CHEM 205 section 03

LECTURE #26 Tues. Apr.08, 2008

ASSIGNED READINGS:

TODAY'S CLASS: Ch.12 overview
study theory at level of notes
but do problems from textbook

- **Final exam: Mon. April 14th (2-5pm)**
- **Covers entire course: Ch.1-5, 20.1, 7-9, 10.1-2, 12**

FINAL EXAMS FROM PREVIOUS YEARS ON WEBSITE:
Moodle site has link to: http://faculty.concordia.ca/rogers

Chapter 12: Gases & their Properties

You are only responsible for learning Ch.12 at the level presented in the lecture and notes
(*i.e.,* read Ch.12 only if you want to…
but must do Ch.12 problems!)

12.1 Properties of Gases
12.2 Gas Laws: Experimental Basis
12.3 The Ideal Gas Law
12.4 Gas Laws & Chemical Reactions
12.5 Gas Mixtures & Partial Pressures
12.6 The Kinetic Molecular Theory
12.7 Diffusion & Effusion
12.8 Some Applications:
hot-air balloons, deep sea diving
12.9 Nonideal Behaviour: Real Gases

Chapter Goals:

- Understand the basis of the gas laws & how to use them
- Use the ideal gas law
- Apply the gas laws to stoichiometric calculations
- Understand kinetic-molecular theory of gases, especially the distribution of molecular speeds (energies)
- Recognize why real gases do not behave as "ideal gases"

12.1: Properties of gases

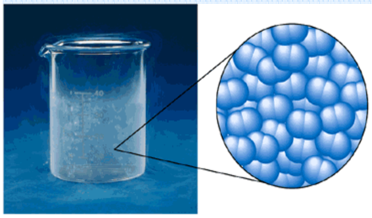
- **Referring to gas-phase substances:**
  - "gas" = substance normally in gaseous state *(phase)* at ambient temperature (T) & pressure (P)
    Table 12.1: He, H_2, O_2, N_2, F_2, Cl_2, CO_2, C_3H_8, etc…
  - "vapour" = gaseous form of substance that is normally a solid or liquid at ambient T & P
    water vapour (steam), gasoline vapour (gas fumes)

Particles (atoms/molecules) in a gas are VERY FAR APART

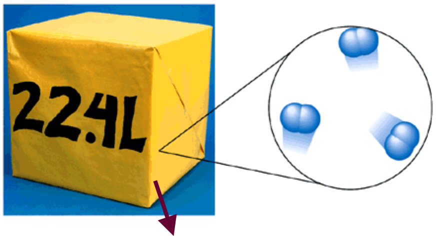
- **lowest density state of matter**
- **particles can be squeezed closer together: compressible**
- **particles don't interact much with each other: simple behaviour!**

Zumdahl's Figure 5.14:

(a) One mole of $N_2(l)$ = 28.13 g
V = ~ 35 mL = ~ $(3.3\ \text{cm})^3$
d = 0.81 g/mL



(b) One mole of $N_2(g)$ at STP
V = 22.4 L
d = 1.2×10^{-3} g/mL



22.4 L = 22.4 dm^3
= $22.4 \times (10\text{cm})^3$
= $22.4 \times 10^3\ cm^3$
≈ 28cm x 28cm x 28cm
≈ roughly 1 cubic foot

Volume of one mole of N_2, as LIQUID *vs.* GAS:

$$V(N_{2(g)}) / V(N_{2(l)})$$

= 22.4 L / 0.035 L
= 640x greater as gas!

Gases exert PRESSURE: what is it?

Force caused by gas particles colliding with container walls

PRESSURE is defined as:
FORCE per unit AREA

- Force = mass x acceleration
  = mass x (velocity change/unit time)
  1 N = 1 kg x (m/s^2) = **definition of "Newton"**
- **SI unit of Pressure: "Pascals" 1 Pa** = 1 N/m^2
  = 1 $(kg \cdot m \cdot s^{-2}) \cdot m^{-2}$
  = 1 $kg \cdot m^{-1} s^{-2}$
- **Typical "atmospheric pressure"** = **1 atm** **(COMMON unit)**
  = **101.325 kPa**
  = **1.01325 bar**
  = **760 mm Hg**
  = **760 torr**

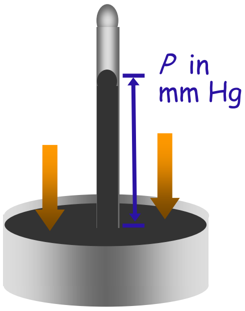
NOTE:
- in everyday life: "psi" (pounds per square inch) where 1 atm = 14.7 psi

Measuring pressure: barometers & manometers

Kotz Fig.12.2

A barometer

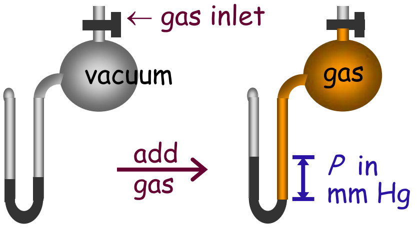
- dish of Hg(*l*) open to atmosphere
- evacuated tube inverted into Hg
- Hg rises until $P_{Hg(gravity)} = P_{atm}$
- P = height of Hg column



Kotz p.550: *A Closer Look*

A manometer

- U-tube, with Hg(*l*)
- sealed on one end
- gas flask on other end
- P = difference in height of two ends of Hg "column" in the U-tube



12.2-3 Gas Laws: Experimental Basis… ⇨ Ideal Gas Law

Physically: All gases essentially behave same way!
(NOT chemically)

Gas behaviour is described by natural "laws"

Based on general observations made in the 17th & 18th centuries…by:

- **Avogadro:** more particles ⇨ larger volume $V = a\,n$
- **Boyle:** higher pressure ⇨ smaller volume $V = b/P$
- **Charles:** higher temperature ⇨ larger volume $V = c\,T$

SUMMARY: The volume (V) occupied by a sample of gas is:
directly proportional to n (#moles) & T (temperature)
inversely proportional to P (pressure)…

…combine laws into one equation: $\boxed{PV = nRT}$ The IDEAL GAS LAW

A proportionality constant: R = "the gas constant"
$= 8.314\ J{\cdot}mol^{-1}K^{-1} = \underline{0.08206\ L{\cdot}atm{\cdot}mol^{-1}K^{-1}}$

Gases behave ideally if their particles don't interact much

In an IDEAL gas, the particles (atoms/molecules)

1) do not interact with each other ⇦ particles are very far apart
2) each have ~zero volume ⇦ most of container is truly empty
3) are in constant motion ⇦ enough KE to overcome all attractions, whether strong *(polar)* or weak *(nonpolar)*

THUS: *Any* gas will behave ideally…

- at LOW pressures ⇦ low concentration of particles
- at "HIGH" temperatures ⇦ particles moving quickly

Under these conditions, gases OBEY THE IDEAL GAS LAW
⇨ PV=nRT accurately describes physical behaviour

Standard Temperature & Pressure: "STP" = 1 atm, 0°C
= conditions where most gases behave ideally

Molar volume: 22.42 L at STP
1 mole of *any* gas occupies 22.42 L at STP
Don't memorize: calculate easily using PV=nRT…

Can use the parent gas laws individually…
…to compare same sample of gas under different conditions

- **Boyle's law:** ↑P ⇨ ↓V $P_1V_1 = P_2V_2$ **when n & T are constant**
- **Charles' law:** ↑T ⇨ ↑V $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ **when n & P are constant**

EXAMPLE: You inflate a 2.0 L balloon with He at room temperature (25°C). You then take it outside on a hot summer day: T = 35°C. Will the balloon expand or contract? What will its new volume be? (assume P is constant)

Can use PV=nRT separately for the two conditions (less memorizing…)
…recognize that the # moles of gas does not change…

- Group the constant terms together: $\frac{V_1}{T_1} = \frac{nR}{P} = \frac{V_2}{T_2}$ *tah dah!*

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow V_2 = V_1 \times \frac{T_2}{T_1} \Rightarrow V_2 = 2.0\text{L} \times \frac{308\text{K}}{298\text{K}} = 2.1\text{ L}$$

expands

Applying the ideal gas law to stoichiometry: Explosions…

What would happen if 25.0g of nitroglycerin ($C_3H_5N_3O_9$, MM 227.1 g/mol) were detonated inside an evacuated, rigid 10.0 L container at 500°C?

$$4\ C_3H_5N_3O_9(s) \rightarrow 12\ CO_2(g) + 6\ N_2(g) + 10\ H_2O(g) + O_2(g)$$

(a) What would the total pressure be inside the container?

ANS: 0.1101 mol $C_3H_5N_3O_9$ ⇨ 0.7982 mol gas ⇨ 5.06 atm

(b) If the hot gases were released out into the atmosphere, where the pressure is 1.00 atm, what would the total volume of gas be? Assume the temperature remains at 500°C.

ANS: 50.6 L

(c) Now consider that the original solid occupied approximately 15.0 cm^3 ($1cm^3 = 1mL$, or $1dm^3 = 1L$). How many times greater is the volume of the products compared to reactants (at 1 atm P)?

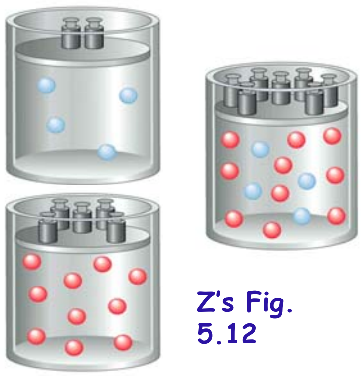
⇨much of destructive force of explosives comes from sudden formation of large volumes of gas
⇨forces everything out of the way…

ANS:
$$50.6\text{ L} \times \frac{(10\text{cm})^3}{1\text{L}}$$
$= 50600\ cm^3$
≈ 3400 x larger!

12.5 Partial Pressures: Dalton's law

For mixture of gases in container: $P_{\text{Total}} = P_1 + P_2 + \ldots + P_n$

Each gas contributes to the total pressure…



Z's Fig. 5.12

BUT…
the **partial pressure** of each gas is **SAME AS IF ALONE** in container!

- P_1 depends only on # moles of gas *1* (use PV=nRT)
- If know P_{total} & mole ratio of gases, can calculate partial pressures

E.g.: Air is 21% O_2, 78% N_2, plus other trace components (by mole)
THUS: if P_{TOT} = 1.00 atm, then
$PO_2 = (0.21 \times 1.00 \text{ atm}) = 0.21$ atm
$PN_2 = (0.78 \times 1.00 \text{ atm}) = 0.78$ atm… *etc…*

Our explosion example: now think about partial pressures

- Think about what would occur if 25.0g of nitroglycerin ($C_3H_5N_3O_9$, MM = 227.1 g/mol) were detonated inside an evacuated rigid 10.0 L container at 500°C.

$$4\ C_3H_5N_3O_9(s) \rightarrow 12\ CO_2(g) + 6\ N_2(g) + 10\ H_2O(g) + O_2(g)$$

(d) What would the partial pressure of oxygen be inside the container?

ANS: 0.174 atm (1/29th of P_{TOT})

QUESTION: Do we need to know the total pressure ?

ANS: no…
Could use stoichiometry to find
$\#n_{O2}$ formed, then convert to P_{O2} using PV=nRT

(e) Imagine this explosion occurred on a large scale in a building, and all the air in the room was displaced by the gaseous reaction products at 1.00 atm. Would a person who survived the explosion be able to breathe comfortably in that room? (assume T = 25°C if use PV=nRT approach)?

ANS: $P_{O2} = (1/29) \times 1.00 \text{ atm} = 0.0345$ atm
but we're used to P_{O2} = 0.21 atm (21% of atmospheric P)
so we might not breathe well now…

12.6 Kinetic Molecular Theory of Gases

THEORY PROPOSED (and accepted)
TO EXPLAIN OBSERVED BEHAVIOUR OF GASES:

1) Gases consist of particles (atoms, molecules), separated by distances much greater than size of particles

2) Particles in constant, random, rapid motion…
…collide with each other and walls of container

3) Temperature determines the average kinetic energy of particles (thus: same for any gas at same T!)

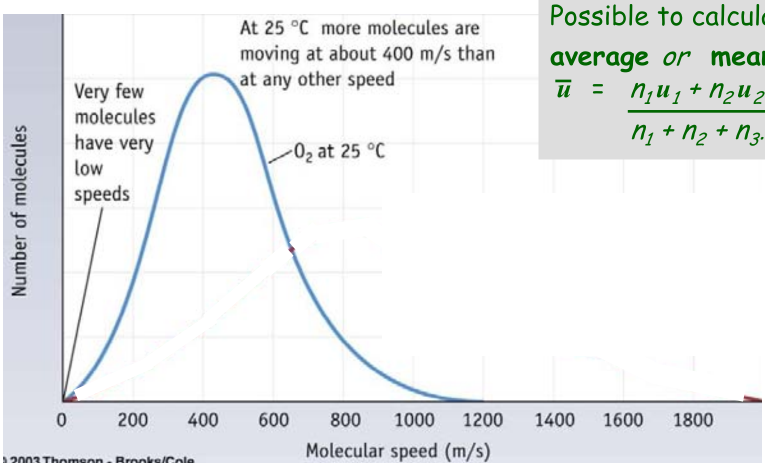
$$\overline{K.E.} = \tfrac{1}{2} m \bar{u}^2$$

mass ↗ ↖ **Average velocity (speed)**

ABOVE THREE POSTULATES: Exactly what we thought about to determine when gases would behave "ideally"…

Fig. 12.14: **Velocities of N_2 molecules at two temperatures**

In a collection of molecules: DISTRIBUTION OF ENERGIES
- Some have high K.E., most have average, some have low K.E.
- Implies: not all molecules in a sample move at same speed…



Possible to calculate (not us…):

average *or* **mean speed**

$$\bar{u} = \frac{n_1 u_1 + n_2 u_2 + n_3 u_3 \ldots}{n_1 + n_2 + n_3 \ldots}$$

Heavier molecules are slower at same temp…

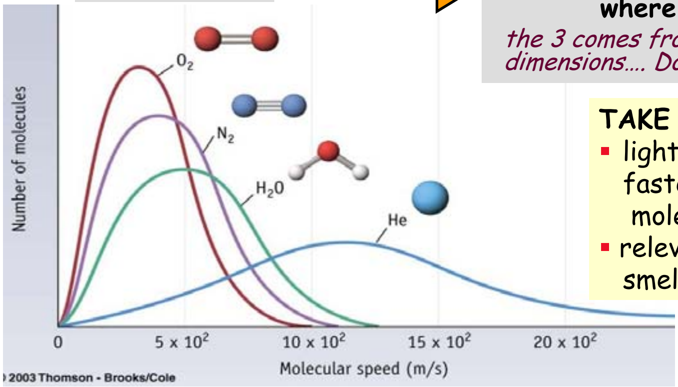
- In reality: velocity has direction *(a vector quantity)*
- Take SQUARE of average velocity then take square root
  - ⇨ removes sign: get <u>directionless velocity</u> called "root mean square velocity" $\overline{u}_{rms}$

- K.E. proportional to mean square velocity ($\overline{u}_{rms}^2$) & **MASS**
- If consider a mole of molecules:

$\overline{KE} = \frac{1}{2} m \overline{u}^2$ in 3D yields… $\overline{u}_{rms} = (3RT/M)^{1/2}$

where M = molar mass

the 3 comes from velocities in 3 dimensions…. Don't worry about how.



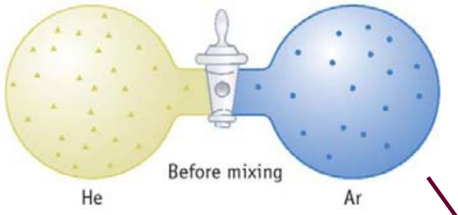
TAKE HOME MESSAGE:

- lighter molecules travel faster than heavier molecules…
- relevant to things like smelling odours!

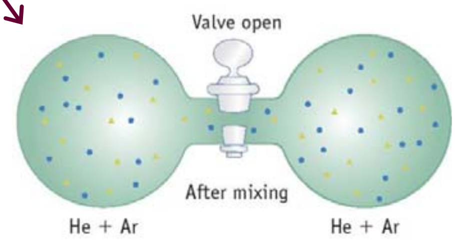
Fig. 12.15

12.7 Diffusion & Effusion: Movement of gas molecules

1. **Diffusion** = mixing of gases due to random molecular motions
   - eventually will mix completely & randomly
   - heavy particles move more slowly ⇨ diffuse more slowly



Open valve & eventually…



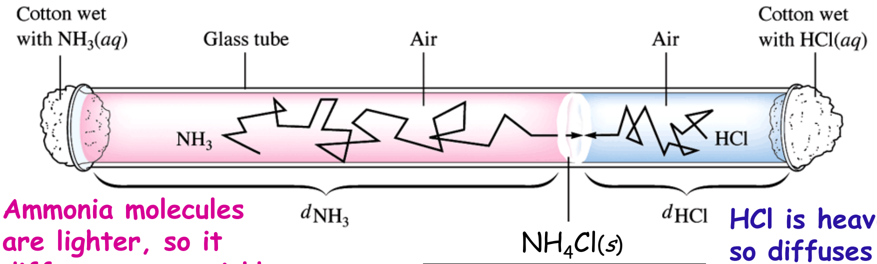
Graham's law governs effusion & diffusion

$$\frac{\text{Rate for A}}{\text{Rate for B}} = \sqrt{\frac{\text{M of B}}{\text{M of A}}}$$

Rate of diffusion/effusion is inversely proportional to gas's molar mass.

Thomas Graham
1805-1869

An experiment to demonstrate different rates of motion:



Ammonia molecules are lighter, so it diffuses more quickly

HCl is heavier, so diffuses more slowly

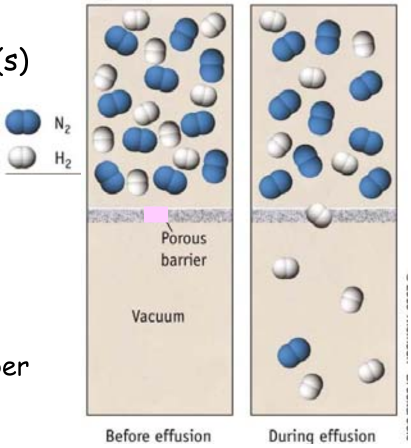
$HCl(g)$ + $NH_3(g)$ form white ring of $NH_4Cl(s)$… →

2. Effusion

= movement of a gas through tiny hole(s)
= faster for lighter molecules…
since they hit barrier more often!

WHY DOES IT HAPPEN?

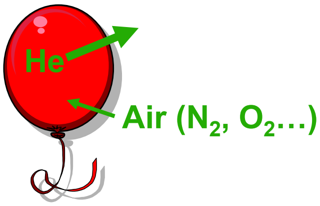
- molecules collide with container walls…
- but if "hit" the hole: go through!



BALLOONS:

- molecules effuse through holes in rubber
- rate (= moles/time) is:
  proportional to temperature
  inversely proportional to molar mass.

Thus: a He balloon deflates after a while…
He effuses out more rapidly than
N_2 & O_2 from air effuse in.



Compare Fig.12.19

12.8 Interesting real-world applications…

Deep sea diving

- **At surface:** normal air, 21% O_2 ⇨ P_{O_2} = 0.21 atm
  78% N_2 ⇨ P_{N_2} = 0.78 atm
- **Using a SCUBA tank:** P's must be balanced inside & out…
  i.e., pressure of air = pressure exerted on body
  = 2 atm at 33 feet below water

  ⇨ because O_2 is still 21% of the air in the tank,
  P_{O_2} = 0.21 x 2 atm = 0.42 atm oxygen
  P_{N_2} = 0.78 x 2 atm = 1.56 atm nitrogen

- **Problems:** high P_{N_2} (depths ~below 100ft) leads to
  huge increase in N_2 dissolved in blood
  ⇨ problems with nerve conduction
  ⇨ poor judgement, giddyness…

& when return to surface: <u>bubbles</u> in blood ⇨ "the bends"

more in Chem206…

12.9 Real Gases behave non-ideally at times

(things to consider if/when we must be VERY accurate)

Must correct for **non-ideal gas behavior** for samples at **high pressure** (smaller volume) and/or **low temperature**.
e.g., in compressed gas cylinders!

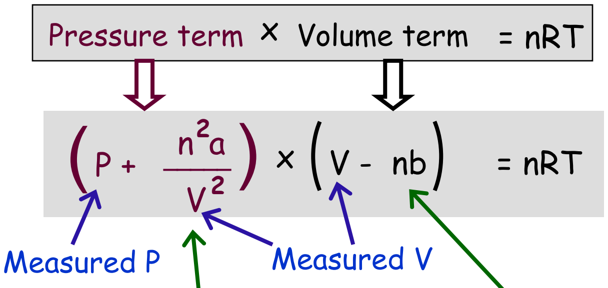
…WHEN INTERACTIONS <u>ARE</u> ACTUALLY SIGNIFICANT…

Zumdahl
Fig.5.29

- **HIGH P *or* SMALL V:**
  - **Particles are closer together**
  - Polar molecules attract each other fairly strongly
  - Nonpolar molecules' interactions small but significant…
- **LOW TEMPERATURE:**
  - **Particles are only moving slowly**
  - If not enough thermal energy to break away from intermolecular interactions, gas will NOT behave ideally!

Cylinder image from: http://www.oseh.umich.edu/OSEH%20Presentations/Rhonda.pdf

To accurately describe real gases: use van der Waals' equation



Pressure term × Volume term = nRT

$$\left(P + \frac{n^2a}{V^2}\right) \times \left(V - nb\right) = nRT$$

Measured P

Measured V

Compensate for intermolecular forces…

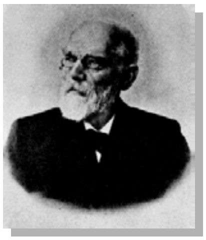
Real gas particles "waste" some energy by interacting with each other

→ Observed pressure is lower than if behaving ideally

"Volume of particles" correction

Real gas particles do NOT each have zero volume

→ Total volume occupied by real gas sample therefore larger than predicted for "ideal" gas



J. van der Waals.
1837-1923, Physics
Prof., Amsterdam.
Nobel Prize 1910.

Van der Waals' constants for various gases: Table 12.2

A real sample of Cl_2 gas: **8.00 moles in a 4.00 L tank at 27.0°C**

Ideally: $P = nRT/V$ *note: 8.00 mol is ~ 284 g of Cl_2*

$P = (8.00\ \text{mol})(0.08206\ \text{L·atm·mol}^{-1}\text{K}^{-1})(300\ \text{K}) / 4.00\ \text{L}$

$= 49.2\ \text{atm}$ ← *if the gas can behave ideally in this tank…*

For "real" Cl_2, experiments have shown: $a = 6.49\ \text{atm·L}^2/\text{mol}^2$

$b = 0.0562\ \text{L/mol}$

$$\left(P + \frac{n^2a}{V^2}\right) \times \left(\underbrace{V - nb}\right) = nRT$$

$= 4.00\text{L} - (8.00\text{mol} \times 0.0562\ \text{L/mol})$

$= 4.00\text{L} - (0.4496\ \text{L}$ of matter)

$= 3.550\ \text{L}$ actual empty space…

$$= \frac{(8.00\ \text{mol})^2 \times (6.49\ \text{atm·L}^2/\text{mol}^2)}{(4.00\ \text{L})^2}$$

$= 25.96\ \text{atm}$ …interactions slow particles down…

…lost KE would be enough to cause this much more P

Thus: $(P + 25.96\ \text{atm}) \times (3.550\ \text{L}) = nRT$

$(3.550\ \text{L})\ P + 92.16\ \text{L·atm} = (8.00\ \text{mol})(0.08206\ \text{L·atm·mol}^{-1}\text{K}^{-1})(300\ \text{K})$

$(3.550\ \text{L})\ P + 92.16\ \text{L·atm} = 196.94\ \text{L·atm}$

$\Rightarrow P = 29.5\ \text{atm}$

Thus: the P we'd observe is MUCH lower than if behaving ideally… implies that it must be relatively crowded in the tank!

FINAL EXAM INFORMATION

- **Final exam: Mon. April 14th (2-5pm)**
- **Covers entire course: Ch.1-5, 20.1, 7-9, 10.1-2, 12**
- The examination room invigilators are VERY STRICT:
  - Student ID card mandatory
  - No programmable calculators
  - **No electronic dictionaries, cell phones, pagers, blackberries, *etc***
  - Book-format translation dictionaries (word-to-word only) allowed, but they will be inspected.
  - Arrive to the exam room early !

FINAL EXAMS FROM PREVIOUS YEARS ON WEBSITE:
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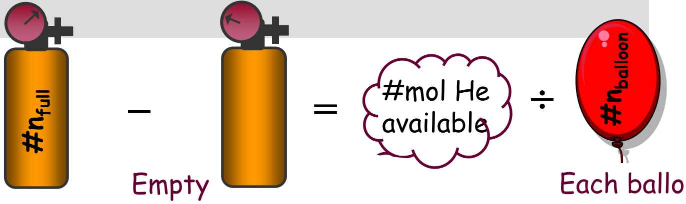
Sample exam question: how many balloons?

Imagine you are filling balloons with helium from a 30.0 L gas cylinder. The "full" cylinder contains 125 atm of He at a temperature of 26°C, and the cylinder is "empty" when the He pressure reaches 1.05 atm (*i.e.,* atmospheric P) at the same temperature. *Assuming ideal behaviour:* how many balloons can be filled to a 3.00 L volume at 1.05 atm & 23°C?

Approaches: conceptually simplest one uses only PV=nRT
1.) Calculate #moles He in "full" *vs.* "empty" tank ⇨ available He
2.) Calculate #moles He in full balloon (note new T)
3.) Divide…



Full
P = 125 atm
V = 30.0 L
T = 26°C

Empty
P = 1.05 atm
V = 30.0 L
T = 26°C

Each balloon
P = 1.05 atm
V = 3.00 L
T = 23°C

ANS: 1168.6 balloons (many ways to reach this answer)
To 3SF : 1170 (= more than can actually fill… ∴ better to report 1168…

Stoichiometry involving gases: *cf* Kotz 6th Ed. Ch.12 #62

Dimethyldichlorosilane $(CH_3)_2SiCl_2$ is a starting material used to make silicones, which are polymeric substances used as lubricants, anti-stick agents and water-proofing caulk. It is formed by the following reaction:

$$\mathbf{Si(s) + 2\ CH_3Cl(g) \rightarrow (CH_3)_2SiCl_2(g)}$$

If you place 2.25g of solid silicon in a 6.56 L flask containing CH_3Cl at a pressure of 585 mm Hg at 25°C…

a) what mass of dimethyldichlorosilane can be formed?
b) what pressure would be exerted by this $(CH_3)_2SiCl_2(g)$ at 25°C?
c) what would be the total pressure in the flask after the reaction?

Please provide FULL details in written calculations on exam, <u>AND</u> comments at each step to explain what you are doing.

Additional questions:

1. What type of reaction is this? How can you tell?
2. How would you describe the reactants?
   a) Element (metal, nonmetal, metalloid?) *vs* compound?
   b) For compounds: ionic *vs* covalent? polar *vs* nonpolar?
   c) Soluble in water?

Stoichiometry involving gases: *cf* Kotz 6th Ed. Ch.12 #62

<u>ANS: provide FULL details on exam – outline given here only</u>

$\#n_{Si}$ = 0.08011 mol *vs.* $\#n_{CH3Cl}$ = 0.2065 (using PV=nRT)
= **1 Si** *to* **2.6 CH_3Cl**

THUS: have excess CH_3Cl, since rxn requires 1:2 ratio ⇨ Si is limiting.

a) Yield of $(CH_3)_2SiCl_2$ (based on 1:1 stoich.) = $\#n_{Si}$ = 0.08011 mol
$MM_{(CH3)2SiCl2}$ = 129.06 g/mol ⇨ $m_{(CH3)2SiCl2}$ = 10.3 g

b) Using PV=nRT: this gas would exert a P of 0.299 atm = 227 mm Hg
= **the partial pressure of $(CH_3)_2SiCl_2$ in the flask**
= $\boldsymbol{P(CH_3)_2SiCl_2}$ …if other gases present, total P will be greater than this…

c) What would be the <u>total</u> pressure in the container after the rxn?

TOTAL pressure: $P_{TOT} = \boldsymbol{P(CH_3)_2SiCl_2 + PCH_3Cl(excess)}$

Excess $\#n_{CH3Cl}$ = $\#n_{initial}$ - $\#n_{reacted}$ ← = 2x $\#n_{Si}$
= 0.2065 mol - 0.1602 mol
= 0.04628 mol

Thus: $\boldsymbol{PCH_3Cl(excess)}$ = 0.173 atm = 131 mm Hg ⇨ P_{TOT} = 227 + 131
= 358 mm Hg