**Unit 9: The Gas Laws**

***The Atmosphere*** → an "ocean" of gases mixed together

***Composition***

nitrogen ($N_2$)……………~78%

oxygen ($O_2$)……………..~21%

argon (Ar)……………….~0.93%

carbon dioxide ($CO_2$)…..~0.03%

water vapor ($H_2O$)………~0.1%

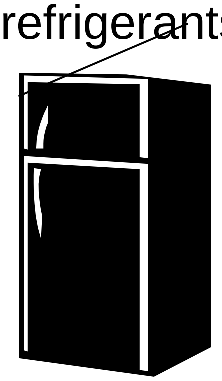
| |
|---|
| Trace amounts of: He, Ne, Rn, $SO_2$, $CH_4$, $N_xO_x$, etc. |

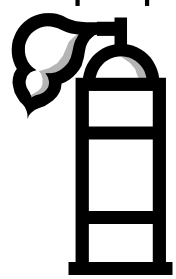
***Depletion of the Ozone Layer***

Ozone ($O_3$) in upper atmosphere blocks ultraviolet (UV) light from Sun. UV causes skin cancer and cataracts.

$O_3$ depletion is caused by chlorofluorocarbons (CFCs).

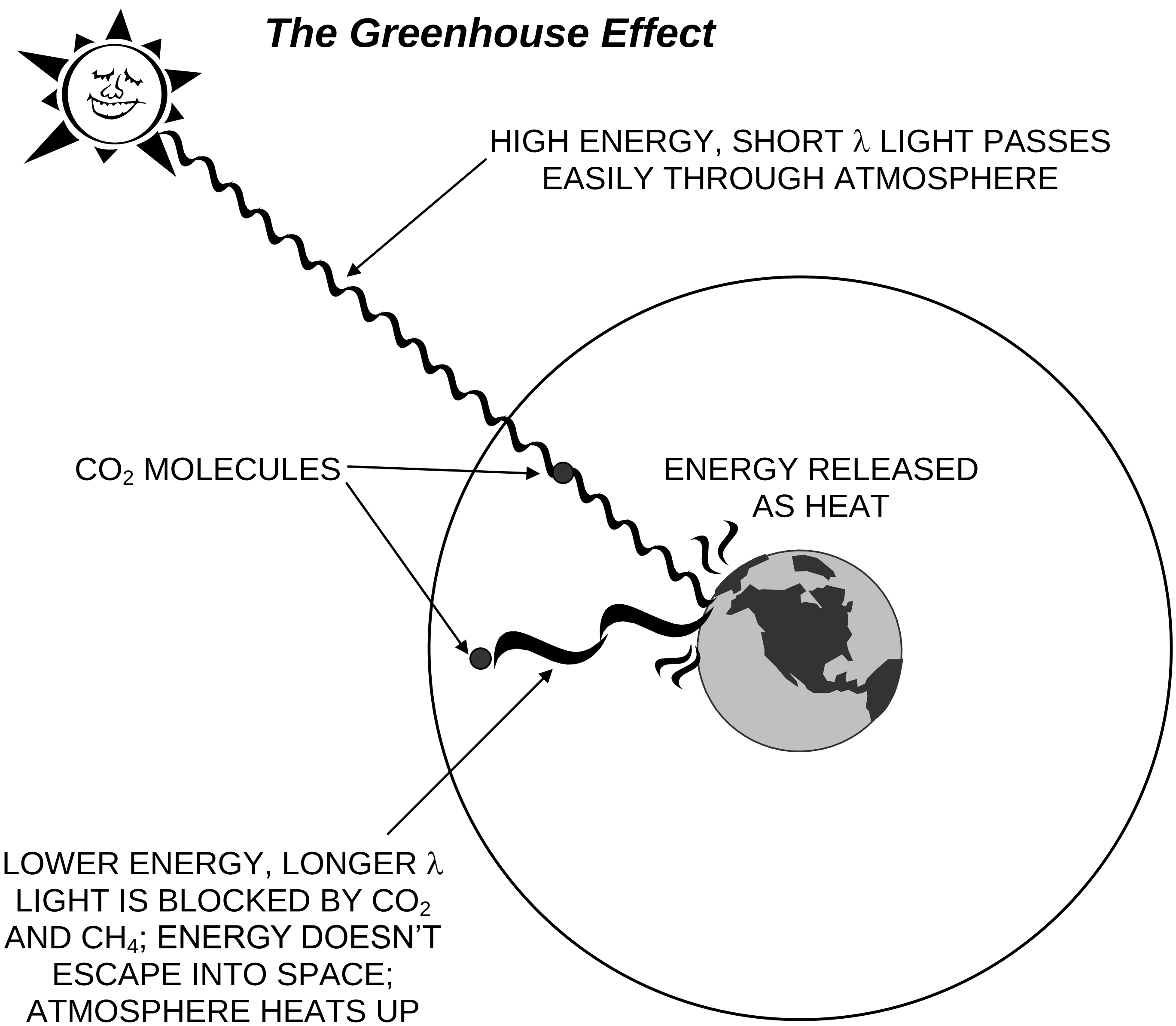
Uses for CFCs: refrigerants aerosol propellants






→ banned in U.S. in 1996

$O_3$ is replenished with each strike of lightning.

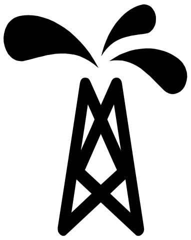



Energy from Sun has short wavelengths (λs) and high energy. $CO_2$ and methane ($CH_4$) let this light in.

Reflected light has longer λs and less energy.

$CO_2$ and $CH_4$ ("greenhouse gases") prevent reflected light from escaping, thus warming the atmosphere.

*Why more $CO_2$ in atmosphere now than 500 years ago?*



<u>burning of fossil fuels</u>

-- coal

-- petroleum

-- natural gas

-- wood

<u>deforestation</u>

-- urban sprawl

-- wildlife areas

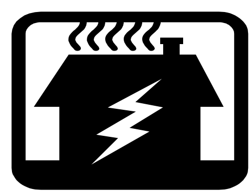
-- rain forests

* The burning of ethanol won't slow greenhouse effect.

*What can we do?*

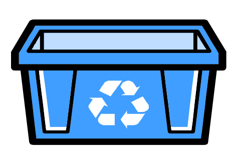
1. Reduce consumption of fossil fuels.

<u>At home</u>: insulate home; run dishwasher full; avoid temp. extremes (A/C & furnace); wash clothes on "warm," not "hot"



<u>On the road</u>: bike instead of drive; carpool; energy-efficient vehicles

2. Support environmental organizations.



3. Rely on alternate energy sources.

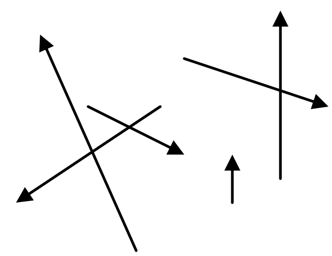
solar, wind energy, hydroelectric power

**The Kinetic Molecular Theory (KMT)**

-- explains why gases behave as they do

-- deals $^{w}$/"ideal" gas particles…

1. …are so small that they are
   assumed to have zero volume
2. …are in constant, straight-line motion



3. …experience <u>elastic collisions</u>
   in which no energy is lost
4. …have no attractive or repulsive
   forces toward each other
5. …have an average kinetic energy (KE)
   that is proportional to the
   <u>absolute temp</u>. of gas (i.e., Kelvin temp.)

AS TEMP. $\uparrow$, KE $\uparrow$

Theory "works," except at high pressures and low temps.

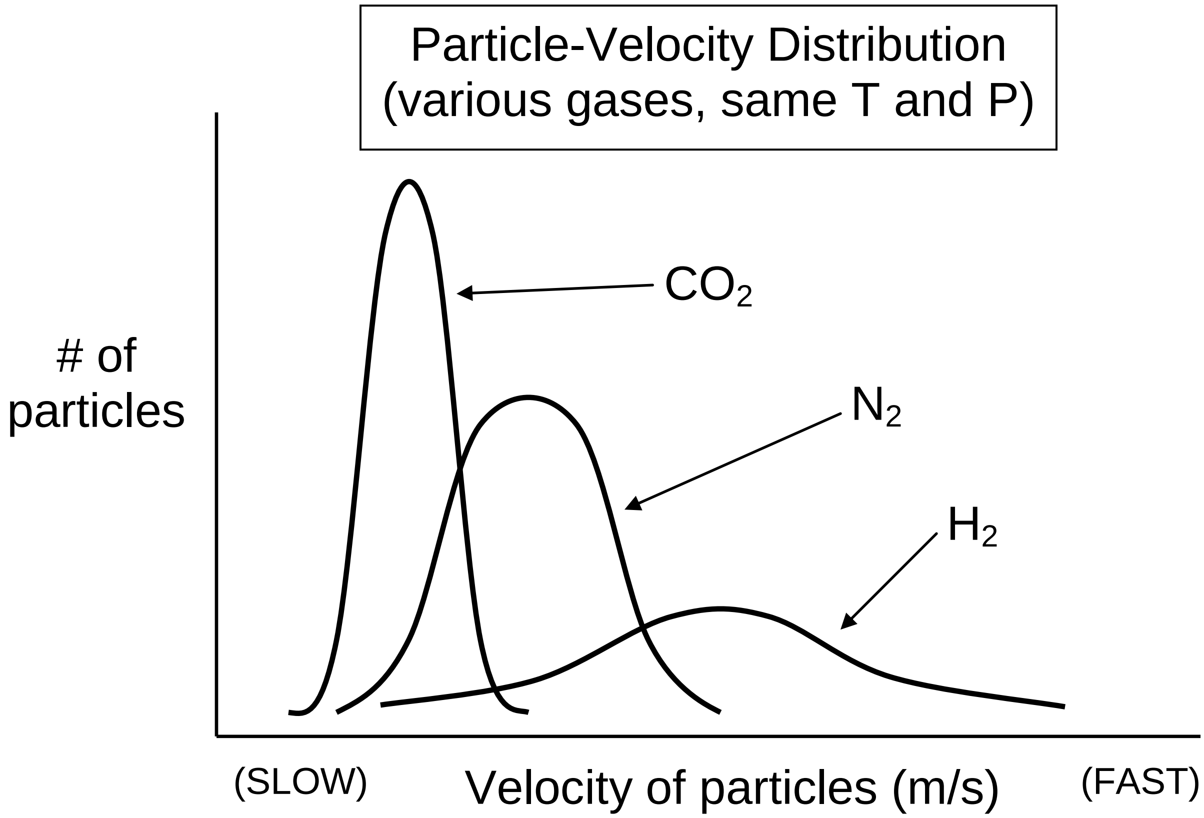
**Two gases $^{w}$/same # of particles and at
same temp. and pressure have the same kinetic energy.

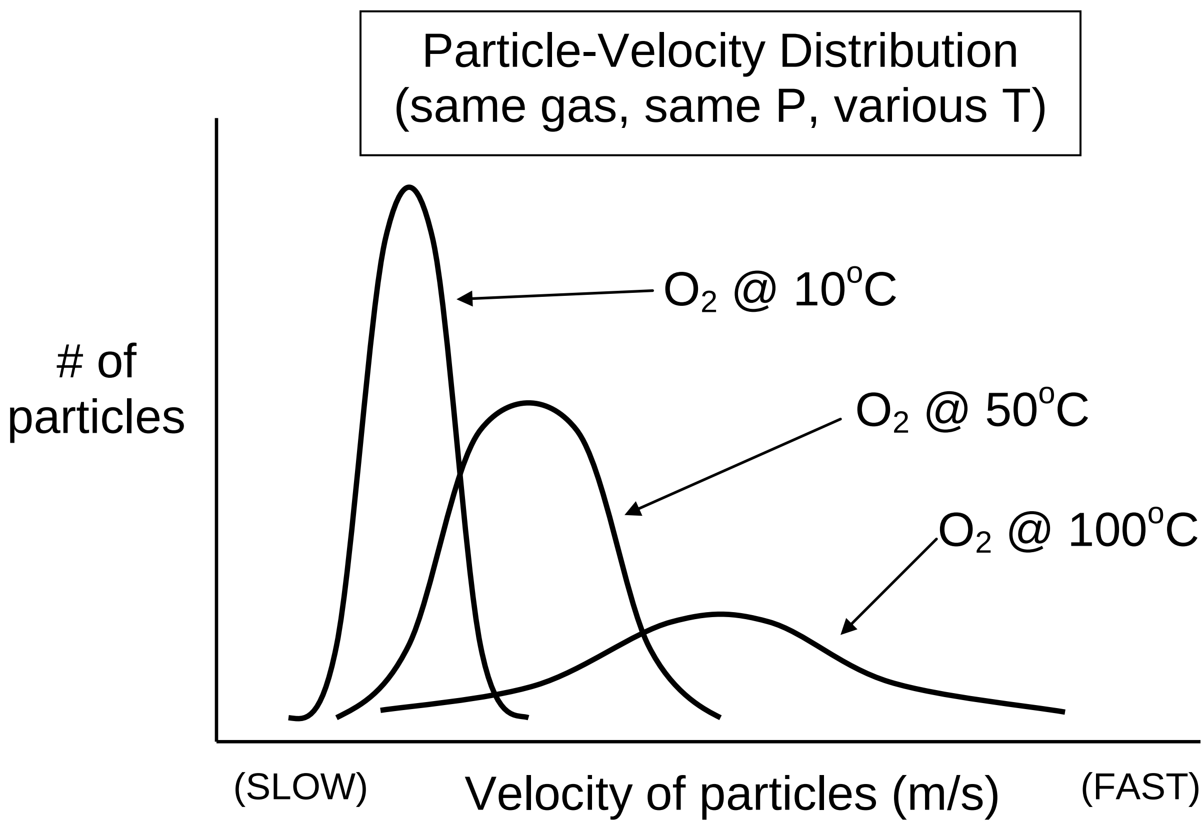
KE is related to mass and velocity (KE = ½ m $v^2$)

To keep same KE, as m $\uparrow$, v must $\downarrow$ OR

as m $\downarrow$, v must $\uparrow$

More massive gas particles are slower than less massive gas particles (on average).



## Graham's Law

Consider two gases at same temp.

Gas 1: $KE_1 = ½\, m_1\, v_1^2$

Gas 2: $KE_2 = ½\, m_2\, v_2^2$

Since temp. is same, then…

$$KE_1 = KE_2$$

$$½\, m_1\, v_1^2 = ½\, m_2\, v_2^2$$

$$m_1\, v_1^2 = m_2\, v_2^2$$

Divide both sides by $m_1\, v_2^2$…

$$\left(\frac{1}{m_1\, v_2^2}\right) m_1\, v_1^2 = m_2\, v_2^2 \left(\frac{1}{m_1\, v_2^2}\right)$$

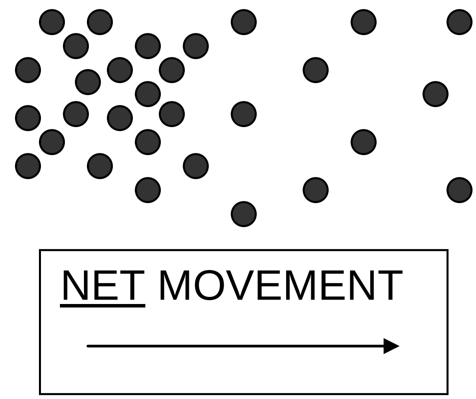
$$\frac{v_1^2}{v_2^2} = \frac{m_2}{m_1}$$

Take sq. rt. of both sides to get Graham's Law:

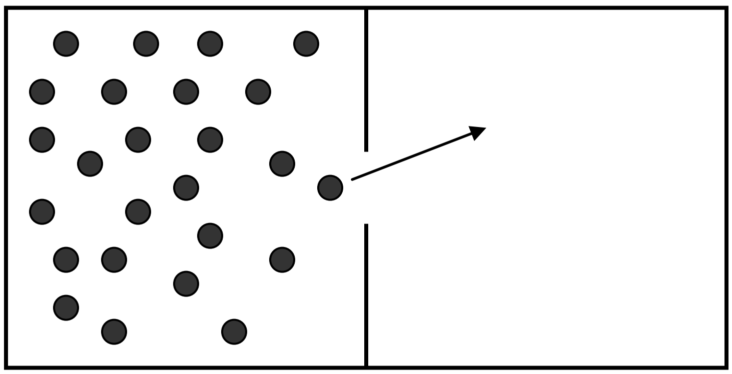
$$\boxed{\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}}$$

To use Graham's Law, both gases must be at same temp.

<u>diffusion</u>: particle movement from high to low conc.




<u>effusion</u>: diffusion of gas particles through an opening



For gases, rates of diffusion & effusion obey Graham's law: more massive = slow; less massive = fast

On avg., carbon dioxide travels at 410 m/s at 25$^{o}$C. Find avg. speed of chlorine at 25$^{o}$C.

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}} \rightarrow \frac{v_{Cl_2}}{v_{CO_2}} = \sqrt{\frac{m_{CO_2}}{m_{Cl_2}}} \rightarrow v_{Cl_2} = v_{CO_2}\sqrt{\frac{m_{CO_2}}{m_{Cl_2}}}$$

$$v_{Cl_2} = 410\ \text{m/s}\sqrt{\frac{44\ \text{g}}{71\ \text{g}}} = \boxed{320\ \text{m/s}}$$

**Hint: Put whatever you're looking for in the numerator.

At a certain temp., fluorine gas travels at 582 m/s and a noble gas travels at 394 m/s. What is the noble gas?

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}} \rightarrow \frac{v_{F_2}}{v_{unk}} = \sqrt{\frac{m_{unk}}{m_{F_2}}} \rightarrow \left(\frac{v_{F_2}}{v_{unk}}\right)^2 = \frac{m_{unk}}{m_{F_2}}$$

$$m_{unk} = m_{F_2} \left(\frac{v_{F_2}}{v_{unk}}\right)^2 = 38\text{ amu}\sqrt{\frac{582}{394}} = 82.9\text{ amu} \rightarrow \boxed{\text{Kr}}$$

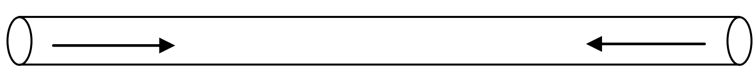
$CH_4$ moves 1.58 times faster than which noble gas?

Governing relation: $v_{CH_4} = 1.58\, v_{unk}$

$$\frac{v_{CH_4}}{v_{unk}} = \sqrt{\frac{m_{unk}}{m_{CH_4}}} \rightarrow \frac{1.58\, v_{unk}}{v_{unk}} = \sqrt{\frac{m_{unk}}{m_{CH_4}}} \rightarrow (1.58)^2 = \frac{m_{unk}}{m_{CH_4}}$$

$$m_{unk} = (1.58)^2\, m_{CH_4} = (1.58)^2\,(16\text{ amu}) = 39.9\text{ amu} \rightarrow \boxed{\text{Ar}}$$

HCl and $NH_3$ are released at same time from opposite ends of 1.20 m horiz. tube. Where do gases meet?

HCl  $NH_3$

1.20 m

$$\frac{v_{NH_3}}{v_{HCl}} = \sqrt{\frac{m_{HCl}}{m_{NH_3}}} = \sqrt{\frac{36.5}{17}} = 1.465 \rightarrow v_{NH_3} = 1.465\, v_{HCl}$$

Velocities are relative; pick easy #s: $v_{HCl} = 1.000\text{ m/s}$

$v_{NH_3} = 1.465\text{ m/s}$

DISTANCE = RATE x TIME

$$1.20 = \text{HCl dist.} + NH_3\text{ dist.} = 1.000\,t + 1.465\,t \rightarrow t = 0.487\text{ s}$$

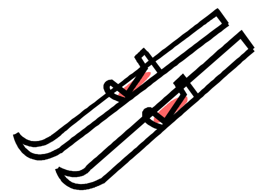
So HCl dist. = 1.000 m/s (0.487 s) = $\boxed{0.487\text{ m}}$

## Gas Pressure

Pressure occurs when a force is dispersed over a given surface area.

$$\boxed{P = \frac{F}{A}}$$

If F acts over a large area… $\dfrac{F}{\Large A} = {\scriptsize P}$

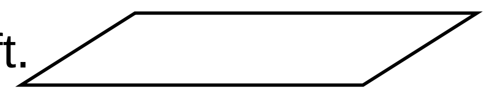


But if F acts over a small area… $\dfrac{F}{\scriptsize A} = {\Large P}$

At sea level, air pressure is <u>standard pressure</u>:

1 atm, 101.3 kPa, 760 mm Hg, 14.7 lb/in$^2$

Find force of air pressure acting $\downarrow$ on a baseball field tarp…




$$A = \left[100\text{ ft}\left(\frac{12\text{ in}}{1\text{ ft}}\right)\right]^2 = 1.44 \times 10^6\text{ in}^2$$

$$F = P A = 14.7\text{ lb/in}^2\,(1.44 \times 10^6\text{ in}^2) = 2 \times 10^7\text{ lb.}$$

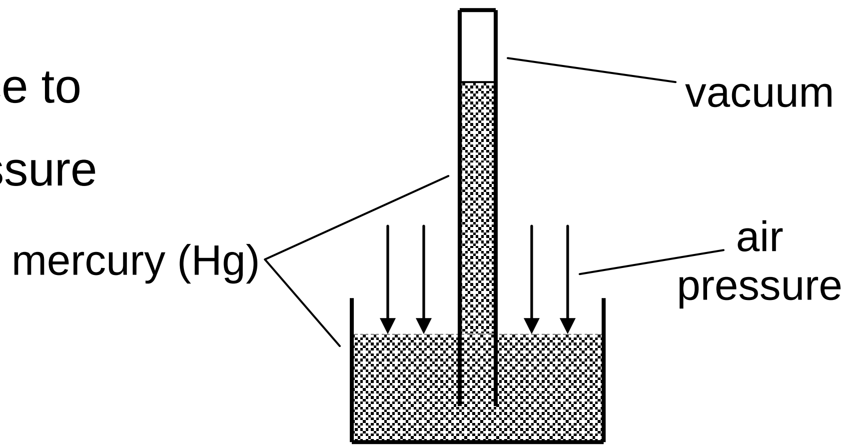
$$F = 2 \times 10^7\text{ lb.}\left(\frac{1\text{ ton}}{2000\text{ lb.}}\right) = \boxed{10{,}000\text{ tons}}$$

Key: Gases exert pressure in all directions.

Atmospheric pressure changes with altitude:

as altitude $\Uparrow$, pressure $\Downarrow$

barometer: device to measure air pressure



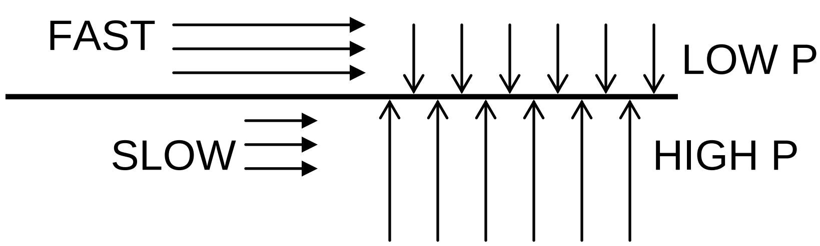

**Bernoulli's Principle**

For a fluid traveling // to a surface:

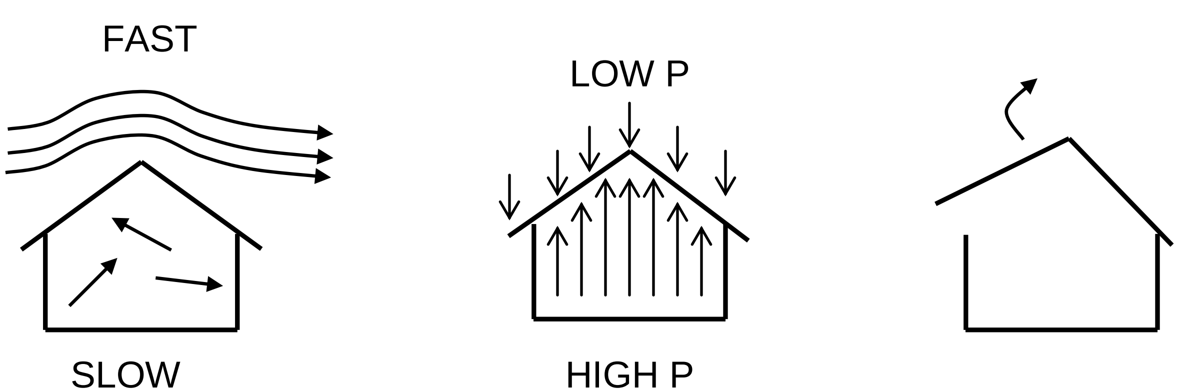
LIQUID OR GAS

…FAST-moving fluids exert LOW pressure

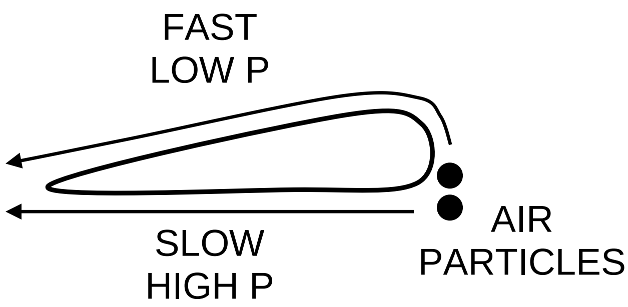
…SLOW- “ “ “ HIGH “

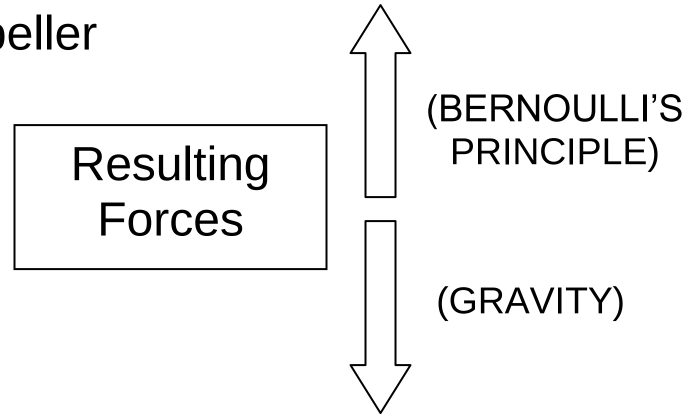



roof in hurricane

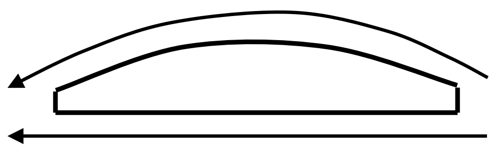


airplane wing / helicopter propeller

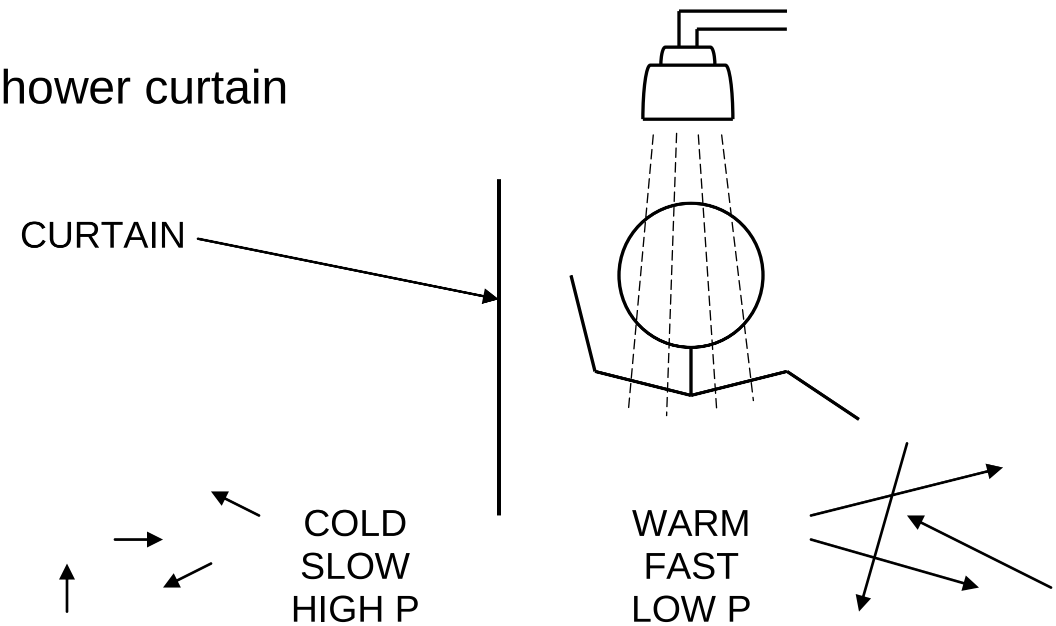


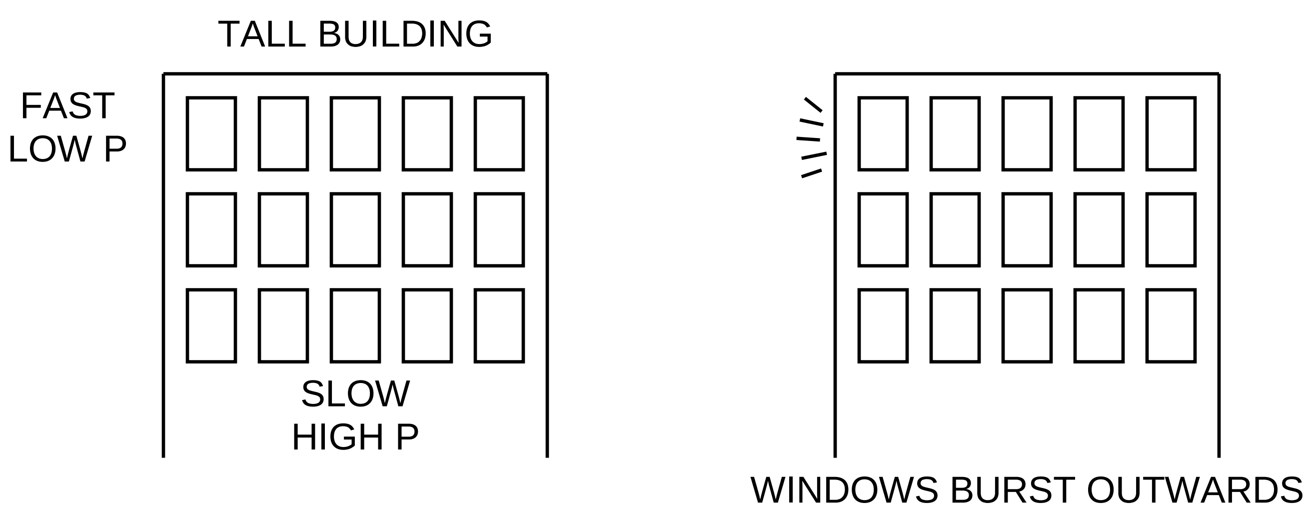

frisbee



creeping shower curtain




windows and high winds (e.g., tornadoes)



## Pressure and Temperature

STP (Standard Temperature and Pressure)

| <u>standard temperature</u> | <u>standard pressure</u> |
|---|---|
| $0^{o}C$ | 1 atm |
| 273 K | 101.3 kPa |
| | 760 mm Hg |

Equations / Conversion Factors:

$K = {}^{o}C + 273$

${}^{o}C = K - 273$

1 atm = 101.3 kPa = 760 mm Hg

Convert $25^{o}C$ to Kelvin.

$$K = {}^{o}C + 273 = 25^{o}C + 273 = \boxed{298\ K}$$

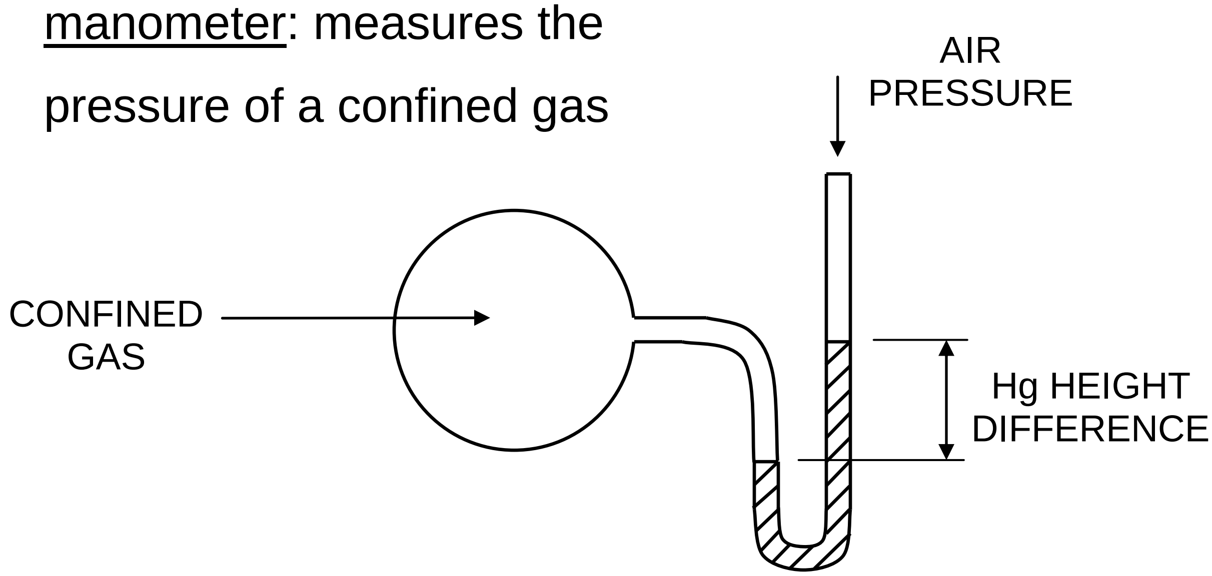
How many kPa is 1.37 atm?

$$X\,kPa = 1.37\,atm\left(\frac{101.3\,kPa}{1\,atm}\right) = \boxed{138.8\,kPa}$$

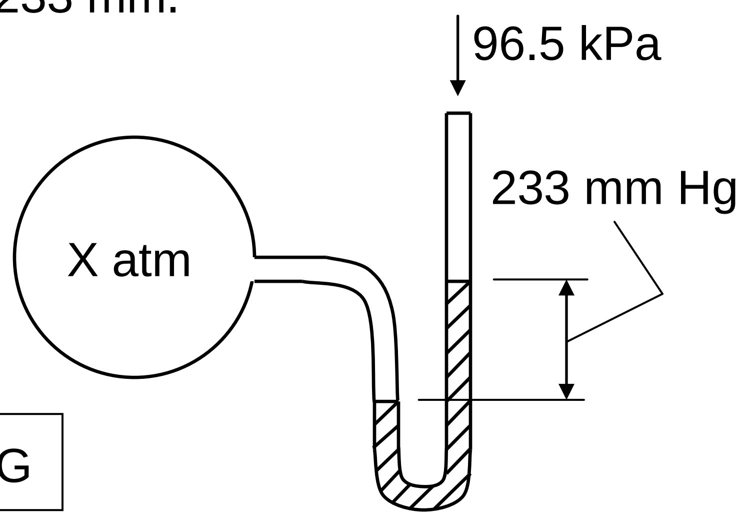
How many mm Hg is 231.5 kPa?

$$X\,mm\,Hg = 231.5\,kPa\left(\frac{760\,mm\,Hg}{101.3\,kPa}\right) = \boxed{1737\,mm\,Hg}$$

manometer: measures the pressure of a confined gas




Atmospheric pressure is 96.5 kPa; mercury height difference is 233 mm. Find confined gas pressure, in atm.




$$\boxed{\text{SMALL} + \text{HEIGHT} = \text{BIG}}$$

96.5 kPa + 233 mm Hg = X atm

$$96.5\ \text{kPa}\left(\frac{1\ \text{atm}}{101.3\ \text{kPa}}\right) + 233\ \text{mm Hg}\left(\frac{1\ \text{atm}}{760\ \text{mm Hg}}\right) = X\ \text{atm}$$

0.953 atm + 0.307 atm = X atm

$$\boxed{X = 1.26\ \text{atm}}$$

## The Ideal Gas Law

$$\boxed{PV = nRT}$$

P = pressure (in kPa)

n = # of moles of gas (mol)

V = volume (in L or $dm^3$)

T = temperature (in K)

R = universal gas constant = $8.314\ \frac{\text{L - kPa}}{\text{mol - K}}$

32 g oxygen at $0^oC$ is under 101.3 kPa of pressure. Find sample's volume.

T = $0^oC$ + 273 = 273 K

$$n = 32\text{ g }O_2\left(\frac{1\text{mol }O_2}{32\text{ g }O_2}\right) = 1.0\text{ mol}$$

$$PV = nRT \rightarrow V = \frac{nRT}{P} = \frac{1\text{mol }(8.314)(273)}{101.3} = \boxed{22.4\text{ L}}$$

0.25 g carbon dioxide fills a 350 mL container at $127^oC$. Find pressure in mm Hg.

T = $127^oC$ + 273 = 400 K

V = 0.35 L

$$n = 0.25\text{ g }CO_2\left(\frac{1\text{mol }CO_2}{44\text{ g }CO_2}\right) = 0.00568\text{ mol}$$

$$PV = nRT \rightarrow P = \frac{nRT}{V} = \frac{0.00568\,(8.314)(400)}{0.35} = 54.0\text{ kPa}$$

$$P = 54.0\text{ kPa}\left(\frac{760\text{ mm Hg}}{101.3\text{ kPa}}\right) = \boxed{405\text{ mm Hg}}$$

## P, V, T Relationships

At constant P, as gas T ↑, its V ↑ .
“ “ “, “ “ T ↓, “ V ↓ .

Charles’s Law

At constant V, as gas T ↑, its P ↑ .
“ “ “, “ “ T ↓, “ P ↓ .

Gay-Lussac’s Law

At constant T, as P on gas ↑, its V ↓ .
“ “ “, “ P “ “ ↓ , “ “ ↑ .

Boyle’s Law

## The Combined Gas Law

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

P = pressure (any unit will work)

V = volume (any unit will work)

T = temperature (must be in Kelvin)

1 = initial conditions

2 = final conditions

A gas has vol. 4.2 L at 110 kPa. If temp. is constant, find pres. of gas when vol. changes to 11.3 L.

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

$$110\ \text{kPa}\,(4.2\ \text{L}) = P_2\,(11.3\ \text{L}) \qquad \boxed{P_2 = 40.9\ \text{kPa}}$$

Original temp. and vol. of gas are $150^{o}$C and 300 $dm^3$. Final vol. is 100 $dm^3$. Find final temp. in $^{o}$C, assuming constant pressure.

$$T_1 = 150^{o}\text{C} + 273 = 423\ \text{K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2} \rightarrow \frac{300\ \text{dm}^3}{423\ \text{K}} = \frac{100\ \text{dm}^3}{T_2}$$

$$300\ \text{dm}^3\ (T_2) = 423\ \text{K}\ (100\ \text{dm}^3) \rightarrow 141\ \text{K} = \boxed{-132^{o}\text{C}}$$

A sample of methane occupies 126 $cm^3$ at $-75^{o}$C and 985 mm Hg. Find its vol. at STP.

$$T_1 = -75^{o}\text{C} + 273 = 198\ \text{K}$$

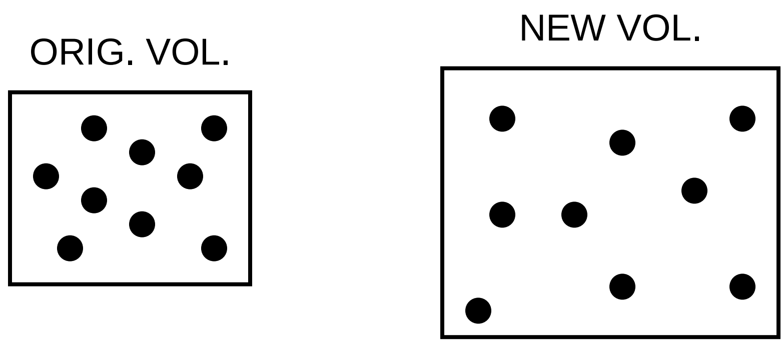
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow \frac{985\ \text{mm Hg}(126\ \text{cm}^3)}{198\ \text{K}} = \frac{760\ \text{mm Hg}\,(V_2)}{273\ \text{K}}$$

$$985\ (126)\ (273) = 198\ (760)\ V_2 \qquad \boxed{V_2 = 225\ \text{cm}^3}$$

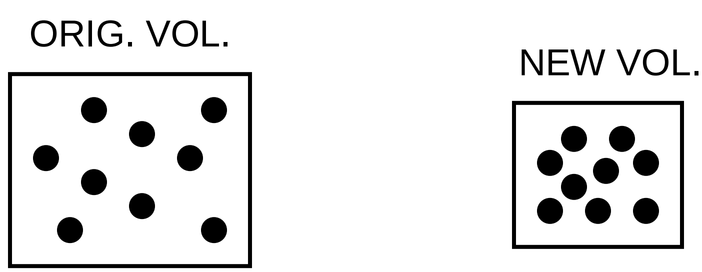
# Density of Gases

Density formula for any substance: $D = \dfrac{m}{V}$

For a sample of gas, mass is constant, but pres. and/or temp. changes cause gas's vol. to change. Thus, its density will change, too.




If V $\Uparrow$ (due to P $\Downarrow$ or T $\Uparrow$), then… D $\Downarrow$




If V $\Downarrow$ (due to P $\Uparrow$ or T $\Downarrow$), then… D $\Uparrow$

Density of Gases Equation: $\dfrac{P_1}{T_1 D_1} = \dfrac{P_2}{T_2 D_2}$

** As always, T's must be in K.

A sample of gas has density 0.0021 g/cm$^3$ at –18$^o$C and 812 mm Hg. Find density at 113$^o$C and 548 mm Hg.

$T_1$ = –18$^o$C + 273 = 255 K      $T_2$ = 113$^o$C + 273 = 386 K

$$\frac{P_1}{T_1 D_1} = \frac{P_2}{T_2 D_2} \rightarrow \frac{812}{255\,(0.0021)} = \frac{548}{386\,(D_2)}$$

$812(386)(D_2) = 255(0.0021)(548) \rightarrow \boxed{D_2 = 9.4 \times 10^{-4}\ \text{g/cm}^3}$

A gas has density 0.87 g/L at 30$^o$C and 131.2 kPa. Find density at STP.

$T_1$ = 30$^o$C + 273 = 303 K

$$\frac{P_1}{T_1 D_1} = \frac{P_2}{T_2 D_2} \rightarrow \frac{131.2}{303\,(0.87\,)} = \frac{101.3}{273\,(D_2)}$$

$131.2(273)(D_2) = 303(0.87)(101.3) \rightarrow \boxed{D_2 = 0.75\ \text{g/L}}$

Find density of argon at STP.

$$D = \frac{m}{V} = \frac{39.9\ \text{g}}{22.4\ \text{L}} = \boxed{1.78\ \frac{\text{g}}{\text{L}}}$$

Find density of nitrogen dioxide at 75°C and 0.805 atm.

D of $NO_2$ @ STP… $D = \frac{m}{V} = \frac{46.0\ g}{22.4\ L} = 2.05\ \frac{g}{L}$

$T_2 = 75°C + 273 = 348\ K$

$$\frac{P_1}{T_1 D_1} = \frac{P_2}{T_2 D_2} \rightarrow \frac{1}{273\,(2.05)} = \frac{0.805}{348\,(D_2)}$$

$1\,(348)\,(D_2) = 273\,(2.05)\,(0.805) \rightarrow \boxed{D_2 = 1.29\ g/L}$

A gas has mass 154 g and density 1.25 g/L at 53°C and 0.85 atm. What vol. does sample occupy at STP?

Find D at STP. $T_1 = 53°C + 273 = 326\ K$

$$\frac{P_1}{T_1 D_1} = \frac{P_2}{T_2 D_2} \rightarrow \frac{0.85}{326\,(1.25)} = \frac{1}{273\,(D_2)}$$

$0.85\,(273)\,(D_2) = 326\,(1.25)\,(1) \rightarrow D_2 = 1.756\ g/L$

Find vol. when gas has that density.

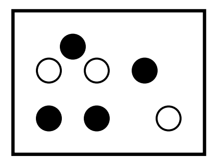
$$D_2 = \frac{m}{V_2} \rightarrow V_2 = \frac{m}{D_2} = \frac{154\ g}{1.756\ g/L} = \boxed{87.7\ L}$$

## Dalton's Law of Partial Pressure

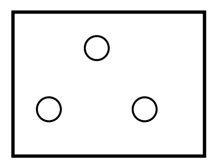
In a gaseous mixture, a gas's **partial pressure** is the one the gas would exert if it were by itself in the container.

The mole ratio in a mixture of gases determines each gas's partial pressure.

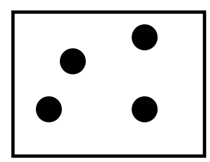
Total pressure of mixture (3.0 mol He and 4.0 mol Ne) is 97.4 kPa. Find partial pressure of each gas.



$$P_{He} = \frac{3 \text{ mol He}}{7 \text{ mol gas}}(97.4 \text{ kPa}) = \boxed{41.7 \text{ kPa}}$$



$$P_{Ne} = \frac{4 \text{ mol Ne}}{7 \text{ mol gas}}(97.4 \text{ kPa}) = \boxed{55.7 \text{ kPa}}$$



**Dalton's Law:** the total pressure exerted by a mixture of gases is the sum of all the partial pressures

$$\boxed{P_Z = P_{A,Z} + P_{B,Z} + \ldots}$$

80.0 g each of He, Ne, and Ar are in a container. The total pressure is 780 mm Hg. Find each gas's partial pressure.

$$80\text{ g He}\left(\frac{1\text{mol}}{4\text{ g}}\right) = 20\text{ mol He}$$

$$80\text{ g Ne}\left(\frac{1\text{mol}}{20\text{ g}}\right) = 4\text{ mol Ne}$$

$$80\text{ g Ar}\left(\frac{1\text{mol}}{40\text{ g}}\right) = 2\text{ mol Ar}$$

Total: 26 mol gas

$P_{He} = {}^{20}/_{26}$ of total

$P_{Ne} = {}^{4}/_{26}$ of total

$P_{Ar} = {}^{2}/_{26}$ of total

$$\boxed{P_{He} = 600\text{ mm Hg},\ P_{Ne} = 120\text{ mm Hg},\ P_{Ar} = 60\text{ mm Hg}}$$

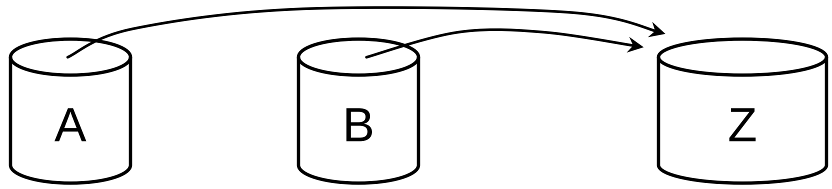
Dalton's Law: $P_Z = P_{A,Z} + P_{B,Z} + \ldots$

Two 1.0 L containers, A and B, contain gases under 2.0 and 4.0 atm, respectively. Both gases are forced into Container B. Find total pres. of mixture in B.


| | $P_X$ | $V_X$ | $V_Z$ | $P_{X,Z}$ |
|---|---|---|---|---|
| **A** | 2.0 atm | 1.0 L | 1.0 L | 2.0 atm |
| **B** | 4.0 atm | 1.0 L | | 4.0 atm |

Total = 6.0 atm

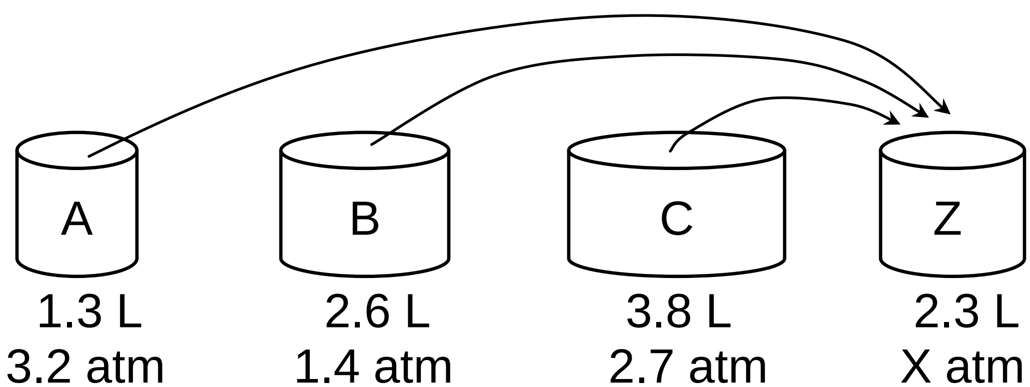
Two 1.0 L containers, A and B, contain gases under 2.0 and 4.0 atm, respectively. Both gases are forced into Container Z ($^{w}$/vol. 2.0 L). Find total pres. of mixture in Z.




| | $P_X$ | $V_X$ | $V_Z$ | $P_{X,Z}$ |
|---|---|---|---|---|
| **A** | 2.0 atm | 1.0 L | 2.0 L | 1.0 atm |
| **B** | 4.0 atm | 1.0 L | | 2.0 atm |

Total = 3.0 atm

Find total pressure of mixture in Container Z.




| | $P_X$ | $V_X$ | $V_Z$ | $P_{X,Z}$ |
|---|---|---|---|---|
| **A** | 3.2 atm | 1.3 L | | 1.8 atm |
| **B** | 1.4 atm | 2.6 L | 2.3 L | 1.6 atm |
| **C** | 2.7 atm | 3.8 L | | 4.5 atm |

Total = 7.9 atm

## Gas Stoichiometry

Find vol. hydrogen gas made when 38.2 g zinc react $^{w}$/excess hydrochloric acid. Pres.=107.3 kPa; temp.= 88$^{o}$C.

**Zn (s) + 2 HCl (aq) → $ZnCl_2$ (aq) + $H_2$ (g)**

38.2 g Zn excess

$V = X\ L\ H_2$
P = 107.3 kPa
T = 88$^{o}$C ***

$$X \text{ mol } H_2 = 38.2 \text{ g Zn}\left(\frac{1 \text{mol Zn}}{65.4 \text{ g Zn}}\right)\left(\frac{1 \text{mol } H_2}{1 \text{mol Zn}}\right) = 0.584 \text{ mol } H_2$$

At STP, we'd use 22.4 L per 1 mol, but we aren't at STP.

$$P\,V = n\,R\,T \rightarrow\ V = \frac{n\,R\,T}{P} = \frac{0.584 \text{ mol}\,(8.314)\,(361)}{107.3} = \boxed{16.3 \text{ L}}$$

What mass solid magnesium is req'd to react $^{w}$/250 mL carbon dioxide at 1.5 atm and 77$^{o}$C to produce solid magnesium oxide and solid carbon?

**2 Mg (s) + $CO_2$ (g) → 2 MgO (s) + C (s)**

X g Mg

V = 250 mL → 0.25 L
P = 1.5 atm → 151.95 kPa
T = 77$^{o}$C → 350 K

$$P\,V = n\,R\,T \rightarrow\ n = \frac{P\,V}{R\,T} = \frac{151.95\,(0.250)}{8.314\,(350)} = 0.013 \text{ mol } CO_2$$

$$X \text{ g Mg} = 0.013 \text{ mol } CO_2\left(\frac{2 \text{ mol Mg}}{1 \text{mol } CO_2}\right)\left(\frac{24.3 \text{ g Mg}}{1 \text{mol Mg}}\right) = 0.63 \text{ g Mg}$$

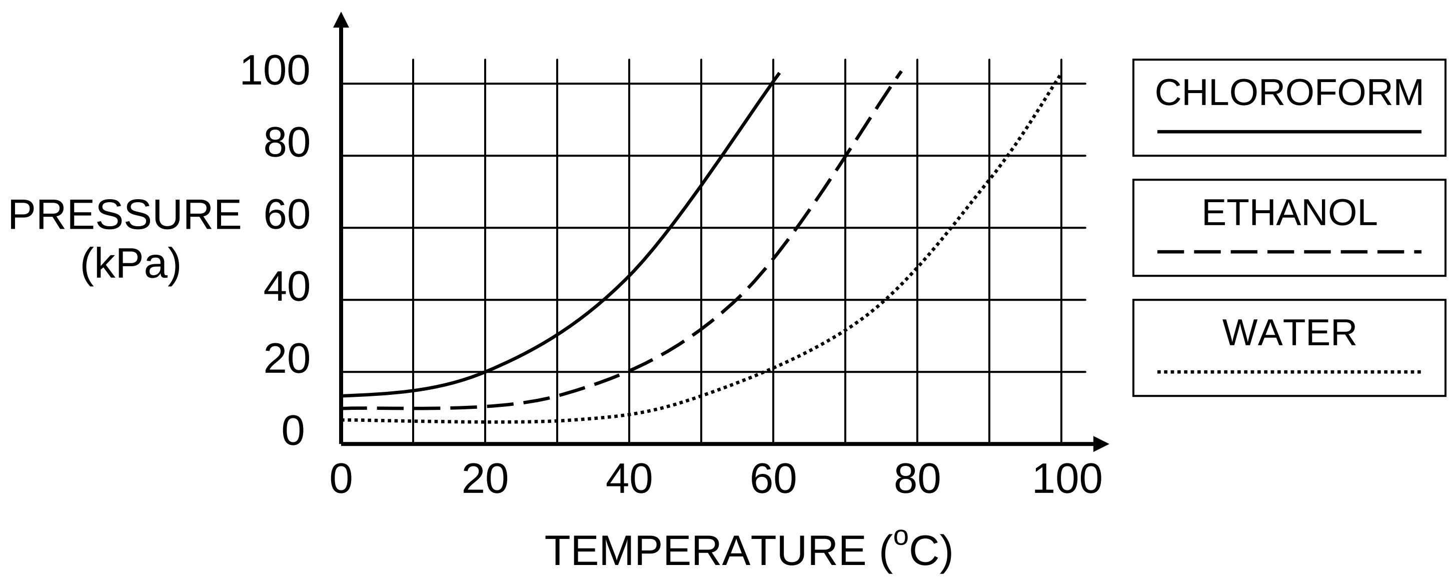
## Vapor Pressure

-- a measure of the tendency for liquid particles to enter gas phase at a given temp.

-- a measure of "stickiness" of liquid particles to each other

| | | | | |
|---|---|---|---|---|
| more "sticky" | ⇨ | less likely to vaporize | ⇨ | In general: LOW v.p. |
| not very "sticky" | ⇨ | more likely to vaporize | ⇨ | In general: HIGH v.p. |

NOT all liquids have same v.p. at same temp.




**Volatile** substances evaporate easily (have high v.p.'s).

BOILING → when vapor pressure = confining pressure (usually from atmosphere)

At sea level and 20$^{o}$C…