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# Physical pharmacy I 

lec2
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# States of matter 

## Part 2

## Learning objectives

$\checkmark$ Perform calculations involving the ideal gas law and molecular weights.
$\checkmark$ Understand the properties of the gaseous state

## The gaseous state

- Gas general properties
- Ideal gas
- Real gas

Ideal gas
(ne intermelectular forces)

Real gas (atiractive forces)

## Gas general properties

> Gases can be expanded infinitively, therefore gases can fill containers and take their volume and shape.
$>$ Gases diffuse and mix evenly and rapidly.
> Gases have much lower densities than liquids and solids(There is a lot of free space in a gas, therefore; It is the most compressible state of matter).


Gas
Gas
Liquid

Gas molecules travel in random paths and collide with one an other and with the walls of the container in which they are kept .A gas exerts a pressure (a force per unit area)expressed in dynes $/ \mathbf{c m}^{2}$,
$>$ Pressure is also recorded in atmospheres or in millimeters of mercury because of the use of the barometer in pressure measurement
$>$ atmospheres or in mmHg (1atm $=760 \mathrm{mmHg}=760$ Torr).
$>$ Gases have volumes that is expressed in liters or cubic centimeters $\left(1 \mathrm{~cm}^{3}=1 \mathrm{~mL}\right)$.
$>$ The temperature involved in the gas equations is expressed by the absolute or Kelvin scale ( $0^{\circ} \mathrm{C}=273.15 \mathrm{~K}$ (Kelvin)).

## Ideal gas

Ideal gas is a gas where no intermolecular interactions exist and collisions are perfectly elastic , and thus no energy is exchanged during collision.
The properties of the ideal gas can be described by the general ideal gas law ,which are derived from Boyle ,Charles and Gay-Lussac laws


## Boyle's law

Boyle's law states that the volume and pressure of a given mass of gas is inversely proportional (i.e. when the pressure of a gas increases, its volume decreases).

$$
\begin{aligned}
& \mathbf{P} \boldsymbol{\alpha} \frac{\mathbf{1}}{V} \text { or } \quad \mathbf{P} \mathbf{V}=\mathbf{k} \\
& \mathbf{P}_{1} \mathbf{V}_{1}=\mathbf{P}_{\mathbf{2}} \mathbf{V}_{2}
\end{aligned}
$$

P:pressure,
K:constant,
V:volume

As volume increases, pressure decreases


$$
\begin{aligned}
& p V=k \\
& p_{1} V_{1}=p_{2} V_{2} \\
& p=k V
\end{aligned}
$$

## Charles law

Charles law states that the volume and absolute temperature of a given mass of gas at constant pressure are directly proportional (i.e when the temperature of a gas increases, its volume increases as well).
$\mathrm{V} \alpha \mathrm{T}$ or
V=kT

$$
\frac{V_{1}}{T_{1}}=\frac{V_{2}}{T_{2}}
$$

$\mathbf{T}$ : temperature in Kelvin


## Gay-Lussac law

The law of Gay-Lussac states that the pressure and absolute temperature of a given mass of gas at constant volume are directly proportional (i.e when the temperature of a gas increases, its pressure increases as well).
Pat or
P=kT

$$
\frac{P_{1}}{T_{1}}=\frac{P_{2}}{T_{2}}
$$



## Example

Suppose you have a gas at 30.0 atm pressure and $100^{\circ} \mathrm{C}$ and the temperature is changed to $400^{\circ} \mathrm{C}$. What is the new pressure of the gas?

$$
\begin{aligned}
& \mathrm{T}_{1}=100^{\circ} \mathrm{C}+273=373 \mathrm{~K} \\
& \mathrm{~T}_{2}=400^{\circ} \mathrm{C}+273=673 \mathrm{~K}
\end{aligned}
$$

$$
\frac{P_{1}}{T_{1}}=\frac{P_{2}}{T_{2}}
$$

$$
\frac{30}{373}=\frac{P_{2}}{673} \Rightarrow P_{2}=54.1 \mathrm{~atm}
$$



## Combined gas law

Boyle ,Gay-Lussac and Charles law can be combined to obtain the familiar relationship:

$$
\frac{P_{1} V_{1}}{T_{1}}=\frac{P_{2} V_{2}}{T_{2}}
$$

The Combined
"Gas Law"


## Example 1

A sample of methane $\mathrm{CH}_{4}$ has a volume of $7.0 \mathrm{~d}^{3}$ at a temperature of $4^{\circ} \mathrm{C}$ and a pressure of 0.848 atm . Calculate the volume of methane at a temperature of $11^{\circ} \mathrm{C}$ and a pressure of 1.52 atm .
$d m^{3}=1 \mathrm{~L}$

$$
\frac{P_{1} V_{1}}{T_{1}}=\frac{P_{2} V_{2}}{T_{2}}
$$

$$
\mathbf{V}_{\mathbf{2}}=4 \mathrm{dm}^{3}
$$



## Example2

The Effect of Pressure Changes on the Volume of an Ideal Gas In the assay of ethyl nitrite spirit, the nitric oxide gas that is liberated from a definite quantity of spirit and collected in a gas burette occupies a volume of 30.0 mL at a temperature of $20^{\circ} \mathrm{C}$ and a pressure of 740 mm Hg . Assuming the gas is ideal, what is the volume at $0^{\circ} \mathrm{C}$ and 760 mm Hg ? Write

$$
\begin{aligned}
\frac{740 \times 30.0}{273+20} & =\frac{760 \times V_{2}}{273} \\
V_{2} & =27.2 \mathrm{~mL}
\end{aligned}
$$



## General ideal gas law

General ideal gas law (also called equation of state) relates the specific conditions, that is , the pressure ,volume , and temperature of a given mass of gas.

$$
\frac{P V}{T}=R
$$

or

$$
P V=R T
$$

in which $R$ is the constant value for the $P V / T$ ratio of an ideal gas. This equation is correct only for 1 mole (i.e., 1 g molecular weight) of gas; for $n$ moles it becomes

$$
P V=n R T
$$

$R=0.08205$ liter atm/mole $K$

If 1 mole of an ideal gas is chosen, its volume under standard conditions of temperature and pressure (i.e., at $0^{\circ} \mathrm{C}$ and 760 mm Hg ) Example
Calculation of Volume Using the Ideal Gas Law. What is the volume of 2 moles of an ideal gas at $25^{\circ} \mathrm{C}$ and 780 mm Hg ?

$$
P V=n R T
$$

$780 \mathrm{mmHg} / 760 \mathrm{mmHg}=1.0263 \mathrm{~atm}$
$25^{\circ} \mathrm{C}+273=298 \mathrm{~K}$
$\left(780 \mathrm{~mm} / 760 \mathrm{~mm} \mathrm{~atm}^{-1}\right) \times V$
$=2 \mathrm{moles} \times(0.08205 \mathrm{liter} \mathrm{atm} / \mathrm{mole}$ deg $) \times 298 \mathrm{~K}$
$V=47.65$ liters

## Molecular weight

The approximate molecular weight of agas can be determined by use of the ideal gas law:

$$
\mathbf{P V}=\mathbf{n R T} \quad \text { since } \mathbf{n}=\mathbf{g} / \mathbf{M}
$$

Then

$$
P V=\frac{g}{M} R T
$$

$$
\mathrm{M}=\frac{\mathrm{gRT}}{\mathrm{PV}}
$$



## Example

If 0.30 g of ethyl alcohol in the vapor state occupies 200 mL at a pressure of 1 atm and a temperature of $100^{\circ} \mathrm{C}$, what is the molecular weight of ethyl alcohol?

$$
\begin{aligned}
& 100^{\circ} \mathrm{C}+273=373 \mathrm{~K} \\
& 200 \mathrm{~mL} \div 1000 \mathrm{~mL}=0.2 \mathrm{~L}
\end{aligned}
$$

$$
\mathbf{M}=\frac{\mathbf{g R T}}{\mathbf{P V}}=\frac{0.3 \times 0.082 \times 373}{1 \times 0.2}=46 \frac{\mathrm{~g}}{\mathrm{~mole}}
$$

## Real gas

$>$ Real gases do not interact without energy exchange ,and therefore do not follow the laws of Boyle ,Charles, and Gay-Lussac.
$>$ Real gases are not composed of infinitely small and perfectly elastic non-attracting spheres.
$>$ They are composed of molecules of a finite volume that tend to attract one another.
$>$ The significant molecular volume and the intermolecular attractions between gas molecules affect both the volume and the pressure of a real gas respectively.

## VanderWaals Equation

The vanderWaals equation is a modified ideal gas equation that takes in to account the factors that affect the volume and pressure of areal gas.

For 1 mole of gas: $\quad\left(\boldsymbol{P}+\frac{\boldsymbol{a}}{\boldsymbol{V}^{2}}\right)(\boldsymbol{V}-\boldsymbol{b})=\boldsymbol{R} \boldsymbol{T}$
For $\mathbf{n}$ moles of gas: $\quad\left(\boldsymbol{P}+\frac{\boldsymbol{a} n^{2}}{\boldsymbol{V}^{2}}\right)(\boldsymbol{V}-\boldsymbol{n} \boldsymbol{b})=\boldsymbol{n} \boldsymbol{R} \boldsymbol{T}$
The term $\boldsymbol{a} / V^{2}$ accounts for the internal pressure per mole resulting from the intermolecular forces of attraction between the molecules;
$\boldsymbol{b}$ accounts for the excluded volume, which is about four times the molecular volume.

The influence of non-ideality is greater when the gas is compressed (At high pressure and low temperature). When the volume of a gas is large(At low pressure and high temperature), the molecules are well dispersed and far apart. Under these conditions, $\mathbf{a} / \mathbf{V}_{\mathbf{2}}$ and $\mathbf{b}$ become in significant with respect to $\mathbf{P}$ and $\mathbf{V}$, respectively, and the vanderWaals equation for the real gas reduces to the ideal gas equation:
PV = n RT
At these conditions, real gases behave in an ideal manner.

## Application of the van der Waals Equation

A 0.193 -mole sample of ether was confined in a 7.35 -liter vessel at 295 K . Calculate the pressure produced using
(a) the ideal gas equation and
(b) the vanderWaals equation.

The vanderWaals a value for ether is 17.38 liter $^{2} \mathrm{~atm} / \mathrm{mole}^{2}$; the $b$ value is 0.1344 liter/mole .To solve for pressure, the vanderWaals equation can be rearranged as follows:

$$
P=\frac{n R T}{V-n b}-\frac{a n^{2}}{V^{2}}
$$

(a)

$$
\begin{aligned}
P & =\frac{0.193 \text { mole } \times 0.0821 \text { liter atm } / \mathrm{deg} \text { mole } \times 295 \mathrm{deg}}{7.35 \text { liter }} \\
& =0.636 \mathrm{~atm}
\end{aligned}
$$

(b)

$$
\begin{aligned}
P= & \frac{0.193 \text { mole } \times 0.0821 \text { liter atm } / \text { deg mole } \times 295 \mathrm{deg}}{7.35 \text { liter }-(0.193 \mathrm{~mole}) \times(0.1344 \text { liter } / \mathrm{mole})} \\
& -\frac{17.38 \text { liter }^{2} \mathrm{~atm} / \mathrm{mole}^{2}(0.193 \mathrm{~mole})^{2}}{\left(7.35 \text { liter }^{2}\right.} \\
= & 0.626 \mathrm{~atm}
\end{aligned}
$$

## Sublimation in freeze drying (lyophilization)

Freeze drying (lyophilization) is widely used in the pharmaceutical industry for the manufacturing of heat-sensitive drugs. Freeze drying is the most common commercial approach to making a sterilized powder. This is particularly true for injectable formulations, where a suspended drug might undergo rapid degradation in solution, and thus a dried powder is preferred. Many protein formulations are also prepared as freeze-dried powders to prevent chemical and physical instability processes that more rapidly occur in a solution state than in the solid state.
freeze drying is a process where a drug suspended in water is frozen and then dried by a sublimation process. The following processes are usually followed in freeze


(a) The drug is formulated in a sterile buffer formulation and placed in a vial (it is important to note that there are different types of glass available and these types may have differing effects on solution stability;
(b) a slotted stopper is partially inserted into the vial, with the stopper being raised above the vial so that air can get in and out of the vial;
(c) the vials are loaded onto trays and placed in a lyophilizer, which begins the initial freezing;
(d) upon completion of the primary freeze, which is conducted at a low temperature, vacuum is applied and the water sublimes into vapor and is removed from the system, leaving a powder with a high water content (the residual water is more tightly bound to the solid powder);
(e) the temperature is raised (but still maintaining a frozen state) to add more energy to the system, and a secondary freeze-drying cycle is performed under vacuum to pull off more of the tightly bound water; and
(f) the stoppers are then compressed into the vials to seal them and the powders are left remaining in a vacuum-sealed container with no air exchange.


These vials are subsequently sealed with a metal cap that is crimped into place. It is important to note that there is often residual water left in the powders upon completion of lyophilization. In addition, if the caps were not air tight, humidity could enter the vial and cause the powders to absorb atmospheric water (the measurement of the ability of a powder/solid material to absorb water is called its hygroscopicity), which could lead to greater instability. Some lyophilized powders are so hygroscopic that they will absorb enough water to form a solution; this is called deliquescence and is common in lyophilized powders. Finally, because the water is removed by sublimation and the compound is not crystalized out, the residual powder is commonly amorphous.

Thank (a) falls

