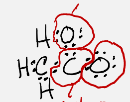
Lecture 5 CH131 Summer 1

Thursday, May 28, 2020

- Gas behavior
- Ideal gas law
- Gas constant R, STP, and SATP
- Gas law calculational recipe
- Gas density
- Partial pressures
- Gas law calculations in chemical reactions

Next lecture: Continue 9.1–9.6.

$6-6=0$



$6-7=\boxed{-1}$

$+4=0$

CH_3COO^-

$0+0-1=-1$

Turning Point
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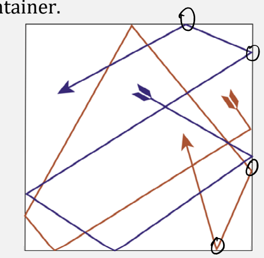
1

Gas behavior

~10x

Let's explore how a gas is affected by changes in T, V, n, and P.

Doing this, visualize gases as collections of widely separated particles, moving faster as temperature increases, generating pressure as a result of collisions with the walls of the container.

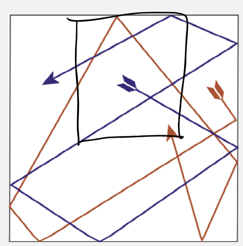


2

2

[TP] A container is filled with gas A. At 20°C the volume of the container is V. If V is decreased, then the pressure P exerted by the gas on the walls of the container ...

13%	1.	goes down
0%	2.	stays the same
87%	3.	goes up
0%	4.	further information needed



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3

0

3

Gas behavior

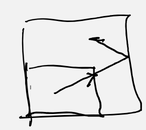
$P \sim \frac{1}{V}$

If V is decreased, then the particles travel less far between collisions with the walls, and so collide with the walls more often, generating greater pressure.

We can express this as P being inversely proportional to V,

$P = c(T,n)\,1/V$

Let's explore next how the constant of proportionality, $c(T,n)$, depends on the number of particles (the number of moles n).



4

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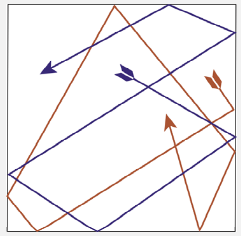
[TP] When more particles are added to the same V at the same T, the pressure ...

0% 1. goes down
0% 2. stays the same
100% 3. goes up
0% 4. further information needed



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5

0

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Gas behavior

$c(T,n) = nc'(T)$

When more particles are added to the same V at the same T, there will be more collisions with the walls, and so the pressure must go up.

We can express this as P being proportional to n,

$P = c'(T)n/V$

Let's explore next how the constant of proportionality, $c'(T)$, depends on the temperature, T.

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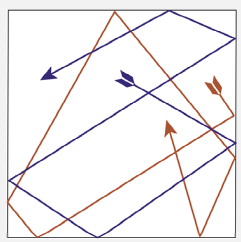
[TP] Heating a gas at constant V, and constant number of moles n, the pressure ...

0% 1. goes down
0% 2. stays the same
100% 3. goes up
0% 4. further information needed



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7

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Gas behavior

Heating a gas at constant V, the particles will move faster, so collide with the wall more often, and so the pressure must go up.

We can express this as P being proportional to T,

$P = c''nT/V$

In this expression temperature is measured in Kelvin,

$T\ (\text{in K}) = t\ (\text{in °C}) + 273.15$

$T = 0$ K is the temperature at which particles would not be moving at all and so would not exert any pressure.

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[TP] Consider 1 mol each of two different gases, A and B, each with the same volume (1 L) and temperature (25°C). The molar mass of A is twice the molecular mass of B. What is the relationship between the pressures of A and B?

- 6% 1. $P_A = 2P_B$
- 6% 2. $P_A = \frac{P_B}{2}$
- 0% 3. $P_A = 4P_B$
- 0% 4. $P_A = \frac{P_B}{4}$
- 88% 5. $P_A = P_B$ ||

$P = c'' n T / V$ 1L

constant that does not depend on what gas we have

How many particles we have

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Ideal gas law

does not depend on which gas we have

In the expression $P = c'' nT/V$, the remaining constant of proportionality, c'', is known as the gas constant R, $P = RnT/V$.

This expression is written as

$PV = nRT$ c'' R

and it is known as the ideal gas law.

The adjective "ideal" signifies that this relation does not depend of what the gas particles are.

It is as true for a gas of O_2 molecules as for a gas of Xe atoms.

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Gas constant R

$PV = nRT$

The value of the gas constant has been determined by measuring V for a given P, n, and T.

$273 + 20 = 293\ \mathrm{K}$

For example, the volume of 1 mol of gas at 20°C and 1 bar = 100000 Pa = 100000 J/m³ is

$V = 0.02437387\ \mathrm{m^3} = \frac{nRT}{P}$ $Pa = \frac{J}{m^3}$

From this we can evaluate that

$$R = \frac{PV}{nT} = \frac{10^5\,\mathrm{J/m^3} \times 0.02437387\ \mathrm{m^3}}{1\ \mathrm{mol}\ 293.15\ \mathrm{K}} = \boxed{8.314472\ \frac{\mathrm{J}}{\mathrm{K\ mol}}}$$

$\frac{J}{K\ mol}$

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Gas constant R

Often, pressures are measured in atm (1.01325 bar) and volumes are measured in L ($1\ \mathrm{L} = 10^{-3}\ \mathrm{m^3}$).

Since $1\ \mathrm{m^3} = 1000$ L and 1 Pa = 1 atm/101325,

$1\ \mathrm{J} = \mathrm{m^3 Pa} = 1000\ \mathrm{L} \times \frac{\mathrm{atm}}{101325} = 0.00986923\ \mathrm{L\ atm}$

From this we can evaluate that

$$R = 8.314472\ \frac{\mathrm{J}}{\mathrm{K\ mol}} \times \frac{0.00986923\ \mathrm{L\ atm}}{\mathrm{J}} = \boxed{0.0820575\ \frac{\mathrm{L\ atm}}{\mathrm{K\ mol}}}$$

In calculations, use the value of R with the most convenient units.

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Gas constant R

Since

$1\ \text{J} = 1\ \text{Pa m}^3 = 10^{-5}\text{bar} \times 10^3\text{L} = 10^{-2}\ \text{L bar}$

an alternative expression for the value of the gas constant

$R = 8.314472 \frac{\text{J}}{\text{K mol}}$

is

$R = 0.08314472 \frac{\text{L bar}}{\text{K mol}}$

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Gas constant R

$R = 8.314472 \frac{\text{J}}{\text{K mol}}$

$R = 0.08314472 \frac{\text{L bar}}{\text{K mol}}$

Finally, pressures are sometimes measured in atm (1.01325 bar) and so a third expression for the value of the gas constant is

$R = 0.08314472 \frac{\text{L bar}}{\text{K mol}} \times \frac{\text{atm}}{1.01325\ \text{bar}} = 0.0820575 \frac{\text{L atm}}{\text{K mol}}$

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Gas constant R

$R = 8.314472 \frac{\text{J}}{\text{K mol}}$

$R = 0.08314472 \frac{\text{L bar}}{\text{K mol}}$

$R = 0.0820575 \frac{\text{L atm}}{\text{K mol}}$

In calculations, use the value of R with the most convenient units.

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STP and SATP

Two different "standard" values of temperature and pressure are defined.

STP is Standard Temperature and Pressure,

$T = 273.15\ \text{K} = 0°\text{C}$ and $P = 1\ \text{bar} = 10^5\ \text{Pa}$

SATP is Standard Ambient Temperature and Pressure,

$T = 298.15\ \text{K} = 25°\text{C}$ and $P = 1\ \text{bar} = 10^5\ \text{Pa}$

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[TP] What is the volume (in L) of 1.00 mol of an ideal gas at standard ambient temperature and pressure, SATP? $R = 8.3145 \frac{\text{J}}{\text{mol K}} = 0.083145 \frac{\text{L bar}}{\text{mol K}}$.

0%	1.	Less than 20 L
0%	2.	20-22 L
11%	3.	22-24 L
83%	4.	24-26 L
0%	5.	26-28 L
0%	6.	28-30 L
6%	7.	More than 30 L

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

$= \frac{1 \cancel{\text{mol}} * (273.15+25)\cancel{K} * 0.083145 \frac{L\,\cancel{bar}}{\cancel{mol}\,\cancel{K}}}{1\,\cancel{bar}}$

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STP and SATP

What is the volume (in L) of 1.00 mol of an ideal gas at standard ambient temperature and pressure, SATP?

$V = \frac{nRT}{P} = \frac{\overset{1.00}{1} \text{ mol } 0.08314 \text{ L bar/(K mol) } 298.15 \text{ K}}{1.00 \text{ bar}} = 24.5 \text{ L}$

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Gas law calculational recipe

The recipe is to rearrange $PV = nRT$ so that what does not change is grouped on one side of the equality and what does change is grouped on the other.

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Gas law calculational recipe

$P_2 = \frac{T_2}{T_1} P_1$

A 2-liter cylinder contains a gas at 250 kPa at 18°C. What will be the pressure at 125°C?

Heating the gas makes the particles move faster, there will be more collisions with the container walls in a given time, and so the pressure will increase.

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Gas law calculational recipe

A 2-liter cylinder contains a gas at 250. kPa at 18°C. What will be the pressure at 125°C?

The volume (V) and amount (n) of gas are constant, so rearrangement gives

$$\frac{nR}{V} = \frac{P_1}{T_1} = \frac{P_2}{T_2} \to P_2 = P_1 \frac{T_2}{T_1}$$

$$P_2 = 250.\text{ kPa} \times \frac{(273.15+125)\text{ K}}{(273.15+18)\text{ K}} = 342\text{ kPa}$$

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Gas law calculational recipe

A piston containing 25.0 dm^3 of gas at 45°C is expanded to 55.0 dm^3.

The increase in volume means the gas particles must travel farther between collisions with the container walls, there will be fewer collisions with the walls in a given time, and so the pressure will decrease.

The original pressure can be restored by heating the gas so that the increased speed offsets the greater distance.

To what temperature must the gas be heated to restore the pressure to that before the expansion?

25.0 dm^3

45°C

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Gas law calculational recipe

A piston containing 25.0 dm^3 of gas at 45°C is expanded to 55.0 dm^3. To what temperature must the gas be heated to maintain the same pressure as before the expansion?

The pressure (P) and amount (n) of gas are constant, so rearrangement gives

$$\frac{nR}{P} = \frac{V_1}{T_1} = \frac{V_2}{T_2} \to \boxed{T_2 = T_1 \frac{V_2}{V_1}}$$

$$T_2 = (273.15 + 45)\text{ K} \times \frac{55.0\text{ dm}^3}{25.0\text{ dm}^3} = 700.\text{ K} = 427\text{°C}$$

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Gas law calculations

mol/L

Calculate the density of water in the gas phase at 100.0°C and 1.00 atm.

Rearrangement of the ideal gas law gives

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.00\text{ atm}}{373\text{ K} *}$$

0.080575 Latm/Kmol

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Gas law calculations

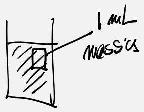
Calculate the density of water in the gas phase at 100.0°C and 1.00 atm.

Rearrangement of the ideal gas law gives

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.00\ \text{atm}}{0.0820575\frac{\text{L atm}}{\text{K mol}}\times 373.25\ \text{K}} = \boxed{0.0327\ \frac{\text{mol}}{\text{L}}}$$

$$\frac{n}{V} = 0.0327\ \frac{\text{mol}}{\text{L}} \times \frac{(2\times 1.008 + 15.999)\ \text{g}}{\text{mol}} \times \frac{\text{L}}{1000\ \text{mL}} = \boxed{0.000588\ \frac{\text{g}}{\text{mL}}}$$

liquid water 1 g/mL



liquid → gas

why so many "friendly"

liquid / # gas = 1630

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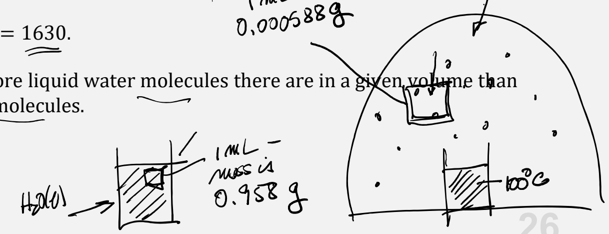
Gas law calculations

At 100.0°C , the density of water vapor is 0.000588 g/mL and that of liquid water is 0.958 g/mL. How much farther apart of water molecules in the gas phase than those in the liquid phase?

The ratio of the densities,

$$\frac{0.958\ \text{g/mL}}{0.000588\ \text{g/mL}} = 1630.$$

is how many more liquid water molecules there are in a given volume than gaseous water molecules.



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Gas law calculations

This means the same volume can hold 1630 times as many liquid water molecules as gaseous water molecules.

Since volume is the cube of distance, the cube root of the ratio, $1630^{1/3} = 11.8$ means the gas particles are about 11.8 times farther apart than liquid particles.

10x

~ 1000

~ 10,000

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Partial pressures

$PV = nRT$

We have seen that the ideal gas law is the same for all gases, since it depends only on the number (moles) of particles but not what kind of particles they are.

This means each kind of gas contributes to the total pressure in only in proportion to its relative number of moles,

$$P = \frac{n_a RT}{V} + \frac{n_b RT}{V} + \cdots = P_a + P_b + \cdots$$

P_a, P_b, …, are the partial pressures of gas a, gas b, etc.

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Partial pressures

A convenient way to calculate partial pressures is to use mole fractions,

$$x_a = \frac{n_a}{n}, x_b = \frac{n_b}{n}, \ldots \qquad n_a \frac{n_a RT}{V} = \frac{n_a}{n}\frac{nRT}{V}$$

Since

$$P = \boxed{\frac{n_a}{n}\frac{nRT}{V}} + \frac{n_b}{n}\frac{nRT}{V} + \cdots = x_a \boxed{\frac{nRT}{V}} + x_b \frac{nRT}{V} + \cdots = x_a P + x_b P + \cdots$$

we see that the partial pressure of each kind of gas is

$$P_a = x_a P, P_b = x_b P, \ldots$$

This is known as Dalton's law of partial pressures.

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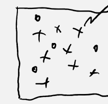
[TP] When 1 mol of $H_2(g)$ is added to a cylinder of volume V and at temperature T the pressure is 1 bar. Then an additional 0.5 mol of gas $CO_2(g)$ is added to the same cylinder keeping the temperature the same. What is the new pressure in the cylinder?

0%	1.	< 1 bar
6%	2.	= 1 bar
22%	3.	Between 1 and 1.5 bar
67%	4.	1.5 bar
0%	5.	Between 1.5 and 2 bar
6%	6.	= 2 bar



1 mol H_2 V, T, P = 1 bar

when P = 1 bar, $\chi_{H_2} = 1$

then $\chi_{H_2} = \frac{1}{1+0.5}$, $\chi_{CO_2} = \frac{0.5}{1+0.5}$

$$P_1 = \frac{n_{H_2}RT}{V} = 1\text{ bar} = \frac{1\text{ mol }RT}{V} = 1\text{ bar}$$

$$P_2 = \frac{(n_{H_2}+n_{CO_2})RT}{V} = \frac{1.5\text{ mol }RT}{V} = 1.5\text{ bar}$$

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Partial pressures

A mixture consisting of 0.513 g of $H_2(g)$ and 16.1 g of $N_2(g)$ occupies 10.0 L at 20.0°C. Calculate the partial pressures of each gas in atm.

First step, calculate the moles of each gas and the total moles.

$$n_{H_2} = 0.254\text{ mol}, n_{N_2} = 0.575\text{ mol}, n = 0.254\text{ mol} + 0.575\text{ mol} = 0.829\text{ mol}$$

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Partial pressures

~~P12.31, page 463~~: ~~A~~ mixture consisting of 0.513 g of $H_2(g)$ and 16.1 g of $N_2(g)$ occupies 10.0 L at 20.0°C. Calculate the partial pressures of each gas in atm.

$$n_{H_2} = 0.254\text{ mol}, n_{N_2} = 0.575\text{ mol}, n = 0.829\text{ mol} \qquad P = \frac{nRT}{V}$$

Second step: Use the total moles to calculate the total pressure.

$$P = \frac{nRT}{V} = 0.829\ \cancel{\text{mol}} \times 0.0820575 \frac{\text{L atm}}{\text{K mol}} \times \frac{293.15\text{ K}}{10.0\text{ L}} = 1.99\text{ atm}$$

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Partial pressures

P 13-31, page 463: A mixture consisting of 0.513 g of $H_2(g)$ and 16.1 g of $N_2(g)$ occupies 10.0 L at 20.0°C. Calculate the partial pressures of each gas in atm.

$n_{H_2} = 0.254$ mol, $n_{N_2} = 0.575$ mol, $n = 0.829$ mol, $P = 1.99$ atm

Final step: Calculate the partial pressures.

$P_{H_2} = x_{H_2}P = \frac{0.254}{0.829} \times 1.99 \text{ atm} = 0.612 \text{ atm}$

$P_{N_2} = x_{N_2}P = \frac{0.575}{0.829} \times 1.99 \text{ atm} = 1.38 \text{ atm}$

Check:

$P = P_{H_2} + P_{N_2} = 0.612 \text{ atm} + 1.38 \text{ atm} = 1.99 \text{ atm}$

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Gas law calculations in chemical reactions

$C_3H_8(g)$ and $O_2(g)$ are placed in a sealed, rigid container. After the container has been heated to 125°C, the partial pressures are $P_{C_3H_8} = 1.00$ atm and $P_{O_2} = 1.00$ atm. A spark then initiates the complete combustion of the mixture, forming $CO_2(g)$ and $H_2O(g)$. What is the total pressure in the container at the end of the reaction at 125°C?

Write the balanced chemical equation.

$P = n\frac{RT}{V}$

100% yield

1.00 atm C_3H_8
1.00 atm O_2
T=125°C
P= 2.00 atm

	C_3H_8	O_2	CO_2	H_2O	P_{total}
initial P	1.00	1.00	0	0	2.00
change					
final P					

6 + 4 = 10

$\boxed{C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O}$

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Gas law calculations in chemical reactions

$P = n\frac{RT}{V}$

$C_3H_8(g)$ and $O_2(g)$ are placed in a sealed, rigid container. After the container has been heated to 125°C, the partial pressures are $P_{C_3H_8} = 1.00$ atm and $P_{O_2} = 1.00$ atm. A spark then initiates the complete combustion of the mixture, forming $CO_2(g)$ and $H_2O(g)$. What is the total pressure in the container at the end of the reaction at 125°C?

$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(g)$

Determine the limiting reagent

1.00 atm C_3H_8 → 3.00 atm CO_2

1.00 atm O_2 → $\boxed{0.600 \text{ atm } CO_2}$

$1.00 \text{ atm } C_3H_8 * \left(\frac{3 \text{ atm } CO_2}{1 \text{ atm } C_3H_8}\right) = 3.00 \text{ atm } CO_2$

$1.00 \text{ atm } O_2 * \left(\frac{3 \text{ atm } CO_2}{5 \text{ atm } O_2}\right) = 0.600 \text{ atm } CO_2$

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