Slide 1

Partial Pressure

When moles are not moles and atmospheres are not atmospheres

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What must be specified for a solution?

A. Volume
B. Mass
C. Volume and Mass
D. Concentration
E. Volume and Concentration
F. Christmas and Easter
G. All of the Above
H. Shut up already

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Chemists are Pragmatists

Most gas phase reactions occur in sealed flasks – you've got to keep the reactants from escaping!

That means that, typically, the volume is fixed and the temperature is known (unless it is a very exothermic or endothermic reaction and the temperature isn't controlled).

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The Gas Law revisited

PV = nRT

In a sealed flask, V is constant and (usually) so is Temperature. Collect the constants!

$$P = n \frac{(RT)}{V} = n * \text{constant}$$

The pressure is directly proportional to n, the number of moles!

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Suddenly bizarre units…

This is critically important for a reaction because, as you know, reactions are all about MOLES! MOLES! MOLES!

For gas phase reactions, the pressure is sometimes a substitute for the number of moles.

YOU CAN ACTUALLY MEASURE THE AMOUNT OF SOMETHING IN ATMOSPHERES!!!!!!

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PV=nRT does not discriminate

While it may not be immediately obvious, there's another interesting thing about PV=nRT…

None of the variables directly depends on the identity of the gas molecules!

P, V, and T are physical properties of the system! Even n is just the number of particles - any particles!

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What's it mean?

It means that the gas laws are additive!!!!!

If I have a mixture of gases, I can look at the physical properties (P, V, T or n) as belonging to one gas separate from the others, or to all the gases collectively.

(Well, except for T, since the gases must all be at the same temperature.)

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Consider Pressure:

What's pressure?

The combined effect of moving gas molecules bouncing off of things.

If you have Hydrogen and Helium mixed in a flask, the total pressure comes from the combined collisions of the Hydrogen and the Helium.

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Keep 'em apart

Hydrogen and Helium independently obey the ideal gas equation.

$P_{He} V = n_{He} R T$

$P_{H2} V = n_{H2} R T$

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Put 'em together

Hydrogen and Helium collectively obey the ideal gas equation.

$P_{total}\ V = n_{total}\ R\ T$

$P_{total}\ V = (n_{He} + n_{H2})\ R\ T$

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Lump the constants..

$P_{total} = \frac{n_{total}\ R\ T}{V}$

$P_{total} = \frac{(n_{He} + n_{H})\ R\ T}{V} = \frac{n_{He}\ RT}{V} + \frac{n_{H2}\ RT}{V}$

$P_{total} = P_{He} + P_{H2}$

The total pressure is the sum of the **partial pressure**

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Partial Pressure

The partial pressure is defined as the pressure exerted by a gas ignoring the presence of any other gases.

(You could also define a partial volume similarly.)

Considering that for an ideal gas, gas molecules don't interact (one of the 2 conditions), this would seem to be a logical result.

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Dalton's Law of Partial Pressures

$P_{total} = P_{He} + P_{H2}$

This is just one specific example of the more general rule:

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

Where P_i is the partial pressure of gas i.

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Calculating partial pressure

As we've seen, the partial pressure is just like any old pressure:

$PV = nRT$

$$P = \frac{nRT}{V}$$

Remember, we are in one flask at one temperature, so RT/V is constant

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Pick a gas, any gas

$$P_{He} = n_{He} \frac{RT}{V}$$

$$P_{total} = n_{total} \frac{RT}{V}$$

In a flask of constant T, T and V are constant for each gas and for the combination of all gases!

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Pick a gas, any gas

$P_{He} = n_{He} \frac{RT}{V}$

$P_{total} = n_{total} \frac{RT}{V}$

$\frac{P_{total}}{n_{total}} = \frac{RT}{V}$

So: $P_{He} = \frac{n_{He} P_{total}}{n_{total}} = \chi_{He} P_{total}$

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Mole Fraction

χ_{He} is called the "mole fraction of He".

χ is a unit of concentration!

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Little Bitty Problem

If I had 0.25 mol H_2 and 0.75 mol He in a 1 L flask at 273 K, what is the partial pressure of each gas and the total pressure in the flask?

$P_{H2} = \frac{n_{H2} R T}{V} = \frac{0.25 \text{ mol} * 0.082058 \text{ L atm} * 273 \text{ K}}{1 \text{ L} \quad \text{mol K}}$

$P_{H2} = 5.6$ atm

$P_{He} = \frac{n_{He} R T}{V} = \frac{0.75 \text{ mol} * 0.082058 \text{ L atm} * 273 \text{ K}}{1 \text{ L} \quad \text{mol K}}$

$P_{He} = 16.8$ atm

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$$P_{tot} = \frac{n_{tot} R T}{V} = \frac{1.0 \text{ mol} * 0.082058 \text{ L atm} * 273 \text{ K}}{1 \text{ L} \quad \text{mol K}}$$

P_{tot} = 22.4 atm = 5.6 atm + 16.8 atm

Notice, I get the same results if I start from the total pressure and divvy it up:

$$P_{H2} = \chi_{H2} P_{tot} = \frac{0.25 \text{ mol}}{1.0 \text{ mol}} * 22.4 \text{ atm} = 5.6 \text{ atm}$$

$$P_{He} = \chi_{He} P_{tot} = \frac{0.75 \text{ mol}}{1.0 \text{ mol}} * 22.4 \text{ atm} = 16.8 \text{ atm}$$

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Tro Problem 5.48

A 1.0 L container of liquid nitrogen is kept in a closet measuring 1.0 m by 1.0 m by 2.0 m. Assuming that the container is completely full, that the temperature is 25.0 C, and that the atmospheric pressure is 1.0 atm, calculate the percent (by volume) of air that would be displaced if all of the liquid nitrogen evaporated. [Liquid nitrogen has a density of 0.807 g/mL]

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The volume of gas in the closet is…

A. 2000 L
B. 2.0 m^3
C. 1999 L
D. I don't know, but it must not be 2000 L
E. 1962.3 L (ish)

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Volume displaced

If you release a second gas into a room, there are two options: either the pressure increases (more moles!) or some of the air in the room escapes.

Unless the room is airtight and sealed, some of the air will escape because the pressure in the room wants to be the same as the pressure outside.

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Volume of air

The air fills the closet.

V_{closet} = l x w x h = 1.0 m x 1.0 m x 2.0 m
= 2.0 m^3

Is this a good unit?

It's the BEST UNIT!!! It's the SI unit!! (But we'd probably rather have L ☺)

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Volume of air

The air fills the closet.

$$V_{closet} = 2.0\ m^3 * \frac{(100\ cm)^3}{(1m)^3} * \frac{1\ mL}{1\ cm^3} * \frac{1\ L}{1000\ mL}$$

V_{closet} = 2000 L

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How much Nitrogen?

I'm sure many of you are tempted to say 1.0 L.

1.0 L is the volume of LIQUID nitrogen. (Which means there's really only 1999 L of air in the room!)

We need to know how much GASEOUS nitrogen is formed when the liquid evaporates.

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1.0 L of liquid is ??? Gas?

????

PV = nRT

What do we know?

We know the R, T, P for sure.
We want to know V
So we need to know n.

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Finding n

We know the volume of the liquid and its density, so we know…

…the mass of the liquid which is the same as…
…the mass of the gas, which can be used to find…
…the moles of gas, by using…
…the molar mass!

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1.0 L N_2 liq * 1000 mL / 1 L * 0.807 g / 1 mL = 807 g N_2 liquid

807 g N_2 liquid = 807 g N_2 gas

807 g N_2 gas * 1 mol N_2 / 28.014 g N_2 = 28.81 mol N_2

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Ideal Gas Law

PV = nRT

V = nRT / P = (28.81 mol) (0.082058) *298 K / 1 atm

V = 704.5 L N_2

704.5 L N_2 should displace 704.5 L air

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% Displaced

704.5 L displaced air / 1999 L air in closet * 100 = 35.24%

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Density in the gas law

- PV=nRT

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

$$PV = \frac{m}{M.M.}RT$$

P(M.M.) = DRT

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Let's actually do some chemistry!

Consider a previously evacuated 1 L sealed flask at 450 C which contains 10 g of H_2 and 10 g of O_2. If I make steam, what is the final pressure in the flask?

Where do we start?

Of course, chemistry ALWAYS starts with a balanced equation!

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Let's actually do some chemistry!

Consider a 1 L sealed flask at 450 C which contains 10 g of H_2 and 10 g of O_2. If I make steam, what is the final pressure in the flask?

$2H_{2\,(g)} + O_{2\,(g)} \longrightarrow 2\,H_2O_{\,(g)}$

And now….???

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YES! It IS a limiting reactant problem!

10 g H_2 * $\frac{1\ mol\ H_2}{2.016\ g\ H_2}$ = 4.96 mol H_2

4.96 mol H_2 * $\frac{2\ mol\ H_2O}{2\ mol\ H_2}$ = 4.96 mol H_2O

10 g O_2 * $\frac{1\ mol\ O_2}{32\ g\ O_2}$ = 0.3125 mol O_2

0.3125 mol O_2 * $\frac{2\ mol\ H_2O}{1\ mol\ O_2}$ = 0.625 mol H_2O

Oxygen is the limiting reagent – and we make 0.625 mol H_2O.

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And so…???

You might be ready to PV=nRT, but…

$2H_{2\ (g)} + O_{2\ (g)} \rightarrow 2\ H_2O_{(g)}$

Note that both the reactants and products are gases. That means all 3 species will contribute to the total pressure at the end, so we need to keep track of the amounts of all of them.

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A little molar accounting

	$2H_{2\ (g)}$	+ $O_{2\ (g)}$	$\rightarrow$ $2\ H_2O_{(g)}$
I	4.96 mol	0.3125 mol	0 mol
C	-2x mol	-x mol	+2x mol
E	(4.96 - 2x)	0 (LR)	0.625 mol

0.3125-x=0

x = 0.3125 mol

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A little molar accounting

$2H_{2\,(g)}$ + $O_{2\,(g)}$ → $2\,H_2O_{\,(g)}$

	$2H_{2\,(g)}$	$O_{2\,(g)}$	$2\,H_2O_{\,(g)}$
I	4.96 mol	0.3125 mol	0 mol
C	-2(0.3125)	-0.3125	+2(0.3125)
E	4.335	0 (LR)	0.625 mol

So the total moles of gas are:
4.335+0.625 = 4.96 mol

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PV = nRT
T = 450 C + 273.15 = 723.15 K

$P = \frac{n_{tot}RT}{V} = \frac{4.96\text{ mol} \cdot 0.082058\text{ L atm} \cdot 723.15\text{ K}}{\text{mol K} \quad 1\text{ L}}$

P = 294 atm

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Another Chemistry problem

32.0 g of $CaCO_3$ (limestone) is placed in a 2.0 L previously evacuated sealed flask with 1.5 atm HCl (g) at 125 C. What is the final pressure in the flask if the following reaction is known to occur:

$CaCO_{3\,(s)} + 2\,HCl_{\,(g)} \rightarrow CaCl_{2\,(s)} + H_2O_{\,(g)} + CO_{2\,(g)}$

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Another limiting reagent problem!

32.0 g $CaCO_3$ * 1 mol $CaCO_3$ / 100.09 g * 1 mol CO_2 / 1mol $CaCO_3$ = 0.32 mol CO_2

PV=nRT for HCl

n = PV / RT = (1.5 atm) (2.0 L) / 0.08206 Latm/mol K (125 C +273.15)

n=0.0918 mol HCl * 1 mol CO_2 / 2 mol HCl =0.0459 mol CO_2

So, HCl is the limiting reagent!

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And again with the molar accounting

$CaCO_{3\ (s)}$ + 2 $HCl_{(g)}$ → $CaCl_{2\ (s)}$ + $H_2O_{(g)}$ + $CO_{2\ (g)}$

I	NA	.0918 mol	NA	0	0
C	NA	-2X	NA	+x	+x
E	NA	0 (LR)	NA	0.0459 mol	0.0459 mol

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Final Pressure

$N_{total} = n_{H2O} + n_{CO2}$ = 0.0459 mol +0.0459 mol = 0.0918 mol

P = nRT / V = 0.0918 mol *0.08206 L atm/mol K*398.15 K / 2.0L

P = 1.5 atm

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Clicker Question #1

2.0 g of hydrogen and 10.0 g of oxygen are added to a sealed, evacuated 10.0 L flask. The mixture is reacted at 550 ºC for 6 hours. Assuming the reaction goes to completion, what is the total pressure in the flask after 6 hours (before it cools down)?

A. 6.8 atm

B. 4.3 atm

C. 2.1 atm

D. 3.8 atm

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2 g H_2 * 1 mol/2 g = 1.0 mol H_2 *(2 H_2O/2 H_2) = 1 mol H_2O

10 g O_2 * 1 mol/32 g = 0.3125 mol O_2 * (2 mol H_2O/1 mol O_2) = 0.625 mol H_2O

	$2H_{2\,(g)}$	+ $O_{2\,(g)}$	$\rightarrow$ $2\,H_2O_{(g)}$
I	1.0 mol	0.3125 mol	0 mol
C	-2x	-x	+2x
E	1-2x	0 LR	2x mol

0.3125-x = 0

X = 0.3125 mol

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	$2H_{2\,(g)}$	+ $O_{2\,(g)}$	$2\,H_2O_{(g)}$
I	1.0 mol	0.3125 mol	0 mol
C	-2(0.3125)	-0.3125	+2(0.3125)
E	0.375	0	0.625 mol

Total moles gas= 0.375 + 0.625 = 1 mol

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PV = nRT

P (10 L) = 1 mol * 0.082056 $\frac{L\ atm}{mol\ K}$ * 823.15 K

P = 6.8 atm