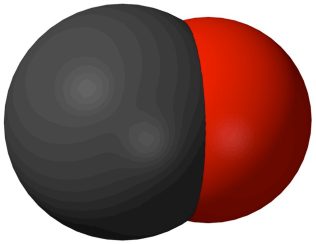
# Lecture C1
# Microscopic to Macroscopic, Part 1: Gases

*Got a temperature?*

Some elements (and compounds) are gases at Room Temperature...



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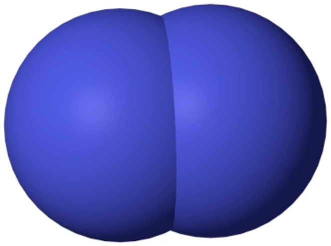
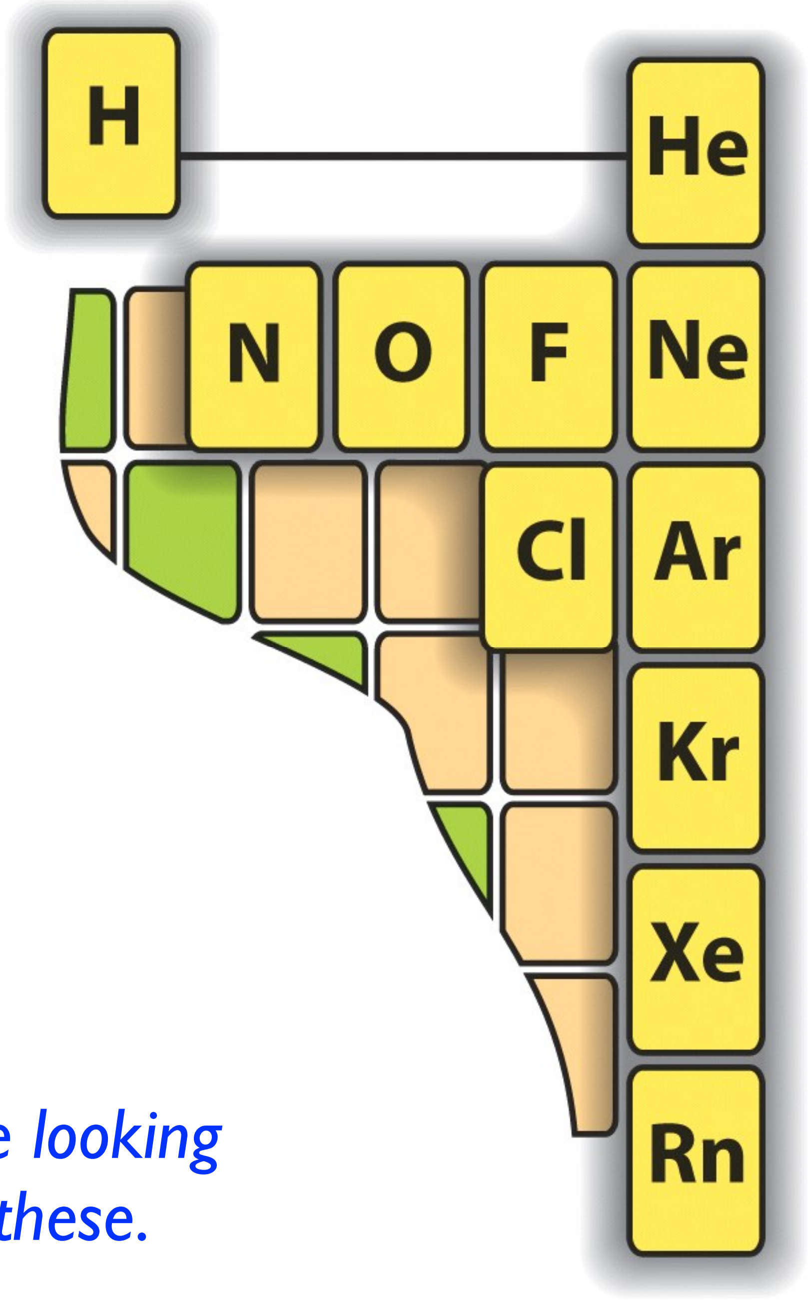


$N_2$



*We've actually spent considerable time looking at the molecular structure of some of these.*

At low pressures, all gases behave similarly.
These behaviors were worked out by a number of scientists:

Robert Boyle (1627-1691)
$PV = constant$

Jacques Charles (1746-1823)
Joseph Louis Gay-Lussac (1778-1850)
$V = constant \times T$
$P = constant \times T$
$T = 0$ @ $-273.15°C$ = Absolute Temperature

Amedeo Avogadro (1776-1856)
$V = n \times molar\ volume = n \times V_m$

Nowadays we put these findings together into a single "equation of state" called..

# The ideal gas law!

$$PV = nRT$$

We can use the ideal gas law to predict changes in V, T and P. If we solve for the constant R and compare two states, we get:

$$R = \frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

*These equations lead to MANY homework problems for high school and college chemistry students.*

For example:

$$R = \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

Hold n, V constant, relate P and T: $P_1/T_1 = P_2/T_2$

Hold n, P constant, relate V and T: $V_1/T_1 = V_2/T_2$

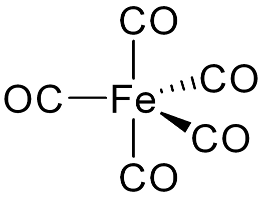
Hold n, T constant, relate P and V: $P_1V_1 = P_2V_2$

*These equations lead to MANY homework problems for high school and college chemistry students.*

# The ideal gas law can be a window:

$$PV = nRT$$

It seems incredibly boring now, but back then, this equation was their window from the macroscopic (people-sized) world to the microscopic (molecular) world!



molecular ↔ macroscale

# An aside about Physical Chemistry:

The physical theories that connect the macroscopic to the microscopic are part of the realm of physical chemistry, which is the branch of chemistry that uses physics and mathematics to describe chemical systems.

A Physical Chemist's toolbox includes:

Quantum Mechanics
Thermodynamics
Statistical Mechanics
Kinetics
Classical Mechanics
Electromagnetism

# An aside about Physical Chemistry:

The physical theories that connect the macroscopic to the microscopic are part of the realm of physical chemistry, which is the branch of chemistry that uses physics and mathematics to describe chemical systems.

The *Kinetic Theory of Gases* is a set of physicochemical equations that make, among other things, a concrete connection between the microscopic motion of gas molecules and the macroscopic measurements of pressure, temperature and volume.

# An aside about Physical Chemistry:

The physical theories that connect the macroscopic to the microscopic are part of the realm of physical chemistry, which is the branch of chemistry that uses physics and mathematics to describe chemical systems.

A Physical Chemist's toolbox includes:

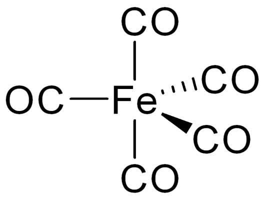
Quantum Mechanics
Thermodynamics
Statistical Mechanics ← *Kinetic Theory of Gases*
Kinetics
Classical Mechanics
Electromagnetism

*KTG is a part of Stat. Mech.*

# Back to the ideal gas law:

$$PV = nRT$$

It seems incredibly boring now, but back then, this equation was their window from the macroscopic (people-sized) world to the microscopic (molecular) world!



molecular ↔ macroscale

# Pressure in the ideal gas law:

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

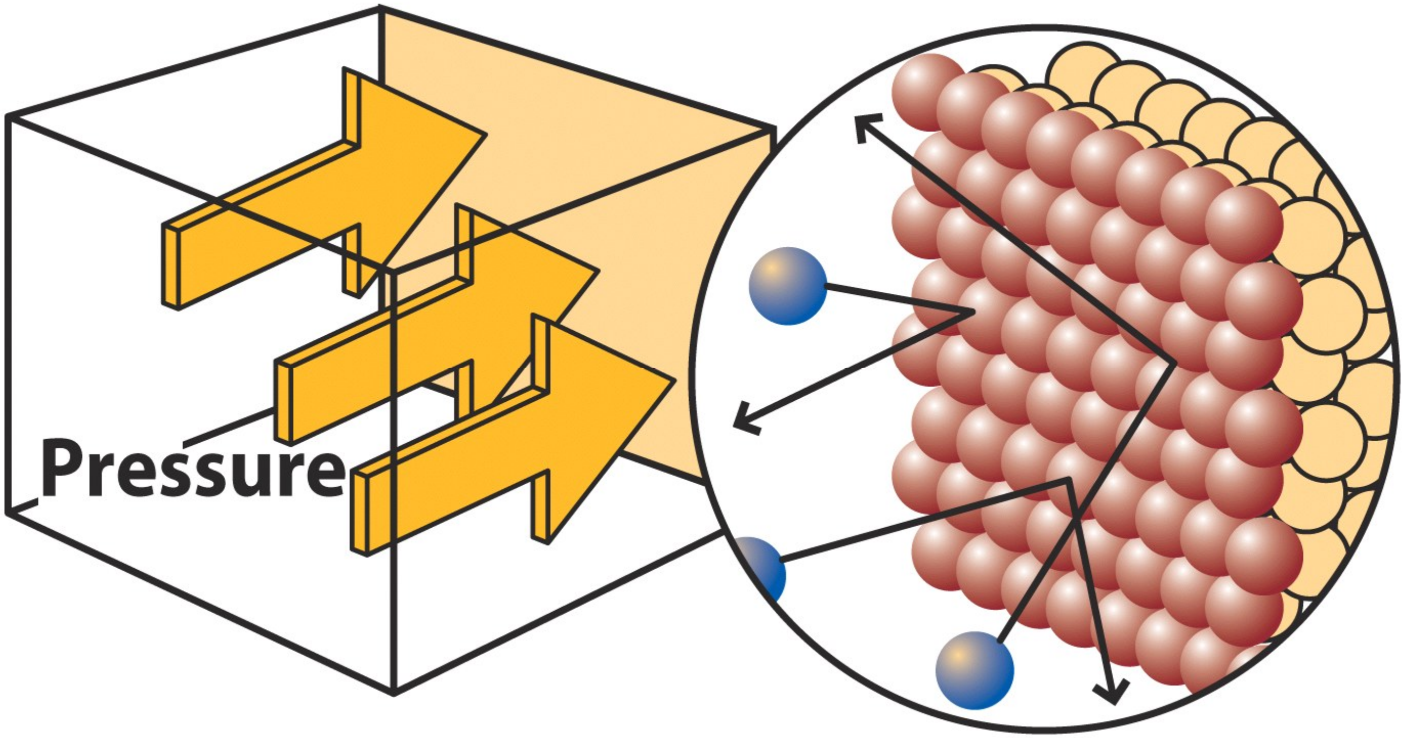
$P$ = pressure

1 atm = 760 Torr = 1.013 bar = 1.013x $10^5$ Pascals.

What is the microscopic picture of gas pressure?

# The Kinetic Theory of Gases: Pressure

A gas contained in a vessel exerts a pressure on its walls. The microscopic origin of pressure is collisions that occur between gas molecules and the walls of the vessel in which they are contained.



# Pressure in the ideal gas law:

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

A microscopic picture of pressure:

P is related to the molar mass (M) and the squared average velocity ($v^2_{rms}$) of the gas particles:

$$P = \frac{nMv^2_{rms}}{3V}$$

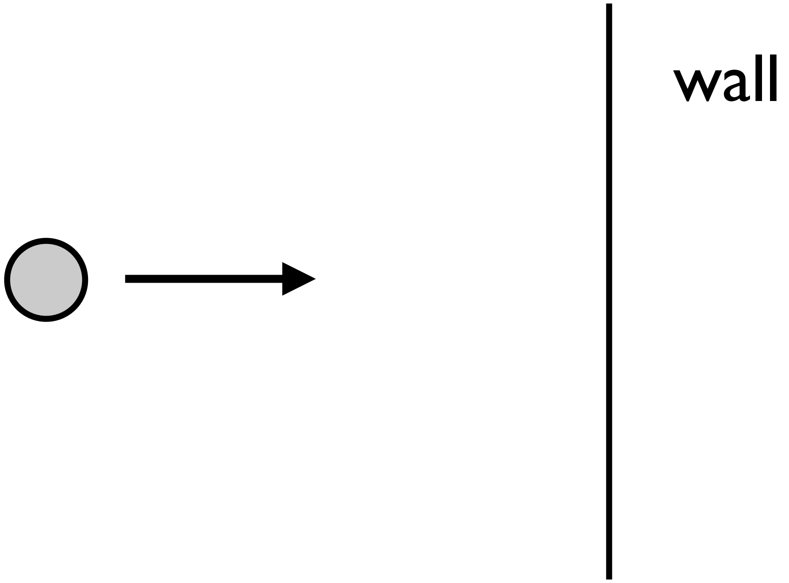
*Let's derive this!*

# The KTG Postulates:

1. Gases consist of particles (atoms or molecules) in continuous, random motion.
2. Collisions between gas particles are *elastic*.
3. The average *energy of translational motion* of a gas particle is directly proportional to temperature, and independent of the identity of the gas!

Let's say we have just one molecule in our vessel traveling in the +x direction. When it collides with the wall, it experiences a change of momentum Δp equal to 2mv. This momentum is also imparted to the wall.

$\Delta p = 2mv_x$ one particle



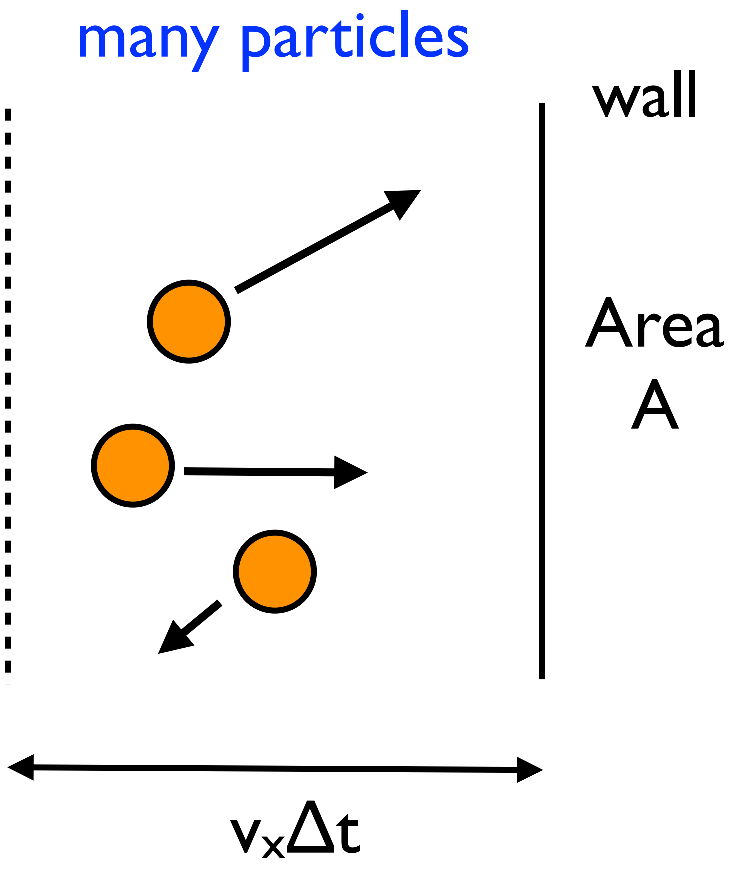
If a vessel of volume V is now filled with N particles, total momentum transfer to an area A of the wall in the time interval $\Delta t$ will be:

$\Delta p$ = (the number of particles close enough) x $2mv_x$

$\Delta p = \frac{1}{2}(N/V) \times (Av_x\Delta t) \times 2mv_x$

$\Delta p = NmAv_x^2\Delta t/V$

where $v_x$ is the average x velocity,
N/V is the particle density,
and the ½ is because only half of the molecules travel in the positive x direction.

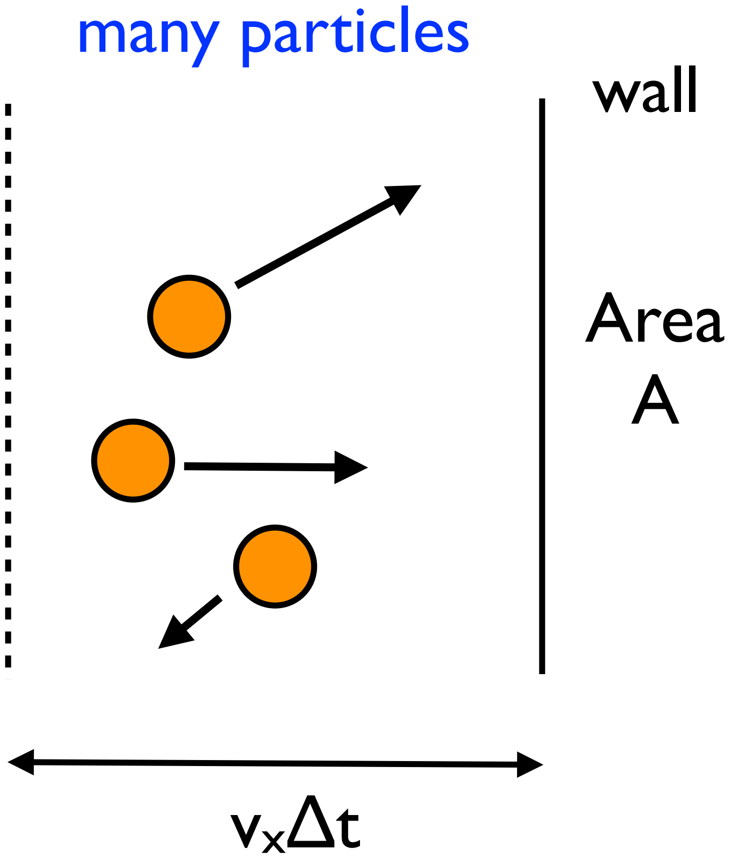


The total force F on area A can be gotten from the momentum transfer and Newton's Law:

$$F = ma = d(mv)/dt = \Delta p/\Delta t$$

$$F = (NmAv_x^2\Delta t/V) \div \Delta t$$

$$F = NmAv_x^2/V$$



# The pressure P on the wall is the force per area:

$P = F/A$

$P = (NmAv_x^2/V) \div A$

$P = Nmv_x^2/V$

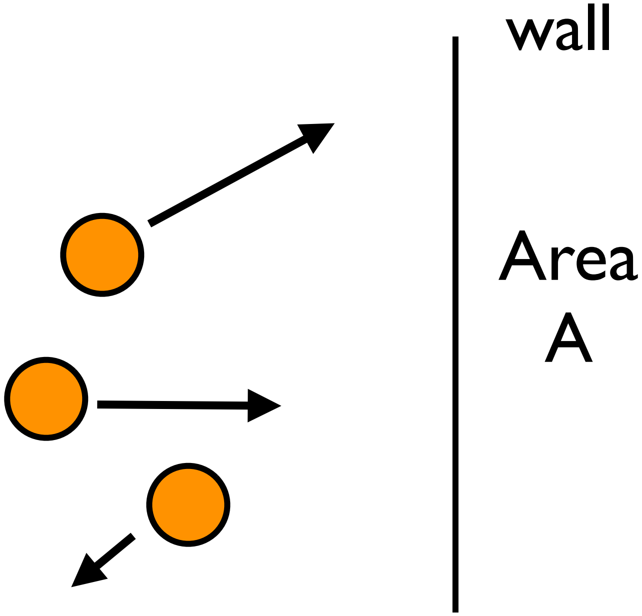
$P = nM\langle v_x^2\rangle/V$

where:

$\langle v_x^2\rangle$ is the average squared x velocity

$M = N_A m$ = molar mass
n = moles of particles

$$P = nM\langle v_x^2\rangle/V$$



# $P = nM\langle v_x^2\rangle/V$

The average squared x velocity can be related to the average squared total velocity $\langle v^2\rangle$:

$$\mathbf{v} = v_x\hat{\mathbf{i}} + v_y\hat{\mathbf{j}} + v_z\hat{\mathbf{k}}$$

$$v_{rms}^2 = \left\langle v^2 \right\rangle = \left\langle v_x^2 \right\rangle + \left\langle v_y^2 \right\rangle + \left\langle v_z^2 \right\rangle$$

$$v_{rms}^2 = 3\left\langle v_x^2 \right\rangle$$ (because x, y, z are on average the same)

therefore: $$P = \frac{nMv_{rms}^2}{3V}$$

*Voila!*

Pressure in the ideal gas law:

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

A microscopic picture of pressure:

P is related to the molecular weight (M) and the squared average velocity ($v^2_{rms}$) of the gas particles:

$$P = \frac{nMv^2_{rms}}{3V}$$

*We've derived this!*

# Temperature in the ideal gas law:

$$PV = nR\boxed{T}$$

$T$ = absolute temperature (0 = -273.15°C)

What is the microscopic theory of Temperature in gases?

# Temperature in the ideal gas law:

$$PV = nR\boxed{T}$$

Temperature is also related to the average velocity!

$$v_{rms} = \left[\frac{3RT}{M}\right]^{1/2} \qquad T = \frac{Mv_{rms}^{2}}{3R}$$

*Let's derive this too!*

The pressure is given by:

$$P = nMv_{rms}^2/3V$$

Rearrange and substitute in the ideal gas law:

$$PV = nMv_{rms}^2/3$$

$$nRT = nMv_{rms}^2/3$$

$$T = Mv_{rms}^2/3R \rightarrow v_{rms} = \left[\frac{3RT}{M}\right]^{1/2}$$

*Voila!*

# Temperature in the ideal gas law:

$$PV = nR\boxed{T}$$

Temperature is also related to the average velocity!

$$v_{rms} = \left[\frac{3RT}{M}\right]^{\frac{1}{2}} \qquad T = \frac{Mv_{rms}^{2}}{3R}$$

$v_{rms}$ = 728 m/s for $N_2$ at 298K

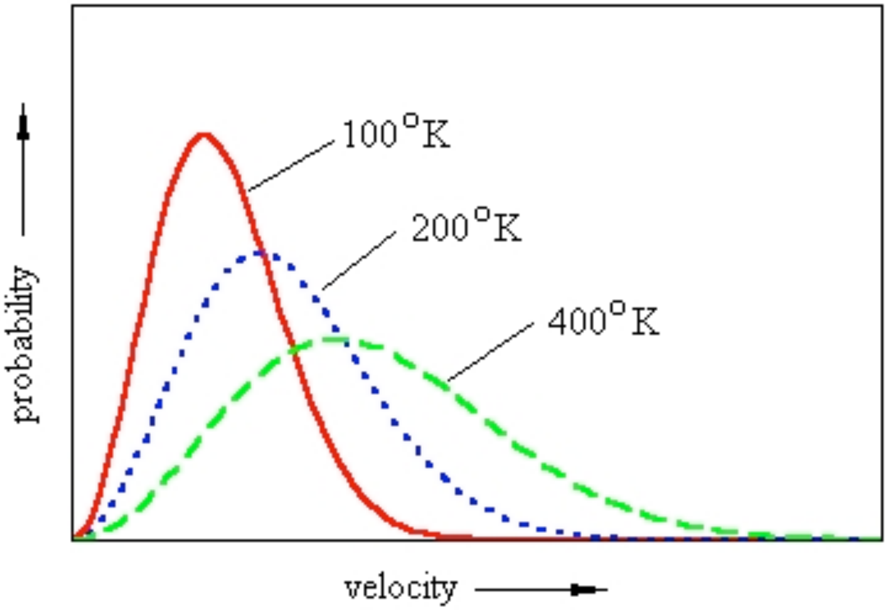
*We've derived this too!*

Temperature also defines the velocity distribution:

$$\frac{\Delta N}{N} = f(v)\Delta v$$

fraction of particles with a velocity in the range from v to v + Δv

$$f(v) = 4\pi\left[\frac{M}{2\pi RT}\right]^{3/2} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$



Maxwell-Boltzmann Distribution

*We will not derive this.*

Finally, the ideal gas law can be a measure of n:

$$PV = \boxed{n}RT$$

$n$ = number of moles

This is no big deal if you know the molecular weight.
But what if you don't know the molecular weight?

*Like Lord Rayleigh, you can use the weight of measured volumes of gas to deduce molecular weights of unknowns!*

# The ideal gas law as a measure of n:

$$PV = \boxed{n}RT$$

We can also follow Chemical Reactions such as the Haber Process:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

We must assume that the ideal gas law holds for all three gaseous species, so that the total pressure is the sum of the PARTIAL pressures for the three species:

The Haber Process: $N_2 + 3H_2 \rightarrow 2NH_3$

partial pressures

$$P_{total} = \boxed{P_{N_2} + P_{H_2} + P_{NH_3}}$$

$$P_{total} = \chi_{N_2} P_{total} + \chi_{H_2} P_{total} + \chi_{NH_3} P_{total}$$

where we have used the mole fractions for $N_2$, $H_2$ and $NH_3$:

$$\chi_{N_2} + \chi_{H_2} + \chi_{NH_3} = 1$$

Mole fractions: $\chi_{N_2} + \chi_{H_2} + \chi_{NH_3} = 1$

$$\chi_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2} + n_{NH_3}}$$

$$\chi_{H_2} = \frac{n_{H_2}}{n_{N_2} + n_{H_2} + n_{NH_3}}$$

$$\chi_{NH_3} = \frac{n_{NH_3}}{n_{N_2} + n_{H_2} + n_{NH_3}}$$

# The Haber Process:

$N_2 + 3H_2 \rightarrow 2NH_3$

$$P_{total} = P_{N_2} + P_{H_2} + P_{NH_3}$$

$$P_{total} = \chi_{N_2} P_{total} + \chi_{H_2} P_{total} + \chi_{NH_3} P_{total}$$

where we have used the partial pressure for $N_2$, $H_2$ and $NH_3$.

**Example:** Consider the Haber Process: $N_2 + 3H_2 \rightarrow 2NH_3$. Let's say we're starting with 2 mol $H_2$ and 1 mol $N_2$ in a 2 liter container at 273.15 K. Calculate the *mole fractions* of these two gases, and their *partial pressures*.

What do we know? 2 mol $H_2$ and 1 mol $N_2$ in a 2 liter container at 273.15 K

mole fractions:

$$\chi_{N_2} = \frac{n_{N_2}}{n_{total}} = \frac{1}{1+2} = 1/3$$

$$\chi_{H_2} = 1 - 1/3 = 2/3$$

**Example:** Consider the Haber Process: $N_2 + 3H_2 \rightarrow 2NH_3$. Let's say we're starting with 2 mol $H_2$ and 1 mol $N_2$ in a 2 liter container at 273.15 K. Calculate the *mole fractions* of these two gases, and their *partial pressures.*

What do we know? 2 mol $H_2$ and 1 mol $N_2$ in a 2 liter container at 273.15 K

partial pressures:

$$P_{total} = \frac{n_{total}RT}{V} = \frac{(3.000)(0.08206)(273.15)}{2.000} = 33.62atm$$

$$P_{N_2} = \chi_{N_2}P_{total} = \frac{1}{3}(33.62) = 11.21atm$$

$$P_{H_2} = \chi_{H_2}P_{total} = \frac{2}{3}(33.62) = 22.42atm$$

# *Which value of R should you use?*

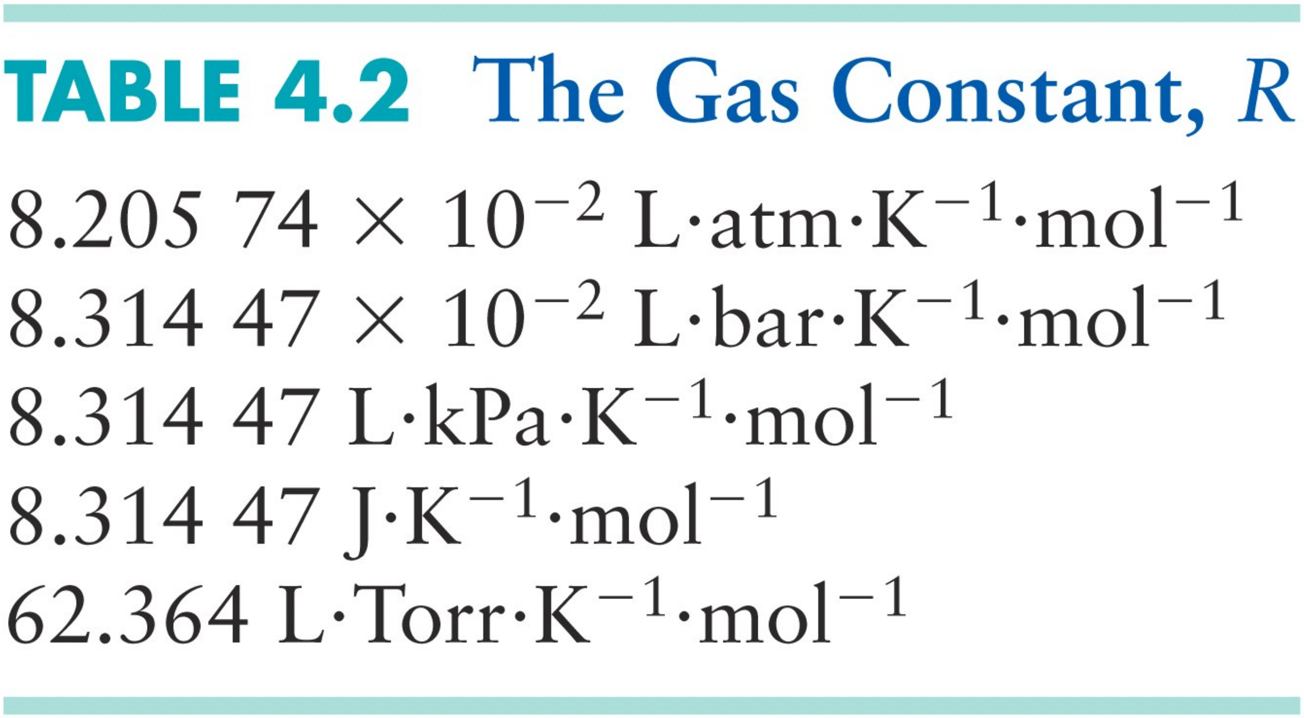


**TABLE 4.2** The Gas Constant, *R*

$8.205\ 74 \times 10^{-2}\ \mathrm{L{\cdot}atm{\cdot}K^{-1}{\cdot}mol^{-1}}$

$8.314\ 47 \times 10^{-2}\ \mathrm{L{\cdot}bar{\cdot}K^{-1}{\cdot}mol^{-1}}$

$8.314\ 47\ \mathrm{L{\cdot}kPa{\cdot}K^{-1}{\cdot}mol^{-1}}$

$8.314\ 47\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$

$62.364\ \mathrm{L{\cdot}Torr{\cdot}K^{-1}{\cdot}mol^{-1}}$

**Example:** Consider the Haber Process: $N_2 + 3H_2 \rightarrow 2NH_3$. Let's say we're starting with 2 mol $H_2$ and 1 mol $N_2$ in a 2 liter container at 273.15 K. Calculate the *mole fractions* of these two gases, and their *partial pressures.*

NOW, *all the hydrogen is reacted.* Calculate $P_{total}$, $P_{NH3}$ and $P_{N2}$.

What do we know? stoichiometry of reaction.

$N_2 + 3H_2 \rightarrow 2NH_3$

also, $P_{H2} = 0$, so $\Delta n_{H2} = 2$ mols.

How many *moles* of $NH_3$ are produced?

Let's divide the balanced chemical equation by 3:

$$(1/3)N_2 + H_2 \rightarrow (2/3)NH_3.$$

So 2/3 mol of $NH_3$ is produced for each mol of $H_2$ consumed: $(2/3) \times 2 =$ 4/3 moles $NH_3$

**Example:** Consider the Haber Process: $N_2 + 3H_2 \rightarrow 2NH_3$. Let's say we're starting with 2 mol $H_2$ and 1 mol $N_2$ in a 2 liter container at 273.15 K. Calculate the *mole fractions* of these two gases, and their *partial pressures*.

NOW, *all the hydrogen is reacted.* Calculate $P_{total}$, $P_{NH3}$ and $P_{N2}$.

4/3 moles $NH_3$ produced.

What about $N_2$?

Well, according to this eqn: $(1/3)N_2 + H_2 \rightarrow (2/3)NH_3$
1/3of a mole of $N_2$ is consumed for each mole of $H_2$.
So we have consumed (1/3)x2= 2/3 moles of $N_2$.

This leaves us with 1- 2/3 = 1/3 moles of $N_2$.

**Example:** Consider the Haber Process: $N_2 + 3H_2 \rightarrow 2NH_3$. Let's say we're starting with 2 mol $H_2$ and 1 mol $N_2$ in a 2 liter container at 273.15 K. Calculate the *mole fractions* of these two gases, and their *partial pressures.*

NOW, *all the hydrogen is reacted.* Calculate $P_{total}$, $P_{NH3}$ and $P_{N2}$.

So finally: 5/3 moles total: 4/3 moles $NH_3$ and 1/3 moles of $N_2$

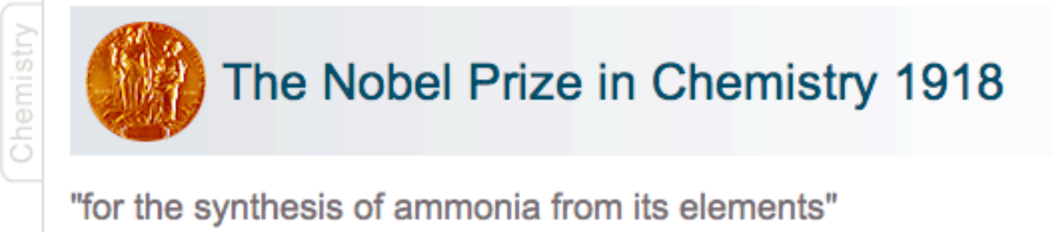
$$P_{total} = \frac{n_{total}RT}{V} = \frac{(5/3)(0.08206)(273.15)}{2.000} = 18.68 atm$$

$$P_{N_2} = \chi_{N_2} P_{total} = \frac{1/3}{5/3}(18.68) = (0.2)(18.68) = 3.736 atm$$

$$P_{NH_3} = \chi_{NH_3} P_{total} = \frac{4/3}{5/3}(18.68) = (0.8)(18.68) = 14.95 atm$$

$P_{total}$ was 33.63 atm before the reaction.

# By the way: Fritz Haber won the Nobel Prize in Chemistry in 1918



The Nobel Prize in Chemistry 1918

"for the synthesis of ammonia from its elements"

**Fritz Haber**

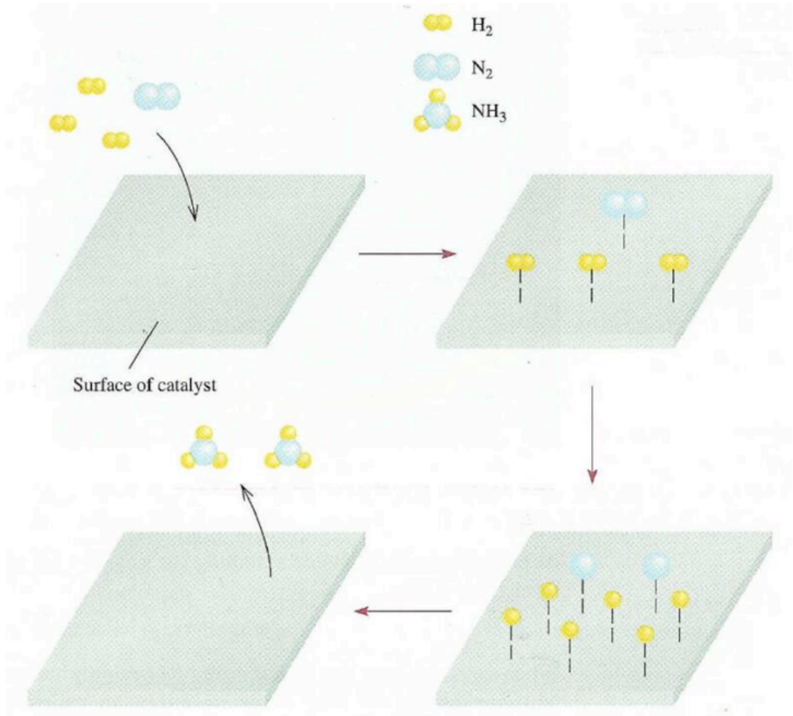
Germany

Kaiser-Wilhelm-Institut
(now Fritz-Haber-Institut)
für physikalische Chemie
und Electrochemie
Berlin-Dahlem, Germany

b. 1868
d. 1934

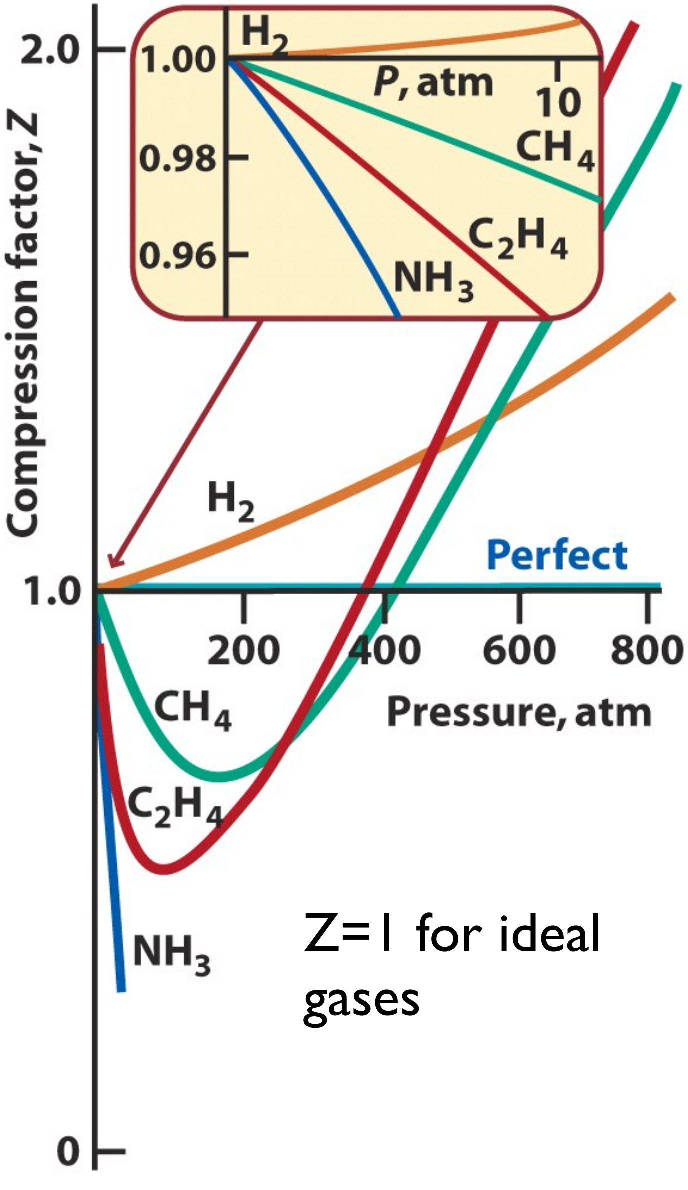
$N_2 + 3H_2 \rightarrow 2NH_3.$

Haber's solution? Speed up this slow step in the process by giving the nitrogens a metal catalyst to bond to...

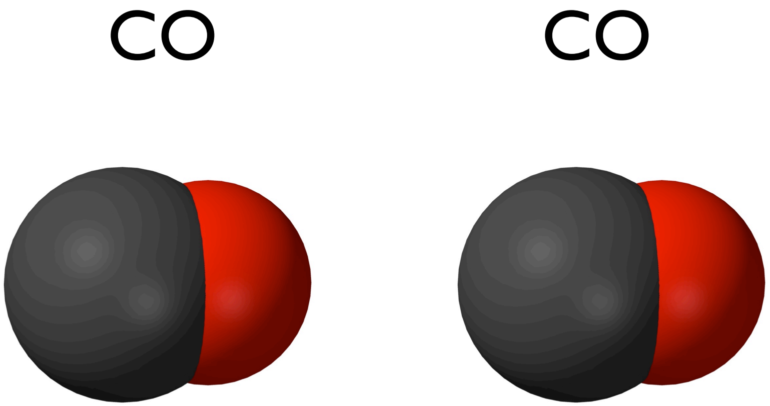


The catalyst was osmium and uranium initially; now it is $Fe_3O_4$.

# Actually, most gases are NOT ideal except at very low pressures:



Z=1 for ideal gases



*Intermolecular interactions come into play at higher pressures -- molecules interact!*

# We will look at the different types of intermolecular interactions next!