

Serial: Amount of substance and temperature

In the fourth episode of this year’s series, we leave mechanics behind and look at quantities associated with thermodynamics and chemistry – temperature and amount of substance, whose historical development has been mutual to some extent and motivated by the nature of matter and its composition.

Amount of substance

As we mentioned in the previous episode, the mass of particles – atoms and molecules – has not been known for a long time. Chemists in the late 18th century discovered the fundamental principles governing chemical reactions – the law of conservation of mass (A. Lavoisier), the concepts of equivalent masses, stoichiometry, and the law of definite proportions (J. B. Richter, J. L. Proust). Their work was followed up in 1805 by J. Dalton with his atomic theory explaining these observations as rearrangements of the fundamental blocks – atoms – during chemical reactions. He also compiled the first tables of relative masses, assigning the lightest element – hydrogen – the mass of one. Gay-Lussac’s progress with experiments on gas reactions, in turn, led Avogadro to assume that under the same conditions, equal quantities of two different gases take on the same volume. In the following decades, this evolved into the kinetic theory of the ideal gas, which we will discuss in the next chapter.

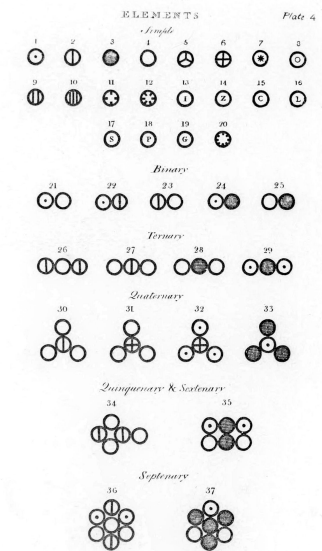


Fig. 1: Dalton’s table of atoms from *A New System of Chemical Philosophy* published in 1808¹

However, hydrogen was not well suited for the experimental determination of the masses of chemical compounds. Oxygen, in contrast, reacts with almost all known elements. J. Berzelius chose a relative mass of the oxygen atom equal to 100 as the base value. That did not last for long, and the definition of $M(\text{O}) = 16$ was adopted, with the same value and precision as the original definition through hydrogen. The following quantities and units are associated with this definition:

- Avogadro's constant N_A – the amount of particles in 32 g of an oxygen molecule O_2 ,
- Dalton 1 Da – the mass equal to 1/32 of the mass of the oxygen molecule O_2 ,
- mole 1 mol – a unit of amount of substance n indicating how many particles of a given substance are in the sample in units of Avogadro's constant $n = N/N_A$.

With the discovery of stable isotopes of the elements in the mid-twentieth century, it was necessary to create a new definition. Physicists began to use the isotope ^{16}O , but chemists preferred to use the natural isotopic composition of oxygen. However, this proved inhomogeneous from various sources, so they switched to a new definition using the carbon isotope in 1960:

One mole is equal to the number of atoms in 12 g of the isotope ^{12}C .

With this change, the definitions of dalton and Avogadro's constant understandably changed.

The amount of substance was adopted as a fundamental quantity in the SI system in 1971. Today's definition of a mole has transferred its essence to the natural constant

The mole (denoted mol) is a unit of the amount of substance, a quantity proportional to the number of elementary particles of a substance. One mole contains exactly $6.022\,140\,76 \cdot 10^{23}$ of elementary particles, which may be atoms, molecules, ions, or other particles. This number is equal to a fixed value of Avogadro's number N_0 and represents the numerical value of Avogadro's constant in units of mol^{-1} .

There are also some derived units associated with the amount of substance

- molar mass – the mass of one mole of a substance,
- molar volume – the volume of one mole of a substance (under defined conditions),
- molar concentration – the amount of a given substance in a sample/solution of a given volume (usually one liter),
- mass fraction – the proportion of particles belonging to a specific substance relative to the total number of particles in a solution or mixture.

Nowadays, we usually determine the amount of substance by accurate weighing and subsequent conversion using a known molar mass value determined from the atomic abundance of the analyzed substance.

¹https://commons.wikimedia.org/wiki/File:A_New_System_of_Chemical_Philosophy_fp.jpg

Temperature

Is it freezing?

People have always perceived the temperature of objects around them. Most of the time, however, it was enough to determine whether something was too warm or cold. The first documented experiments with heat took place in ancient Greece, where Philo of Byzantium and Heron of Alexandria created apparatus to transport water utilizing the expansion of heated air. Later, the Roman physician Galen created a temperature scale by mixing various amounts of boiling water and ice. Nevertheless, these advancements, along with numerous other scientific concepts, faded into oblivion in Europe. It was not until the Renaissance, marked by the resurgence of archaic texts that scientific inquiry resumed. For instance, Galileo Galilei reenacted ancient experiments and devised the thermoscope during this period. If a heated glass flask is immersed neck down in the water, the cooling air will draw the water into the flask. Afterward, we can deduce the temperature from the position of the water. The first air thermometer was created by adding a simple scale. However, these instruments are affected by the change in atmospheric pressure.

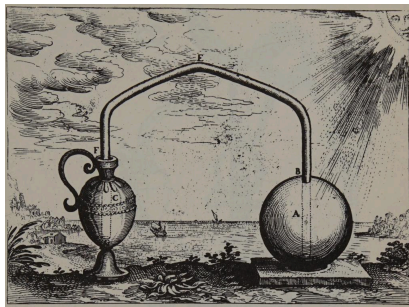


Fig. 2: Drawing of the apparatus of Philo of Byzantium²

Another significant development occurred with the illustrations by J. S. Delmedigo, which inspired the construction of the first liquid thermometer in the mid-17th century by Ferdinando II de Medici. A thin capillary protruded from a flask filled with brandy, which was air-sealed at the top. The liquid expanded due to the temperature change, indicating the temperature on the attached scale. Similar instruments rapidly became popular across Europe. However, standardization became a pressing issue concerning both the filling substance used (typically a mixture of alcohol and water to depress the freezing point) and the calibration scale. Consequently, by the end of the century, scientists advocated for standardizing scales by employing various reference temperatures. Advances in measurement accuracy came with the work of D. G. Fahrenheit, who constructed a thermometer containing mercury in 1714. Such a thermometer had an increased range of measured values and a fixed composition of contents. Fahrenheit also defined a new scale, which later obtained his name, with a zero point at the temperature of a mixture of ice and ammonium chloride and a value of 90°F at human body temperature.

²https://commons.wikimedia.org/wiki/File:Fludd_figure_of_philo_experiment.png

However, these values are not reproducible accurately enough, so a temperature scale devised by A. Celsius has been adopted, using the melting point of ice and the boiling point of water at standard atmospheric pressure at sea level as reference points and dividing their difference into one hundred degrees.³ The calibration of the thermometer was thus performed by recording the position of the liquid column in the capillary in an equilibrium mixture of ice and water, the position in the boiling water, and then dividing the scale evenly into one hundred parts. An example of significant practical use is Six's maximum and minimum thermometer, capable of recording the highest and lowest temperatures experienced within a given timeframe, such as 24 hours. Similarly, the once-prevalent medical mercury thermometer operates on the same principle. However, the problems with such thermometers are the properties of the liquids used – their solidification and boiling values limit the operable range of measured temperatures. Furthermore, volumetric expansion typically is not consistent with temperature variations. For instance, water expands in volume at temperatures below four degrees Celsius despite further cooling.

Lastly, it is worth noting that bimetallic thermometers also operate based on thermal expansion principles. They utilize a strip composed of two different metals with distinct expansion coefficients. When the temperature fluctuates, one side of the strip expands more than the other, causing the attached needle to rotate accordingly. We can encounter this type of thermometer even in our households, e.g., while baking.

You cannot go any lower!

Research into thermodynamics started in the second half of the 17th century. The following laws were derived by experimenting with gases at changing temperature t , pressure p , and volume V :

- in 1662, the Boyle-Mariott law, where at constant temperature $pV = \text{const}$,
- Gay-Lussac also verified the dependence at constant volume, where $\Delta p/p = \beta \Delta t$ (this is known as Charles's law),
- and the dependence at constant pressure $\Delta V/V = \gamma \Delta t$ now known as Gay-Lussac's law.

At the time, the last three relationships showed that at the temperature $t_0 = -267^\circ\text{C}$ (later called absolute zero), the product of pressure and volume of any amount of gas approaches zero. These laws, combined with Avogadro's law, form the ideal gas law

$$\frac{pV}{nT} = R_m,$$

where R_m is the molar gas constant, n is the amount of substance of gas, and $T = t + t_0$ is the so-called absolute thermodynamic temperature, which used kelvins - in honor of W. Thomson (Lord Kelvin), who invented the scale.

The temperature scale in degrees Kelvins begins at absolute zero temperature and has a fraction as large as the Celsius scale.

Later measurements showed that the melting point of ice also depends on pressure (Celsius already knew this about boiling point), so it went from melting and boiling at standard pressure to a more precise definition using the triple point of water – the equilibrium state between

³The original definition had the values reversed, stating that water boils at 0 degrees and ice melts at 100 degrees.

water vapor, liquid water, and ice, which occurs at a pressure of about 611 Pa and a temperature 0.01 °C higher, than the melting point. After the precise determination of the value of absolute zero in 1954, a newer formulation from 1968 omitted the degree from the unit's name to align its naming with other units.

The unit of thermodynamic temperature is the kelvin, its magnitude given as $1/273.16$ the value of the thermodynamic temperature of water.

The various dependencies of melting and boiling point of water have become deeply studied phenomenons. However, it was later established that the temperature of the triple point depends on the isotopic composition. Consequently, a resolution was enacted in 2005 that ordered the measurements to take place under the Vienna Standard of Mean Ocean Water. Rankine, a scale of absolute temperature based on degrees Fahrenheit is sometimes used in place of kelvin based on degrees Celsius.

In the relation expressing the pressure of an ideal gas, the product nR stands out. After determining the number of particles of a substance by measuring Avogadro's constant N_A it was possible to go from the amount of substance to the number of gas particles themselves

$$pV = Nk_B T,$$

where $k_B = R/N_A$ is Boltzmann's constant. This constant is fundamental to the statistical description of thermodynamics. In the second half of the 19th century, R. Clausius, J. C. Maxwell, and L. Boltzmann developed the kinetic theory of gases, where they considered individual elastic collisions between the molecules and the wall of the container. They succeeded in deriving the ideal gas law and also the Maxwell-Boltzmann velocity distribution of gas particles – the number of particles $f(v)$ moving with velocity v

$$f(v) \propto 4\pi v^2 e^{-\frac{mv^2}{2k_B T}},$$

which the gas reaches in dynamic equilibrium between its particles. The following generalization is the Boltzmann energy distribution

$$p_i \propto e^{-\frac{E_i}{k_B T}},$$

describing the probability p of occupying a state i with energy E_i at a given temperature. One notable consequence of these relationships is the equipartition theorem, which states that in thermodynamic equilibrium, each quadratic degree of freedom of motion within the system possesses an average kinetic energy of $E = k_B T/2$. Due to the importance of this connection and the desire to separate the definition of the kelvin from material characteristics, a new definition of the kelvin was introduced in 2019:

Kelvin, symbol K, is the SI unit of thermodynamic temperature. It is defined by fixing the numerical value of the Boltzmann constant $\{k_B\} = 1.380\,649 \cdot 10^{-23}$ expressed in units of $\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{K}^{-1}$.

Based on the relations for the ideal gas, it is possible to measure the absolute temperature directly. One possibility is to use a gas thermometer – either by measuring the change in pressure at constant volume or the change in volume at constant pressure. However, we cannot treat real gases as ideal – the size of the gas particles and the van der Waals interaction between

the particles cause variations when they are close together. Therefore, the sparser the gas, the more accurate the thermometer becomes. A variant with higher precision is an acoustic gas thermometer measuring the speed of sound u in the gas, for which

$$u^2 = \frac{\gamma k_B T}{m},$$

where m is the mass of the gas molecules and γ is the ratio of the heat capacity at constant pressure and volume (it is equal to $5/3$ for monatomic gases). We can determine the speed of sound from the resulting standing waves of known frequency in a gas-filled cavity, whose dimensions have previously been determined, e.g., by microwave resonances. The measurement is made for different gas pressures and extrapolated to the limit of zero pressure, for which the real gas behaves as an ideal gas (for which the relationship above was derived). Temperature values determined this way may have relative accuracy up to $1 : 10^6$.

At low temperatures, we encounter a different problem –the gases liquefy. Temperature of condensation of nitrogen is 77 K, the lowest condensation temperature under atmospheric pressure has helium, only 4.2 K for the isotope ^4He and 3.2 K for helium ^3He . At lower temperatures, alternative measuring methods are necessary. A convenient approach involves determining the saturation vapor pressure of helium ^3He , although its dependency requires calibration through another primary method for determining absolute temperature.

It heats, it emits, it shines

As anyone who has ever sat by a fire knows, hot bodies transmit energy into the surrounding area not only by direct contact but also by radiation. Even in the Middle Ages, people working in metallurgy used color to tell if a heated body was hot enough. Quantitative research on the thermal and luminous radiation of hot bodies began to flourish in the second half of the 19th century with the work of B. Stewart and G. Kirchhoff, culminating in the formulation of Kirchhoff's law of thermal radiation – in thermal equilibrium, for a body of temperature T is the ratio of the radiated energy and the fraction of incident absorbed radiation on a given wavelength λ is the same and given by the function $B(\lambda, T)$ characterizing an absolute blackbody.

Quantitative research into the thermal and luminous radiation of hot bodies saw significant development in the latter half of the 19th century through the contributions of B. Stewart and G. Kirchhoff. This era culminated in the formulation of Kirchhoff's law of thermal radiation, which states that in thermal equilibrium, the ratio of radiated energy to the fraction of incident absorbed radiation at a given wavelength λ is consistent and determined by the function $B(\lambda, T)$, characterizing an absolute blackbody with temperature T .

Determining this function proved to be a challenging task. On one hand, advancements over time and improvements in experimental techniques led to the discovery of the Wien radiation law. On the other hand, through theoretical physics reasoning, Jeans' law emerged. While these two relations provided accurate descriptions of experimental values in the shortwave and longwave regions of the spectrum, they failed to make accurate predictions between those two regions. Nowadays, we recognize these laws as approximations of Planck's radiation law, which was initially derived empirically to fit measured values in its first publication in 1900. In 1901, Planck provided a mathematical derivation of this law using quantum radiation principles. The concept that radiation can only occur in discrete "packets" of energy, known as quanta,

was further established in 1905 through Einstein's theoretical explanation of the photoelectric phenomenon. Today, the blackbody radiation law has the form

$$B_{\lambda}(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1},$$

where B_{λ} represents the amount of energy radiated from a unit surface area per unit wavelength and spatial angle.

Practically, the temperature of hot bodies is measured using thermal radiation properties. Primary radiation thermometry involves measuring the optical power of the body with a radiometer of known spectral sensitivity and defined spatial angles using apertures. Alternatively, we can measure and compare relative intensities with known calibration points. This method is preferred for temperatures around 1235 K (the melting point of silver) and can achieve measurement errors of about 0.1 K at temperatures up to 2800 K. We use the melting points of metals like silver, gold, or copper to calibrate radiometers.

Pyrometers (non-contact thermometers) work on a similar basis – by detecting radiation over a wide spectral range using the Stefan-Boltzmann law – an integral form of Planck's law describing the total radiated energy on all wavelengths. Hence, thermal radiation stands out as one of the few techniques for gauging the temperature of celestial bodies, including stars, planets, and other space objects, which are beyond physical reach.

Electrical properties of substances

In practice, temperature measurement often employs secondary methods that measure another parameter with a precisely known temperature dependence rather than directly measuring temperature. It should not surprise us that the most commonly used temperature-measuring instruments today are resistance thermometers, thermistors, and thermocouples, owing to advancements in electrical measurements.

The electrical resistance of conductors arises from the hindrance of conduction electrons due to collisions with the vibrating nuclei in the crystal lattice. As temperature decreases, these vibrations diminish, leading to a decrease in resistance to a constant value determined by lattice defects and impurities at extremely low temperatures in the order of a few kelvins. W. Siemens noted this phenomenon in 1871 and developed the first resistance-based thermometer in later years. In high school physics textbooks, we often come across the following relationship

$$R = R_0 (1 + \alpha (T - T_0))$$

describing the dependence of electrical resistance on temperature as a linear function. For broader temperature ranges and higher measurement precision, employing a polynomial expansion with an increased number of coefficients becomes necessary. We can determine the corresponding temperature from the measured resistance value by applying simple numerical calculations. Precision resistance thermometers typically feature a platinum resistor (often a coiled thin wire right at the probe's tip) connected to a resistance bridge. Simultaneously, we measure voltage with the help of a galvanometer. A platinum resistance thermometer enables us to assess temperatures ranging from approximately 10 K to 1300 K, with accuracy below 1 mK across most of this range with a single instrument.⁴

⁴A large number of reference materials for high-precision temperature measurements are available on the website of Bureau International des Poids et Mesures (BIPM) <https://www.bipm.org/en/committees/cc/cct/guides-to-thermometry>



Fig. 3: Standard platinum resistance thermometer⁵

Another option is using a thermistor – a semiconductor component whose electrical resistance varies with temperature by influencing the number of free charge carriers in the semiconductor. Thus, their change in electrical resistance is more significant than in the case of resistance thermometers. They are viable only for a smaller range of temperatures of about one hundred kelvin with an accuracy of the order of tenths of a kelvin. We distinguish between two types – thermistors with a negative coefficient α , composed of metallic oxides of the ferrous group, and species with a positive coefficient composed of ceramic doped materials. In practice, they commonly serve as a straightforward method for measuring temperature or regulating current, often in place of fuses.

Another related device is the thermocouple, which exploits the thermoelectric phenomenon. In 1821, T. J. Seebeck observed that heating one end of a conducting wire generates a measurable voltage between its ends. Different metals exhibit different voltage values. We can create a stable current by connecting two different metals into a loop and maintaining the junctions at different temperatures. The voltage on a thermocouple with temperatures of the junctions T_1 and T_2 is given by

$$U = \int_{T_2}^{T_1} (S_B - S_A) dT,$$

where S_i are the Seebeck coefficients (nonlinear functions of temperature) of the conductors. The thermocouple does not need an external power supply to measure temperature, but its accuracy is smaller when compared to previous methods (only in a few units of kelvin). In addition to temperature measurement, it is possible to use thermocouples to generate electricity from heat, such as in a radioisotope thermoelectric generator. An intriguing application of this

⁵https://commons.wikimedia.org/wiki/File:SPRT_Glass_Capsule_-_RTD.jpg

phenomenon is the Peltier cooler serving as a cooling element utilizing electrical energy and operating on the reverse principle.

Just as with liquid thermometers, it is essential to calibrate any thermometer operating on the principle of variable electrical resistance. To achieve this, a comprehensive list of precise temperature values corresponding to various reproducible states, such as melting and boiling points of pure substances, has been compiled to serve as temperature standards. This compilation, known as the International Temperature Scale of 1990 (ITS 1990), spans from the triple point of hydrogen at approximately 13.8 K to the melting point of copper at 1357.8 K, later extended to 0.65 K. However, for measurements at even lower temperatures, a new standard needed to be established – the PLTS-2000 (established in 2000) covers the range from 1 K to 0.9 mK, albeit requiring different measurement techniques. In both cases, precise procedures are defined, including the state, calibration, and calibration function to be employed and executed. New tables detailing deviations from these temperature scales emerge with more recent and accurate measurements conducted through primary methods.

Advanced techniques

There are also many other techniques for measuring temperature. Polarization gas thermometry determines the density of a gas by measuring its electrical properties. Utilizing the Clausius-Mossotti relation along with the equation of an ideal gas, we can derive the relationship between the relative electrical permittivity ϵ_r , pressure p and the temperature T of a noble gas

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{A_e p}{RT},$$

where A_e is the molar electric polarizability given by the chemical composition of the gas used. Its value must be determined through theoretical quantum-mechanical calculations, and it is only accurately known for atomic helium gas, with a value of $A_e = 0.52 \text{ cm}^3 \cdot \text{mol}^{-1}$. The measurement procedure involves determining the capacitance of a capacitor (denoted as C , with helium gas held between its plates) from the well-established relation

$$C = \frac{\epsilon_r \epsilon_0 S}{d},$$

which utilizes certain simplifications and is valid if the surface area of the plates, denoted as S , is significantly larger than the distance between the plates, represented by d . Another possibility is to measure the refractive index of air and determining its temperature using the equations from the last serial problem.

The Johnson noise thermometer operates on a completely different principle. It relies on the electrical resistance, denoted as R , which generates noise on the measured voltage or current due to thermal motions. When measuring a constant voltage V , its value fluctuates around the average value with a certain dispersion

$$\sigma_V^2 = 4k_B T R \Delta f,$$

where k_B is the Boltzmann constant and Δf is the width of the frequency range at which we measure the noise. This range of frequencies can be conceptualized as follows – a single measurement point is acquired for time t_1 and the entire measurement takes time t_2 . Therefore, it is not possible to record noise on longer or shorter time scales. Various measurement configurations exploit this phenomenon, enabling temperature measurements from a few hundred kelvins to tens of millikelvins.

Derived quantities

Temperature is associated with a large number of derived quantities describing the change in properties of objects and materials, such as thermal expansion in units $\text{m}^3 \cdot \text{K}^{-1}$, or thermal conductivity in units $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. You have probably also come across heat capacity (with the unit $\text{J} \cdot \text{K}^{-1}$), which describes the change in temperature of an object when a certain amount of energy is supplied to it (for materials, we often also encounter specific heat capacity per unit mass). These material constants are usually measured from definitional relationships measuring the change in a given property on temperature.

One physical quantity, however, holds a distinct status – entropy. It characterizes a system’s capacity to perform work. According to the second law of thermodynamics, the entropy of a closed system remains non-decreasing over time. One of the well-established relationships from statistical physics says

$$S(E) = -k_B \sum_i p_i(E) \ln p_i(E),$$

where the entropy is equal to a product of Boltzmann’s constant and the term describing the probability $p_i(E)$ that the system will be in state i at total energy of the system E . From this relationship, we can see that the entropy increases with the disorderliness of the system –that is, a more even representation of the individual states. The question remains, however, how to measure entropy. The most appropriate formula for this is the relationship

$$dS = \frac{\delta Q}{T},$$

where a small entropy gain of the system equals the ratio of the heat input and the system’s temperature during a reversible process. For calculating the entropy change of a substance between two states, it is essential to execute a reversible process connecting them and measure the heat transfer within the system. The absolute value of entropy relies on a principle postulated by the third law of thermodynamics – an ideal crystal at absolute zero temperature possesses zero entropy.

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