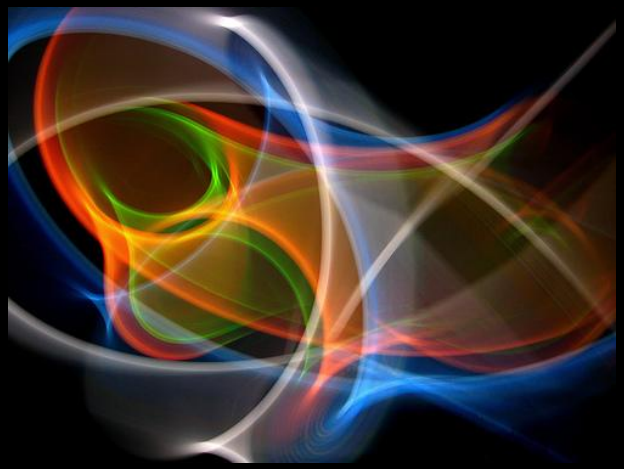

Gas Laws

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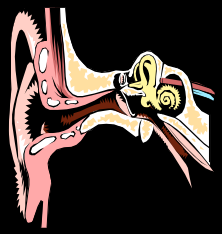
LPT

Rigid and Flexible Gas Containers

Walls: rigid
Volume: constant
Rupture when internal pressure exceeds container strength
Example: compressed gas cylinder

Walls: flexible
Volume: constant if internal & surroundings pressures equal
Volume: changes if internal & surroundings pressures unequal
Rupture when internal pressure exceeds container strength
Examples: balloon, internal air spaces (lungs, ears, sinus, gut)



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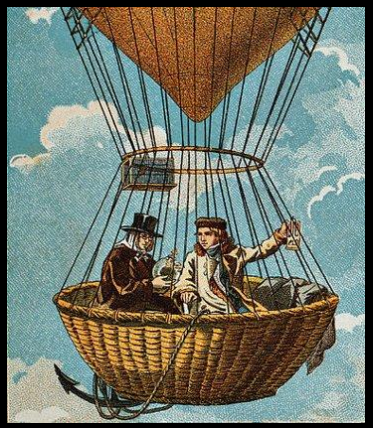
LPT

Joseph Louis Guy-Lussac

French chemist
Student of Jacques Charles
Studied Gases In Chemical Reactions



Pressure - Temperature relationship (1809)
Maybe called Charles's Law or Charles's Law #2
Sometimes called Amonton's Law
(Proposed relationship, but lacked technology to prove)
But,
Guy-Lussac was first to experimentally document P-T relation

His observations - primary source of absolute temperature scale

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LPT

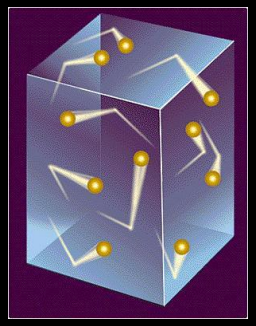
Guy-Lussac's Law

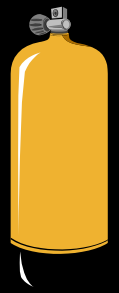
Heat energy increases molecular motion.

Volume of cylinder cannot increase, the pressure increases

At constant *volume*, in a RIGID container:
pressure is directly proportional to the absolute temperature

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





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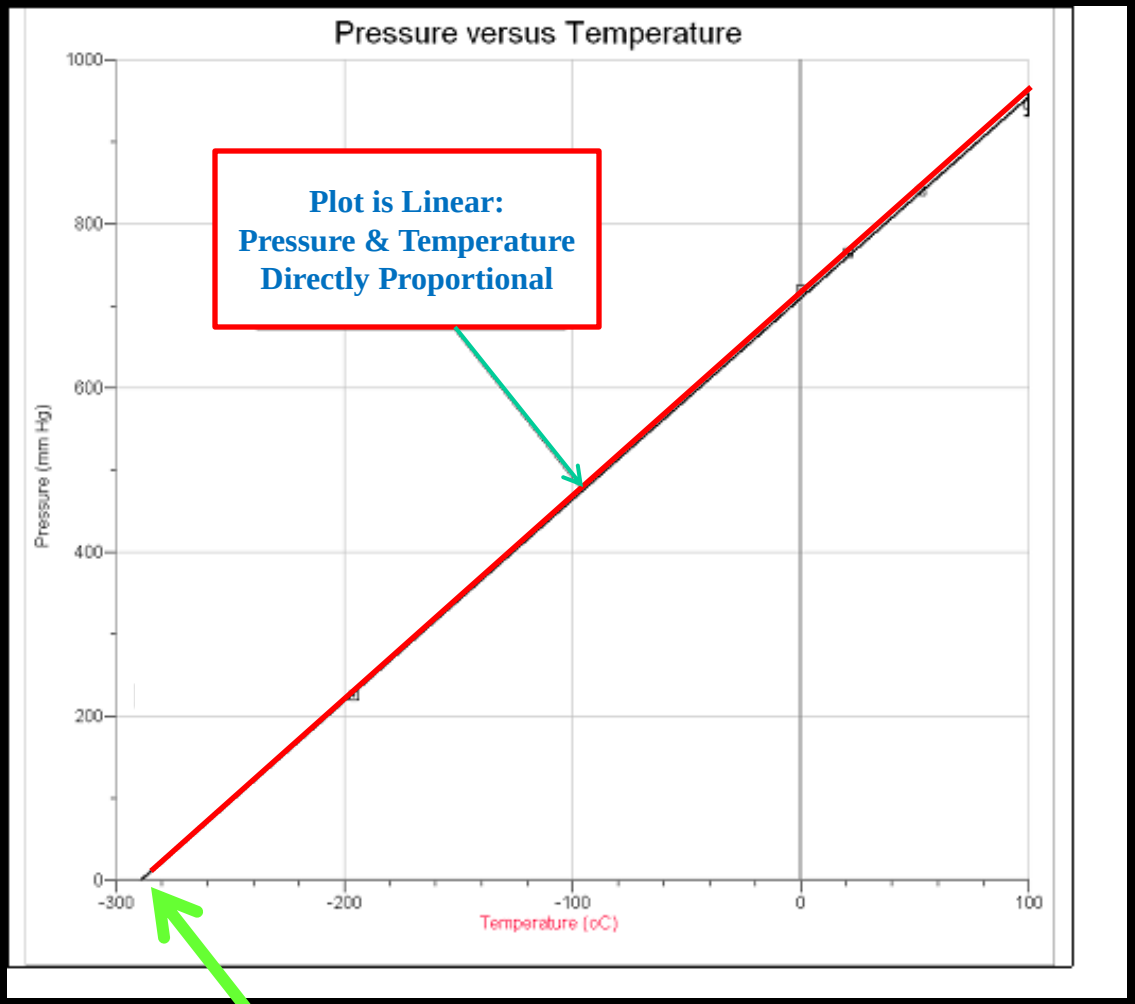
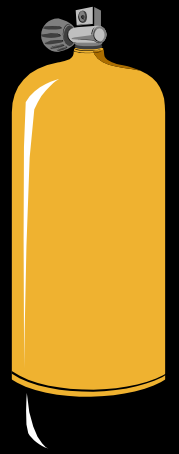
LPT

Guy-Lussac's Law





Absolute Zero (-273.16 ºC)

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LPT

A sample of oxygen has a pressure of 1420. mm Hg at a temperature of 75 °C. What is the pressure of this gas sample if temperature is lowered to 19° C?

	Pressure (torr)*	Volume	Temperature (°C)	→	Temperature (K)
Initial	1420	constant	75	+ 273	348
Final	?	constant	19	+ 273	292

Volume constant, use Guy-Lussac's Law

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

$$\frac{1420 \text{ torr}}{348 \text{ K}} = \frac{P_2}{292 \text{ K}} \longrightarrow \frac{(1420 \text{ torr})(292 \text{ K})}{348 \text{ K}} = P_2$$

$P_2 = 1191.49$ torr ➔ 1190 torr ➔ 1190 mm Hg

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*** 1 mm Hg = 1 torr**

LPT

Calculate the pressure a gas will exert at 65 °C if the gas has a pressure of 830. torr at 52 °C.

	Pressure (torr)	Volume	Temperature (°C)	→	Temperature (K)
Initial	830	constant	52	+ 273	325
Final	?	constant	65	+ 273	338

Volume constant, use Guy-Lussac's Law

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

$$\frac{830 \text{ torr}}{325 \text{ K}} = \frac{P_2}{338 \text{ K}} \longrightarrow \frac{(830 \text{ torr})(338 \text{ K})}{325 \text{ K}} = P_2$$

$P_2 = 863.2$ torr ➔ 863 torr

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LPT

A sample of nitrogen has a pressure of 1420. torr at a temperature of 75 °C. What is the ° C temperature of this gas if the pressure is lowered to 258 torr?

	Pressure (torr)	Volume	Temperature (°C)	→	Temperature (K)
Initial	1420	constant	75	+ 273	348
Final	258	constant	?	+ 273	?

Volume constant, use Guy-Lussac's Law

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

$$\frac{1420 \text{ torr}}{348 \text{ K}} = \frac{258 \text{ torr}}{T_2} \longrightarrow \frac{(258 \text{ torr})\,(348 \text{ K})}{(1420 \text{ torr})} = T_2$$

$T_2 = 63.2262 \text{ K} \rightarrow T_2 = 63.2 \text{ K}$

$T_2 = 63.2 \text{ K} - 273 = -210 \text{ ° C}$

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LPT

Jacques Charles

French chemist

Scientific Advisor to Montgolfier brothers

Volume - Temperature Relationship (1787)

1783 – First hot air balloon

Sack cloth and paper with 1800 buttons

Redesigned the way hot-air balloons were built:

- **Silk instead of paper construction**
- **Hydrogen instead of hot air**
- **Valve line**
- **Wicker basket passenger compartment**

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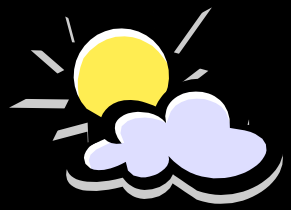
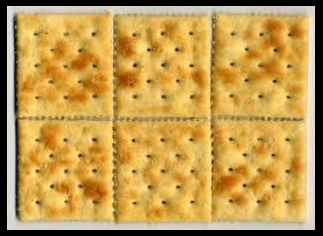
LPT



Charles' Law



Heat energy increases molecular motion.

Volume of flexible container increases

At constant *pressure*, in a FLEXIBLE container volume is directly proportional to the absolute temperature

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

If T = negative, volume = negative (not realistic)

Need temperature to be positive

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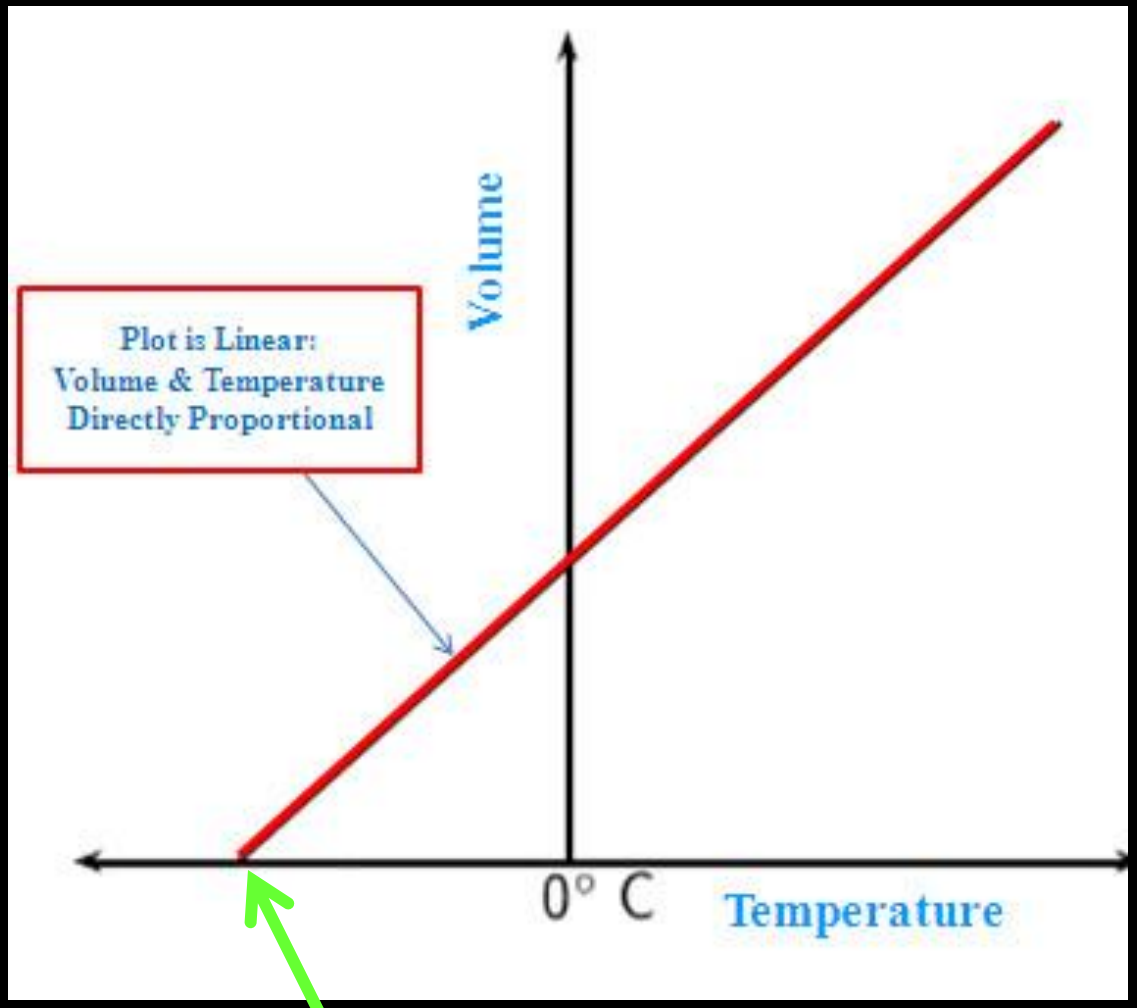
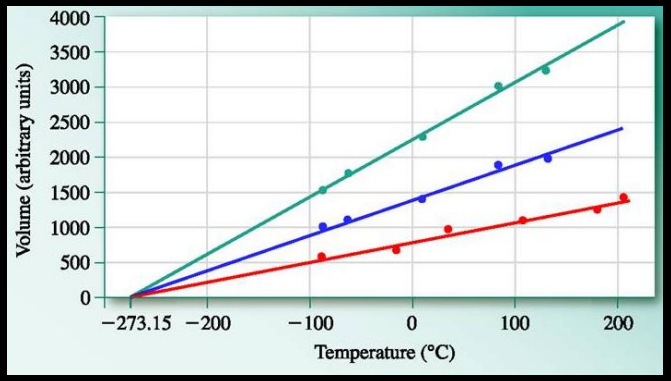
LPT

Charles' Law





Absolute Zero (-273.16 °C)

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LPT

A sample of oxygen occupies a volume of 1240 mL at temperature of 45° C. What is the volume of this gas sample if the temperature is raised to 85° C?

	Pressure	Volume (mL)	Temperature (^oC)	→	Temperature (K)
Initial	constant	1240	45	+ 273	318
Final	constant	?	85	+ 273	358

Pressure constant, use Charles' Law

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

$$\frac{1240\ mL}{318\ K} = \frac{V_2}{358\ K} \longrightarrow \frac{(1240\ mL)(358\ K)}{318\ K} = V_2$$

$V_2 = 1395.97\ mL \rightarrow 1400\ mL \quad (1.40 \times 10^3\ mL)$

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LPT

Calculate the volume a gas will occupy at 15 °C if the gas has a volume of 830. mL at 42 °C.

	Pressure	Volume (mL)	Temperature (^oC)	→	Temperature (K)
Initial	constant	830	42	+ 273	315
Final	constant	?	15	+ 273	288

Pressure constant, use Charles' Law

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

$$\frac{830\ mL}{315\ K} = \frac{V_2}{288\ K} \longrightarrow \frac{(830\ mL)(288\ K)}{315\ K} = V_2$$

$V_2 = 758.857\ mL \rightarrow 759\ mL$

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LPT

Calculate the final temperature in °C of a gas initially at 39 °C whose volume changes from 348 ml to 657 mL. The pressure remains constant.

	Pressure	Volume (mL)	Temperature (°C)	→	Temperature (K)
Initial	constant	348	39	+ 273	312
Final	constant	657	?	+ 273	?

Pressure constant, use Charles' Law

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

$$\frac{348\ mL}{312\ K} = \frac{657\ mL}{T_2} \longrightarrow \frac{(657\ mL)\ (312\ K)}{(348\ mL)} = T_2$$

$T_2 = 589.038 \rightarrow 589\ K$

$T_2 = 589\ K - 273 = 316\ ^oC$

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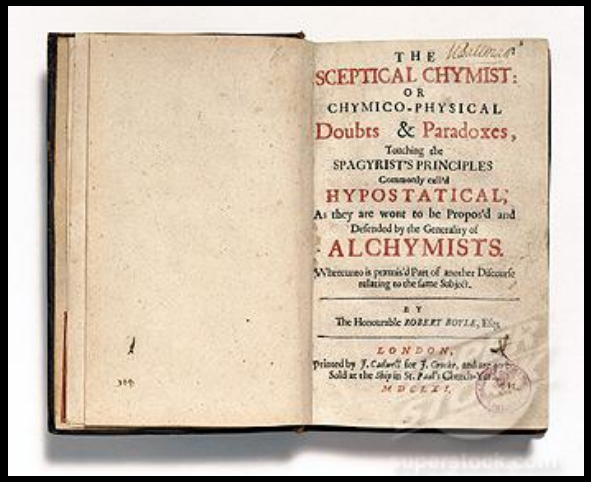
LPT

Robert Boyle

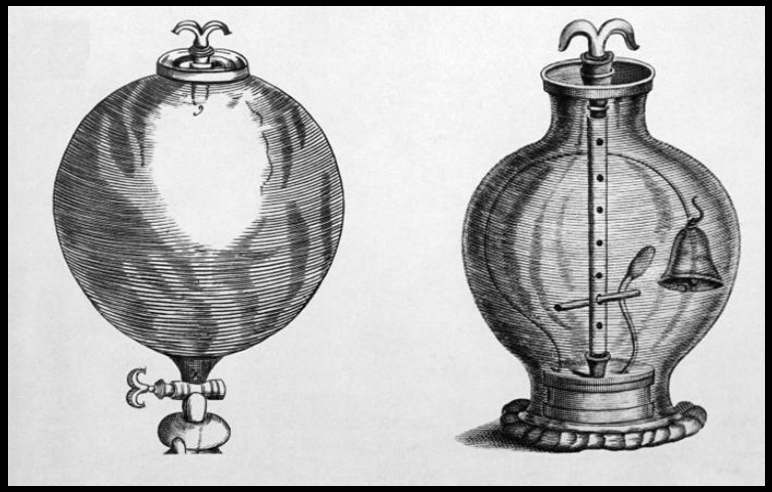
Irish Alchemist
Father of modern chemistry
Founder of Royal Society


THE
SCEPTICAL CHYMIST:
OR
CHYMICO-PHYSICAL
Doubts & Paradoxes,
Touching the
SPAGYRIST'S PRINCIPLES
Commonly called
HYPOSTATICAL,
As they are wont to be Propos'd and
Defended by the Generality of
ALCHYMISTS.
Wherunto is premis'd Part of another Discourse
relating to the same Subject.
BY
The Honourable ROBERT BOYLE, Esq;
LONDON,
Printed by J. Cadwell for J. Crooke, and are to be
Sold at the Ship in St. Paul's Church-Yard.
MDCLXI.

Pressure - Volume relationship (1660)

New Experiments: Phsico-Mechanical Touching the spring of air and their effects (1660)

The Sceptical Chymst (Air, Earth, Fire, & Water not elements) (1661)



In an evacuated chamber
Observed bubble in snake's eye
Reduced Pressure Changes Physiology
Bell produced no sound
Air needed to carry sound

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LPT

Boyles's Law Apparatus

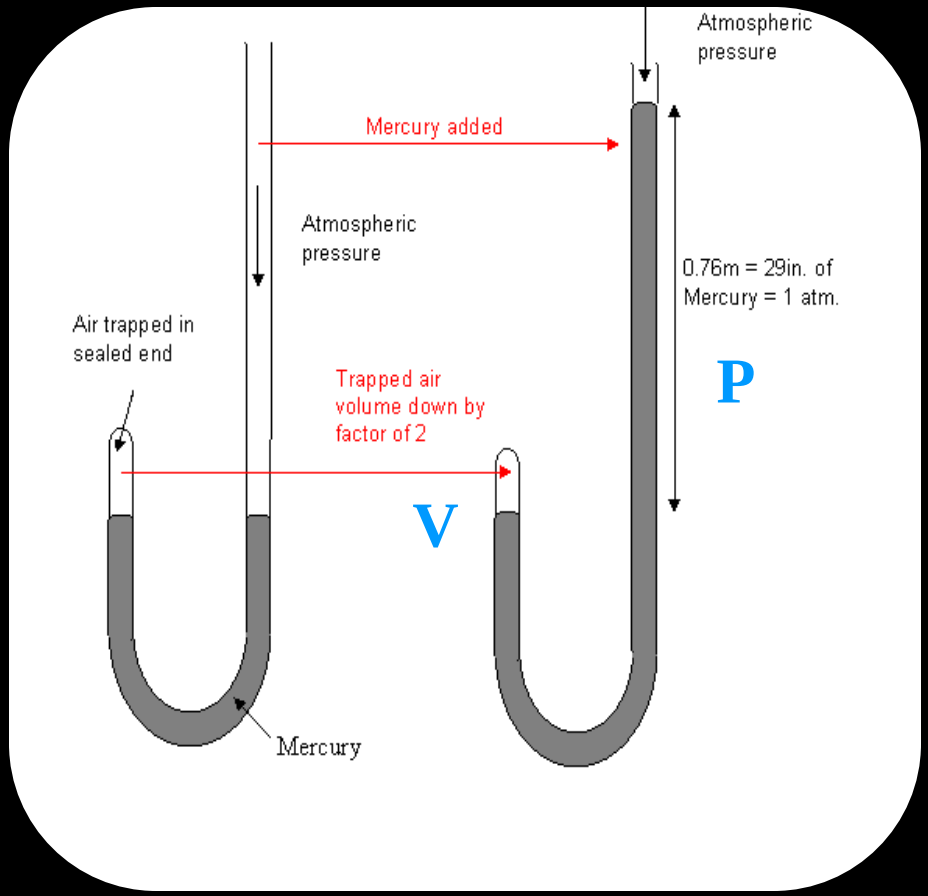
Measure height mercury (P)
Measure Volume (V)

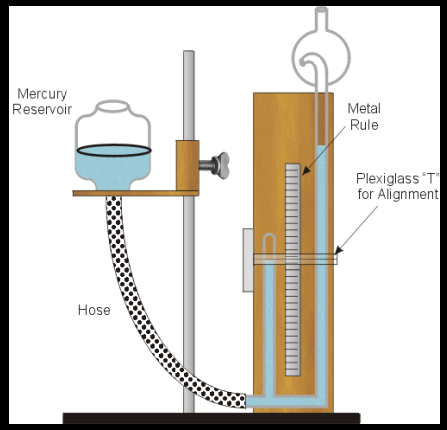
$P_1V_1 = k$
$P_2V_2 = k$
$P_3V_3 = k$

Set Equalities

$P_1V_1 = k = P_2V_2$

$P_1V_1 = P_2V_2$





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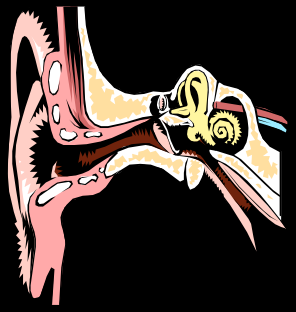
LPT

Boyles's Law



At constant *temperature*, the volume of a flexible container depends upon the surrounding pressure

At constant *temperature*, in a FLEXIBLE container volume is indirectly proportional to the absolute pressure

$$P_1 V_1 = P_2 V_2$$

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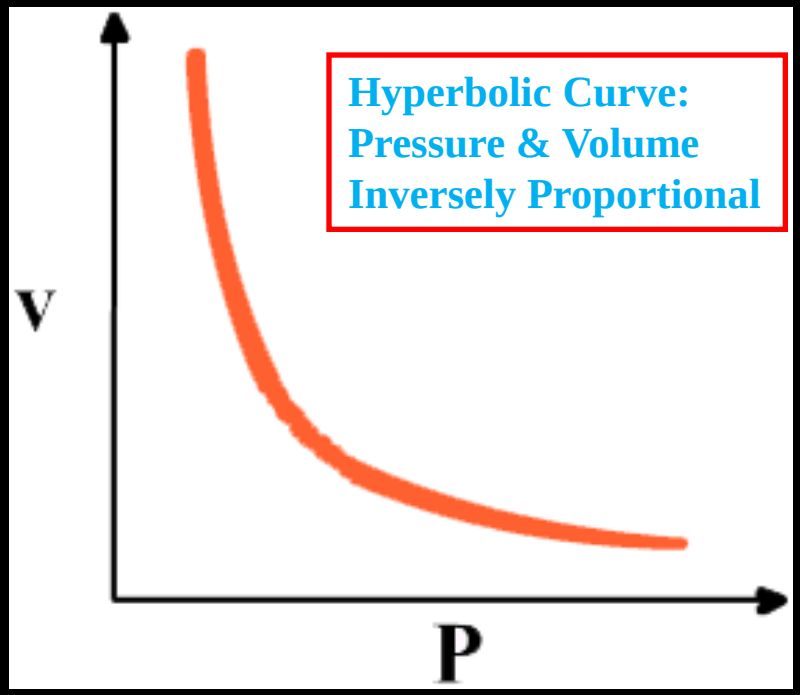
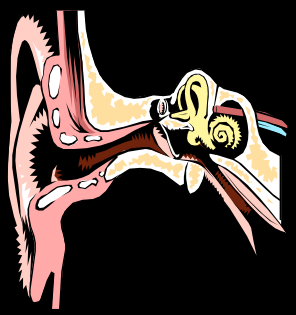
LPT

Boyles's Law



Greatest volume change:
pressure near zero

Means greatest risk to tissue:
shallow water



Explains:

Ear Discomfort while ascending / descending
Grandpa's knee forecasting weather
Changes in all gas volumes with altitude / depth
Changes in pressure with altitude / depth

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LPT

At 723 mm Hg a gas has a volume of 294 mL. What is the new volume of this gas if the pressure is changed to 585 mm Hg?

	Pressure (mm Hg)	Volume (mL)	Temperature (°C)	Temperature (K)
Initial	723	294	constant	constant
Final	585	?	constant	constant

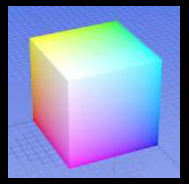
Temperature constant, use Boyle's Law

$$P_1 V_1 = P_2 V_2$$

$$(723 \text{ mm Hg})(294 \text{ mL}) = (585 \text{ mm Hg}) V_2$$

$$\frac{(723 \text{ mm Hg})(294 \text{ mL})}{(585 \text{ mm Hg})} = V_2$$

$$V_2 = 363.354 \text{ mL} \rightarrow 363 \text{ mL}$$



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LPT

At 723 torr a gas has a volume of 294 mL. What is the new pressure of this gas if the volume is changed to 1256 mL?

	Pressure (torr)	Volume (mL)	Temperature (°C)	Temperature (K)
Initial	723	294	constant	constant
Final	?	1256	constant	constant

Temperature constant, use Boyle's Law

$$P_1 V_1 = P_2 V_2$$

$$(723 \text{ torr})(294 \text{ mL}) = (1256 \text{ mL}) P_2$$

$$\frac{(723 \text{ torr})(294 \text{ mL})}{(1256 \text{ mL})} = P_2$$

$$P_2 = 169.237 \rightarrow 169 \text{ torr}$$

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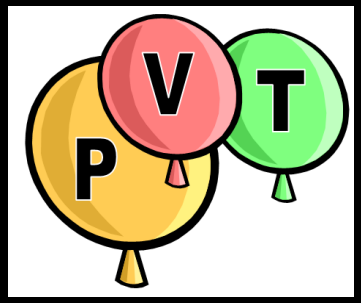
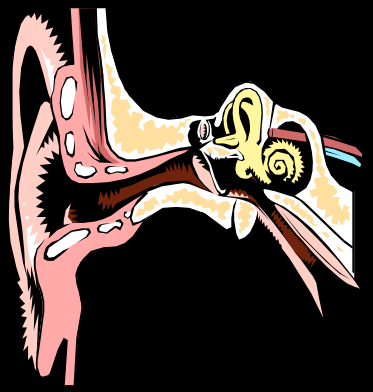
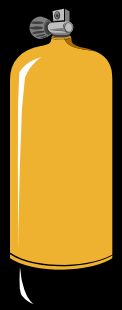
LPT



General Gas Law



$$\frac{p_1 v_1}{t_1} = \frac{p_2 v_2}{t_2}$$



Units need to be same on both sides of =

P & T must be in absolute measures

Class assumes given P is absolute

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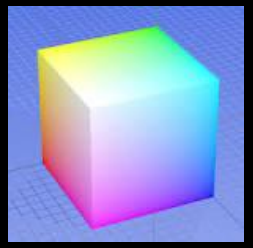
LPT

General Gas Law

$$\frac{p_1 v_1}{t_1} = \frac{p_2 v_2}{t_2}$$



If P constant:

$$\frac{v_1}{t_1} = \frac{v_2}{t_2}$$

Charles

If V constant:

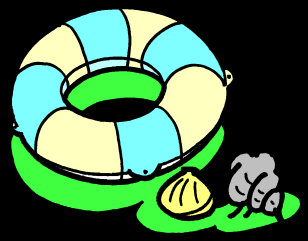
$$\frac{p_1}{t_1} = \frac{p_2}{t_2}$$

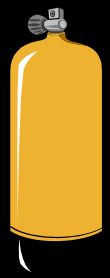
Guy-Lussac

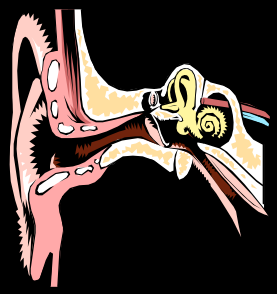
If T constant:

$$p_1 v_1 = p_2 v_2$$

Boyle







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LPT

A sample of neon with a volume of 825 mL at a temperature of 37 °C and a pressure of 600. torr is heated to a temperature of 68 °C and a pressure of 940. mm Hg. What is the new volume of the gas?

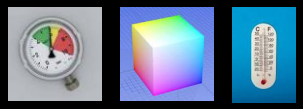
	Pressure (torr)	Volume (mL)	Temperature (°C)	→	Temperature (K)
Initial	600	825	37	+ 273	310
Final	940	?	68	+ 273	341

Pressure, Volume & Temperature change, use General Gas Law

$$\frac{p_1 v_1}{t_1} = \frac{p_2 v_2}{t_2}$$

$$\frac{(600 \text{ torr})(825 \text{ mL})}{310 \text{ K}} = \frac{(940 \text{ torr})\, v_2}{341 \text{ K}} \rightarrow \frac{(600 \text{ torr})(825 \text{ mL})(341 \text{ K})}{(310 \text{ K})(940 \text{ torr})} = v_2$$

$$V_2 = 579.255 \text{ mL} \rightarrow 579 \text{ mL}$$



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A sample of argon with a volume of 4.37 L at a temperature of 58 °C and a pressure of 725 torr is cooled to a temperature of 22 °C and a pressure of 615 mm Hg. What is the new volume of the gas?

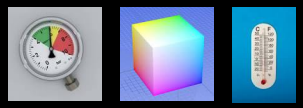
	Pressure (torr)	Volume (L)	Temperature (^oC)	→	Temperature (K)
Initial	725	4.37	58	+ 273	331
Final	615	?	22	+ 273	295

Pressure, Volume & Temperature change, use General Gas Law

$$\frac{p_1 v_1}{t_1} = \frac{p_2 v_2}{t_2}$$

$$\frac{(725 \text{ torr})(4.37 \text{ L})}{331 \text{ K}} = \frac{(615 \text{ torr})\, v_2}{295 \text{ K}} \rightarrow \frac{(725 \text{ torr})(4.37 \text{ L})(295 \text{ K})}{(331 \text{ K})(615 \text{ torr})} = v_2$$

$$V_2 = 4.59133 \text{ L} \rightarrow 4.59 \text{ L}$$



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LPT

A sample of nitrogen with a volume of 14.7 L at a temperature of 95 °C and a pressure of 485 torr is brought to STP. What is the new volume?

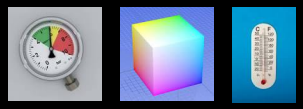
	Pressure (torr)	Volume (L)	Temperature (°C)	→	Temperature (K)
Initial	485	14.7	95	+ 273	368
Final	760	?	0	+ 273	273

Pressure, Volume & Temperature change, use General Gas Law

$$\frac{p_1 v_1}{t_1} = \frac{p_2 v_2}{t_2}$$

$$\frac{(485 \text{ torr})(14.7 \text{ L})}{368 \text{ K}} = \frac{(760 \text{ torr})\, v_2}{273 \text{ K}} \rightarrow \frac{(485 \text{ torr})(14.7 \text{ L})(273 \text{ K})}{(368 \text{ K})(760 \text{ torr})} = v_2$$

$$V_2 = 6.95922 \text{ L} \rightarrow 6.96 \text{ L}$$



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A sample of neon at STP has a volume of 286 L. What is the pressure in atmospheres if the temperature is changed to 95 °C at a new volume of 26.5 L?

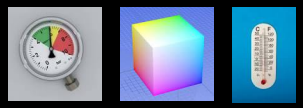
	Pressure (ata)*	Volume (L)	Temperature (^oC)	→	Temperature (K)
Initial	1.00	286	0	+ 273	273
Final	?	26.5	95	+ 273	368

Pressure, Volume & Temperature change, use General Gas Law

$$\frac{p_1 v_1}{t_1} = \frac{p_2 v_2}{t_2}$$

$$\frac{(1.00 \text{ ata})(286 \text{ L})}{273 \text{ K}} = \frac{P_2(26.5 \text{ L})}{368 \text{ K}} \rightarrow \frac{(1.00 \text{ ata})(286 \text{ L})(368 \text{ K})}{(273 \text{ K})(26.5 \text{ L})} = P_2$$

$P_2 = 14.5481$ ata ➔ 14.5 ata



* ata = atmospheres absolute

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A sample of xenon with a volume of 825 mL at a temperature of 37 °C and a pressure of 600. torr is changed to a pressure of 940. mm Hg at a volume of 628 mL. What is the temperature in °C of the gas?

	Pressure (torr)	Volume (mL)	Temperature (°C)	→	Temperature (K)
Initial	600	825	37	+ 273	310
Final	940	628	?	+ 273	?

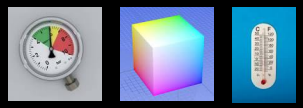
Pressure, Volume & Temperature change, use General Gas Law

$$\frac{p_1 v_1}{t_1} = \frac{p_2 v_2}{t_2}$$

$$\frac{(600 \text{ torr})(825 \text{ mL})}{310 \text{ K}} = \frac{(940 \text{ torr})(628 \text{ mL})}{T_2} \rightarrow \frac{(940 \text{ torr})(628 \text{mL})(310 \text{ K})}{(600 \text{ torr})(825 \text{ mL})} = T_2$$

$T_2 =$ 369.695 K ➔ 370 K

$T_2 =$ 370 K – 273 = 97 °C



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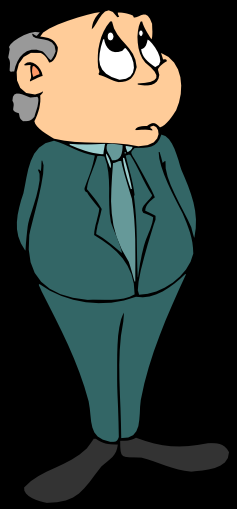

Proportional Thinking

$$\frac{pv}{t} = k$$

$$\frac{p_1 v_1}{t_1} = k = \frac{p_2 v_2}{t_2}$$

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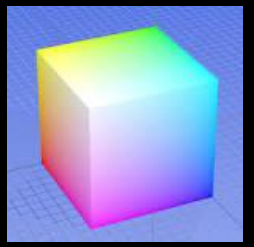
Proportional Thinking

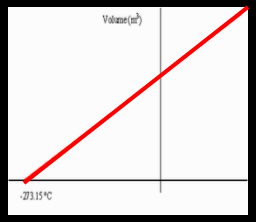


$$\frac{pv}{t} = k$$

If P constant:

$$\frac{v}{t} = k$$

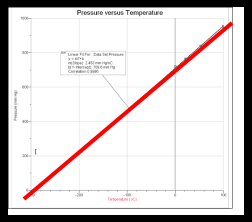
Charles' Law
Direct Proportion



If V constant:

$$\frac{p}{t} = k$$

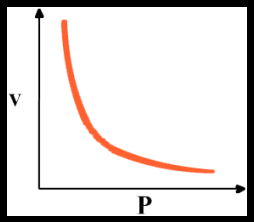
Guy-Lussac's Law
Direct Proportion



If T constant:

$$pv = k$$

Boyle's Law
Inverse Proportion



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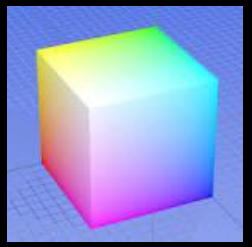
Proportional Thinking



$$\frac{pv}{t} = k$$

Variables change to keep k constant

If P constant:

$$\frac{\uparrow v}{\uparrow t} = k$$

v and t change (increase or decrease) in same direction

If V constant:

$$\frac{\uparrow p}{\uparrow t} = k$$

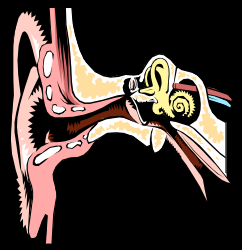
p and t change (increase or decrease) in same direction

If T constant:

$$pv = k$$

$\uparrow \downarrow$

p and v change (increase or decrease) in opposite direction



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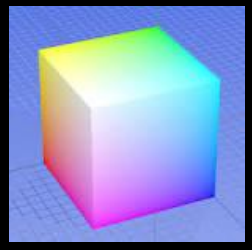
Proportional Thinking: Word problems

At constant volume, if temperature decreases, pressure _____

At constant pressure, if temperature increases, volume _____

At constant temperature, if pressure increases, volume _____



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Proportional Thinking: Word problems

At constant volume, if temperature decreases, pressure **decreases**

$\frac{p}{t} = k \rightarrow \frac{p}{t} = k$

P & T Move same direction

At constant pressure, if temperature increases, volume **increases**

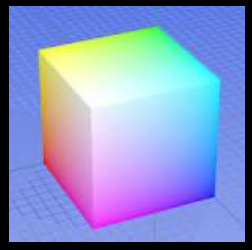
$\frac{v}{t} = k \rightarrow \frac{v}{t} = k$

V & T Move same direction

At constant temperature, if pressure increases, volume **decreases**

$pv = k \rightarrow pv = k$

P & V Move opposite direction



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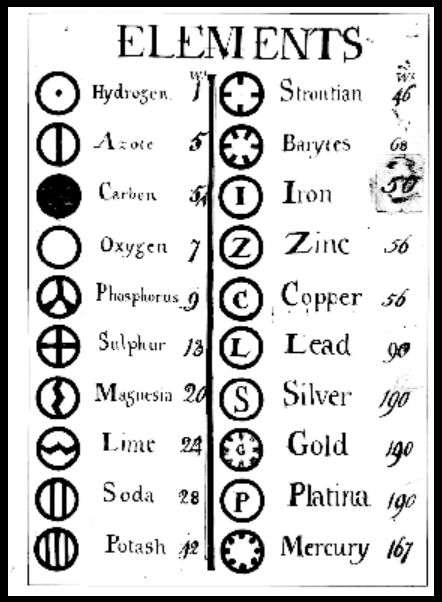
John Dalton

School teacher with contributions to:
- **Atomic Theory**
- **Understanding Color Blindness**
- **Studies on Gas Behavior**



Dalton's Law of Partial Pressure (1803)

$$P_{total} = P_1 + P_2 + P_3 + \ldots P_n$$

For a mixture of ideal gases,
total pressure = sum of the partial pressures of gases present

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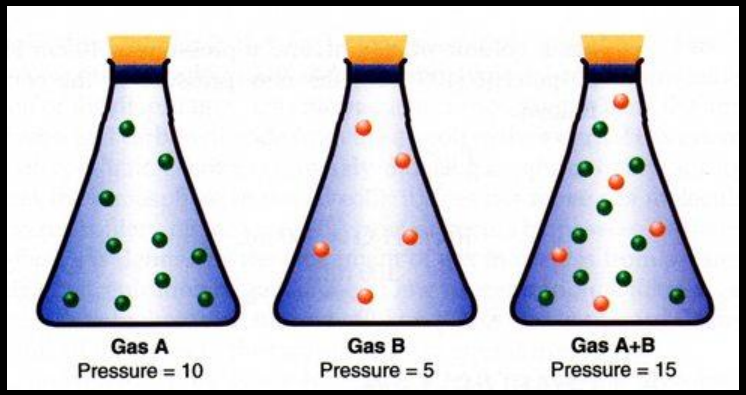
Dalton's Law: Partial Pressures

Dalton's law: In a mixture of gases, the total pressure is the sum of the partial pressures of the individual components

$$P = P_1 + P_2 + P_3 + \ldots + P_n$$

The partial pressure of a gas is the product of the fraction of that gas times the total pressure

$$P_g = F_g \times P_{total}$$



Where

P_g = partial pressure of the component gas

F_g = fraction of the component gas in the mixture

P_{total} = the total pressure of the gas mixture

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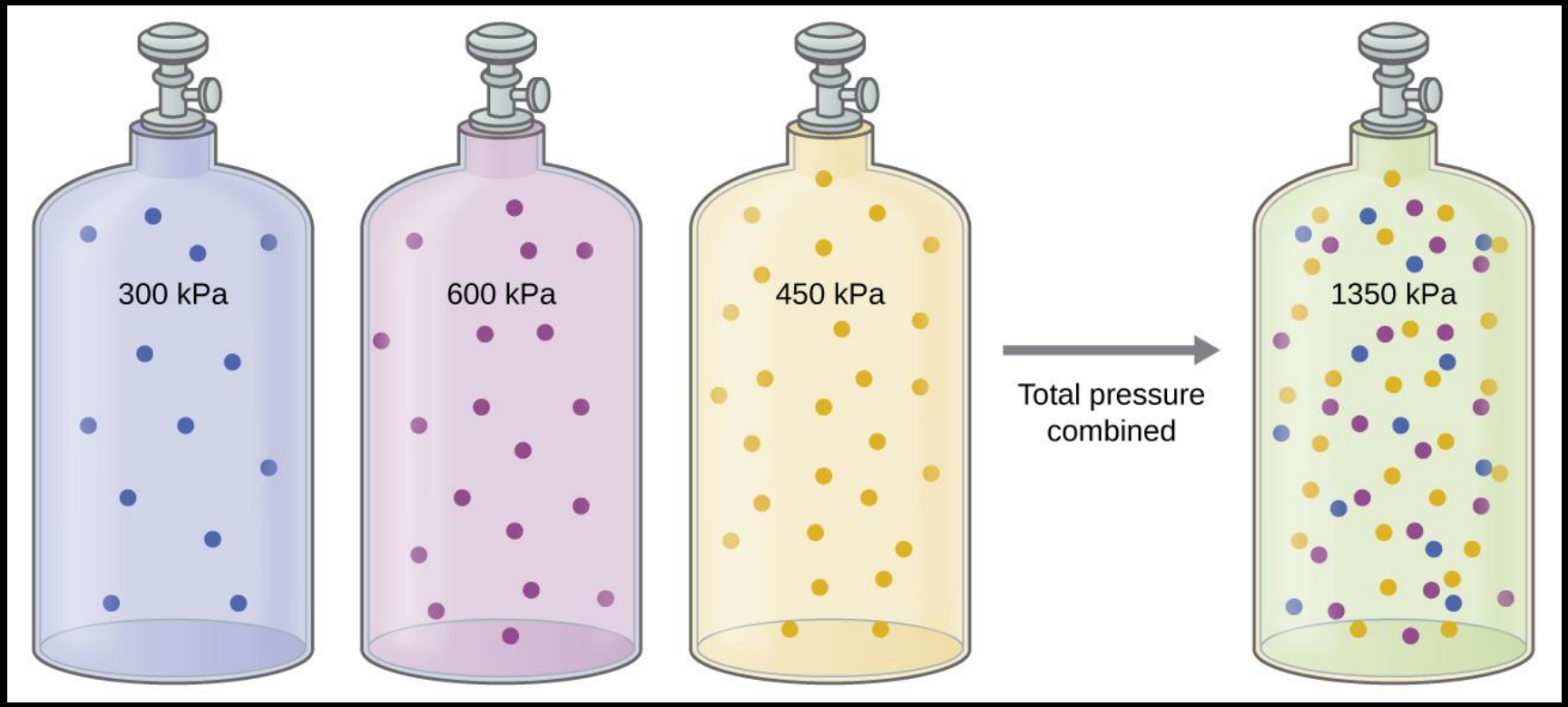
Dalton's Law: Partial Pressures



Total pressure is always the sum of component gas pressures

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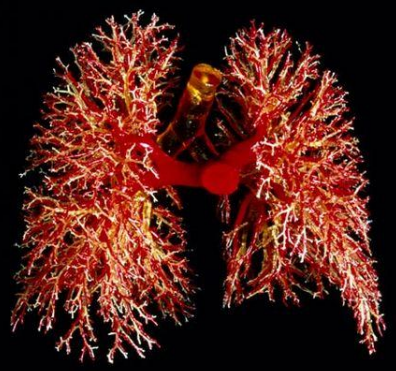
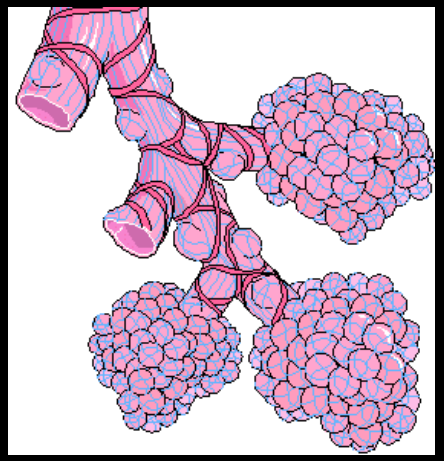
Dalton's Law: Partial Pressures

Pressure in alveolar spaces immediately equilibrates with blood

	Inspired air	Alveolar air
H_2O	Variable	47 mmHg
CO_2	000.3 mmHg	40 mmHg
O_2	159 mmHg	105 mmHg
N_2	601 mmHg	568 mmHg
Total pressure	760 mmHg	760 mmHg





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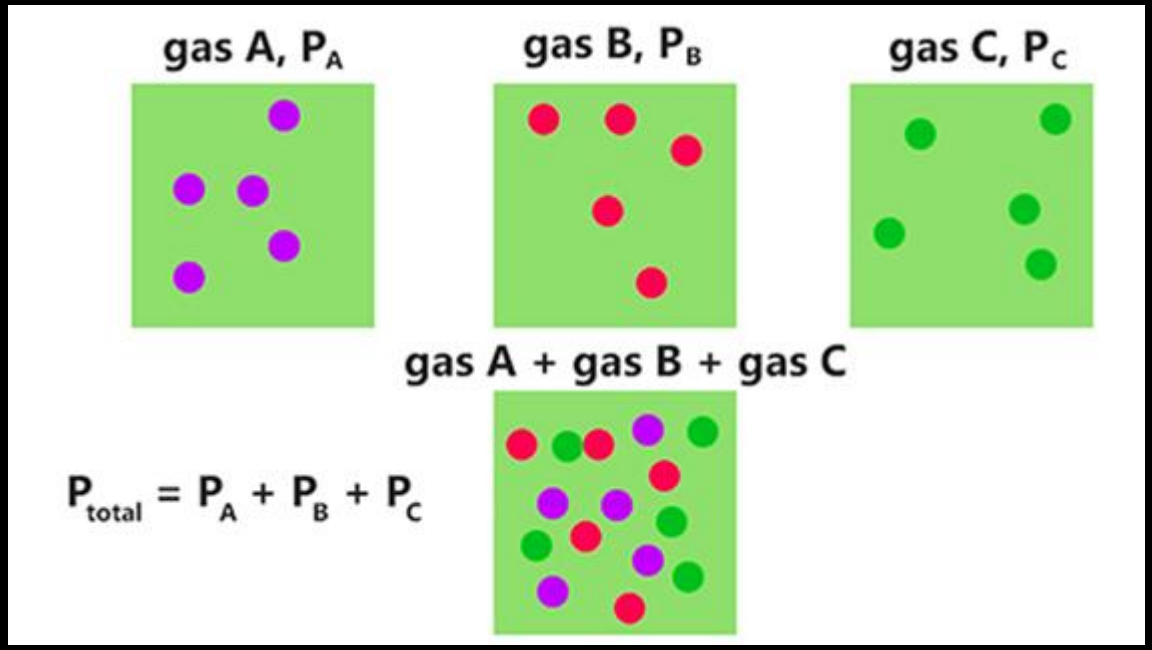
A mixture of gases at 760 torr contains 55.0 % N_2, 25.0 % O_2, and 20.0 % CO_2 by volume. What is the partial pressure of each gas?

N_2: 55.0/100 x 760 torr = 418 torr

O_2: 25.0/100 x 760 torr = 150 torr

CO_2: 20.0/100 x 760 torr =152 torr

Total (check) = 760 torr



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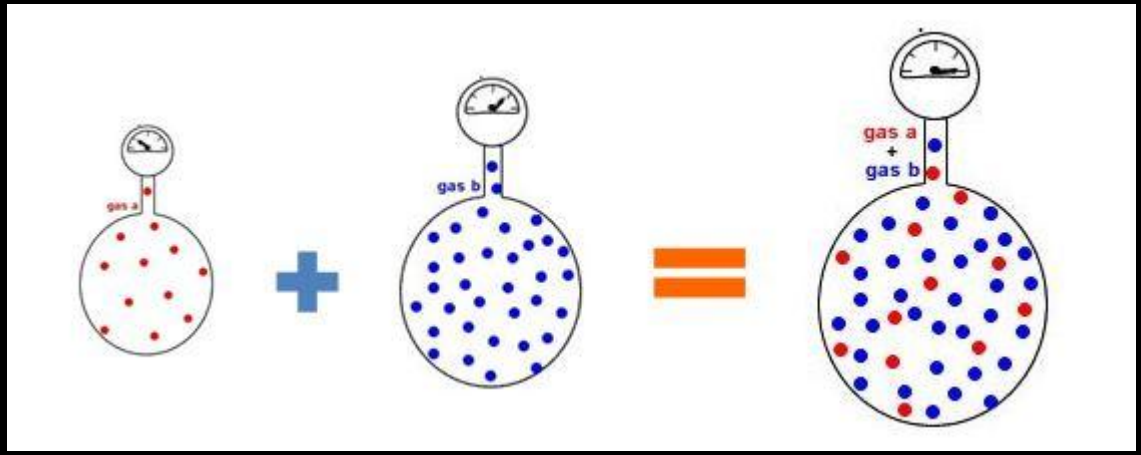
A 200 mL flask contains O_2 at 220 torr and a 300 mL flask contains N_2 at 100 torr. The flasks are connected and the gasses are allowed to completely fill the system. There is no temperature change. What is the partial pressure of each gas and the total pressure?

The final volume is 200 mL + 300 mL = 500 mL

O_2: 220 torr (200 / 500) = 88 torr

N_2: 100 torr (300 / 500) = 60 torr

Total: 60 torr + 88 torr = 148 torr



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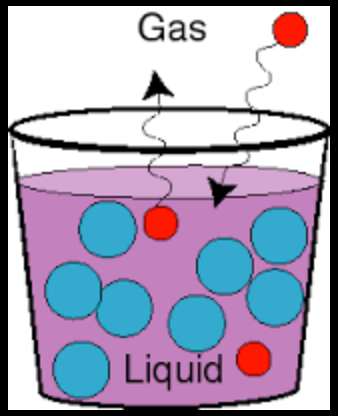
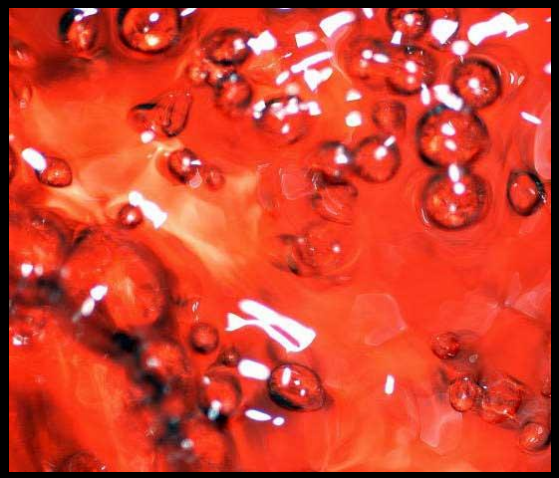
William Henry

British chemist
Solubility of gases
Composition of HCl and NH_3
Disinfecting powers of heat



Gas in liquid solubility: Henry's Law (1803)

Determined solubility of gases in liquids a function of:
- Partial pressure of the gas
- Temperature of the system
- Characteristics of the liquid



Very important when environmental pressure changes (alters gasses dissolved in the body)

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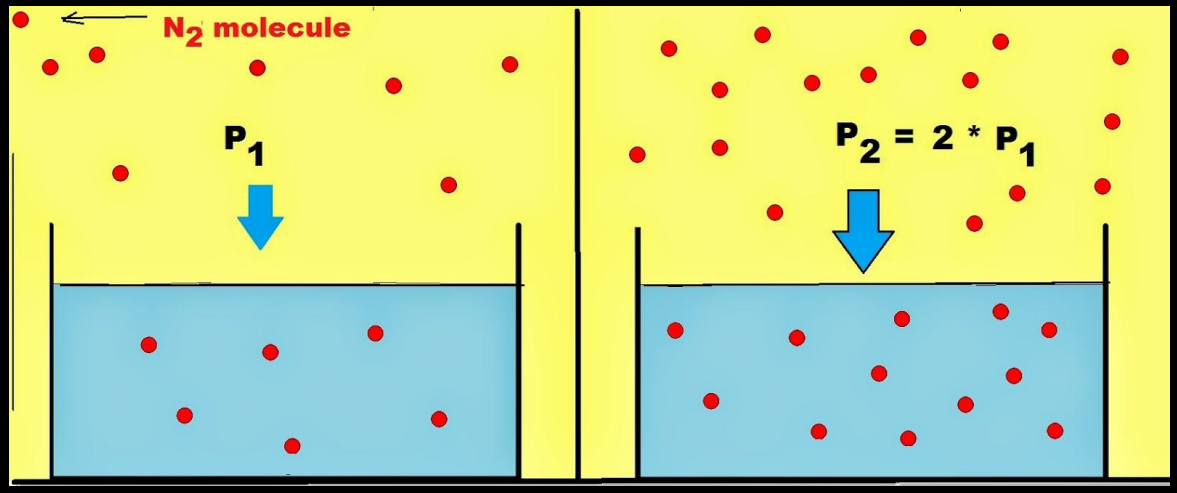
Henry's Law

The amount of any given gas that will dissolve in a liquid at a given temperature is a function of the partial pressure of the gas that is in contact with the liquid and the solubility coefficient of the gas in the particular liquid

$$S_g = K_H \times P_g$$

S_g solubility of the gas
K_h liquid solubility constant
P_g Partial pressure of the gas



Increase in pressure → increase in solubility
Decrease in pressure → decrease in solubility

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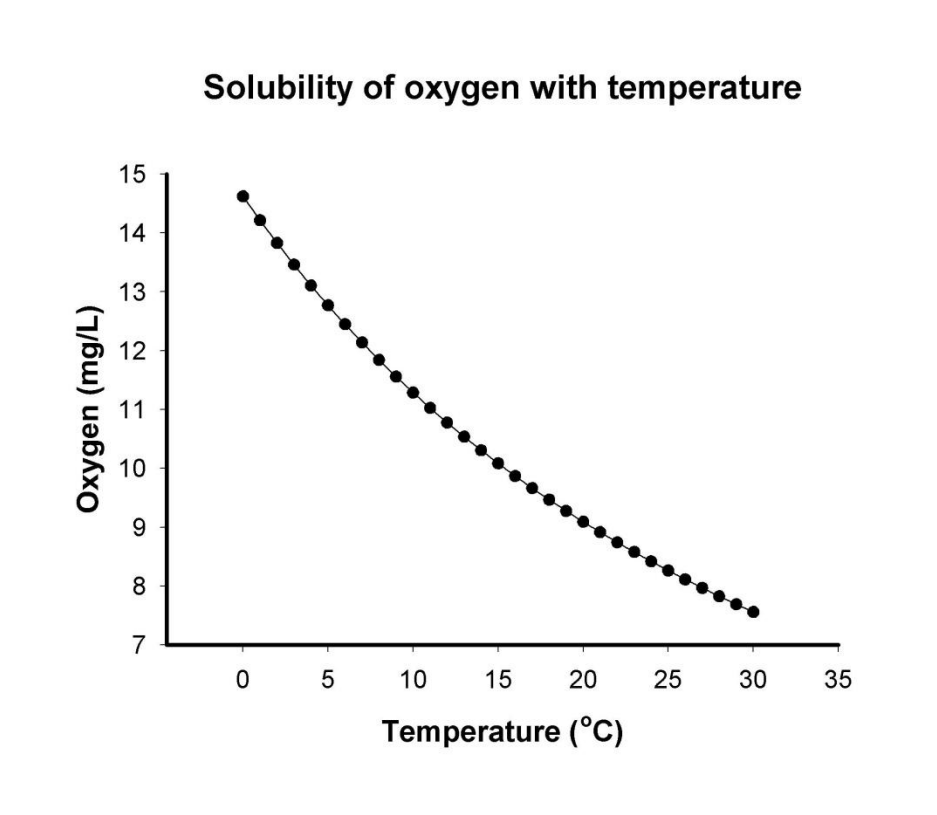
Henry's Law

Gas solubility changes with temperature



Colder water (Great Lakes): Divers carry additional gas loads

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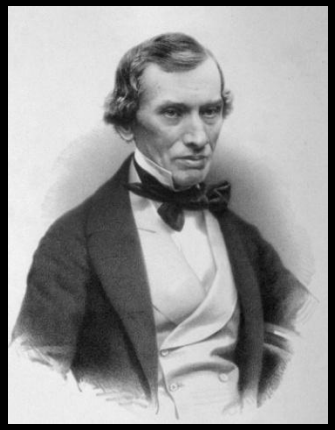
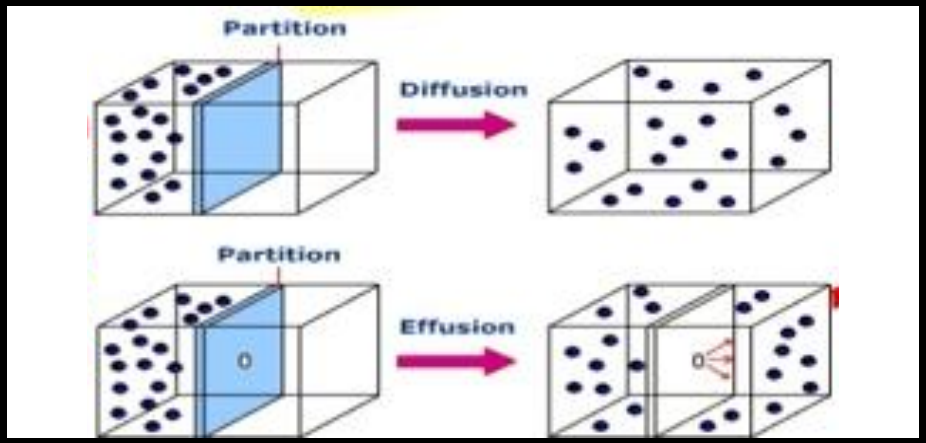


Graham's Law

The speed of gas diffusion (gas mixing due to kinetic energy) or effusion (gas moving through a tiny opening) is inversely proportional to the square root of their molar masses.

This is commonly written for effusion:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\frac{M_2}{M_1}}$$



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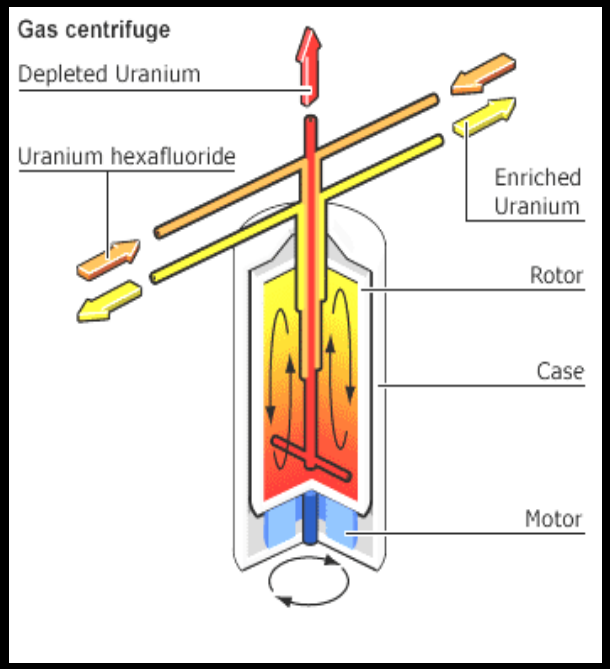
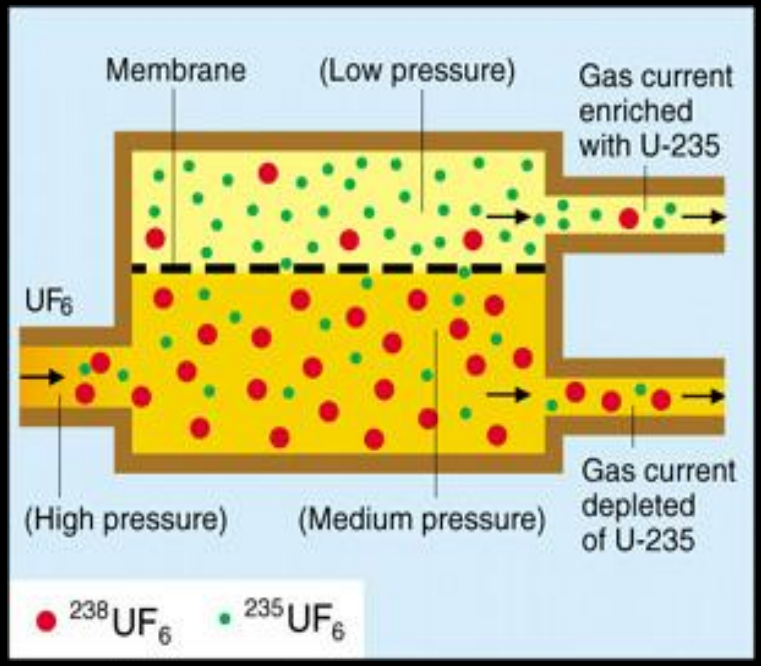
Graham's Law

Useful for:

- **separation of gases of different densities**
- **separation of isotopes**
  - **prime means for producing nuclear material**
- **determining molar mass of unknown material**





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Compare the relative rates of effusion of H_2 and CO through a fine pinhole.

Molar masses:
CO = 28.0
H_2 = 2.00

$$\frac{\text{Rate } H_2}{\text{Rate CO}} = \sqrt{\frac{28.0}{2.00}} = 3.74$$

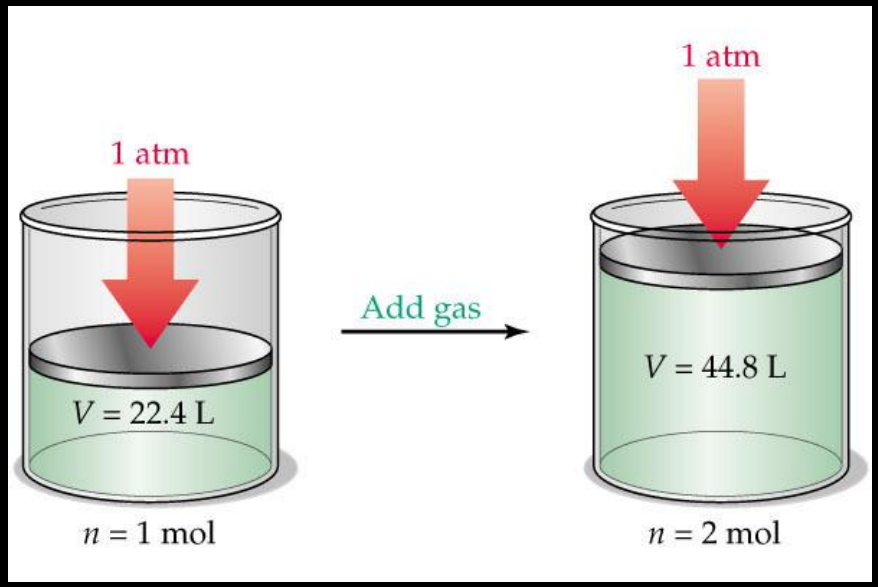
Compare the relative rates of effusion of H_2 and O_2 through a fine pinhole.

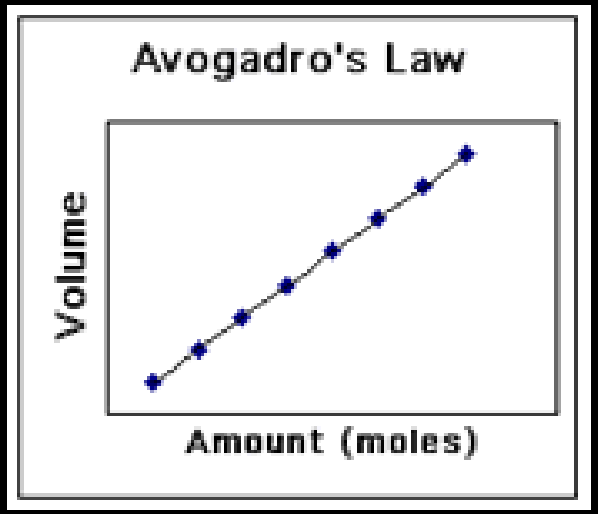
Molar masses:
O_2 = 32.0
H_2 = 2.0

$$\frac{\text{Rate } H_2}{\text{Rate } O_2} = \sqrt{\frac{32.0}{2.0}} = 4.0$$

Avogadro's Law (1811)

More Moles (Molecules) means more molecular collisions





Plot is Linear:
Volume & # moles
Directly Proportional

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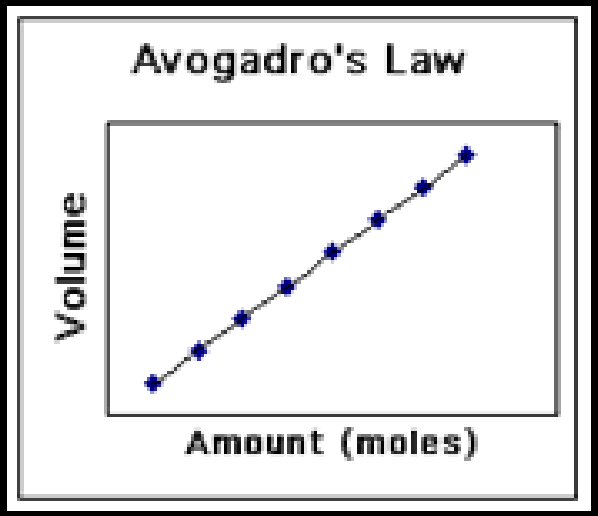
Avagadro's Law



At constant *temperature and pressure,*
volume is directly proportional to the number of moles present

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

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1.00 mole of gas occupies 1.45L. If the quantity of gas is increased to 2.50 moles, what is the new volume of gas?

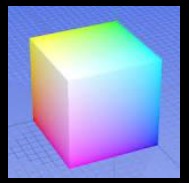
	Pressure (torr)	Volume (L)	# moles
Initial	constant	1.45	1.00
Final	constant	?	2.50

Pressure constant, use Avagadro's Law

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

$$\frac{1.45\ L}{1.00\ m} = \frac{V_2}{2.50\ m} \longrightarrow V_2 = \frac{(1.45\ L)\ (2.50\ m)}{1.00\ m}$$

$$V_2 = 3.625\ L \longrightarrow 3.63\ L$$



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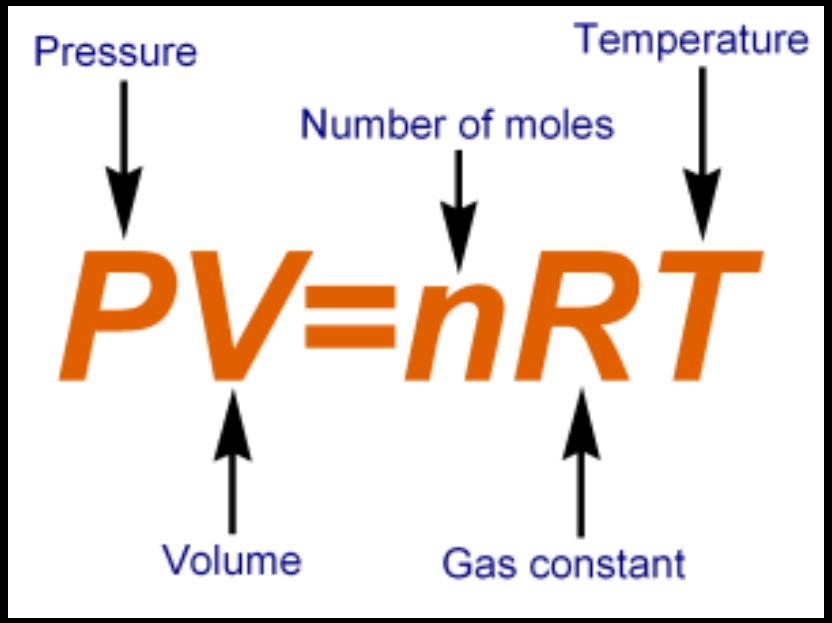
Ideal Gas Law

$$PV = kT$$



$$R = \frac{PV}{nT}$$

R makes "numbers work"

For:

P in atm; V in L; T in K

R = universal gas constant: 0.08206 L · atm / K · mol

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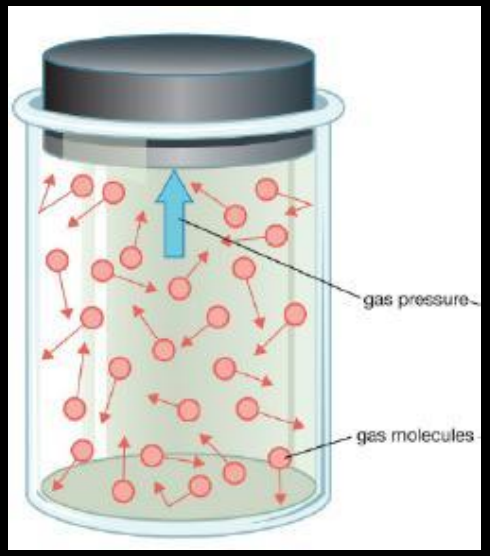
Ideal Gas Law



PV = nRT
Based on kinetic theory of gases
Primary use is single point determination

Assumes:
- **Volume of individual gas molecules is negligible**
- **There is no attraction between individual molecules**

Strongest correlation between calculated and measured:
- **Low pressure**
- **High temperature**
- **Monatomic gases**

Ideal gas law assumes vast distances between gas molecules

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Calculate the pressure of a 2.50 mole sample of a gas in a 5.50 L container at 27 °C.

Only one condition given ➔ use Ideal Gas Law:

PV = nRT

P (5.50 L) = (2.50 mole) (0.08206 L-atm/K-mol) (27 + 273 K)

$$P = \frac{(2.50 \text{ mole}) (0.08206 \text{ L-atm/K-mol}) (300 \text{ K})}{(5.50 \text{ L})}$$

P = 11.19 atm ➔ 11.2 atm

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How many moles of a gas occupy 2.67 L at STP?

Only one condition given ➔ use Ideal Gas Law:
STP: Standard Temperature & Pressure ➔ 1 atm and 273 K

$$PV = nRT$$

$$(1.00\ atm)\ (2.67\ L) = n\ (0.08206\ L\text{-}atm/K\text{-}mol)\ (273\ K)$$

$$n = \frac{(1.00\ atm)\ (2.67\ L)}{(0.08206\ L\text{-}atm/K\text{-}mol)\ (273\ K)}$$

$$n = 0.119184 \rightarrow 0.119\ mole$$

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Real (Non-Ideal) Gases

Ideal gases (because of decreased distance between molecules) often will differ in behavior from ideal gas equations. Modifications of ideal laws to account for molecular volumes and attractions are termed Real or non-ideal situations.

Van der Waals' Real Gas Equation

Modifies ideal gas law to account for molecular volume and attractions

New Volume term: V-nb (n = moles; b= specific constant for each gas)

New Pressure term: $P + an^2 / V^2$ (a= specific constant for each gas)

$$(P + an^2 / V^2)(V-nb) = nRT$$

Values of a and b available in gas tables

Complex calculations best done by calculator / computer

Solving Gas Law Problems:
Merely a Matter of Paying Attention to Details!

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