The irregularity of Avogadro’s hypothesis and determination of the gas constant value ($R$)

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Abstract. Avogadro’s hypothesis, which in reality is used as a "basis" in determining/calculating various thermodynamic variables, and decreasing various derivative equations, is less understandable. Avogadro’s hypothesis is a "hypothesis", not a "law" that has been widely and correctly proven both analytically and empirically. For this reason, this paper discusses the objections associated with the hypothesis, as well as alternative solutions to determine the gas constant value $R$ (not the universal gas constant as obtained from Avogadro’s hypothesis) which depends on the type of gas. These gas constants are obtained through a simple assumption, that is from the definition that 1 (one) mole of gas is a unit related to the number of gas molecules in a certain volume measured at STP conditions (pressure 1 atm, and temperature $25^\circ$C = 298$^\circ$K). With this assumption, it is clear that the gas constant is unique, so it becomes the character of the gas (for gas type X is $R_X=V_X/298$ litters $\cdot$ mol$^{-1} \cdot$ atm $\cdot$ K$^{-1}$).

1. Introduction
The history of civilization/human development has shown the human tendency to know and reveal the secrets of various natural phenomena. Along with its development, its curiosity is increasingly diverse, both quantitative and qualitative. To reveal the various phenomena, humans form various theories based on assumptions, analogies, postulates, axioms, hypotheses, laws, experiments, and so on.

In addition, the variety of phenomena requires that humans do classification or grouping based on the type or scope of the phenomenon. In scientific terminology, this classification is an embodiment of one of the global paradigms of science, namely optimization [1]. Classifications based on the scope of natural phenomena give rise to a variety of scientific disciplines. Related to that, in its assessment, specialization and professionalization is needed to get truly optimal results.

An analysis, testing, and proof of hypotheses, theories, arguments, and laws in any branch of science needs to be done. The results of that step will contribute greatly to the improvement and progress of science itself. Actually hypotheses, theories, arguments, and laws are realized or not are "measuring instruments or tools” created by humans to answer various basic questions related to various phenomena that are observed. For example, in laboratory, the ability of Type II Endonuclease Retention enzymes to cut DNA has a repeatability, perfect specificity and accuracy at optimum conditions. On the basis of this fact, combined with the fact that plasmids can enter and enter between cells and replicate semi-independently in them, modern biotechnology is developed (the position of facts is stronger than law). Newton’s law is used as a measure and a decrease in the derivative
equations of physics. The application of the two examples above are true, and therefore must be accepted. Another example is the "Avogadro hypothesis" which is used as the basis of thermodynamics, although the position of the hypothesis can be said to be weak before there is theoretical or empirical evidence.

An irregularity in scientific rules, both the basic assumptions used, the hypothesis, and various subsequent derivatives, need to be clarified. Regarding this issue, this paper presents a discussion on testing the hypothesis of Avogadro in theoretical logic [2-4]. In addition, an alternative theory is also based on the determination of gas $R$ parameters that depend on the type of gas being reviewed.

By testing and analysing it is expected to clarify the status of Avogadro's hypothesis, whether the hypothesis is still acceptable (with or without correction) or failed/rejected.

2. The irregularity of Avogadro's hypothesis

Avogadro's hypothesis says that one mole of any gas, in STP conditions (pressure of 1 atm, and temperature of 25°C = 298 K), has a volume of 22.4 liters. The hypothesis also raises Avogadro's Number which states the number of molecules or atoms contained in each mole, which is $6.022 \times 10^{23}$ molecules ($N_A = 6.022 \times 10^{23}(30) \times 10^{23} \text{mol}^{-1}$). As a result of the hypothesis we can obtain, through the relation $PV = nRT$, the $R$ value is 0.082 liter-atm-mol$^{-1}$-K$^{-1}$ which is as a universal gas constant. Furthermore, this $R$ value is used in all calculations/determinations of various parameters and thermodynamic variables, such as pressure $P$, volume $V$, temperature $T$, and so on.

Avogadro's hypothetical product is also used in various derivative equations, including $\Delta G = -2.303 \ R \ T \ \log K$, Van Hoff's equation to determine the value of osmotic pressure $\pi = (n/V) \ R \ T = MRT$, determining the chemical equilibrium value of gas at a certain temperature $K_p = K_c \ (RT) \ \Delta n$, the determination of heat of the gas reaction at a fixed pressure is $\Delta H = \Delta E + \Delta n_{\text{gas}} \ R \ T$, and there are many more equations in the thermodynamic domain.

Now we connect the two statements of Avogadro. For the hypothesis statement, we take a concrete example, 1 mole of Helium (He) gas compared to 1 mole of Radon gas (Rn), both gases are noble gases, group VIII A. In that group, the radius of the Helium atom is the smallest and the radius of the Radon atom is the largest. One (1) mole of Helium gas = $6.022 \times 10^{23}$ Helium molecules, 1 mole of Radon gas = $6.022 \times 10^{23}$ Radon molecules (the actual physical meaning of the two gases), so 1 mole of the two gases contains the same number of molecules / atoms. As a simple illustration, it is assumed that Helium atoms are the size of marbles, and Radon atoms are the size of a football. One (1) mole of He gas = 5 Helium atoms, 1 mole of Radon gas = 5 Radon atoms. How can 5 marbles need a place as large as 5 balls (22.4 liters)? Surely the volume needed for 5 Helium atoms is smaller than the volume needed for 5 Radon atoms.

Avogadro's hypothesis links volume with the same temperature and pressure for Helium and Radon gas, which is 25°C or 298 K and a pressure of 1 atm. Review the influence of temperature, assuming the temperature has an influence on the radius of the atom. Because $V$ is proportional to $T$ so if the temperature increases the volume also increases, both for Helium and Radon, and vice versa. That means, the volume needed for 5 Helium atoms is still smaller than the volume needed for 5 Radon atoms. Review the effect of pressure, because $V$ is inversely proportional to $P$, so if the pressure increases it will reduce the volume of the Helium atom, but the same thing happens to Radon atoms, the volume of radon atoms also decreases, the result is the same as the analysis of the effect of temperature.

From the simple analysis above, there appears to be an odd assumption (if not wrong) in Avogadro's hypothesis.

3. Atomic Spectrum as "Fingerprints"

The irregularity of Avogadro's hypothesis is also evident from the observation of the atomic spectrum by Balmer (known as the Balmer spectrum array). Related to the results of his observations, Balmer stated that the atomic spectrum is a fingerprint of that atom. From observing the atomic spectrum, it can be determined not only the atomic pathway but also the "path" of "each" orbit of electrons. None of the researchers refuted Balmer's statement. Other researchers have also obtained a spectrum of atoms under different conditions of temperature and pressure. Their observations turned out to also
show the same results as Balmer's observation[11]. That means that temperature and pressure have no effect on the atomic path, or in other words, they also refute Avogadro's hypothesis.

The atomic spectrum is the absorption of $h\nu$ from the emission of light used, then by the absorption atom $h\nu$ is emitted again. So it concerns the change of "absorption-emission" energy level $E_1$ to $E_2$, $E_2$ to $E_3$, $E_3$ to $E_4$, etc. The delta value (difference) of energy $E_2-E_1$, $E_3-E_2$, $E_4-E_3$, and so on is "certain", because the atomic spectrum is unique; is a fingerprint of that atom. Delta (difference) from the energy levels "determines" the radius of the atom, while the radius of the atom determines the volume of atoms. Therefore, each atom has a "different" atomic volume. That is a fact, and the fact "must" be accepted as truth.

The atomic spectrum is obtained by heating, but the effects of heating also cause electron excitation, or in other words electrons absorb energy.

From the spectrum of Hydrogen atoms, Balmer obtained the equation:

$$\nu = R_Hc \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$

where \( \nu = \text{frequency} \), \( R_H = \text{Rydberg constant} \), \( c = \text{speed of light} \), and \( n = 3, 4, 5, \ldots \). Niels Bohr obtained the equation, also from the spectrum of Hydrogen atoms:

$$E_n = -13.6 \text{ eV} \left( \frac{1}{n^2} \right)$$

where $E_n$ is the energy in the $n^{th}$ orbit, and $n = 1, 2, 3, \ldots$ is the principal quantum number associated with distance ($r$) of the atomic nucleus. For example, at $n = 1$, $r = A_0 = 0.53\text{angstroms}$.

The energy level for hydrogen-like atoms, in this case what is meant by hydrogen-like atoms is an atom with the outer shell $n_e$ (one), such as Sodium, Potassium, etc., can be determined through quantum mechanical calculations. However, the values obtained are irregular or, in other words, less successful. The failure of quantum mechanics becomes greater if atoms do not resemble hydrogen-like atoms, or the outer electrons are not $n_e$ (one), for example for atoms with outer electrons $n_p$ (two), $n_p$ (five), like Br atom.

Another fact that can show the awkwardness of Avogadro's hypothesis is the event of light absorption by the sample material in the AAS (Atomic Absorption Spectrophotometry) device[12]. The study was almost the same as the spectrum study and Balmer's statement. In AAS, if we are going to analyse Al, we have to use Al (aluminium) lights. Aluminium lamp emits light waves from the ground state to the first excitation state with energy, say, $E_{Al}$. This light emission is absorbed by the sample Al, from the base level to the first excitation level, which is "equal" to $E_{Al}$. In this case, we cannot use another lamp, for example, the K lamp, since the K lamp will emit light waves from the base level to the first excitation level with $E_K$ energy that is different from $E_{Al}$. If a lamp with another atom is used, the emission energy of that atom will be absorbed by the sample atom, but there is no comparison between the amount of energy absorption of the emission and the number or concentration of sample atoms, so that AAS cannot be used.

The two reasons above show that the delta-energy of an atom is proportional to the radius of the atom, and the radius of the atom is proportional to the volume of the atom. So each atom has a unique or certain atomic volume, which means different atomicvolumes.

4. Definition of 1 (one) mole and determination of $R$

From the simple analysis, it is clear that Avogadro's hypothesis states that one mole of any gas, in a STP condition pressure 1 atm, and temperature 25°C = 298°K), has a volume of 22.4 liters, which results in a single $R$ value for all gases, must be corrected. For the reason that the molecular radius is unique for each type of gas, the volume of a gas in the STP state will be different from the other gas.

Assuming that in STP conditions all gases have the same number of molecules and units of moles of gas associated with the number of particles/gas molecules, it can be defined (different from Avogadro's hypothesis) that (one) mole of gas is a unit related to the number of gas molecules in a certain volume measured in STP conditions (pressure 1 atm, and temperature 25°C = 298°K).

Based on the definition of one mole of gas above, and the relationship of the ideal gas
\[ PV = nRT \text{ or } V = R \left( \frac{n}{p} \right), \]  

(3)

It is clear that under STP conditions, which means 1 (one) mole, the value of R depends on the volume. Because two different gases have different volumes (in STP conditions), the R value for both is also different. Therefore, the R value is unique and only applies to the gas, in other words, the gas constant R is not a universal gas constant. Thus, from equation (3) is obtained

\[ R_X = V_X \left( \frac{p}{T} \right) = \frac{V_X}{298} \text{ liter} \cdot \text{mol}^{-1} \cdot \text{atm} \cdot ^\circ \text{K}^{-1} \]  

(4)

where \( R_X \) and \( V_X \) are the gas constant and the volume, respectively, of gas X obtained from the experimental result on STP conditions.

Proof of Avogadro's objection and at the same time proving the uniqueness of \( R_X \) values can be done through experiments; the flowcharts and experimental designs are described in Figures 1 and 2, respectively. In the path of proof, it is assumed that in the STP condition the gas tested is 1 mol (because the mole is not related to volume, but with the number of particles). If the result shows that the volume of various gas tests is the same (more specifically 22.4 liters), Avogadro's hypothesis is correct. Meanwhile, if the test results show that the volume of each test gas is different, the hypothesis fails, which results in the value of R being unique for each gas.

**Figure 1.** Flowchart of verification of Avogadro's hypothesis and determination of the value of \( R_X \) if Avogadro's hypothesis is failed.
Figure 2. Experiment design to obtain $R_X$ values and test Avogadro's hypothesis. The coat contains water and electronic components to maintain temperature stability. The cylinder cap can rise and fall according to the volume of gas in the STP condition. As a test gas, He, O$_2$, H$_2$, N$_2$, and Ne gas can be used.

5. Conclusion and Suggestion

5.1. Conclusion
By reasoning the molecular radius is unique for each type of gas (for two different gases the radius is different), the volume of the gas in STP conditions will be different from the other gases. Therefore, Avogadro's hypothesis needs to be reviewed.

Assuming that in STP conditions all gases have the same number of molecules and a unit of mole of gas associated with the number of particles/molecules making up the gas, it can be defined that (one) mole of gas is a unit related to the number of gas molecules in a volume measured in STP conditions.

From the two assumptions, it is clear that the value of $R$ depends on its volume on STP conditions. In other words, the value of $R$ is unique and only applies to that gas, whose value for the type of gas $X$ is given by $R_X = \frac{V_X}{298} \text{liter} \cdot \text{mol}^{-1} \cdot \text{atm} \cdot \text{oK}^{-1}$.

5.2. Suggestion
It is necessary to do a real experiment to review Avogadro's hypothesis with a flow diagram and instrumentation model as described in Figures 1 and 2.

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