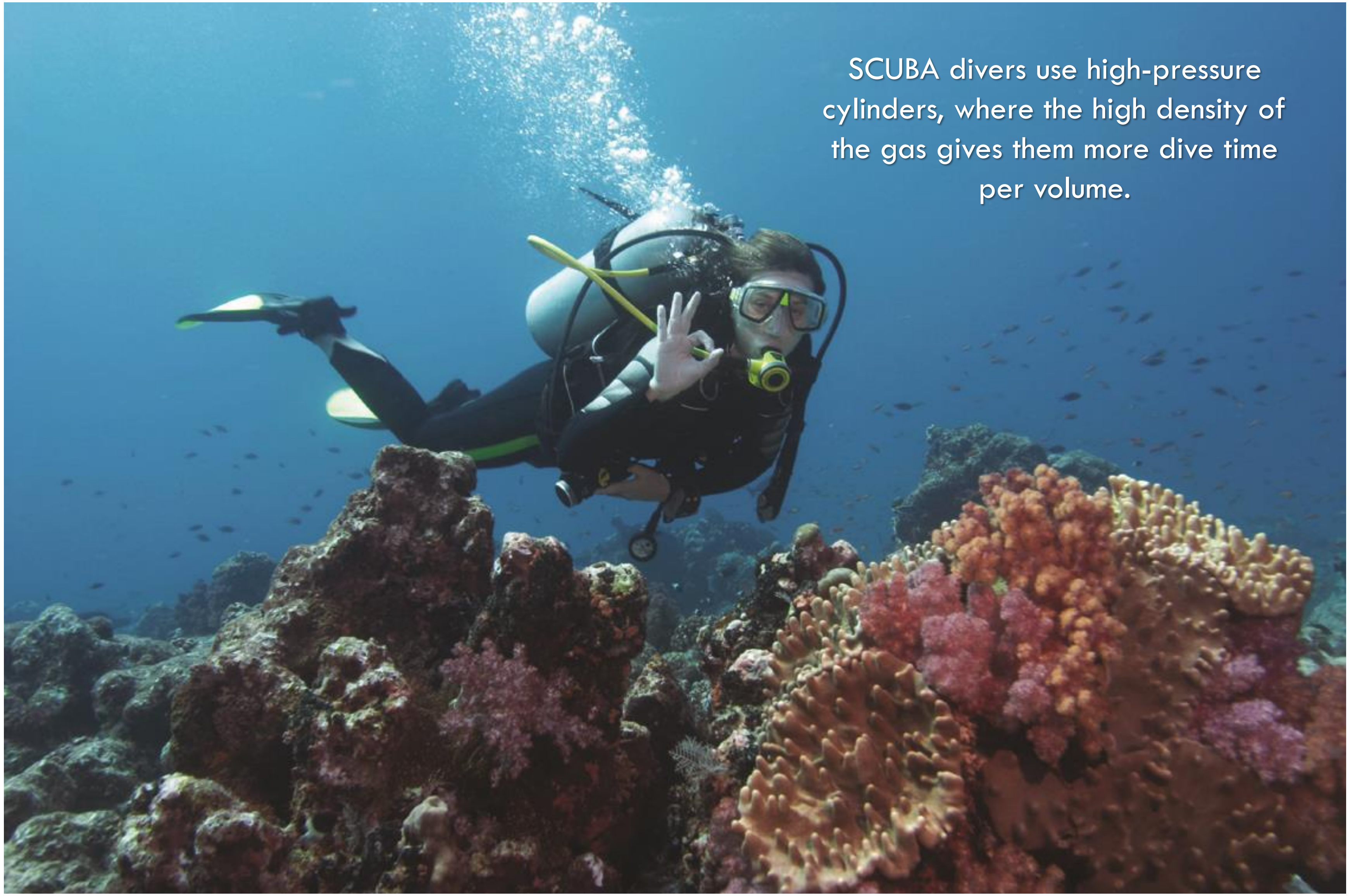
SCUBA divers use high-pressure cylinders, where the high density of the gas gives them more dive time per volume.

# MOLAR MASS FROM THE DENSITY OF A GAS

We can use a simple rearrangement of the gas law to determine the molar mass of an unknown gas or volatile liquid:

$$n = \frac{m}{M_r} = \frac{PV}{RT} \quad \text{so} \quad \boxed{M_r = \frac{mRT}{PV}}$$

Recall… $\rho = \frac{m}{V}$

Hence $\boxed{M_r = \frac{\rho RT}{P}}$

# EXAMPLE

Calculate the molar mass of a gas if 0.455 g occupies a volume of 250.0 mL at 27 $^{o}C$ and 772 mmHg.

Calculate the molar mass of a gas if 0.455 g occupies a volume of 250.0 mL at 27 $^{o}$C and 772 mmHg.

*Use the formula* $$M_r = \frac{\rho RT}{P}$$

*Remember to change to an appropriate set of units! (So we can chose appropriate value for R)*

Using volume in litres, pressure in atm, temperature in K: gives R = 0.08206 atm L mol$^{-1}$ K$^{-1}$
Volume = 250.0/1000 litres, 0.2500 L
Density ($\rho$) = mass/ volume = 0.455/0.25 = 1.82 g/L
Pressure converted to atmospheres = 772/760 atm = 1.016 atm
Temperature = 27 + 273.15 = 300.15 K

$M_r$ = (1.82 x 0.08206 x 300.15)/ 1.016 = 44.12 g/mol

*Units for the answer is grams since we used a mass in grams*

# HOMEWORK 1

From worked example 6.1 what would the pressure be if the tank was stored in a hot shed where the temperature reached 42°C?

# HOMEWORK 2

A sample of helium gas is held at constant temperature inside a cylinder with a volume of 0.80 L when a piston exerts a pressure of $1.5 \times 10^5$ Pa. If the external pressure on the piston is increased to $2.1 \times 10^5$ Pa, what will the new volume be?