

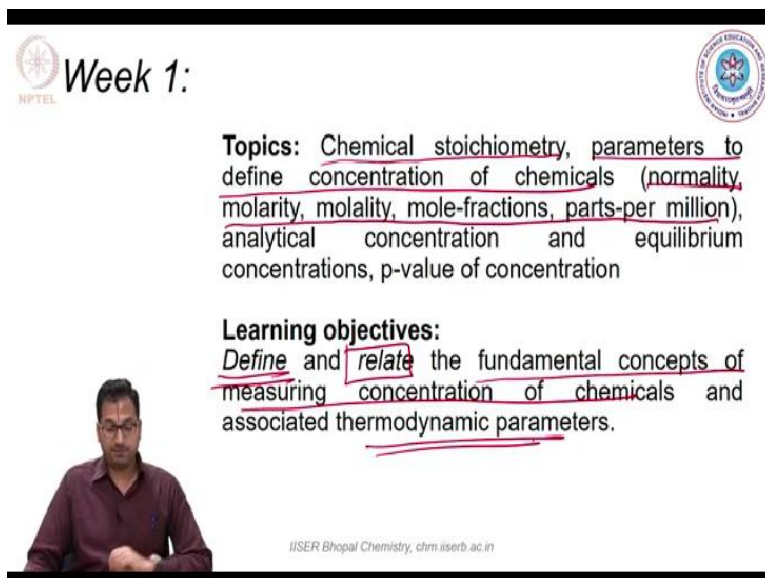
Quantitative Methods in Chemistry
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Lecture-01

A Brief History of The Beginning of Quantitation In Chemistry, Defining Chemical Stoichiometry and Molarity

Hi, welcome to the course quantitative methods in chemistry. I am Bharathwaj Sathyamoorthy, as we had explained in the introductory video will be handled by Dr. Aasheesh Srivastava and myself. For the first week of lectures, I will be handling the topics as we had decided before in this course.

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Week 1:

Topics: Chemical stoichiometry, parameters to define concentration of chemicals (normality, molarity, molality, mole-fractions, parts-per million), analytical concentration and equilibrium concentrations, p-value of concentration

Learning objectives:
Define and relate the fundamental concepts of measuring concentration of chemicals and associated thermodynamic parameters.

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The topics that will be covered for this week would be chemical stoichiometry and the parameters to define concentration of chemical so basically this is important for chemists to understand how to quantify different chemicals, as we will be dealing with different reactions as we go forward. And the different types of concentrations will be defined here namely the normality, molarity, molality, mole fractions, ppm that is parts per million.

And also understanding analytical concentrations and equilibrium concentration in terms of thermodynamic parameters, and also p value for a given concentration. Let us go a little bit in

detail about the learning objective here, here will be defining various parameters that we would like to understand and relate them across each other meaning that how was molarity related to normality, morality and so on and so forth.

And how the fundamental concepts of concentration of chemicals would help us deal with defining different chemicals that we might end up using in any of the reactions going forward. And of course, the last part will be associating them with thermodynamic parameters, which will see us at the end of this week of lectures.

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The slide features a speaker in the bottom left corner. The main content includes the title "Avogadro's number" in blue, a bullet point stating "1820: Equal volumes of different (ideal) gases contain the same number of 'particles' at a given constant temperature and pressure.", and handwritten red text: "1 mol = 22.41 L @ 1 atm 0°C". To the right is a portrait of Amedeo Avogadro with the caption "Amedeo Avogadro 1766-1856 Credit: Getty Images". Logos for NPTEL and IISER Bhopal are also present.

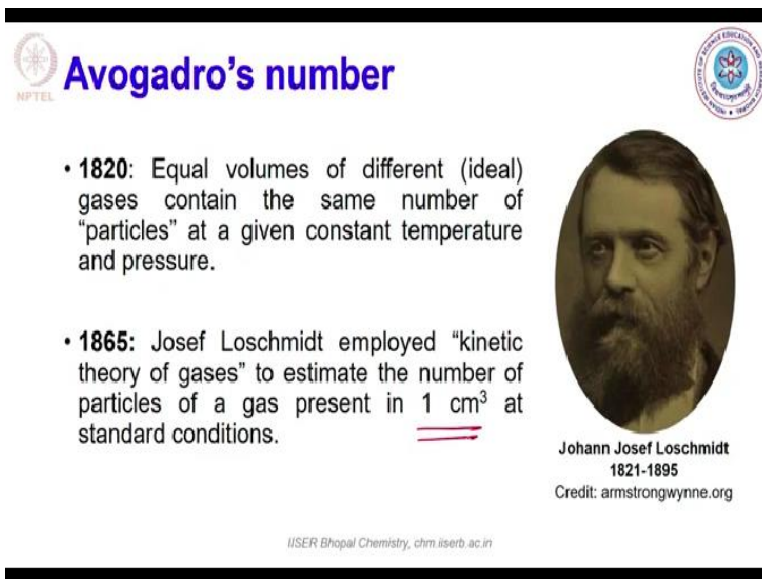
To start with the first point that one should always remember that quantitation of chemical concentration came back from Avogadro at this time and in 1820 Avogadro hypothesized that equal volumes of different gases contain the same number of particles at a constant temperature and pressure. There are 2 words that I have put up here which is ideal at that point the definition of ideal gas was still being under works or it was not completely done.

Basically, it is assumed that ideal gases of equal volume had the same number of particles at a given pressure and temperature and remember here be different particles is largely because sometimes there are gases, which are just single atoms. And sometimes gases could also be made of molecules. So, that is where the particle is a general term given for atoms molecules. So this

was an important step largely because one would understand that defining a given number of molecules for a chemical started with such a definition.

Here, as he mentioned, one mole of a gas occupies 22.41 liters at 1 atmosphere pressure and at 0 degrees Celsius. So, this was the definition that was given by Avogadro towards quantifying the number of particles presented across different chemicals, in this case the gases.

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The slide features a title "Avogadro's number" in blue text. On the left, there are two bullet points: the first states that in 1820, equal volumes of different ideal gases contain the same number of particles at constant temperature and pressure; the second states that in 1865, Josef Loschmidt used kinetic theory to estimate the number of particles in 1 cm³ at standard conditions. On the right, there is a portrait of Johann Josef Loschmidt, a man with a full beard, and a caption identifying him as Johann Josef Loschmidt (1821-1895) with credit to armstrongwynne.org. The slide also includes logos for NPTEL and IISER Bhopal.

- **1820:** Equal volumes of different (ideal) gases contain the same number of "particles" at a given constant temperature and pressure.
- **1865:** Josef Loschmidt employed "kinetic theory of gases" to estimate the number of particles of a gas present in 1 cm^3 at standard conditions.

Johann Josef Loschmidt
1821-1895
Credit: armstrongwynne.org


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This was followed by Josef Loschmidt, who employed kinetic theory of gases of course, here is where the definition of ideal gases was completely put forth, saying that there are no attractive or repulsive forces between the molecules and the molecules occupy very much smaller volume than the container itself. Using this theory, he was able to determine how many particles are present in a 1 centimeter cube at standard conditions. Once again standard conditions here defined as 1 atmosphere and 0 degrees Celsius.


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Avogadro's number

- **1820:** Equal volumes of different (ideal) gases contain the same number of "particles" at a given constant temperature and pressure.
- **1865:** Josef Loschmidt employed "kinetic theory of gases" to estimate the number of particles of a gas present in 1 cm³ at standard conditions.
- **1909:** Jean Baptiste Perrin estimated Avogadro's number using Brownian motion.



Jean Baptiste Perrin
1870-1940
Credit: nobelprize.org



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Moving forward with these 2 definitions, it was indeed in 1909, the Jean Baptiste Perrin estimated the Avogadro number using Brownian motion, one should understand that getting an idea of Avogadro number requires measuring mass of a molecule. And at the same time in its macroscopic fashion, that is you need to measure mass of a molecule and mass of a given number of particles, so that you can determine mass per particle and so on and so forth.

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Avogadro's number

- **Faraday's constant:** 96485.34 C.mol⁻¹ of charge per mole of electrons
- **1909:** Millikan's oil drop experiment that provided charge of an electron (1.6 x 10⁻¹⁹ J, 1 eV)

$$F = eN_A$$

$$N_A = 6.022 \times 10^{23} \text{ particles.mol}^{-1}$$


Robert Millikan
1868-1953
Credit: nobelprize.org



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The Avogadro's number was precisely determined by in fact, the Millikan's oil drop experiment. Until that time it was known that the Faraday's constant is given by something approximately equal to 96500 colon per mole of electrons. Once Millikan was able to determine precisely the charge of an electron by his experiment that is 1.6 10 to the power - 19 joule that is equal to 1

eV, then a simple division of the Faraday's constant with that of the electronic charge gives us what is the value of the Avogadro's number.

As we see here and most commonly, people have known this, this is approximately equal to 6.022 into 10 to 23 particles per mole, in case that you are dealing with atoms will be atoms per mole, in case you are dealing with molecules, number of molecules per mole, and so on and so forth.

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Mole and molecular weight

- One mole of a substance has a mass equal to its molecular mass
- Molecular weight – a.m.u /g.mol⁻¹ /Da
- What is the molecular mass of CO₂?

Handwritten calculations:
 $1 \times 12 = 12$
 $2 \times 16 = 32$
 44 g/mol

Periodic table and element cards for Carbon (C, 12.0107) and Oxygen (O, 15.999).

Credit (table): iupac.org
Credit (atom info): vectorstock.com

So now let us get into the idea of what is mole and molecular weight. One mole of a substance has a mass that is equal to its molecular weight. As you see here molecular weight is defined in atomic mass units or gram per mole, or Daltons. And to the right hand side here, what you see is the periodic table given by a IUPAC which attributes different features such as the molecular mass of a given atom, and it is isotope.

Let us take for an example. What is the molecular mass of carbon dioxide. And as you see here in the periodic table, it is given by the mass number down here, the mass number for carbon is given as 12 amu approximately, and then that of oxygen is given a 16 amu. This indicates the total number of electrons that is present while the mass number is indicated by the mass of the protons and neutrons that are present in the nucleus.

So as we go forward, let us ask ourselves what is the molecular weight of carbon dioxide. This is given by 1 atom of carbon and then 2 atoms of oxygen. This results in 44 grams per mole of carbon dioxide. So basically 1 mole of carbon dioxide weighs 44 grams.

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Isotopes and molecular weight

• What is the molecular mass of CO₂?

Isotope	Atomic Mass	Abundance	Stability
¹² C	12.00000	98.89%	Stable
¹³ C	13.00335	1.11%	Stable
¹⁴ C	14.0	t _{1/2} = 5715 yrs	Radioactive Cosmogenic/ anthropogenic
¹⁶ O	15.9949	99.76%	Stable
¹⁷ O	16.9991	0.04%	Stable
¹⁸ O	17.9991	0.20%	Stable

Handwritten calculations:

$$^{12}\text{C} + ^{16}\text{O}_2 = (0.9889 \times 0.9976) (12 + 16 \times 2)$$

$$^{12}\text{C} + ^{17}\text{O}_2 = (0.9889 \times 0.0004) (12 + 17 \times 2)$$

~ 44.01 g/mol.

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So, as we move forward okay is this the right molecular weight of carbon dioxide because carbon tends to have different isotopes, as shown here carbon could be present as C 12, C 13, or C 14 and the same time carbon dioxide, the oxygen and carbon dioxide could be present as O 16, O 17 or O 18. And as the numbers indicate below the carbon 12 is the most stable and the abundant nuclear with carbon 13 being present at 1% abundance, while C 14 is traces.

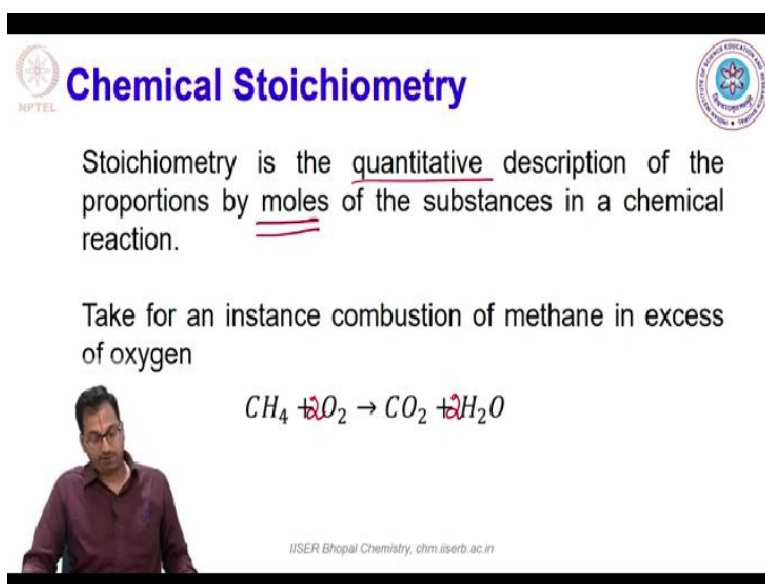
So, for all practical purposes, we will not be employing this further calculation going forward. On the other hand, oxygen 16 is the most abundant followed by O 18. Then followed by O 17. The previous slide showed you the calculation of molecular weight assuming that the isotope of carbon is C 12 and that of oxygen is O 16. Now let us take a look at the fact what if we consider that **poverty** population waiting.

So basically what is going to end up happening is that for C 12 + O 16, you are going to have the calculation that is driven by the fact that 0.9889 times 0.9976 times 12 + 16 times 2, this is where you are getting C O 2 where 12 and 16 are factor. On the other hand, if you are going to have 12

C + 17 O you are going to get something like 0.9889 times 0.04 sorry 0.004 for 12 + 17 times 2. If you do the math, you are going to get something close to 44.01 grams per mole.

We tend to assume that C 12 O 16 constitute towards a molecule weight of carbon dioxide and therefore, we tend to say 44 grams per mole is the molecular weight of carbon dioxide. As you have seen in this detailed discussion that isotopes do end up mattering. So depending upon the concentration of these isotopes, one has to be careful defining what is a molecular weight for a given chemical.

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The slide features a title "Chemical Stoichiometry" in blue text, flanked by two circular logos. Below the title, a definition states: "Stoichiometry is the quantitative description of the proportions by moles of the substances in a chemical reaction." The words "quantitative" and "moles" are underlined in red. Below this, it says "Take for an instance combustion of methane in excess of oxygen". A chemical equation is shown: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, with the coefficients 2, 1, and 2 written in red above the respective molecules. At the bottom left, there is a small video inset of a man in a purple shirt. At the bottom center, the text "IISER Bhopal Chemistry, chem.iiserb.ac.in" is visible.

So let us quickly define what is chemical stoichiometry. Stoichiometry is the quantitative definition or description of proportions by moles. Once again, we just define moles. In a chemical reaction, let me repeat stoichiometry is the quantitative description of the proportion by moles of the substances in a chemical reaction. Let us take for instance combination of methane. Methane is CH 4 and combustion happens in the presence of oxygen.

That results in the formation of carbon dioxide and water of course, here we are assuming it is complete combustion. First thing that we have to end up doing is that we understand you have 2 atoms of oxygen here while you have 3 atoms of oxygen here. So the first step that would be involved in getting a chemical reaction to understand stoichiometry would be balancing it. So the

first act of balancing would be one where let us take a look at the number of carbon atoms here, 1 carbon atom to left side 1 to the right side that means it is already balanced.

Here 4 atoms of hydrogen, but you have 2 atoms of hydrogen on the right hand side. So it might make sense to add 2 there. And then when you pay close attention, you see that you have 2 atoms of oxygen on the left side while you have 4 on the right side. So therefore it makes sense to have $CH_4 + 2 O_2$ giving $CO_2 + 2 H_2O$. So this process is called then it is called balance of chemical reaction that helps us understand stoichiometry.

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The slide features a title 'Chemical Stoichiometry' with logos for IPTL and IISER Bhopal. It displays a balanced chemical reaction: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$. Handwritten annotations show molecular weights: $12 + 4 = 16 \text{ g/mol}$ for CH_4 , $16 \times 2 \times 2 = 64 \text{ g}$ for $2O_2$, 44 g for CO_2 , and $(2 + 16) \times 2 = 36 \text{ g}$ for $2H_2O$. A bullet point states: 'When reagents are added stoichiometric amounts, then upon completion of reaction, neither will reagents be present in excess nor required any further'. A presenter is visible in the bottom left. A text box at the bottom right says: 'One is also able to see that we are employing the law of conservation of mass as we balance chemical reactions'. The footer reads: 'IISER Bhopal Chemistry, chem.iiserb.ac.in'.

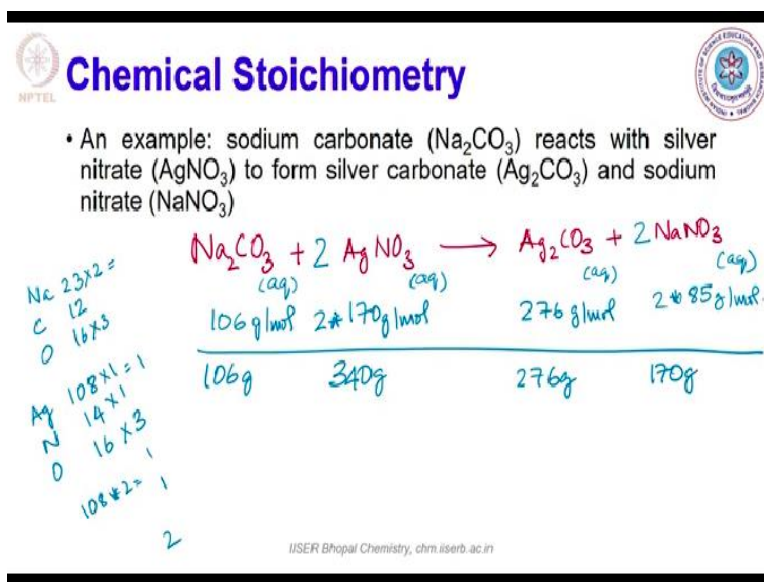
Once that we have balanced this equation with the appropriate number on either side of the reaction, the next step would be understanding what is stoichiometry that is involved. CH_4 the molecular weight of CH_4 is going to be $12 + 4$, that is going to be 16 grams and oxygen at 16 times 2 and you have 2 of those. So basically, you are going to have 16 times 2 times 2, that is going to be 64 grams.

And carbon dioxide as we have just discussed a few moments back as 44 grams. And water is going to be $2 + 16$ times 2. That is going to make it 18 times 2 on the right hand side, basically this is going to be 36 gram. Understand that you have 1 mole of methane reacting with 2 moles of oxygen to give 1 mole of carbon dioxide and 2 moles of water. As you see here, the

equivalence of the stoichiometry that goes is that 16 grams of methane reacts with 64 grams of oxygen, it will result in the formation of 44 grams of carbon dioxide and 36 grams of water.

So, basically, this is what we mean by stoichiometry. And the important thing one has to understand when the reagents are added in stoichiometry amounts, then upon completion of the reaction, neither will the reagents be present in excess not be required any further, this just indicates the fact that all of the reagents will be used, and there will be none, that will be required any further because all the other reagents would have been completed.

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Let us try to take an example to understand this a little further. The example being sodium carbonate reacts with silver nitrate. So let us start writing and there are at least a few more things that should be added in addition to the grams that is given for this stoichiometry one also gives the standard states at which a at least the different reactants and the products are present.

In this case methane will be present as a gas, oxygen will be present as a gas, carbon dioxide will also be present as a gas, water is a liquid or gas depending upon the temperature that we are dealing with here in this combustion process. So, the temperature is high enough, it is not going to condense and you are going to see water vapor. So, in this example, we are going to be looking at sodium carbonate plus silver nitrate resulting in the formation of silver carbonate plus sodium nitrate.

As always, the first step is going to be balancing this reaction. As we see on the left hand side we see 2 atoms of sodium and only one on the right side. So, let us see whether we like 2 whether it helps or not, just for the sake of clarity, let me try to change the color of the pen I was using just to indicate the balancing. So let us add a 2 here, that is 2 atoms of sodium on the right and we already had 2 on the left, carbon is present as 1 atom on both sides.

Oxygen, on the other hand, left hand side has 6, on right hand side now has 9. Let us go on and see that silver there are 2 atoms on the right and 1 on the left. So it might make sense to add a 2 here. This takes care of the nitrogen and oxygen being carefully balanced. So basically, this is the balanced reaction. And all of these are present under aqueous conditions okay, now that we have balanced the reaction, let us try to ask ourselves what is stoichiometry meaning.

How many grams per mole are required for each one of this sodium is 23, Carbon is 12 and oxygen is 16. So basically you are going to have $46 + 12 + 48$. That takes it 106, the 106 grams per mole. Now that we have obtained the molecular weight of all of these constituents of this reaction, let us try to understand how many of what is required. So 106 grams of sodium carbonate will react with 340 grams of silver nitrate to give 276 grams of silver carbonate, and then 170 grams of sodium nitrate. So basically this is a stoichiometry that we are looking forward for such a reaction.

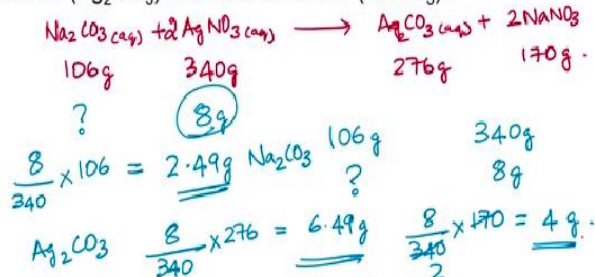
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Chemical Stoichiometry



- How many grams of sodium carbonate (Na_2CO_3) is required to completely convert 8 g of silver nitrate (AgNO_3) to silver carbonate (Ag_2CO_3) and sodium nitrate (NaNO_3)?



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Going forward, let us take a question here. How many grams of sodium carbonate is required to completely convert 8 grams of silver nitrate to silver carbonate and sodium nitrate. So let us quickly rewrite the whole equation again. I am going to go back to red. So the question here is that if you are having 8 grams of silver nitrate, how much of sodium carbonate is required for completely using all the silver nitrate that is present.

So for instance, all that we have to do here is that for 106 grams, 340 grams is required. So for 8 grams how much is required, so it is going to be equal to 8 by 340 times 106 that is going to be equal to 2.49 grams of sodium carbonate. And now that we have understood 2.43 grams of sodium 2.49 grams of sodium carbonate is required. That is also determine how much of Ag 1 CO 3 that the silver carbonate will be found.

Using the same formula, you are going to have 8 by 340 times 276 which is going to be equal to 6.49 grams. And how much of Na NO 3 it is going to be equal to 8 by 340 times 170, which is going to be equal to this is only 4 grams. So basically if you have 8 grams of silver nitrate that is present, you need to add about 2.49 grams of sodium carbonate, which will lead you 6.49 grams of silver carbonate and then 4 grams of sodium nitrate.

So this I hope helps you understand how does stoichiometry go, depending upon the concentration of one reagent the other is carefully added such that no more of the reagents are required to form the products and none exists at the end of it.

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The slide is titled "Chemical Stoichiometry" and features the NPTEL logo on the left and the Indian Institute of Space Science and Technology logo on the right. The main content is a chemical reaction: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$. Below the reaction, handwritten notes in blue ink show the masses: 16g for CH_4 , 64g for $2O_2$, 44g for CO_2 , and 36g for $2H_2O$. A second row shows 8g for CH_4 and 32g for O_2 , with the 32g circled. The text " CH_4 limiting" is written to the right. A presenter is visible in the bottom left corner of the slide frame.

• Concept of limiting reagent

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

16g 64g 44g 36g
8g 32g CH_4 limiting

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So, let us quickly understand the concept of limiting reagent which is understood that 16 grams of methane reacts with 64 grams of oxygen to be 44 grams of carbon dioxide and 36 grams of water. And one has to remember that what happens if you just had 8 grams of methane while you had still 64 grams of oxygen. When this happens, what you are able to realize is that 8 grams of methane is only going to about use 32 grams of oxygen.

This results in an excess of 32 grams of oxygen. So basically, this is a reaction where the methane appears to be a limiting reagent. What do we mean by that, we mean that since the concentration of methane is less, it limits the reaction to go any further, although oxygen is present in mole excess. So this is an example where one is able to understand these are not given stoichiometry ratios resulting in one reagent being in excess.

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Molecular weight

- Atoms
- Molecules
- Macromolecules

Isotopic data for Carbon:

¹² C	¹³ C	¹⁴ C
12.00000	13.00335	14.00324
98.89%	1.11%	(E) = 575 pm

Water: H2O (18 g)

Sodium carbonate hydrate: Na2CO3 · 10H2O (106 + 180 = 286 g/mol)

Glucose: 180 g/mol

Fructose: 180 g/mol

Sucrose: 180.1 g/mol × 2 = 360, minus 18 = 342 g/mol

Myoglobin, PDB: 1MBN
C783H1240N216O216S2
 17,199 g/mol = 17.2 kDa

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So going back little bit to molecular weight. Let us recap a small portion of this, you understand that atoms, weight is going to be given based on an isotope, molecules such as water, which has 18 grams per mole is given by the sum such atomic weights. And you could also have chemicals we just saw an example where sodium carbonate which is going to be 46 + 12 + 48 making it 106 grams per mole is assuming there is no water of hydration present, you could be purchasing salts that has water of hydration meaning that these waters cannot be removed from the final solid product that has been obtained.

As an example as taken here sodium carbonate that has 10 water of hydration. This is sodium carbonate that are hydrate is going to have 106 grams + 18 grams times 10 which is going to be 180, so this molecular weight of the same is going to be 286 grams per mole. On the other hand if you are going to larger molecules as you see here, this is a molecule of sucrose, sucrose is made with combination of glucose and fructose.

And as you would all know, glucose and fructose are isomers of each other meaning that they have the same molecular weight, they are about 180 grams per mole. And sucrose is formed by the condensation of glucose and fructose with elimination of 1 water molecule. So basically that is going to be 360 - 18, which results in 342 grams per mole. So, what one is able to understand here is that molecular weights can be determined from the constitute atoms and molecules that help forming them.

Going to macromolecules as in the case of proteins are shown here. This is a famous protein called myoglobin. It has a lot of atoms are seeing here it has 783 carbon atoms, 1240 hydrogen atoms, 216 nitrogen atoms and 216 oxygen atoms and 2 sulfur atoms. Of course, you can take all day to sit and calculate its molecular weight, I had the comparable here, this is about 17199 grams per mole. Generally in the field of proteins, this is going to be called as Dalton. So, this is also referred to us 17.2 kilo Dalton, which indicates the molecular weight of myoglobin.

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Molarity

- Molarity

Number of moles present in a liter of solution

$$M = \frac{\text{no. of moles}}{\text{Vol. of soln. (L)}} = \frac{\text{weight of chemical (g)}}{\text{mol. wt. (g)} * \text{Vol. of soln. (L)}} = \text{mol. L}^{-1}$$

Calculate molarity of 10 g sodium carbonate in 500 mL of water. *soln.*

$\text{Na}_2\text{CO}_3 = 106 \text{ g/mol}$

$$M = \frac{10 \text{ g}}{\frac{106 \text{ g/mol} * 0.5}{10}} = \frac{1}{5} = \underline{0.2 \text{ M}}$$

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Now, let us go to the first concentration unit that we will most commonly use in this field of chemistry. So, that is called molarity. Molarity is defined as the number of moles present in a given volume of solution. So, basically molarity M is given by number of moles which is unit less divided by the volume of solution in liters. And as we just saw, the number of moles is going to be given, let us say the weight of the solute of the chemical in grams, dividing that by the molecular weight, which we just understood how to calculate, times the volume of solution, and liters.

So this will end up as a unit such as moles per liter. So this is the definition of molecular weight. Let us go back to our sodium carbonate. In this case, let us not assume it is a decahydrate to start with. So the question here is what is the molarity of 10 grams of sodium carbonate in half a liter

of solution. In this case, we are assuming addition of 10 grams to half a liter of water results and half a liter of solution, which may not be the case all the time.

But let us assume the same to start with. So we know that the molecular weight of sodium carbonate is 106 grams per mole. And we have 10 grams of it. So the molarity is now going to begin by 10 grams divided by 106 grams per mole. Just for the sake of easiness let us assume we have 10.6 grams of sodium carbonate that makes our math easier times volume of solution and liters and you have 500 ml of solution let us say.

So that is going to be 0.5. So basically this is going to be something like 10, this is too 1 by 5 is equal to, so 10 grams of sodium carbonate in water and half a liter water constitutes 0.2 molar.

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Molarity

Calculate the amount in mg of myoglobin present in 100 μL of 5 mM solution

$$5 \times 10^{-3} \text{ M} = \frac{\text{wt.}}{\text{mol. wt} \times V (\text{L})} = \frac{\text{wt. (g)}}{\frac{17.2 \times 10^3 \text{ g/mol}}{100 \times 10^{-6} \text{ L}}}$$

$$\text{wt (g) myoglobin} = 5 \times 10^{-3} \times 17.2 \times 10^3 \times 10^{-4}$$

$$= 8.6 \times 10^{-3} \text{ g} = \underline{\underline{8.6 \text{ mg}}}$$

Handwritten calculation on the left:

$$\begin{array}{r} 31 \\ 172 \\ \hline 5 \\ \hline 860 \end{array}$$

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We have just determined the molarity of sodium carbonate and half a liter of water and you have 10.6 grams of sodium carbonate. Let us try to twist the question over NASA same thing in a slightly different manner. We are asking how much amount of myoglobin is present and 100 microliters of solution that is having 5 millimolar concentration of myoglobin. Let us go back to a definition molecular weight is given by weight by molecular weight times volume of solution in liters.

Here volume of the solution is 100 microliters. So, you are asking what is the weight in grams. What is the molecular weight which is now it is 17.2 into 10 to the power of 3 grams per mole. And volume of solution in liters it is 100 microliters. So therefore the way to determine how much weight is present and remember, the left hand side is 5 millimolar. So therefore the weight in grams of myoglobin is going to be equal to 5 into 10 power - 3 times 17.2 into 10 to the power of 3 multiplied by 10 power - 4.

So, this is going to finally result in 17.2 times 5. So, basically it is going to be 8.6 into 10 to the power of -3 grams, which is 8.6 milligrams. So basically if you dissolve 8.6 milligrams of myoglobin in 100 microliters solution, you are going to finally end up with a 5 millimolar concentration of myoglobin. With this let us stop the first lecture, we will continue the forthcoming lectures by trying to define other units of concentration such as normality, molarity, weight percent and so on and so forth.

And try to go forward in understanding how all these different units of concentration help us understand or define concentration of chemicals that we use in different reactions. Thank you.