Beauty of Physical Chemistry – Part 1

New definitions of SI Units and Physical Chemistry

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Learning physical chemistry is equally important as other areas in Chemistry. Unfortunately, lot of students (and also lecturers) give less attention to it. However, concepts in physical chemistry such as quantum mechanics, thermodynamics, kinetics, statistical mechanics, etc. are really important to understand the fascinating world of Chemistry. Considering this, I wish to make this series of articles an eye opener and to boost your curiosity in learning physical chemistry. To get the full benefit, please explore the concepts and problems given in boxes by yourselves.

Let's begin with something everyone knows, SI units! Everyone of us applies them, but do you know the concept behind its definitions? Very recently definitions of SI units were changed and they are now defined by natural constants of nature. Concepts of these new definitions relate more towards physical chemistry principles. Let's explore!

Historically, humans learned to measure even before they learned to write. Our ancestors used their fingers to count, the position of the sun to tell time, feet or hand to measure length, earthly objects to measure weight. However, from civilization to civilization and country to country measurement units were different until the establishment of the International System of Units which is commonly known as SI units or metric system. Today, trade, construction, travel, astronomy, and scientific research are impossible without precise measurements based on SI units. Technical regulations for quality assurance of products are decided by commonly accepted standards which are essentially based on SI measurement units.

There are seven SI base units as depicted in Table 1 and all other measurement units are derived using them. For example, Newton (unit of force) is a derived unit that is expressed in kilograms, meters, and seconds.

Initial discussion for SI units began at the Metre Convention of 1875 at the General Conference on Weights and Measures in France but the system was published and established internationally only in 1960. The international body responsible for SI units and measurement standards and is the Bureau of Weights and Measures (BIPM) located in France (BIPM stands for Bureau International des Poids et Mesures in French).

Early definitions of SI units were based on artifacts and physical measurements. For example, a kilogram and meter were defined using special artifacts made from Platinum – iridium alloys. Experimental uncertainties in physical measurements of these artifacts were a major concern among the scientific community. Therefore, in order to improve the precision, reliability, reproducibility, and accuracy with reduced measurement uncertainty initial definitions were changed from time to time in history. The last redefinition was in May 2019 during which four of the base SI units such as the kilogram (mass), mole (amount of substance), Kelvin (temperature), and Ampere (current) were redefined. With these changes, current SI base unit definitions are entirely based on the several physical constants of nature as shown in the third column of Table 1. Nevertheless, the new definitions do not change the values of SI units, so we can still use the existing measurements without any issue.

Table 1: Seven SI base units

	Quantity	Unit	Physical constants associated with the new definition
1	Time	second (s)	Hyperfine transition frequency of Cesium
2	Length	meter (m)	Speed of light
3	Mass	kilogram (kg)	Planck constant
4	Amount of substance	mole (mole)	Avogadro number
6	Temperature	Kelvin (K)	Boltzmann constant
5	Current	Ampere (A)	Electron charge
7	Luminous intensity	Candela (cd)	Monochromatic radiation of frequency 540 Hz

Following discussions summarize the historical definitions and introduce the new or current definitions of the seven base units.

Time (second)

Definition of time has a long history similar to the many other units of measurement. I suggest you read the article https://www.nist.gov/si-redefinition/second-past to explore more.

Atomic clocks

By the 19th century, the mechanical clock was widespread, but scientists realized that these were not suitable to set standards because they were/are prone to errors due to friction and changes in temperature. Later, physicist James Maxwell proposed the use of atomic vibrations as the "natural standard" to measure time. The frequency of atomic transitions is unique and does not change with disturbances. Over the years, highly precise 'atomic clocks' were developed based on the hyperfine energy splitting of the Cs-133 isotope.

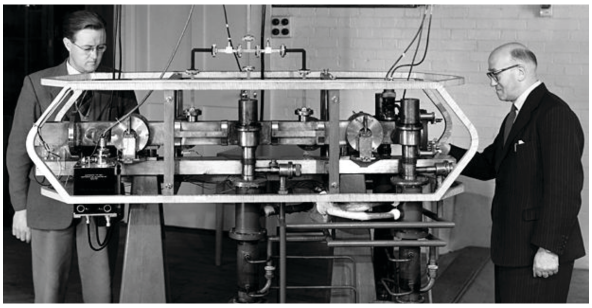

Figure 1: World's first Cs-133 atomic clock developed by Louis Essen and Jack Parry in 1955 at the National Physical Laboratory in the UK (https://www.wikiwand.com/en/Atomic_clock)

Atomic clock is indeed a fascinating concept which involves ***physical chemistry****. Now it is your turn to explore it. Read and find out more about the types of atomic clocks, ultrafine energy splitting, type of spectroscopy etc. We'll discuss them in detail in the future articles of this series.*

Definition of a second; old and new

The early definition of a second was based on the period of earth's rotation which is not a very accurate measurement. Therefore, in 1967, the SI definition of a second was revised based on the hyperfine energy splitting of C-133.

The energy gap between two hyperfine energy states of Cs-133 in a magnetic field was experimentally expressed in units of Hz as $\Delta v_{cs} = 9192631770$ Hz (1 Hz=1 s^{-1}). This is indeed a very accurate value.

Therefore, the definition of 1 s is given by,

$$1s = \frac{9192631770}{\Delta v_{Cs}} \qquad (1)$$

In other words, 1 s is 9192631770 times longer than the time of the transition, which is the new definition of 1 s. The atomic clocks are so accurate that it was found that the one built at NIST won't lose or gain a second in 6 million years (Refer NIST: National Institute of Standards and Technology).

Length (meter)

A brief account on the long history

In the past, different countries used different standards to measure distances. The first widely accepted one-meter length standard was a prototype bar of platinum and named the French meter, as it was set up in France. However, it was impossible to verify whether copies of this meter bar have the same lengths. This prototype was later changed to a platinum-iridium bar since it was significantly more durable than the pure platinum bar and remained as the standard until 1927. The next length standard was based on the interferometry technique which enabled the measurement of the wavelength of waves precisely. Accordingly, in 1940, measurement scientists were able to develop a reproducible and convenient methodology to define the meter using the precise measurement of the wavelength of the green emission light of mercury-198. However, in 1960, another length standard was defined using the wavelength of the krypton-86 atom at 605.8 nm. Nonetheless, the krypton standard didn't last long, and ultimately, the speed of light has become the measurement standard of length until now.

Figure 2: Platinum – iridium meter standard. (https://www.nist.gov/si-redefinition/meter)

> *Even though mercury and krypton wavelengths are now not being used to determine length standards now, it is indeed another fascinating idea in **Physical Chemistry**. Find out what these characteristic wavelengths of atoms are and how they are found precisely before I discuss it in detail in the future.*

The new definition of a meter

The speed of the light was accurately calculated by using the wavelength and frequency measurements of characteristic laser light. The accurate value for the experimental speed of light was found to be 299,792,458 meters per second in a vacuum.

The meter is defined as the distance that light travels in 1 s divided by the numerical value of the speed of light in vacuum c to be 299,792,458 when expressed in the unit m s^{-1}. Definition of second is then applied in terms of $\Delta\nu_{cs}$

$$1m = \frac{c}{299792458s} = \frac{9192631770}{299792458s}\frac{c}{\Delta\nu_{Cs}} = 30.63319\frac{c}{\Delta\nu_{Cs}} \qquad (2)$$

The length was now no longer an independent standard but rather was derived from the extremely accurate standard of time and a newly defined value for the speed of light.

Mass (kilogram)

International Prototype of Kilogram (IPK) to Planck constant

Before the introduction of SI units, different methods/artifacts were used as mass standards. One of such methods was the measurement of the mass of water at a given volume and a specified temperature. In 1875, at the Meter Convention, the kilogram was defined using the International Prototype of Kilogram (IPK) which is an artifact made of an alloy of 90% platinum and 10% iridium (Figure 3). IPK and its six replicas were kept inside triple-locked vaults at the BIPM in France. All other countries have to keep their primary 1 kg standards and calibrate against IPK periodically at their national metrology institutes. These laboratories have to maintain their own working standards to calibrate the balances in the country.

However, this has been a very laborious task and also problematic since each of these individual standards is changed or drifted by a small amount over time. Owing to this situation the relative uncertainties increased during scaling down of standards such as standards of mg range and below. As researchers, we know how important it is to measure milligram to microgram quantities accurately in research work. Moreover, even the mass of the IPK can drift over time. Accordingly, these drawbacks led the international measurement science community to decide to change the IPK based mass standards to a system where scaling measurements do not increase uncertainty. As a result, the kilogram is now defined by taking the fixed numerical value of the **Planck constant**.

Figure 3: A replica of an IPK in a Science Museum (https://en.wikipedia.org/wiki/International_Prototype_of_the_Kilogram)

Quantum mechanics & the Planck Constant

Planck constant was named after the eminent physicist Max Planck who first introduced the concept of energy 'quanta' which has led to the development of quantum mechanics in the early 20th century.

> *Quantum mechanics is the major breakthrough of modern science. Max Planck in fact made a big role in development of this theory. Recall quantum mechanics you learnt under **physical chemistry** (if you have) and think what will happen to science if quantum mechanics has not evolved. Do you agree or not with the above underlined statement?*

He applied this concept to explain the spectrum of blackbody radiation (energy released from a hot object) which couldn't be explained using classical physics. He postulated that the 'quanta' or energy of a photon is proportional to the frequency of the electromagnetic radiation (ν) and this proportionality constant was named as the Planck constant (h). Everyone who studies science today knows the famous relationship, $E=nh\nu$

where n is a positive integer. Accordingly, the Planck constant is fixed by nature and the value will never change.

How was the Planck constant used to redefine kilogram units?

During the late 20th century scientists were able to determine the value of the Plank constant with extraordinary precision as a result of two physical constants related to voltage and resistance. These are the Josephson constant (KJ = 2e/h) and the von Klitzing constant (RK = h/e^2).

From these experiments the accurate value of Planck constant, h was determined as $6.62607015 \times 10^{-34}$ J s. Here the unit of h is equal to kg m^2 s^{-1}. Meter and second were defined in terms of c and $\Delta\nu_{Cs}$ as mentioned in the above sections. Thus, we can obtain the value of 1 kg from

$$1\ kg = \frac{h}{6.62607015 \times 10^{-34}} \frac{1\ s}{(1\ m)^2} = 1.47552214 \times 10^{40} \frac{h\Delta\nu_{Cs}}{c^2} \qquad (3)$$

if we know the accurate value of h, $\Delta\nu_{Cs}$ and c.

So, how do we find the value of the Planck constant experimentally using a primary standard understanding the definition of a kilogram?

Currently, there are two methods that are capable of doing it.

1. Using the Kibble balance
2. Using silicon spheres

Kibble balance

A special instrument known as Kibble balance could be used to measure the unknown value of h using an exactly defined mass. Therefore, one can measure unknown mass (whatever the standard material) by substituting in Equation 3.

Kibble balance was first developed by British physicist Bryan Kibble in 1975 at the National Physical Laboratory (NPL) of the United Kingdom to determine the value of h. However, currently, there are only a few Kibble balances in operation for this purpose.

Silicon spheres

Silicon sphere is a 1 kg of an almost perfect sphere made solely of **ultra-pure silicon-28**. This is made with single crystal silicon and has a diamond-type crystal system with the cubic unit cell as shown in Figure 5. The value of the Avogadro constant can be accurately determined using the silicon sphere.

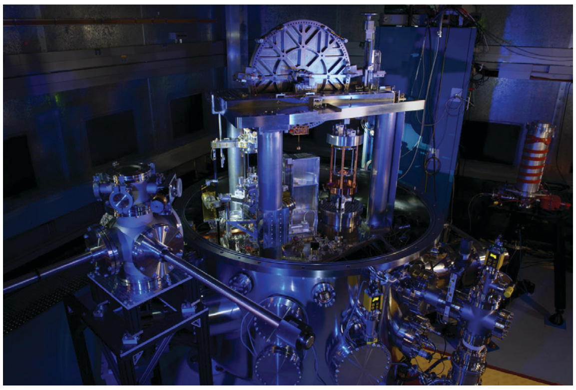

Figure 4: Kibble balance at NIST USA (https://www.nist.gov/si-redefinition/kilogram-mass-and-plancks-constant)

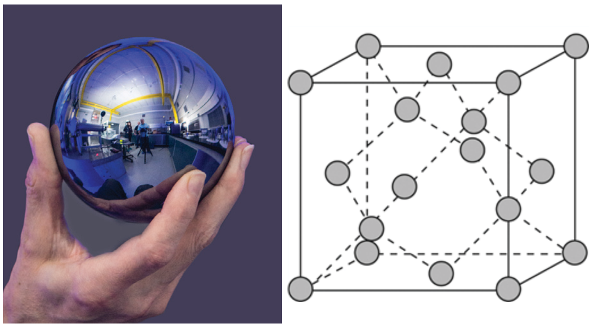

Figure 5: Left: True silicon sphere in NIST laboratory, USA. Right: Cubic unit cell of a Si crystal

> *What is the most abundant element in the world? Is it Silicon? No. It is the second, but, silicon is the game changer of the world! and one of the most important elements in **Physical Chemistry**. Silicon spheres are really fascinating. Find out more before we discuss it next time.*

Primary and secondary mass standards

Now we know how mass is defined using the Planck constant. The next question is how to calibrate the working standards. There are two types of mass standards such as primary and secondary mass standards. The primary mass standard can be an artifact (object) which is practically determined in terms of the Planck constant by the formal definition of the kilogram. Silicon spheres are the most acceptable primary standards. Secondary standards are calibrated using the primary standards and they are used to disseminate the mass unit.

Amount of substance (Mole)

Before the new definition, one mole was defined as "the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilograms of carbon-12 isotope". Avogadro number was defined as the number of atoms of carbon-12 isotope has in a mass of 0.012 kg. This is what every one of us has learned in Chemistry Textbooks in our high schools. Accordingly, the relative atomic mass of an isotope of an element was defined as the weight in grams of the number of atoms of the element contained in 12 g of Carbon-12. For example, the relative atomic mass of copper was found to be 63.546 and that mean 63.546 g of copper contains the same number of copper atoms as 12 g of Carbon-12. Thus, it requires precise measurement of weight to experimentally determine the molar masses.

However, the carbon-12 definition is no longer in use. A new definition for mole has a direct relationship to the Avogadro number.

One mole contains exactly $6.02214076 \times 10^{23}$ elementary entities. This number is the fixed numerical value of the Avogadro constant, NA, when expressed in the unit mol^{-1} and is called the Avogadro number.

Inverting this relationship gives an exact expression for the mole in terms of the defining constant N_A:

$$1\ mol = \frac{6.02214076 \times 10^{23}}{N_A} \qquad (4)$$

As explained in the previous discussion, the Avogadro number can be found using **silicon spheres**. Accordingly, in the future, any particular experiments involving mass measurements are not required to define a mole and therefore, do not involve any experimental uncertainties. Please do the following quiz to test your knowledge of silicon spheres.

Quiz on Silicon Spheres

Determine the number of silicon atoms in the above unit cell (n)

Length of each side of the unit cell given above is a (in meters) and atomic mass of silicon is m (m =28.09 Da).

Write an equation for the density (d) of silicon sphere using n, m, a, and NA. (NA is the Avogadro number)

Rest of the SI units will be covered in the next article.

Those who are interested in this subject further please go through the following references.

- National Institute of Standard and Technology - https://www.nist.gov/si-redefinition
- The International Bureau of Weights and Measures - https://www.bipm.org/en/home
- http://hyperphysics.phy-astr.gsu.edu/hbase/acloc.html