



Gas Laws



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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

 ${\bf His\ observations\ -\ primary\ source\ of\ absolute\ temperature\ scale}$

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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

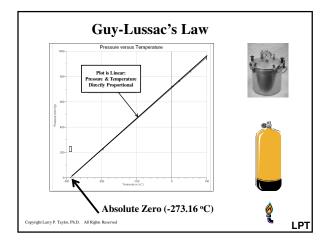


$$\frac{\mathbf{P}_1}{\mathbf{T}_1} = \frac{\mathbf{P}_2}{\mathbf{T}_2}$$



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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

$$\underline{\mathbf{P}}_1 = \underline{\mathbf{P}}_2$$

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



 $P_2 = 1191.49 \text{ torr} \implies 1190 \text{ torr} \implies 1190 \text{ mm Hg}$

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* 1 mm Hg = 1 torr

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)	\rightarrow	Temperature (K)
Initial	830	constant	52	+ 273	325
Final	?	constant	65	+ 273	338

Volume constant, use Guy-Lussac's Law

$$\frac{\mathbf{P}_1}{\mathbf{T}_1} = \frac{\mathbf{P}_2}{\mathbf{T}_2}$$

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



 $P_2 = 863.2 \text{ torr } \implies 863 \text{ torr}$

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A sample of nitrogen has a pressure of 1420. torr at a temperature of 75 $^{\rm o}C$. What is the $^{\rm o}$ C temperature of this gas if the pressure is lowered to 258 torr?

		Pressure (torr)	Volume	Temperature (°C)	\rightarrow	Temperature (K)
Γ	Initial	1420	constant	75	+ 273	348
Ī	Final	258	constant	?	+ 273	?

Volume constant, use Guy-Lussac's Law

$$\frac{\mathbf{P}_1}{\mathbf{T}_1} = \frac{\mathbf{P}_2}{\mathbf{T}_2}$$

$$\frac{1420 \text{ torr}}{348 \text{ K}} = \frac{258 \text{ torr}}{\text{T}_2} \xrightarrow{} \frac{(258 \text{ torr}) (348 \text{ K})}{(1420 \text{ torr})} = \text{T}_2$$



 $T_2 = 63.2262 \text{ K} \implies T_2 = 63.2 \text{ K}$ $T_2 = 63.2 \text{ K} - 273 = -210 \text{ °C}$

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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



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Hydrogen instead of hot air Valve line Wicker basket passenger compartment

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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

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

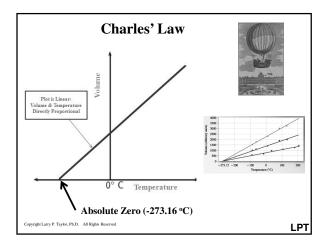


If T = negative, volume = negative (not realistic)

Need temperature to be positive

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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 (°C)	→	Temperature (K)
Initial	constant	1240	45	+ 273	318
Final	constant	?	85	+ 273	358

Pressure constant, use Charles' Law

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

$$\frac{1240 \text{ mL}}{318 \text{ K}} = \frac{\underline{V_2}}{358 \text{ K}}$$

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



 $V_2 = 1395.97 \text{ mL} \implies 1400 \text{ mL} \quad (1.40 \text{ x } 10^3 \text{ mL})$

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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 (°C)	\rightarrow	Temperature (K)
Initial	constant	830	42	+ 273	315
Final	constant	?	15	+ 273	288

Pressure constant, use Charles' Law

$$\frac{\mathbf{V}_1}{\mathbf{T}_1} = \frac{\mathbf{V}_2}{\mathbf{T}_2}$$

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



 $V_2 = 758.857 \text{ mL} \implies 759 \text{ mL}$

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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)	\rightarrow	Temperature (K)
Initial	constant	348	39	+ 273	312
Final	constant	657	?	+ 273	?

Pressure constant, use Charles' Law

$$\underline{\mathbf{V}}_1 = \underline{\mathbf{V}}_3$$

$$\frac{348 \text{ mL}}{312 \text{ K}} = \frac{657 \text{ mL}}{\text{T}_2} \longrightarrow \frac{(657 \text{ mL}) (312 \text{ K})}{(348 \text{ mL})} = \text{T}_2$$



 $T_2 = 589.038 \implies 589 \text{ K}$

 $T_2 = 589 \text{ K} - 273 = 316 \,^{\circ}\text{C}$

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Robert Boyle

Irish Alchemist
Father of modern chemistry
Founder of Royal Society



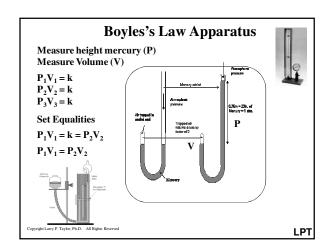
Pressure - Volume relationship (1660)

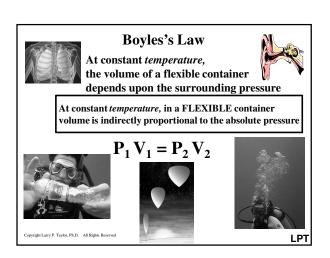
New Experiments: Phsico-Mechanical Touching the spring of air and their effects (1660) The Sceptical Chymst (Air, Earth, Fire, & Water not elements) (1661)

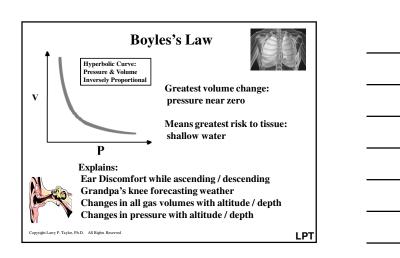


In an evacuated chamber Observed bubble in snake's eye Reduced Pressure Changes Physiology Bell produced no sound Air needed to carry sound

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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

$$\mathbf{P}_1\mathbf{V}_1 = \mathbf{P}_2\mathbf{V}_2$$

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

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



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

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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

$$\mathbf{P}_1\mathbf{V}_1 = \mathbf{P}_2\mathbf{V}_2$$

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

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



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

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General Gas Law







Units need to be same on both sides of = P & T must be in absolute measures
Class assumes given P is absolute

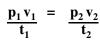






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General Gas Law









LPT

If P constant:

If V constant:



If T constant: $\mathbf{p}_1 \mathbf{v}_1 = \mathbf{p}_2 \mathbf{v}_2$

Guy-Lussac

Boyle







A sample of neon with a volume of 825 mL at a temperature of 37 $^{\rm o}{\rm C}$ 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)	\rightarrow	Temperature (K)
Initial	600	825	37	+ 273	310
Final	940	?	68	+ 273	341

Pressure, Volume & Temperature change, use General Gas Law

$$\frac{\mathbf{p}_1 \mathbf{v}_1}{\mathbf{t}_1} = \frac{\mathbf{p}_2 \mathbf{v}_2}{\mathbf{t}_2}$$

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

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



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A sample of argon with a volume of 4.37 L at a temperature of 58 $^{\rm o}{\rm C}$ and a pressure of 725 torr is cooled to a temperature of 22 $^{\rm o}{\rm C}$ and a pressure of 615 mm Hg. What is the new volume of the gas?

	Pressure (torr)	Volume (L)	Temperature (°C)	\rightarrow	Temperature (K)
Initial	725	4.37	58	+ 273	331
Final	615	?	22	+ 273	295

Pressure, Volume & Temperature change, use General Gas Law

$$\frac{\mathbf{p}_1 \mathbf{v}_1}{\mathbf{t}_1} = \frac{\mathbf{p}_2 \mathbf{v}_2}{\mathbf{t}_2}$$

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

 $V_2 = 4.59133 L \implies 4.59 L$



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A sample of nitrogen with a volume of 14.7 L at a temperature of 95 $^{\rm o}C$ 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

$$\frac{\mathbf{p}_1 \mathbf{v}_1}{\mathbf{t}_1} = \frac{\mathbf{p}_2 \mathbf{v}_2}{\mathbf{t}_2}$$

 $\frac{(485 \text{ torr}) (14.7 \text{ L})}{368 \text{ K}} = \frac{(760 \text{ torr}) \text{ v}_2}{273 \text{ K}} \quad \longrightarrow \quad \frac{(485 \text{ torr}) (14.7 \text{ L}) (273 \text{ K})}{(368 \text{ K}) (760 \text{ torr})} = \text{ v}_2$

 $V_2 = 6.95922 L \implies 6.96 L$



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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 $\,95$ $^{\circ}C$ at a new volume of 26.5 L?

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

Pressure, Volume & Temperature change, use General Gas Law

$$\frac{\mathbf{p}_1 \mathbf{v}_1}{\mathbf{t}_1} = \frac{\mathbf{p}_2 \mathbf{v}_2}{\mathbf{t}_2}$$

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



* ata = atmospheres absolute

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A sample of xenon with a volume of 825 mL at a temperature of 37 $^{\circ}C$ 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 $^{\circ}C$ of the gas?

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

Pressure, Volume & Temperature change, use General Gas Law

$$\frac{\mathbf{p}_1 \mathbf{v}_1}{\mathbf{t}_1} = \frac{\mathbf{p}_2 \mathbf{v}_2}{\mathbf{t}_2}$$

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

 $T_2 = 369.695 \text{ K} \implies 370 \text{ K}$



 $T_2 = 370 \text{ K} - 273 = 97 \,^{\circ}\text{C}$

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Proportional Thinking







$$\frac{\mathbf{p}_1 \, \mathbf{v}_1}{\mathbf{t}_1} = \mathbf{k} = \frac{\mathbf{p}_2 \, \mathbf{v}_2}{\mathbf{t}_2}$$



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Proportional Thinking







If P constant:

Charles' Law Direct Proportion



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If V constant:

Guy-Lussac's Law Direct



Proportion



If T constant:

pv = k

Boyle's Law Inverse Proportion



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Proportional Thinking







 $\mathbf{p}\mathbf{v} = \mathbf{k}$

Variables change to keep k constant

If P constant:

$$\uparrow \underline{\mathbf{v}} = \mathbf{k}$$

v and t change (increase or decrease) in same direction If V constant:



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

If	Т	co	ns	tant:
	p	V	=	k

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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Droportional Thinkings Word problems	
Proportional Thinking: Word problems At constant volume, if temperature decreases, pressure decreases	
At constant processes if temperature increases valume increases	
$\frac{\mathbf{v}}{\uparrow \mathbf{t}} = \mathbf{k} \implies \frac{\uparrow_{\mathbf{v}}}{t} = \mathbf{k} \text{V & T Move same direction}$	
At constant temperature, if pressure increases, volume decreases p v = k pv = k P & V Move opposite direction	
↑ Tavinove 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)	
Understanding Color Blindness Studies on Gas Behavior Studies of Gas Behavior On Description of Compact Assets of Comp	
Dalton's Law of Partial Pressure (1803) $ \bigoplus_{\substack{\emptyset \text{ Patrial } y \in \\ \text{Postal } p \text{ Patrial } y \in \\ \text{Postal } p \text{ Patrial } y \in \\ \text{Postal } p \text{ Patrial } y \in \\ \text{Postal } p \text{ Patrial } y \in \\ \text{Postal } p \text{ Patrial } y \in \\ \text{Patrial } p \text{ Patrial } y \in \\ $	-
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

$$P = P_1 + P_2 + P_3 + ... + P_n$$

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

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



 $P_{\rm g}$ = partial pressure of the component gas $F_{\rm g}$ = fraction of the component gas in the mixture $P_{\rm total}$ = 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

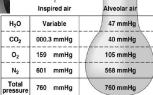
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Dalton's Law: Partial Pressures

Pressure in alveolar spaces immediately equilibrates with blood









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A mixture of gases at 760 torr contains 55.0 % N₂, 25.0 % O₂, and 20.0 % CO₂ by volume. What is the partial pressure of each gas?

N₂: 55.0/100 x 760 torr = 418 torr
O₂: 25.0/100 x 760 torr = 150 torr
CO₃: 20.0/100 x 760 torr = 152 torr
Total (check) = 760 torr

gas A, P_A

gas B, P_B

gas C, P_C

pas B, P_B

Gas C, P_C

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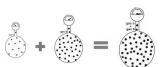
A 200 mL flask contains O_2 at 220 torr and a 300 mL flask contains N_2 at 100 torr. The flasks are connected and the gasses are allowed to completely fill the system. There is no temperature change. What is the partial pressure of each gas and the total pressure?

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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LPT



William Henry

British chemist Solubility of gases Composition of HCl and NH₃ 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 (afters gasses dissolved in the body)

(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

$$S_g = K_H x P_g$$

 $S_{\rm g}$ solubility of the gas $K_{\rm h}$ liquid solubility constant $P_{\rm g}$ Partial pressure of the gas





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

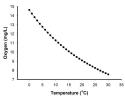
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Henry's Law

Gas solubility changes with temperature

Solubility of oxygen with temperature





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

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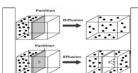
Graham's Law

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.

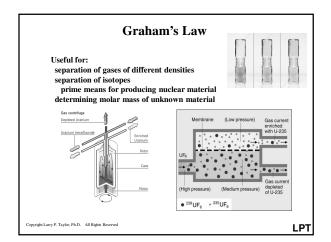
This is commonly written for effusion:

$$\frac{Rate_1}{Rate_2} = \sqrt{\frac{M_2}{M_1}}$$





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Compare the relative rates of effusion of \mathbf{H}_2 and CO through a fine pinhole.

Molar masses: CO = 28.0 $H_2 = 2.00$

$$CO = 28.0$$

H = 2.00

Rate H₂ =
$$\sqrt{\frac{28.0}{2.00}}$$
 = 3.74

Compare the relative rates of effusion of \mathbf{H}_2 and \mathbf{O}_2 through a fine pinhole.

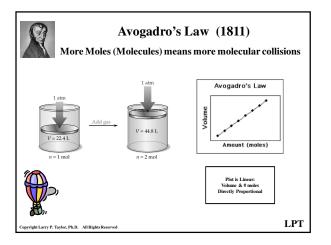
Molar masses:

$$O_2 = 32.0$$

 $H_2 = 2.0$

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

Rate O_2





Avagadro's Law





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



$$\frac{\mathbf{v}_1}{\mathbf{n}_1} = \frac{\mathbf{v}_2}{\mathbf{n}_2}$$

LPT

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

$$\frac{\mathbf{V}_1}{\mathbf{n}_1} = \frac{\mathbf{V}_2}{\mathbf{n}_2}$$

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



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

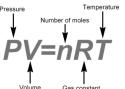




LPT

Ideal Gas Law

$$PV = kT$$



R makes "numbers work"

For:

P in atm; V in L; T in K

 $R = universal\ gas\ constant:\ 0.08206\ L \cdot atm\ /\ K \cdot mol$

Ideal Gas Law	
PV = nRT Based on kinetic theory of gases Primary use is single point determination Assumes: Volume of individual gas molecules is negl There is no attraction between individual	0
Strongest correlation between calculated ar	
High temperature Monatomic gases	
Ideal gas law assumes vast distances between	n gas molecules
	LPT

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 = (2.50 mole) (0.08206 L-atm/K-mol) (300 K)

(5.50 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-atm/K-mol) (273 K)

n = (1.00 atm) (2.67 L)
(0.08206 L-atm/K-mol) (273 K)

n = 0.119184 → 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!













Committee Larry P. Taylor, Ph.D. All Pinhte Passana