La química en la historia,
para la enseñanza

Development of the concept of absolute zero temperature

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Resumen

La posibilidad de un cero absoluto de la temperatura fue introducida en una etapa temprana del desarrollo científico. La existencia del Primum Firgidum, un cuerpo supremamente frío, fue objeto de mucha discussion entre filósofos y científicos hasta el siglo diecisiete. Aun cuando científicos famosos como Gay-Lussac negaron la posibilidad de un cero absoluto, la idea prendió de a poco y un gran número de valores diferentes fueron propuestos para su ubicacion bajo el punto de congelación del agua. Hubo que esperar hasta el trabajo funamental de Lord Kelvin para establecer la escala absoluta de temperatura que llevó al valor aceptado hoy en día de –273.15 C.

Abstract

The possibility of an absolute zero temperature was introduced very early in the development of science. The existence of the Primum Frigidum, a body supremely cold, was the subject of much discussion among philosophers and scientists well up to the seventeenth century. Although famous scientists such as Gay-Lussac negated the possibility of an absolute zero, the idea took ground little by little and a large number of widely different values were proposed for its actual location below the freezing point of water. It took the seminal work of Lord Kelvin to establish an absolute scale of temperatures that led to the accepted value of –273.15 C.

The physiological sensation of heat and cold has accompanied mankind from the very beginning. Heat and cold are mentioned in the Bible in the book of Genesis as natural phenomena that existed before the deluge and that will continue to occur afterwards: "While the earth remaineth, seed time and harvest, and cold and heat, and summer and winter, and day and night, shall not cease" (Genesis 8:22). Later on, the allegory of the vision of the prophet Ezekiel contains a symbol of extreme cold: "And over the heads of the living creatures there was the likeness of a firmament, like the colour of the terrible ice, stretched forth over their heads above" (Ezek. 1:22).

Observations of various natural and man-made phenomena led the ancients to postulate theories that led to our modern concepts about the nature of heat and heat transfer. Thermometry started from the recognition of the need to quantify these differences more precisely than by adjectives like hot and cold. The original apparatus, called *thermoscopes*, served merely to show the changes in the temperature of its surroundings. Eventually the need arose for quantifying these observations and the different thermometers began to be developed. Astronomers built most of these instruments, particularly for measuring low temperatures (Wisniak, 2000). Development of thermometric scales such as those of Réaumur, Fahrenheit and Celsius, led in a natural way to the question whether there was a lower limit to temperature, and correspondingly, to the behaviour of materials under those circumstances. Simultaneously, many scientists devoted part of their efforts to understand the nature of heat and cold as well as to find the laws that described them. Already by the seventeenth century detailed memoirs had been published describing all the available information and the theories about the nature of heat, the most famous (and lengthy) ones being those of Francis Bacon (1561-1626) (Bacon, 1651, 1955) and Robert Boyle (1627-1691) (Boyle 1999). Later on, scientists such as Isaac Newton (1642-1727), Antoine-Laurent Lavoisier (1743-1794), John Dalton (1766-1844), Joseph Fourier (1768-1830), Pierre-Simon Laplace (1749-1827), Joseph-Louis Gay-Lussac (1778-1850), Sadi Carnot (1796-1832), James Prescott Joule (1818-1889), and William Thomson (Lord Kelvin, 1824-1907) would develop the mathematics of the phenomenon and the concepts of absolute temperature and absolute zero that accompany us today.

Francis Bacon (1561-1626) dealt extensively with the concept of heat and cold, as seen in his major works *Novum Organum* (Boyle, 1955) and *Sylva Syl-*

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varum (Boyle, 1651). The latter contains an entry entitled *Experiments in Consort Touching the Production of Cold*, where Bacon writes: "The production of cold is a thing worthy of the inquisition both for the use and disclosure of causes. For heat and cold are nature's two hands whereby she chiefly worketh, and heat must have in readiness in respect of the fire, but for cold we must stay till it cometh back or seek it in deep caves or high mountains, and when all is done we cannot obtain it in any degree, for furnaces of fire are much hotter than a summer sun, but vaults and hills are not much colder than a winter's frost." He went on to describe what he believed were the seven means of producing cold, or its causes (the inside of the earth, the contact of cold bodies, the primary nature of all tangible bodies, the density of bodies, a quick spirit enclosed in a cold body, the chasing and driving away the spirits, and the exhaling or drawing out of the warm spirits). The first mean is particularly interesting because it reflects some of the wrong ideas prevalent at that time: "The first means of producing cold is that which Nature preferenth us whithal; namely the expiring of Cold out of the inwards parts of the Earth in Winter, when the Sun hath no power to overcome it; the Earth being, as has been noted by some (*Primum Frigidum*). This has been asserted, as well as by Ancient, as by Modern Philosophers such as Parmenides, Plutarch, andTelesius" (in other words, the inside of the earth was the source of the maximum cold).

In 1682 Boyle read a paper to the Royal Society on "New Experiments and Observations Touching Cold, or an Experimental History of Cold" (Boyle, 1999) where he described the many experiments he had done on frigorific mixtures, and the general effect of such upon matter. His multiple experiments led him to conclude that cold was a privation of that local motion of the particles of bodies which was requisite to constitute heat, and was not a positive entity at all. He said: "if a body being cold signify to more than its not having its sensible parts so much agitated as those of our sensorium, it suffices that the sun or the fire or some other agent, whatever it were, that agitated more vehemently its part before, does either now cease to agitate them or agitates them but very remissly, so that till it be determined whether cold be a positive quality or but a privative it will be needless to contend what particular body ought to be esteemed the primum frigidum" (Boyle, 1999).

According to Boyle the dispute about the actual identity of the Primum Frigidum was well known among Naturalists, the various candidates being the earth, water, air, or nitre. Although there was argument about its *nature*, all agreed that there must exist a body that by its own nature was "supremely cold" and that its participation in a phenomenon led other bodies to obtain that property. Boyle believed that before arguing about the nature of the factor, scientists should first discuss (and agree) if it existed or not. According to him " it is disputable enough, whether cold be a positive quality, or a bare privation of heat, and till this question be determined, it will be somewhat improper to wrangle solicitously, which may be the Primum Frigidum. For if a Body being cold, signifies no more, then its not having its insensible parts so much agitated there will be no cause to bring in a Primum Frigidum. In the mean time, having discoursed thus long against admitting a primum frigidum, I think it not amiss to take notice once more, that my design in playing the Sceptik on this subject, is not so much to reject other men's probable opinions, of a primum frigidum, as absolutely false, as it is to give an account, why I look upon them, as doubtful."

Between 1703 and 1704 Guillaume Amontons (1663-1705) published several papers (Amontons, 1703a,b, 1704) where he reported the phenomena he had observed while studying the proper way to calibrate an air thermometer. The greatest climatic cold on the scale of units adopted by Amontons was marked 50 and the greatest summer heat 58, the value of boiling water being 73, and the zero being 51.5 units below the freezing point. He noticed that when the temperature was changed between the boiling point of water and ambient temperature, equal drops in temperature resulted in equal decreases in the pressure of theair. Since degrees in his thermometer were registered by the height of a column of mercury, "which the heat was able to sustain by the spring of the air", it followed that the extreme cold of the thermometer would be that which reduced the air to have no power of spring. In there must be a lowest temperature beyond which air, or any other substance could not be cooled. According to Amontons, this lowest temperature represented a greater cold than what we call "very cold', because his experiments showed that when the "spring of the air" (pressure) at the boiling point of water was 73 inches, the degree of heat which remained in the air when brought to the freezing point of water was still very great, for it could maintain the spring of 5.5 inches. Thus Amontons was the first to recognize that the use of air as a thermometric substance led to the inference of the existence of a zero of temperature. Extrapolation of Amonton's experiments indicated that the air would have no spring left if it were cooled below the freezing point of water, to about 2.5 times the temperature range. On the basis of the 100 degrees difference between the freezing and the boiling points of water the zero of Amonton's air thermometer would be located at –240° C.

The next reference to the existence of an absolute zero came some seventy years later when Johann Heinrich Lambert (1728-1777) repeated Amonton's experiments and endorsed his results (Lambert, 1779). Lambert's observations were made with greater care and better instruments and resulted in correcting the value of the zero of the air scale to –270°C as compared to Amonton's –240°C. Lambert remarked that the degree of temperature that was equal to zero should be called *absolute cold*; at this temperature the volume of air would be practically nothing, the particles of the air would fall together, touch each other, and become dense like water. From this Lambert inferred that the gaseous condition was caused by heat.

Joseph Black's (1728-1799) took an undefined position regarding the existence of the absolute zero. In his book *Lectures on the Elements of Chemistry* (Black, 1803) he wrote: "Weare very ignorant of the lowest possible degree or beginning of heat. Some ingenious attempts have been made to estimate what it may be, but they have not proved satisfactory. Our knowledge of the degrees of heat may be compared to what we should have of a chain, the two ends of which are hidden from us and the middle only exposed to our view. We may put distinct marks on some of the links, and number the rest according as they are nearest to or further removed from the principal links, but not knowing the distance of any links from the end of the chain we could not compare them together with respect to their distance, or say that one link was twice as far from the end of the chain as another."

Dalton, in his book *A New System of Chemical Philosophy* (Dalton, 1808), compared the abstraction of heat from a body to the emptying of a vessel; eventually the body would be exhausted of the fluid (caloric). He believed that "it was extremely important in the doctrine of heat to determine how many degrees of the ordinary scale of the temperature a body must be depressed before it would lose all its heat or become absolutely cold." Although this parameter could not be determined by direct experiment, it could be so using data on specific heat or the heat of reaction. Dalton went on to estimate the absolute zero by several methods and obtained the following results:

Method	Absolute zero, °F
Melting of ice	–1500
Mixture of sulphuric acid and water	–1500 to –6000 (depending on the dilution)
Reaction between CaO and water	–4160
Reaction between CaO and HNO_3	–11000
Combustion of hydrogen	5400
Combustion of phosphorus	5400
Combustion of charcoal	6000
Combustion of oil, wax or tallow	–6900
Combustion of ether	6000

*Below the melting point of ice.

Dalton's calculations will be illustrated with his first procedure, to exemplify the ideas prevalent at his time. He considered that at 32° C the heat capacities of ice and water were in the ratio 9 to 10 and that the heat of fusion of ice was equivalent to the amount of heat required to heat liquid water from 32° to 182°F. By performing a heat balance based on the idea that for a given amount of heat the heat capacity varied in inverse proportion to the temperature difference, he arrived at the equation

$$x = \frac{Cn}{C - c} \tag{1}$$

where C and c are the heat capacities of the hot and cold body respectively, n the change in temperature (150°F in this case), and x the number of degrees down to the absolute zero. Using the ratio $C/c = 10/9$ he obtained $x = -1500$°F.

John Leslie (1766-1832) distinguished between the three modes of heat propagation, abduction (conduction), recession (convection), and pulsation (radiation) (Leslie, 1804). He showed experimentally that the cooling power of an air stream varied with its velocity and suggested that an appropriate thermometer could be used as an anemometer. He accepted the notion of an absolute zero of temperature, which he put at –750°C.

In their memory on heat (Lavoisier and Laplace, 1780) Lavoisier and Laplace indicated that every known body contains a large amount of heat that is impossible to eliminate completely, no matter how much we reduce their temperature. Hence, zero temperature in a thermometer (they used one based on degrees Réaumur) represented still the presence of a large amount of heat and it was of interest to determine “cette chaleur commune au systeme entier des corps terrestres” (to determine this amount of heat common to all terrestrial objects).To do so it was simply enough to determine “the amount of absolute heat absorbed by a body at zero degrees that increases its temperature by one degree.” After making what Lavoisier and Laplace considered reasonable hypotheses as to the relation between specific heat and total heat they used different processes (similar to the ones used by Dalton, see table above) to calculate the position of the zero below the melting point of ice. Their results varied between 1538° to 3242° Réaumur and attributed the wide range of values to the lack of accuracy in the experimental values of the specific heats. Notwithstanding, they concluded that the absolute zero should be located at least 600° Réaumur below the freezing point.

Lavosier, in his book *Elements of Chemistry* (Lavoisier, 1789), published in 1792, went further in the direction of indefinitely lowering the zero of temperature when he stated: “When we have heated a solid body to a certain degree and have thereby caused its particles to separate from each other, if we allow the body to cool, its particles again approach each other in the same proportion in which they were separated by an increase in temperature; the body returns through the same degrees of expansion which it before extended through; and, if it be brought back to the same temperature from which we set out at the commencement of the experiment, it recovers exactly the same dimensions which it formerly occupied. But, as we are still very far from being able to arrive at the degree of absolute cold, or deprivation of all heat, being unacquainted with any degree of coldness which we cannot suppose capable of still further augmentation, it follows that we are still incapable of causing the ultimate particles of bodies to approach each other as near as it is possible and, consequently, that the particles of all bodies do not touch each other in any state hitherto known, which though a very singular conclusion, is yet impossible to be denied.”

In 1815 Gay-Lussac made a large number of observations of the cooling effect produced by the evaporation of liquids and remarked that under certain conditions the heat of vaporization would be equal to the heat transferred through the walls of the vessel (Gay-Lussac, 1822). However, if the liquid evaporated into a vacuum surrounded by a freezing mixture the cooling effect could be increased indefinitely as long as the liquid exerted an appreciable vapour pressure. Gay-Lussac reported that he had succeeded in freezing mercury by evaporating water in a vessel surrounded by a freezing mixture. Gay-Lussac had no doubt that with a volatile liquid it would be possible to obtain even lower temperatures.

According to Gay-Lussac, if the liquid evaporated in a perfectly dry gas instead of a vacuum the cooling would not be so great because the gas pressing the liquid would retard the evaporation process. The cold achievable had a maximum value corresponding to the equilibrium between the caloric (heat) absorbed by the vapour and the caloric lost by the air (A reading of the arguments given by Gay-Lussac, in modern terms, would represent what today we define as the wet-bulb temperature of air).

Gay-Lussac then proceeded to develop the following formula describing the degree of cold x (*degree de froid*) produced by evaporation:

$$P^\circ\, \delta\, \Delta H = [P - P^\circ(T)]\, (t_{air} - t)\, c \tag{2}$$

where, δ, ΔH, and c where the density, heat of vaporization, and heat capacity of the vapour at the temperature t in question, and P° *and* P the vapour pressure and the pressure, both in atmospheres.

In a second publication (Gay-Lussac, 1818)Gay-Lussac analysed the production of cold by the expansion of a gas. He realized that cooling by evaporation was limited and pointed out that the minimum temperature achieved was only –80°C. He believed that it was possible to achieve lower temperatures by using the equivalence between cooling caused by the expansion of a gas and heating caused by compression. It was known that compressing the air to one-fifth of its original volume increased the temperature 300°C and Gay-Lussac thought that the temperature might be increased to 1000°C or even 2000°C, if the process was rapid enough. If air was first compressed to five atmospheres, then allowed to cool to atmospheric temperature, and finally allowed to expand, it should absorb as much heat as was given out in its compression and its temperature should be *lowered* by 300°C. From these results he believed that "en prenant une masse d'air comprimée par cinquante, cent, etc., atmospheres, le froid produit par sa dilatation instantanée n'aura point de limit" (if we take a mass of compressed air to 50, 100, etc., atmosphères, the cold produced by its instantaneous expansion will have not limit). In other words, it would be possible to achieve unlimited cold by the expansion of gases.

Gay-Lussac concluded his paper stating: "S'il est incontestable que, par la dilatation des gaz, on peut produire un froid illimité, la determination du zéro absolu de chaleur doit paraître une question tout-à-fait chimérique" (If it is undisputable that expansion of a gas can produce an unlimited amount of cold, then the determination of the absolute zero of heat must seem a complete fantasy), agreeing with the general ideas that Lavoisier had expressed earlier.

An interesting fact is that Gay-Lussac's results were interpreted in a completely different manner by Charles-Bernard Desormes (1777-1862) and Nicolás Clément (1779-1842), who argued that they could actually be used not only to demonstrate the existence of an absolute zero but also to calculate its location. Gay-Lussac had written that the determination of the absolute zero of heat seemed a complete fantasy, but according to Désormes and Clément to support the idea of unlimited cooling, that is, that the temperature could be decreased infinitely, was the same as admitting that the quantity of heat that constitutes this temperature was infinite. If this were the case, then heat would be unlike any other measurable thing or quality.

They presented their ideas paper on the subject to the French Academy in September 1812, on occasion of the prize competition for an essay on the problem of determination of specific heats (competition that was won by Dulong and Petit). The pertinent memoir was not accepted for publication in the journal *Annales de Chimie*, but seven years later it was accepted for publication in another journal (Desormes and Clément, 1815a).

Desormes and Clément were of the opinion that the methods and arguments used by others to analyse the possibility of the existence of an absolute zero, as well as determining its position, were vitiated by the lack of enough information about the caloric and the difficulty of its measurement. For these reasons, they adopted a completely different approach: "On concevra aisément que si au lieu de vouloir estimer le calorique qui forme la température des corps, on dirige ses recherches sur celui qui n'est engage dans aucun corps, sur celui d'un espace vide d'air, tous les invonvéniens des anciennes méthodes inutilement employées disparoissent. Nous allons donc chercher à bien apprécier le calorique de l'espace. Cette connoissance nour conduira à celle du zero absolu de la température, et quand nour l'aurons fixé par cette méthode, nous le vérifierons par quelques autres moyens" (We realize that if instead of trying to determine the caloric that composes the temperature of a body we address our research to that that is not held by a body, that of an empty space, all the inconveniences of old methods disappear. We will estimate the caloric of space. This knowledge will take us to that of the absolute zero of temperature and once we have determined it by this procedure we will verify it by other methods) (Desormes and Clément, 1815a).

As will be discussed below, although Desormes and Clément relied on a hypothesis that we know today to be faulty, they were able to arrive by several different methods to a value of the absolute zero quite close to the one accepted today.

In order to determine the caloric of space Desormes and Clément utilized the well-known phenomena that air heated when it flowed suddenly into a space in which there was absolute vacuum, or it cooled when dilated. To them, these results reflected the effect of the absolute temperature of space. Caloric propagated in vacuum like magnetism and light, elimination of the air did not eliminate the caloric fluid. Thus, when air rushed into empty space its caloric joined the one present in the space and consequently, it heated up.

It was known that temperature was proportional to the amount of caloric, as long as there were no phase changes. Since caloric was an elastic fluid, it must have similar laws as a gas; one of the important properties of gases was that they expanded in vacuum at a constant velocity (417 m/s), independent of their original pressure. Consequently, their mass flow rate was proportional to their density and not to their speed, a behaviour substantially different from that of liquids, for which the density was constant under different pressures and their mass flow rate was proportional to the square root of their pressures.

Comparing the cooling of a body to the flow of caloric and the temperature to the driving force (pressure drop), meant that if we had an elastic fluid then its flow rate should be proportional to the *active temperature*, that is, to the temperature difference. This was exactly what Newton had stated, that the amount of caloric lost was proportional to the temperature difference. Another immediate consequence was that the capacity of dilated air for caloric was the mean between that of air at a high pressure and that of pure space (vacuum).

Using these ideas, Desormes and Clément performed a series of experiments to determine the absolute caloric contained in space by expanding air at atmospheric pressure into an empty vessel maintained at 12.5°C. Their results indicated that "le vide parfait à la temperature de 12.5°C contient une quantité de calorique absolu, capable d'élever de 99 ° un volume d'air atmospherique qui à 766.8 mm Hg, seroit égal à lui, et qui ne changeroit pas" (absolute vacuum at 12.5°C contains a quantity of absolute caloric able of raising by 99°C the temperature of a amount of air having the same volume at 766.8 mmHg). This result was the same for dry or humid air. When the temperature was 18°C (or 98°C) the corresponding increase in temperature was 102°C (or 152°C).

Desormes and Clément realized that the actual heating effect was lower than the maximum one because their apparatus was non adiabatic. After estimating the heat losses they concluded that under adiabatic conditions the heating effect would be 132.62°C, instead of the 99°C observed. To the credit of Desormes and Clément we must say that their estimate was very good. Using modern thermodynamics we can show that when an ideal gas is expanded into empty space, the initial stage of the expansion is adiabatic and its final temperature, T_f, is given by $T_f = \gamma\ T_i$, where T_i is the upstream temperature and g the ratio of the specific heats. For a diatomic gas like air $\gamma = 1.4$ so that $T_f = 1.4\ (12.5 + 273.15) = 285.65\ \mathrm{K} = 126.76°\mathrm{C}$.

Desormes and Clément proceeded then to determine the specific caloric of space (vacuum) at constant volume by comparing it with that of air measured at two different pressures, and using the expression

$$C' = \frac{NC + nc}{N + n} \tag{3}$$

where C and C' are the capacity of air at two different pressures, c that of space, and N and n the volumes of the air and of space, respectively. Their final result was $c = 400$, compared with 1000 for air at 18°C and 762 mmHg pressure.

It was now a question of simple proportions to determine the position of the absolute zero, since temperatures are in the inverse ratio of the capacities. Since air at 98°C had a capacity of only 870 the actual temperature increase should have been 0.870×152 = 132.24°C. The difference in temperature in the empty space (98°– 18° = 80°C) had resulted in a parallel increase of the air temperature of 132.24° −102° = 30.24°C. Consequently the zero of the absolute temperature should be at

$$t = \frac{102 \times 80}{30.24} = 269.8°\mathrm{C} \tag{4}$$

below the zero of the ordinary temperature.

Désormes and Clément also calculated the position of the absolute zero by another procedure. Gay-Lussac had determined that the coefficient of thermal expansion of air at constant pressure was 1/266.66 at 0°C and that it remained constant up to a temperature of 500°C. The value of the expansion coefficient meant that for a given volume of air at atmospheric pressure and 0°C subtraction of the quantity of heat that changed the temperature by one degree would decrease the volume of the air by 1/266.66. If Gay-Lussac's law remained constant then the limit of the reduction in volume would be at 266.66°C below zero. Below this temperature it was impossible to reduce the temperature any further and hence no further cooling was possible. Hence, 266.66°C below zero represented the absolute zero of temperature.

In a second paper (Desormes and Clément, 1815b) Désormes and Clément presented the objections that had been raised against the doctrine of absolute temperature and their refutations of the same: (a) Assumption of the existence of caloric in space free of matter (vacuum), (b) The possibility of measuring the caloric of space, and (c) The possibility of determining the absolute zero of temperature. In addition, they provided two additional procedures to determine the position of the absolute zero of temperature.

The first one was based again on Gay-Lussac's results of the value of the thermal expansion coefficient, considering this time the influence of heat on the expansive force (pressure) of a constant volume of gas: Arbitrarily we can assign the value 266.66 to the pressure existing in a fixed volume of gas at 0°C. Again, each degree of decrease in the temperature will diminish the pressure by one unit, hence the pressure of the gas will reach zero when the temperature has decreased 266.66° below the original one (0°C).

The second procedure was based on the increase of the specific heat of ice upon fusion. Desormes and Clément indicated that at 0°C the specific heat of ice was 720 (0.72) and that of liquid water 1000 (1.00). Assuming that the absolute temperature of ice melting was 266.66° if it were to pass spontaneously from solid to liquid without addition of caloric its capacity would increase from 720 to 1000 with the corresponding decrease in temperature. Again, the ratio of the new temperature to the initial one would be in an inverse ratio to their capacities, that is (266.66) (720/1000) = 192°C. The temperature had thus decreased by (266.66 – 192) = 74.66°C. In order to return the water to its original temperature would be necessary to add a quantity of heat equal to 74.66°. Since the heat of fusion has been determined experimentally to be 75°, this calculation justified the assumption that the absolute temperature of fusing ice was 266.66°C.

Location of the absolute zero

After Joule had determined the mechanical equivalent of heat, William Thomson (Lord Kelvin, 1824-1907) approached the question from an entirely different point of view and went on to devise a scale of absolute temperature, which was independent of the properties of any particular substance and was based solely on the fundamental laws of thermodynamics (Thomson, 1911).

In his groundbreaking paper on the subject (Thomson, 1911) Thomson wrote that the problem of determination of the temperature had achieved a practical solution and that thermometers were already available for accurate determinations. On the other hand, the theory of thermometry was as yet far from being in a satisfactory state: "The principle to be followed in constructing a thermometric scale might at first sight seem to be obvious, as it might appear that a perfect thermometer would indicate equal additions of heat, as corresponding to equal elevations of temperature, estimated by the numbered divisions of its scale. It is however recognized (from the variations in the specific heat of bodies) as an experimentally demonstrated fact that themometry under this condition is impossible, and we are left without any principle on which to found an absolute thermometric scale" (Thomson, 1911).

An important question was the possibility of establishing an absolute scale that was independent of the properties of any particular kind of matter. Solution of this problem would allow the exact comparison of observations made by different experimenters in various positions and circumstances. The most common scale in use was that of the air thermometer where equal absolute expansions of the mass of air or gas in the instrument, under a constant pressure, indicated equal differences of the number on the scale. In the air thermometer the length of a degree was fixed by dividing in equal steps the temperature interval between the freezing and the boiling points of water. Hence, this scale could not be considered as absolute, although the temperature measurement was very accurate.

According to Thomson, in the air thermometer *infinite* cold should correspond to a *finite number of degrees* below zero, since the graduation method would necessarily end at a point corresponding to zero air volume. Assuming 0.366 as the coefficient of expansion of the air, this point would be marked as –100/0.366 = –273°0.

Thomson approached the question of an absolute scale using the principles developed by Sadi Carnot (1796-1832) when analyzing the efficiency of a heat engine. According to Carnot's results the thermal efficiency of a reversible heat engine depended only on the quantities of heat transferred and the temperature of the hot and cold source. Since a definite system for the measurement of heat was available, this result furnished a measure for intervals according to which absolute differences of temperature could be estimated.

On this basis Thomson proposed a new temperature scale characterized by the fact that each of its degrees had the same value, that is, a unit of heat flowing from a body A at temperature T_0 of this scale, to a body B at the temperature ($T_0 - 1$) would give out the same mechanical effect, whatever the number T_0. This scale was certainly absolute since it was clearly independent of the physical properties of any specific substance. To do so is was necessary to demonstrate that Carnot's function (derivable from the properties of any substance whatever, but the same for all bodies at the same temperature), or any arbitrary function of Carnot's function, could be defined as temperature, and be therefore the foundation of an absolute system of thermometry.

Joule and Thomson showed (Joule and Thomson, 1854) that Carnot's function varied nearly in the inverse ratio of what had been called "temperature from the zero of the air thermometer", that is, the centigrade temperature of the air thermometer increased by the reciprocal of the coefficient of expansion. Thus temperature could be defined simply as the reciprocal of Carnot's function and: "If any substance whatever, subjected to a perfectly reversible cycle of operations, takes in heat only in a locality kept at a uniform temperature, and emits heat only in another locality kept at a uniform temperature, the temperature of these localities are proportional to the quantities of heat taken in or emitted at them in a complete cycle of the operations."

In order to determine the unit or degree for the numerical measurement of temperature, it was necessary to select only *one* fixed point, such as that of melting point of ice, and assign it a value of one, or any number desired, or choose *two* fixed temperatures such as that of melting ice and the normal boiling point of water, and call the difference of these temperature any number we pleased, 100 for instance. Joule and Thomson stated that in the present state of science the second choice was the only one that could be made conveniently, but that the former was far preferable and must be adopted ultimately. Adopting the second convention required knowing the exact value of the temperature of melting ice. According to Joule and Thomson the experimental data available did not enable them to assign the temperature of melting ice to perfect certainty within less that two or three-tenths of a degree, but they believed that is value was probably about 273.7°, agreeing with the value of $t = J/\mu$ at 0°C found before (where J is the mechanical equivalent of heat and μ Carnot's function).

Within the following years criticism of the convention of using a two-fixed point scale began to grow. For example, Giauque (Giauque, 1939) remarked that a two-point defined the size of the degree and thus the number of degrees between the ice point and the absolute zero. Hence, as a consequence of this procedure, the values of the ice point and the boiling point of water on the absolute scale were frequently changed, depending on the experimental observations accepted as being the more reliable. When an experiment was performed to measure a temperature by means of Kelvin's scale, the final result contained not only the experimental error of the measurement itself, but also any error, which existed in the particular value of the ice point, which had been adopted as the "best value". Giauque's point is better understood by looking at the basic equations of gas thermometry

$$T_{0°\mathrm{C}} = \frac{100}{[(PV)_T/(PV)_{0°\mathrm{C}}] - 1} \tag{5}$$

$$T = T_{0°\mathrm{C}} \frac{(PV)_T}{(PV)_{0°\mathrm{C}}} \tag{6}$$

where in each case PV is the product of gas pressure and volume corrected for gas imperfection and T is the absolute temperature.

In eq (5) the per cent error in $T_{0°\mathrm{C}}$ is 3.73 times that in the experimental ratio $(PV)_{100°\mathrm{C}}$ and this error is superimposed on the experimental error involved in the determination of the ratio $(PV)_T/(PV)_{0°\mathrm{C}}$ of eq (6).

According to Giauque the errors in temperatures on the thermodynamic scales, which have their origin in eq (5), could be eliminated by changing the two fixed points procedure used by a one-point convention, namely, by defining $T_{0°\mathrm{C}}$ as equal to a suitable number. He believed, as Joule and Kelvin had stated before, that it was unlikely that a reference point more useful and satisfactory that the ice point may be found (Giauque, 1939).

Eventually, this position was recognised as the proper one and in 1948 the *Advisory Committee on Thermometry and Calorimetry* recommended that the zero of the thermodynamic centigrade scale be defined as being 0.0100 degree below the triple point of water. The committee recognized the principle of an absolute thermodynamic scale requiring only one fixed point, which should be the triple point of pure water, for which the absolute temperature was approved in 1954 to be 273.16 K (resolution adopted in October 1954): "TheTenth General Conference on Weights and measures decides to define the thermodynamic temperature scale by means of the triple point of water as the fundamental fixed point, by assigning to it the temperature of 273.16 K exactly" (Anonymous, 1948).

On the basis of this decision the size of the degree does not alter owing to newer and better measurements; rather the boiling point of water instead of being 373.15 K by definition, may vary in the last place. Since this variation will represent at most a few parts in 37,000, it is insignificant for most purposes. Adoption of this new standard has two important advantages. Since most thermodynamic formulas involve T, any revision of the value of T_i at once necessitates small changes in every thermodynamic scale. Adoption of a fixed value for T_i eliminates this necessity. Further, on low temperature work the new scale is much preferable than the old one. Suppose an experimental temperature of –272.00°C is reported. Conversion of this to the Kelvin scale requires selection of a value for T_i. The uncertainty in ($T_i - 272.00$) may well be a hundred times as larger as that in the original number $t = -272.00$°C. The new redefined Kelvin scale avoids this difficulty.

Epilogue

In the opening paragraph we mentioned the part of the vision of the prophet Ezekiel where he described a firmament having the colour of the terrible ice. Can this be a hint that the lower temperature, the primum frigidum, is present in space? The temperature of space is a subject that has been much discussed an analysed. The French physicists of the early nineteenth century rejected the hypothesis of an absolute cold of space. For example, Joseph Fourier (1768-1830) postulated the existence of a physical effect that moderated the temperature and the heat effects observed on the surface of the earth. He identified it with the absolute cold of space; the absolute cold being the temperature that the space would achieve if the sun and all the stars ceased to exist (Fourier, 1824). Claude Pouillet (1790-1868) calculated the temperature of interplanetary space as −142° and John Herschel (1792-1891) as −150°C.

William John Macquorn Rankine (1820-1872) assumed that the interstellar medium was perfectly transparent and diathermanous, incapable of acquiring any temperature, and hence must be at the absolute zero (Nevertheless, if a thermometer would be put in space it would give a reading of 2.73 K because it is not transparent and diathermanous; it will absorb radiation from the sun and other stars, and become warmed; see below). John Henr Poynting (1852-1914) analysed the situation of a body in space heated by radiation from the sun and the stars and showed that the energy received from the sun was at least one thousand times larger than that received from the stars (Poynting, 1903). In other words, bodies in the solar system could be regarded as being situated in a zero enclosure except in so far as they received radiation from the sum. He calculated that by solar radiation alone a small absorbing sphere at the distance of Mercury from the sun would have its temperature raised to 483 K, at the distance of Venus to 358 K, of the earth to 300 K, of Mars to 243 K, and of Neptune to only 54 K. At larger distances the effective temperature of space would drop to about 10 K.

Clearly empty space does not a temperature at all, since only matter and radiation can be described by this term. It is necessary then, to talk about the temperature of objects located in space. The actual cosmos contains the red-shifted remnant of the Big Bang. When the Universe first became transparent, it emitted light like a black body with a temperature of about 3000 K. Since this beginning, the expansion of the Universe has cooled that radiation to correspond to the emission of a black body with a temperature of 2.725 K (roughly the temperature of liquid helium). This radiation is called Cosmic Microwave Background radiation (CMBR) and has a general spectrum shape very similar to that of the sun, except that it peaks at a wavelength of about 1 mm. CMBR can be interpreted as the temperature which would be reached by a body far from stars and planets, simply by cooling by the radiation of its own initial warmth, until it reached a balance between the radiation received from space and the emission due to its own temperature.

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