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Institute for Theoretical Physics University of Amsterdam: The Netherlands

Temperature as a Basic Physical Quantity

By

J. DE BOER

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With 8 Figures in the Text

Abstract

The various aspects of the concept of temperature as a basic quantity in physics are discussed. After a brief historical introduction, the thermodynamic basis of the definition of temperature is given. In § 3 the statistical definition of temperature in terms of the canonical ensemble of statistical mechanics is presented and the equivalence with the thermodynamic definition is stressed. Attention is given also to the physical meaning of negative temperatures. In § 4 the realization of the thermodynamic temperature scale based on the laws of ideal gases, ideal paramagnetic and nuclear magnetic substances and black body radiation is discussed. The international practical temperature scale is very briefly discussed in § 5. Finally in § 6 some remarks are made about the "basic" character of temperature concept and it is stressed that proposals to change the definition of this quantity have so far not offered an improvement.

1. Historical introduction

The temperature, or more precisely the "thermodynamic" temperature, is now generally accepted as one of the fundamental quantities on which are based the description of physical phenomena in terms of well defined physical quantities and also of mathematical equations expressing physical relations between these quantities. The concept of temperature is certainly a very old one and in a brief historical introduction it is tempting to go into the early history [1] starting with the first centuries A. D. and ending with the first introduction of a thermoscope based on the thermal expansion of air by GALILEO GALILEI [2] round 1600. However, this would lead us too far. After the introduction of the thermoscope as an instrument indicating the "degree of heat or cold", it still took more than a century to arrive at a more quantitative definition of the concept "temperature".

First it was necessary to obtain deeper insight into the behaviour of gases as a function of pressure, which was mainly the work of BOYLE (1662) and MARIOTTE (1679). The use of the pressure of a gas as a measure of its "temperature" was explored in particular [2] by AMANTONS (1700), who proposed the use of the pressure of a given volume of air as a measure for what we would now call the absolute temperature. He estimated that the ratio of the greatest "summer heat"

to the "greatest cold" in Paris was approximately 6:5 and expressed as his view that the lowest temperature which could exist at all, would correspond to a gas with pressure zero — really a quite remarkable and advanced feeling for the concept of absolute temperature.

Unfortunately the early definitions of temperature were not based on the thermal expansion of gases but on *thermal expansion of liquids* (alcohol, mercury). It may be sufficient to mention here the names of RØMER (1708) and FAHRENHEIT (1724 to 1726): Apparently [1] RØMER had the idea of introducing a scale with *two fixed points* at the temperatures of melting ice and human blood, and with a zero point lying below the ice point by as much as one half of the distance between the two fixed points. FAHRENHEIT then decided to follow the same principle. He divided the temperature interval between these two fixed points in 64 degrees and attached the values of 32 degrees to the ice point and 96 degrees to the "blood point" respectively. The temperature of boiling rainwater turned out to be 212 degrees on this ("FAHRENHEIT") scale. The zero point of this scale corresponded approximately to the lowest temperature known at that time. It was the Swedish astronomer CELSIUS (1742) who made another essential step with the introduction of a *centigrade scale* of 100 degrees for the temperature interval between two fixed points, for which he chose the ice point and the boiling point of water. The finishing touch apparently was given by his colleague STRÖMER who reversed the two fixed points introduced by CELSIUS and defined the ice point and boiling point of water to be 0 and 100 degrees respectively.

After the first experiments of BOYLE, MARIOTTE and AMANTONS many more experiments on the thermal expansion of gases and liquids were made. In particular the experiments of CHARLES (1787), DALTON (1801), GAY-LUSSAC (1802 to 1816) and REGNAULT led to the important conclusion that all gases had the *same thermal expansion coefficient or pressure coefficient* α . The advantage of defining a temperature scale in terms of the thermal expansion of gases was put forward in particular also by DULONG and PETIT

in a famous investigation from the year 1817; different principles could be followed [2]:

I. Temperature definition with two fixed points:

The temperature t is then defined to be *proportional to the increase in pressure* (at constant volume) $(p - p_0)/p_0 = \alpha t$. The pressure has a standard value p_0 at one fixed point, the ice point. A second fixed point is then needed to define the constant of proportionality α . Choosing the boiling point of water as the second fixed point: with a temperature $t = 100$ degrees, it turns out that $\alpha \approx 0.003661$ degree⁻¹. This completes the definition of the "Celsius temperature" in terms of the pressure coefficient or thermal expansion coefficient of gases, which turned out to be practically the same as the original definition in terms of the thermal expansion of mercury.

II. Temperature definition with one fixed point:

This second principle is due to AMANTONS [2]: the temperature T could be defined to be *proportional to the pressure* (at constant volume) of the gas: $p/p_0 \simeq T$. For the definition of this so called "absolute temperature" T only one fixed point would be needed to determine the constant of proportionality.

In fact however this simple procedure was not followed. Originally the absolute temperature was defined in terms of the Celsius temperature to be $T = \alpha^{-1} + t$, by writing: $p - p_0 = p_0 \alpha t$ in the form: $p = p_0 \alpha (\alpha^{-1} + t)$. The absolute temperature of the ice point then turns out to be $T_0 = \alpha^{-1} \approx 273.15$ degrees approximately.

III. Logarithmic temperature scale:

It may be interesting to mention still a third principle for defining the temperature which was put forward by DALTON: He proposed defining a temperature Θ such that Θ increases always by the same amount when the volume is increased in the same proportion, i.e. $\ln(v/v_0) \simeq \Theta$. Obviously a temperature so defined would be related to the present absolute temperature T by $\ln T \simeq \Theta$: the "absolute zero" $T = 0$ would go to $\Theta = -\infty$, $T = T_0$ would correspond to $\Theta = 0$ and $T = \infty$ to $\Theta = \infty$. Fortunately DALTON's proposal has not been followed but we will come back briefly on this in the next section.

The situation created by choosing for the temperature definition the principle (I), using two fixed points, was however extremely unfortunate and inconvenient. As has been indicated above this principle defines most naturally the Celsius temperature t having the values $t = 0$ °C and $t = 100$ °C at the two fixed points. The absolute temperature T is then defined in terms of the Celsius temperature to be $T = T_0 + t$ where $T_0 = \alpha^{-1}$ is a numerical value which has to be determined experimentally. The two main objections to the temperature definition based on the ice and steam points are (a) $T_0 = \alpha^{-1}$ is the key figure for the conversion from the Celsius temperature, generally used at room temperatures, to the absolute temperature, used at low temperatures, and the experimental accuracy with which its value can be determined is not better than 0.01 or 0.02 degrees. (b) The principles of thermodynamics to be presented briefly in the next section show that the more fundamental temperature concept defined in thermodynamics, the so called "thermodynamic temperature", has to be identified with the "absolute temperature"

defined by the gas thermometer and *not* with the "Celsius temperature".

The concept absolute temperature thus appears to be more fundamental than the Celsius temperature and the recently existing situation in which the absolute temperature was defined in terms of the Celsius temperature (based on two fixed points) was unsatisfactory.

Before coming to more recent developments as regards the temperature definition we turn now to the development of thermodynamics, which has led to a more fundamental approach to the temperature concept.

2. The thermodynamic definition of temperature

2.1 "Classical" thermodynamics

A very much deeper insight in the fundamental importance of the concept of temperature was obtained in the development of the theory of thermodynamics in particular by CLAUSIUS and by THOMSON, the later Lord KELVIN, round the middle of the last century. Although much of this is very well known, it is necessary to mention briefly the basic thermodynamic facts on which the present thermodynamic temperature definition is based.

In the considerations of CLAUSIUS and THOMSON leading to the second law of thermodynamics [2] a central role was played by the Carnot theorem, implying that the efficiency of a heat engine performing a reversible Carnot-cycle depends only on the two temperatures between which the Carnot-cycle operates and does not depend on the working substance. If, in particular, we consider a Carnot-cycle operating between two temperatures differing by an infinitesimal amount dT , the ratio of the infinitesimal amount of work δW , which is done by the engine performing the cycle, to the amount of heat Q which goes from higher to lower temperatures is proportional to dT :

$$\delta W/Q = \mu(T) \cdot dT \quad (1)$$

where $\mu(T)$ is a function of temperature only and, as was mentioned already, does not depend on the working substance of the Carnot-cycle.

One may also interpret this equation as representing the result of a cooling machine with a negative reversible Carnot-cycle, running in the opposite direction. δW is then the infinitesimal amount of work which is required to run the cycle which transports an amount of heat Q from a lower temperature T to a higher temperature $T + dT$ (compare Fig. 1). This interpretation expresses the so called *principle of Clausius*, which states that there exists no cyclic process that has as its only result the transfer of heat from one heat reservoir to another one at a higher temperature. A certain amount of work must be performed on the system for this purpose. In the present case the temperature difference is infinitesimal and correspondingly the amount of work to transport Q from T to $T + dT$ is also infinitesimal, proportional to dT , and given by $\delta W = Q \mu(T) dT$.

As the quantity $\mu(T)$ is *only* a function of temperature, CLAUSIUS and THOMSON realized that there existed the possibility of an independent thermodynamic definition of the temperature concept. THOMSON [3] contemplated defining a temperature Θ by taking $\mu(\Theta) \equiv 1$. In that case the equation would read

$dW = Q d\Theta$ having the simple physical meaning that in a negative Carnot process the amount of work dW needed to transport an amount of heat Q from a given temperature to a temperature which is $d\Theta$ higher, divided by that amount Q , would be simply equal to the temperature difference $d\Theta$. Joule pointed out to THOMSON [3] however that experiments on compression of air had shown that $\mu(T)$ was inversely proportional to the absolute temperature as defined by the ideal gas law. In order to make the new definition of the degree not too different from the customary definition, THOMSON therefore proposed to write $\mu(T) = 1/T$ giving

$$\boxed{dW/Q = dT/T} \quad \text{or} \quad \boxed{Q'/Q = T'/T} \quad (2)$$

where the two equations apply to a Carnot-cycle operating between an infinitesimal (dT) and a finite ($T' - T$) temperature difference respectively.

[The relation between this temperature T defined by $\mu(T) = 1/T$ and the temperature Θ obtained by

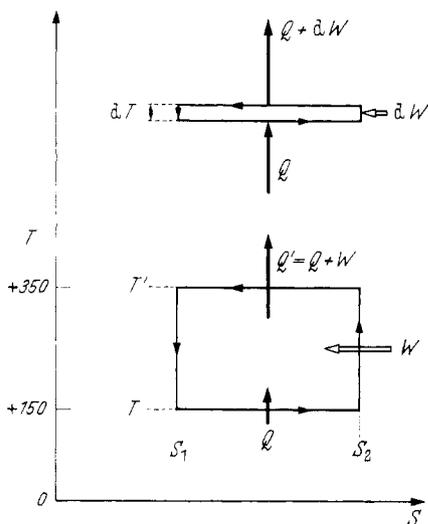


Fig. 1. Finite and infinitesimal "negative" Carnot-cycle for transfer of heat from lower to higher temperatures

$\mu(\Theta) = 1$ is: $\Theta \simeq \ln T$. The temperature Θ is essentially the temperature proposed by DALTON, discussed in the previous section: the absolute zero would be shifted to minus infinity, which in certain respects would be more logical. There is little doubt however that THOMSON's choice was the best, as will be seen in the next section where we discuss the statistical mechanics point of view.]

It can be shown quite generally, by operating the Carnot-cycle (2) with an ideal gas as working substance, that the thermodynamic temperature T is proportional to the gas thermometric absolute temperature T^* . T is defined, except for a constant of proportionality, by equation (2), and T^* is defined by the ideal gas law: $pV \simeq T^*$. Using the first law of thermodynamics $dQ = dU + pdV$ one obtains along the isotherms T^* and $T^{*'}$ in Fig. 1, because $dU = 0$:

$$Q \simeq T^* \ln(V_2/V_1) \quad Q' \simeq T^{*'} \ln(V_2'/V_1')$$

Along the adiabatics 1 and 2 one has $dQ = 0$ giving $dU/T^* \simeq dV/V$. Using the fact that for an ideal gas U is only a function of T^* one obtains

$$\ln(V_2'/V_2) = \ln(V_1'/V_1) \simeq \int_{T^*}^{T^{*'}} dU/T^*$$

Combining these two results one obtains in general $Q'/Q = T^{*'}/T^*$, showing that the gas thermometric absolute temperature and the thermodynamic temperature defined by a Carnot process are proportional to each other.

2.2 The definition of the thermodynamic temperature

The proportionality between the thermodynamic temperature and the gas thermometric absolute temperature made it possible for THOMSON, to make these two temperatures coincide by defining the thermodynamic temperature difference between the boiling point of water and the icepoint as 100 degrees exactly (as was the case for the gas thermometric absolute temperature). Although this choice was fortunate in the sense that no differences were created between the thermodynamic temperature scale and the then existing gas thermometric scale, this now takes us back to the serious disadvantages of a system based on two fixed points mentioned already at the end of section 1.

From the way in which the temperature concept is introduced in thermodynamics using eq. (2) it is obvious that a much more straightforward definition of the thermodynamic temperature would consist of attaching by definition an exact numerical value to only one carefully chosen temperature fixed point. This proposal, which was stressed by GIAUQUE in particular in the years before the war, is essentially the same as that proposed by AMANTONS [principle (II), section 1].

In 1954 the Tenth General Conference on WEIGHTS and MEASURES decided to drop the THOMSON definition and to redefine the thermodynamic temperature by founding this on one fixed point only: the thermodynamic temperature of the triple point of water was defined to be exactly 273.16 degrees Kelvin. The name "degree Kelvin" (symbol: °K) for this unit of thermodynamic temperature should underline the thermodynamic origin of this concept of temperature and its definition. The triple point of water was known to be easy to establish and highly reproducible to within much better than a millidegree and represented therefore a very good choice for this very fundamental role to define the thermodynamic temperature unit.

The icepoint was known to be located approximately 0.00993 degrees below the triple point of water. This zero-point of the Celsius temperature definition could therefore within the experimental accuracy also be redefined to be located at $T_0 = 273.15$ °K exactly, i.e. exactly 0.01 degree below the triple point.

It is obvious that according to this new definition of thermodynamic temperature the boiling point of water is not exactly 373.15 °K: at present the thermodynamic temperature of the boiling point of water is still within the experimental error of a few millidegrees equal to 373.15 °K but future measurements of increased precision might lead to results which deviate slightly from this value.

We have thus arrived at a new thermodynamic definition of the Celsius temperature, being defined as $t = T - T_0$. According to this new definition the Celsius temperature is now derived from the thermodynamic or absolute temperature by subtracting $T_0 = 273.15$ °K exactly, whereas previously on the contrary the absolute temperature was obtained

from the Celsius temperature by *adding* the experimental value of $T^\circ = \lambda^{-1}$. Through this new thermodynamic temperature definition the Celsius temperature concept has become a derived quantity of less importance than the thermodynamic temperature itself.

2.3 Axiomatic approach to thermodynamics

Before closing this section on the thermodynamic definition of the concept of temperature some remarks have to be made about the so called "*axiomatic foundation*" of thermodynamics. It is well known that the foundation of the concept of temperature on the principles of KELVIN and of CLAUSIUS has been criticized. In particular M. BORN [4] has expressed the feeling that a foundation of thermodynamics on such "new and strange concepts which are obviously borrowed from engineering" is only "unhealthy conservatism". BORN has certainly done a very good thing to draw attention to this and to stimulate his student friend, the mathematician Carathéodory, to set up a more axiomatic foundation of thermodynamics which is really more logical [5].

Carathéodory started with the equation expressing the first law of thermodynamics in differential form

$$\delta Q = dU - \delta W = dU - \sum_{\alpha} Y_{\alpha} dX_{\alpha} \quad (3)$$

expressing the fact that the heat absorbed by a system in an infinitesimal process must be equal to the increase in energy of the system minus the work done on the system. For the latter one may write quite generally: $\sum Y_{\alpha} dX_{\alpha}$ where X_{α} are the extensive "mechanical" parameters determining the state of the system and the Y_{α} are the conjugated intensive parameters which are called "generalized forces". For a homogeneous system one set of these parameter couples is given by volume and pressure: $(X, Y) = (V, -p)$. It is well known that this equation can *not* be interpreted as representing the increase dQ of a certain quantity $Q(U, X_{\alpha}, X_{\beta}, \dots)$ as a function of the infinitesimal increases of the parameters: $dU, dX_{\alpha}, dX_{\beta}, \dots$. The "heat" is no such "thermodynamic state function" (i.e. a function of the parameters which is determined by the thermodynamic state of the system) and it is for that very reason that we have written δQ and not dQ ; δQ is merely an infinitesimal amount of heat (and *not* an infinitesimal increase of a function Q). There may exist however the possibility of dividing the whole equation with a factor $\lambda(U, X_{\alpha}, X_{\beta}, \dots)$, such that

$$d\eta(U, X_{\alpha}, X_{\beta}, \dots) = \frac{1}{\lambda} dU - \sum_{\alpha} \frac{Y_{\alpha}}{\lambda} dX_{\alpha} \quad (4)$$

where now $d\eta$ has the property of being the *infinitesimal increase* of a thermodynamic state function $\eta(U, X_{\alpha}, X_{\beta}, \dots)$ expressed in terms of $dU, dX_{\alpha}, dX_{\beta}, \dots$. Carathéodory has shown that the necessary and sufficient condition that such an "integrating factor" $\lambda(U, X_{\alpha}, X_{\beta}, \dots)$ exists is the requirement that there exist in the vicinity of any given thermodynamic state other states which are *adiabatically inaccessible*. If this "principle of Carathéodory" of the adiabatic inaccessibility of certain neighbouring states is satisfied then such a state function $\eta(U, X_{\alpha}, X_{\beta}, \dots)$ exists. Although we shall not go into the complete argument here, it can be shown that this state function η has to be identical with the entropy

$S(U, X_{\alpha}, X_{\beta}, \dots)$ of the system and the quantity $\lambda = (\partial S / \partial U)_{X_{\alpha}, X_{\beta}, \dots}$ with the reciprocal thermodynamic temperature. This is expressed by:

$$dS = \frac{1}{T} dU - \sum_{\alpha} \frac{Y_{\alpha}}{T} dX_{\alpha} \quad \text{or} \quad \frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{X_{\alpha}, X_{\beta}, \dots} \quad (5)$$

It is, however, largely a matter of taste and of personal preference which method one prefers in setting up thermodynamics, particularly because of the somewhat more involved mathematics which is required to understand Carathéodory's reasoning. Personally I have the feeling that not withstanding the more beautiful and logical setup of Carathéodory's treatment, the association of the introduction of the temperature concept to a Carnot-cycle which expresses the work needed to transport heat from lower to higher temperatures also has its charms because this Carnot-cycle is a very fundamental one which brings forward one of the essential features of the concept of temperature.*

3. The statistical definition of temperature

3.1 Kinetic temperature definition

A little after the introduction of the thermodynamic definition of the temperature concept by CLAUSIUS and THOMSON in the middle of the last century, the molecular or kinetic theory of gases started to develop more rapidly, mainly as a result of the important contributions of KRÖNIG (1856) and CLAUSIUS (1857). A further important step was made by MAXWELL (1859) and BOLTZMANN (1868) who gave the well known expressions for the velocity or energy distribution of the molecules in thermal equilibrium, according to which the probability that a molecule of a system has an energy between ϵ and $\epsilon + d\epsilon$ is given by:

$$p(\epsilon) d\epsilon \simeq g(\epsilon) e^{-\epsilon/kT} d\epsilon \quad (6)$$

where $g(\epsilon) d\epsilon$ is a weight function being equal to the available phase space for a molecule with an energy between ϵ and $\epsilon + d\epsilon$. The BOLTZMANN constant k defines at every temperature T a characteristic energy of molecular size kT which determines the velocity or energy distribution of the molecules and leads to an average for the square of the velocity of the molecules given by $\langle v^2 \rangle = 3kT/m$. Comparison with the expression of CLAUSIUS for the same quantity in terms of the molar gas constant R corresponding to a molar mass M : $\langle v^2 \rangle = 3RT/M$ gave the relation $R = Nk$ between the universal gas constant R occurring in the macroscopic ideal gas law and the BOLTZMANN constant k occurring in the molecular energy distribution law.

The importance of this discovery of MAXWELL and BOLTZMANN is obvious: from then on the temperature concept, defined before in terms of thermodynamic quantities like heat and work, got an entirely new *kinetic definition* on a molecular basis. It could be interpreted as a *quantity, characterizing the energy distribution of the molecules in a system*. The kinetic theory of gases developed very rapidly and important progress was made in the last decades of the nineteenth century in explaining the macroscopic equilibrium properties, the transport properties of gases and

* In a recent paper LANDSBERG [25] and TITULAER and VAN KAMPEN [26] have proved that Carathéodory's principle can be deduced entirely from KELVIN's principle.

the approach to equilibrium in terms of the molecular theories of MAXWELL and BOLTZMANN. However, the theory was seriously limited by the fact that it could be applied only to systems of *independent*, non-interacting particles, i.e. in practice only to gases. Obviously this also restricted very much the area of validity of this kinetic definition of temperature and it could not be expected that on this basis the kinetic definition could ever compete with the thermodynamic definition given in section 2, which is quite general and applicable to arbitrary systems.

3.2 Temperature definition of statistical mechanics

An entirely new development initiated however from the development of the so called "statistical mechanics" by BOLTZMANN and by GIBBS (1902). Instead of considering the distribution of single molecules or particles over various states, GIBBS considered the distribution of a *whole system* of N molecules dash gas, liquid or solid dash over the various states of the system. For such a system in thermal equilibrium he introduced for the probability $P(E) dE$ of

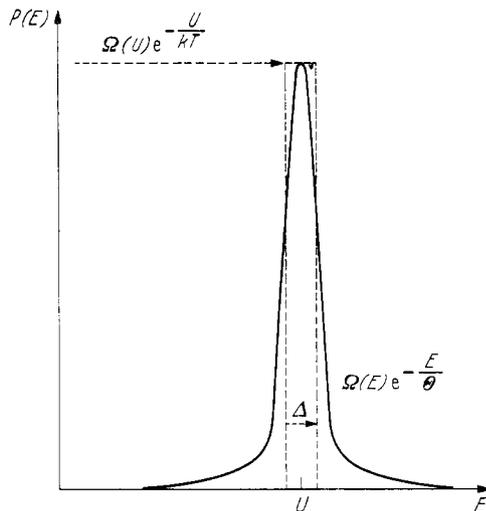


Fig. 2. Canonical probability distribution over various energies; — indicates the approximation of this distribution function by a rectangle

finding the system with total energy between E and $E + dE$, the following "canonical" probability distribution law:

$$P(E) dE \approx \Omega(E) e^{-E/\Theta} dE \quad (7)$$

Here $\Omega(E) dE$ is the available phase space for the whole N -particle system between E and $E + dE$, or in quantum language: the number of accessible states between E and $E + dE$, this being the phase space divided by h^{3N} . This number of accessible states increases rapidly with E (e.g. for an ideal gas $\approx E^{3N/2}$).

The second factor $\exp(-E/\Theta)$ is a rapidly decreasing function of E . The characteristic parameter Θ , determines essentially the speed of decrease of this function. The product of these two factors thus leads to a sharp maximum (see Fig. 2) at an energy E for which:

$$U = E_{\max} \quad \Omega^{-1} (d\Omega/dE)_{E_{\max}} = 1/\Theta \quad (8)$$

The larger Θ is, the larger the value $E_{\max} = U$ where the maximum occurs. This energy is identified with the *thermodynamic energy* of the system.

One may introduce now an *effective number of states* $W(U)$, which essentially counts the states which contribute to a distribution corresponding to the parameter Θ :

$$\int_0^\infty \Omega(E) e^{-E/\Theta} dE = W(U) \cdot e^{-U/\Theta} \quad (9)$$

This amounts essentially to replacing the curve in Fig. 2 by a "microcanonical" distribution, i.e. by a rectangle. Approximating the canonical distribution curve in the top by a GAUSSIAN curve gives:

$$W(U) = \Omega(U) \cdot \Delta \quad \Delta = \Theta (d\Omega/d\Theta)^{1/2} \sqrt{2\pi} \approx \Theta \sqrt{N} \quad (10)$$

The effective width Δ thus turns out to be proportional to Θ . The logarithm of this effective number of accessible states has to be identified with the *thermodynamic entropy of the system*:

$$S(U) = k \ln W(U) \quad (11)$$

This relation is often quoted as the "BOLTZMANN relation" between the entropy $S(U)$ and the effective number of states $W(U)$. It is obvious that both the entropy (11) and the energy (8) are increasing functions of the parameter Θ , determining the distribution. Comparison of (8) and (11) shows that

$$\frac{dS}{dU} = k \frac{d \ln W}{dU} = k \frac{d \ln \Omega}{dU} = \frac{k}{\Theta} \quad (12)$$

Thermodynamics shows however that $dS/dU = 1/T$. It is thus possible to make the following identification:

$$\Theta = kT \quad (13)$$

The parameter Θ , characterizing the canonical distribution of Gibbs, is thus identical with kT , where T is the thermodynamic temperature of the system. This important result thus gives the molecular interpretation of the thermodynamic temperature T as being essentially the distribution parameter Θ in the canonical distribution law for the total energy of a system in the thermal equilibrium. This statistical mechanical interpretation of the temperature is quite generally valid, for all systems in thermal equilibrium, at all temperatures and for classical as well as for quantum mechanics. It serves as a completely general molecular counter part of the thermodynamic definition. The identity between the two definitions follows from relation (12). The statistical mechanical concepts and the thermodynamical ones are linked together by BOLTZMANN'S constant k !

3.3 Negative temperatures

The previous section has shown that in statistical mechanics the temperature is essentially introduced as a parameter $\Theta = kT$ in the canonical distribution law for the states of the system. The question arises whether negative values of Θ make sense and have any physical meaning. Obviously negative values of Θ would lead to a distribution function $P(E) \approx \Omega(E) \cdot \exp(-E/\Theta)$ which goes to infinity for $E \rightarrow \infty$ and which therefore could not be normalized in the case of systems for which the energy has no upper bound. Therefore in a gas or liquid or in a system like that of the thermal lattice motions of a crystal for which there is no upper limit of the kinetic energy, negative

temperatures make no sense and cannot exist. For systems however for which an upper limit for the energy exists, there is no objection in principle to considering also negative values of Θ , or $T = \Theta/k$. An example of a system in which this condition is satisfied is the system of paramagnetic spins or nuclear magnetic spins of a magnetic substance. The upper and lower bound for such a system in a magnetic field H is given by $\pm M \cdot H$ (where M is the magnetization) so that this basic requirement is fulfilled.

A second necessary requirement is of course that there exists temperature equilibrium in the system. However for the lattice waves of the magnetic substance negative temperatures are impossible, and so we have to look for situations where the spin system itself is in thermal equilibrium but where the spin system is not in equilibrium with the lattice. This condition is actually satisfied for some dilute paramagnetic salts and for nuclear magnetic substances: the internal thermal equilibrium is reached in a time ($10^{-8} - 10^{-5}$ second) which is very much shorter than the relaxation time for the spin-lattice thermal equilibrium, which at low temperatures may be of the order of minutes or more. The concept of an independent temperature for the spin system has been introduced by CASIMIR and DU PRÉ [6] in their theory of paramagnetic relaxation phenomena and by BROER [7] and BLOEMBERGEN [8] for the nuclear spin system. POUND, PURCELL and RAMSEY [9] studied in particular situations in the nuclear spin system which correspond to negative temperatures, while many general aspects have been discussed by RAMSAY [10] and ABRAGAM [11]. Because of its great interest a few general remarks on negative temperatures will be made in this article.

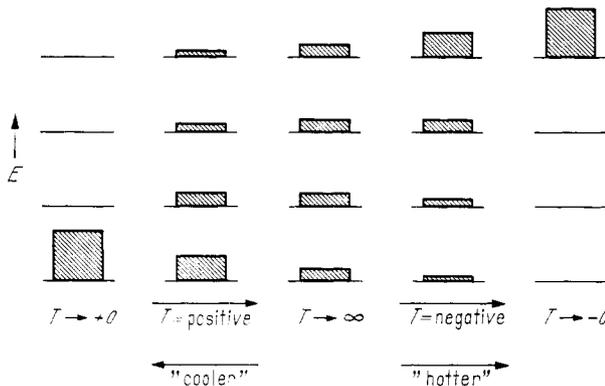


Fig. 3. Population of 4 equidistant spin levels at various positive and negative temperatures

In Fig. 3 we give the populations of a spin system in the various spin levels for set of temperatures ranging from positive to negative T . It is then clear that according to this sequence negative temperatures really correspond to situations which link up much better to the infinitely high positive temperatures $T \rightarrow \infty$ than to $T = 0$: negative temperatures are "hotter" than positive temperatures. We will therefore follow the now generally adopted practice of using the sequence $T = +0 \dots +\infty, -\infty \dots -0$, which corresponds to the values of $-1/T$ ranging from $-\infty \dots 0 \dots +\infty -\infty \dots 0 \dots +\infty$.

As an example we give in Fig. 4 the entropy and the energy for a system of N magnetic spins distrib-

uted over 4 equidistant levels:

$$\frac{3}{2}w, \frac{1}{2}w, -\frac{1}{2}w, -\frac{3}{2}w$$

where $w = \mu H$. The minimum energy $U = -\frac{3}{2}N \cdot w$ corresponds to all magnetic moments directed in the direction of H and at $U = +\frac{3}{2}N \cdot w$ all magnetic moments are opposite. These two completely ordered states both have an entropy $S = 0$ and correspond respectively to $T \rightarrow +0$ and $T \rightarrow -0$ respectively. On the other hand the state of maximum entropy occurs at $T \rightarrow \infty$, corresponding to $-w/kT \rightarrow 0$. In the same figure is also given the entropy versus energy, curve, symmetrical round $U = 0$, $S = \text{maximum}$, which is related to the temperature by the thermodynamic relation: $\partial S/\partial U = 1/T$.

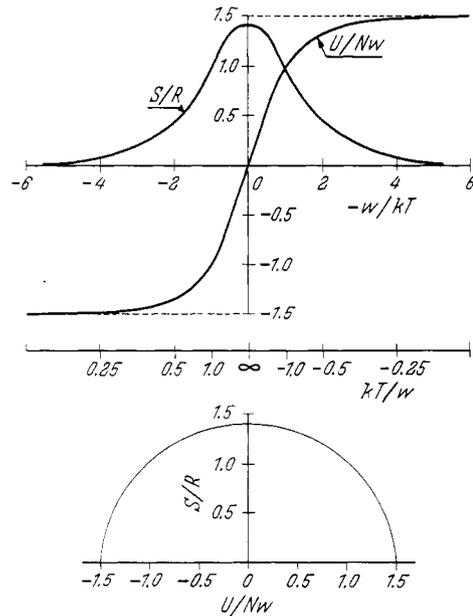


Fig. 4. Entropy and energy of N magnetic spins distributed over 4 equidistant levels; $w = \mu H$, taken from RAMSEY [10]

It is possible to extend thermodynamics so as to include also negative temperatures. If temperatures are ordered according to the order of $-1/T$ heat energy appears to flow always from the "hotter" to the "cooler" system if they are brought in thermal contact with each other. The first law of thermodynamics obviously holds quite generally, because it is the energy conservation law. As regards the second law it should be noted that in agreement with the picture of Fig. 4 supply of heat to a system at negative temperatures increases the energy but decreases the entropy, because the proportionality factor $1/T$ in $dS = \delta Q/T$ is negative. Irreversible flow of heat from a "hotter" system to a "cooler" system at negative temperatures is however again connected with an increase in entropy, as in the normal case. The principle of CLAUSIUS formulated in the form: "There exists no cyclic process that will produce no other effect than transfer of heat from a cooler to a hotter reservoir", is generally valid for positive as well as for negative temperatures. The difference between the two cases being that at positive temperatures work is converted into heat which is also delivered at the higher temperature, whereas at negative temperatures, as is shown in Fig. 5, part of the heat extracted from the cooler reservoir is converted into work. The

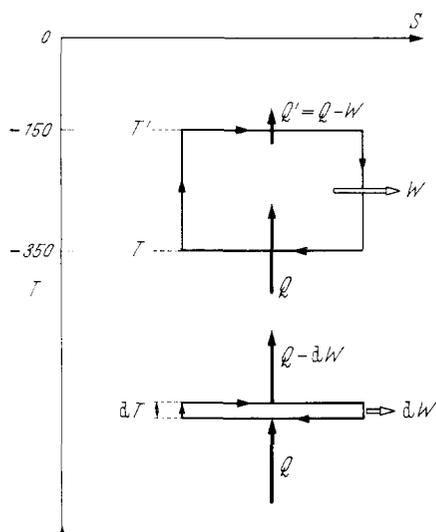


Fig. 5. Finite and infinitesimal Carnot-cycle for transfer of heat from cooler to hotter temperatures at negative temperatures

concept of negative temperature thus represents a useful extension of the ordinary temperature concept, but for a more complete discussion of all its properties we have to refer to the literature quoted above [10].

4. Realization of the thermodynamic temperature scale

4.1 Gasthermometry

As was mentioned in section 1, the definition of temperature was based originally on the Boyle-Gay-Lussac's law for an ideal gas $pV_m = RT^*$ where we have provided the temperature with an asterisk because this temperature T^* should be distinguished from the thermodynamic temperature T . One method of making this identification $T^* = T$ is by making a Carnot-cycle with an ideal gas as a working substance (comp. section 2.1). However a more satisfactory argument is the possibility of deriving the following power series expansion for real gases from statistical mechanics:

$$pV_m = RT [1 + B/V_m + C/V_m^2 + \dots] \quad (14)$$

where $R = Nk$ and the virial coefficients $B(T)$, $C(T)$, etc. are theoretically known functions of temperature. Here T is the thermodynamic temperature occurring in the canonical distribution law of statistical mechanics. For the limit of low densities (large molar volume V_m) the series approaches the ideal gas limit, but in a case for which corrections for non ideality have to be made one can make use either of known experimental values for these coefficients $B(T)$ and $C(T)$ or rely upon theoretical calculations. Consequently the temperature T occurring in $pV_m = RT$ is identical with the thermodynamic temperature.

Gas thermometers are now available in various laboratories and are used up to the high temperature region of the freezing point of gold at 1336 °K to establish the thermodynamic temperature scale. For further discussion however we refer to the literature.

A method which is based on a similar series expansion is the "dynamical method" based on the determination of the velocity of sound [12]. This approaches at low densities the value: $c_0^2 = RT (c_p/c_v)_{p=0}$, which again depends only on the thermodynamic temperature T . At present however this method [13] cannot yet compete with the more accurate gas thermometric methods.

4.2 Paramagnetic temperature scale

At low temperatures it becomes more and more difficult to use the gas thermometer for the realization of the thermodynamic temperature scale. A new possibility here however is to determine the temperature by measuring paramagnetic susceptibility. The analogue of the ideal gas law for a system of non-interacting paramagnetic ions is given by CURIE's law for the magnetic susceptibility $\chi = C/T$, where the $C = n\mu^2/3k$ is the Curie constant. As this law can be derived for a system of non-interacting ions from statistical mechanics there is no doubt that T is the thermodynamic temperature: measurement of the susceptibility of such a paramagnetic salt may therefore be used to determine the thermodynamic temperature of the system. The constant C can then be calibrated at somewhat higher temperatures where non-magnetic methods are available for the temperature determination: the susceptibility of the magnetic substance then provides us with the "magnetic" temperature $T^\oplus = C/\chi$ in the unknown region of low temperatures. The sign \oplus refers to the fact that correction to a spherical sample has been made, taking into account demagnetisation effects.

Selected dilute paramagnetic salts like chromic potassium alum or cerium magnesium nitrate [$\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$], because of the relatively large mutual distance at which the ions are situated, follow CURIE's law down to temperatures of about 1 °K, which makes it possible to identify the obtained magnetic temperatures T^\oplus with the thermodynamic temperature T of the system down to that temperature. At lower temperatures deviations occur which are due to the splitting of the energy levels of the paramagnetic ion caused by the electric crystalline field from the surrounding ions and water molecules and the magnetic interaction with other paramagnetic ions. CURIE's law can then be replaced by a series expansion of the form

$$\chi = \frac{C}{T} [1 + \frac{C_1}{T} + \frac{C_2}{T^2} + \dots] \quad (15)$$

or in many cases by CURIE-WEISS' law:

$$\chi = \frac{C}{T + \Theta} \quad (16)$$

where C_1 , C_2 , ... and Θ are constants. The main difficulty of using the magnetic temperature scale is the fact that usually theoretical calculations are not accurate enough to make completely reliable calculations of the coefficients C_1 , C_2 , ... or Θ as would be required if expressions like (16) were to be used for determining the temperature T from the susceptibility χ alone.

In order to solve this difficulty we go back to the fundamental thermodynamic law relating the thermodynamic temperature to the energy and entropy of the system. In zero field this law can be written as:

$$T = \left(\frac{\partial U}{\partial S} \right)_{H=0} = \frac{(\partial U / \partial T^\oplus)_{H=0}}{(\partial S / \partial T^\oplus)_{H=0}} \quad (17)$$

The denominator can be obtained directly from the empirical results $S = S(T^\oplus)$ of the adiabatic demagnetization experiments, whereas in the numerator $U(T^\oplus)$ has to be determined from a caloric measurement. The temperature determination thus requires here two sets of measurements which will be discussed very briefly.

The *adiabatic demagnetization* starts at a temperature in the liquid helium region, where the thermodynamic temperature is known. The amount of entropy which is squeezed out of the sample at the initial temperature $T_i = T_i^\oplus$ when a magnetic field H_i is applied, is obtained from thermodynamics and the known magnetic equation of state at T_i . Adiabatic demagnetization for various fields $H_i = H_1, H_2, \dots$ then gives a series of final magnetic temperatures $T_f^\oplus = T_1^\oplus, T_2^\oplus, \dots$ which still depend slightly on the final magnetic field

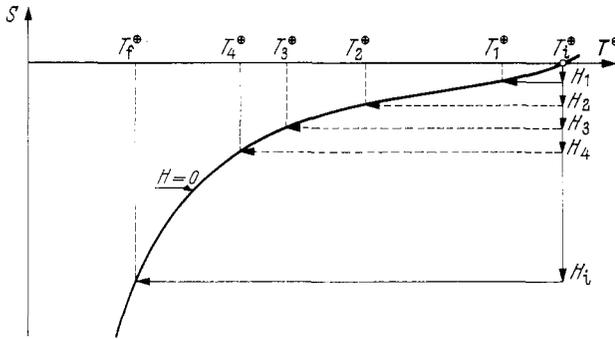


Fig. 6. $S - T$ diagram indicating adiabatic demagnetization experiments from various initial fields $H_1, H_2, H_3, H_4, \dots, H_i$ at the initial temperature T_i to $H = 0$.

H_f required for the susceptibility measurement. Extrapolation to $H_f = 0$ for various initial fields (or entropies) then provides us with the required $T^\oplus(S)$ - or $S(T^\oplus)$ relation.

Independent *caloric measurements*, providing the paramagnetic salt with a known uniform supply of energy in the form of alternating current losses or of röntgen- or gamma radiation, then gives also the energy $U(T^\oplus)$ as a function of T^\oplus .

It has to be mentioned that an independent caloric measurement is *not* essential: Integration of the

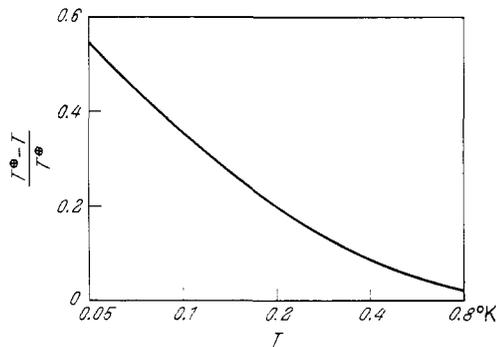


Fig. 7. Relative difference between magnetic temperature T^\oplus and thermodynamic temperature T as a function of temperature (logarithmic scale) obtained by paramagnetic demagnetization of ferric ammonium alum by COOKE, MEYER and WOLF [16]

thermodynamic expression $dU = T dS - M dH$ along an isentropic shows that the energy U can be obtained as function of S and H by integration from magnetic measurements alone, as was stressed in particular by GLAUQUE [17], but it seems that the caloric method is more accurate for the temperature determination [18].

Using these methods the temperature scale has been extended from the liquid helium region into the millidegree region. Cerium magnesium nitrate, which follows CURIE's law down to 0.01 °K, seems to be one of the best paramagnetic salts to be used for low

temperature thermometry. For a full discussion we refer however to review articles e.g. those given by AMBLER and HUDSON [14] and by VAN DIJK [15]. As an example for the magnitude of the deviations from CURIE's law and thus for the differences between T^\oplus and T we give in Fig. 7 the values of $(T^\oplus - T)/T^\oplus$ plotted as function of T for ferric ammonium alum, as given by COOKE, MEYER and WOLF [16].

4.3 Nuclear magnetic temperature scale

The lowest temperatures which can be obtained by paramagnetic demagnetization experiments are essentially limited by the level splitting and paramagnetic interaction: this is expressed by the well known formula for the final temperature: $T_f = H_{eff} T_i / H_i$ where H_{eff} is some effective internal field which, following ABRAGAM and PROCTOR [11], characterizes the strength of these limiting interactions. Even for cerium magnesium nitrate H_{eff} is still 40 oersted and it is not very probable that the interaction can be reduced very much more except of course by further diluting the substance, i.e. by replacing paramagnetic by diamagnetic ions. Then however also the entropy drop is reduced in the same ratio, which effects seriously the cooling capacity of the system. The system of *nuclear magnetic moments* however, which are about 1000 times smaller than atomic magnetic moments and which therefore have a very much smaller interaction, has for that reason become a new tool for bringing the temperature further down to the region of $10^{-5} - 10^{-6}$ °K.

It is not the purpose of this very brief survey to review or even to mention all the problems related to nuclear demagnetization experiments [19]. It is only the intention to mention some of the aspects which have a bearing on the concept of temperature as such. It is well known that one of the main problems in this

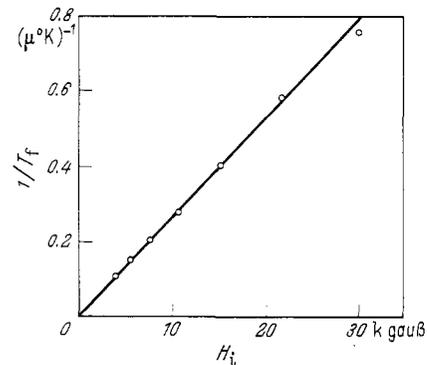


Fig. 8. Temperatures in the microdegree region obtained with nuclear spin demagnetization of copper by KÜRTI and HOBDENS [22]

region of very low temperatures is the thermal contact between the spin system used for the temperature determination and the lattice vibrations of the substance itself. Already, in the case of the paramagnetic ion spins, paramagnetic relaxation phenomena [20] show that the establishment of thermal equilibrium in the spin system goes very much faster (relaxation times of the order of 10^{-9} s) than that between spin and lattice ($10^{-5} - 10^{-2}$ s). For the nuclear spin system the nuclear spin-lattice relaxation time becomes very large: in the case of dielectric crystals the nuclear spin-lattice relaxation time becomes even too

long to allow the entropy to be squeezed out of the sample in a reasonable time at the initial temperature (0.01 °K) of the nuclear demagnetization experiment. For metals, however, energy transfer from the nuclear spin system to the conduction electrons is somewhat easier: the relaxation times are [21] of the order 10 – 100 seconds. For its intrinsic interest we give in Fig. 8 the results obtained by KÜRTI and HOB DEN [22] with nuclear demagnetisation of copper, starting at an initial temperature $T_i = 0.012$ °K and various initial magnetic fields H_i , giving at the highest values of H_i final temperatures $T_f \approx 1.2 \times 10^{-6}$ °K.

4.4 High temperatures

After the excursion to the region of very low temperatures in the previous section we now turn to the region of high temperatures; temperatures of 1500 °K up to 10000 °K and more. In this temperature region gas thermodynamic methods become impossible to use and independent methods based on the radiation emitted or absorbed by hot substances or plasma's can serve to define the thermodynamic temperature for such systems in agreement with the principles of statistical mechanics. Only two methods will be mentioned very briefly based on:

a) radiation of a black radiator

b) intensity distribution in rotational vibrational or electronic spectra and line broadening of spectral lines.

a) *Black-body radiation*: The energy density of the radiation in a cavity which is in equilibrium with a surrounding body of thermodynamic temperature T is given by STEFAN-BOLTZMANN's law:

$$w = (4\sigma/c) T^4 \quad (18)$$

where $\sigma = 2\pi^5 k^4/15 c^2 h^3 = 5.6697 \times 10^{-8}$ W. m⁻². °K⁻⁴ is the radiation constant of STEFAN-BOLTZMANN. The spectral concentration of the energy density, giving the distribution function for this radiation over the various wavelengths λ is given by PLANCK's distribution function:

$$w = \int w_\lambda d\lambda \quad w_\lambda = \frac{8\pi h c}{\lambda^5} \frac{1}{\exp(hc/\lambda kT) - 1} \quad (19)$$

Usually these two radiation laws are formulated in terms of the radiant emittance M of a black body, which is related to the radiation density by $M = (c/4) w$, $M_\lambda = (c/4) w_\lambda$, giving:

$$M = \sigma T^4 \quad (20)$$

$$M_\lambda = \frac{c_1}{\lambda^5} \frac{1}{\exp(c_2/\lambda T) - 1} \quad (21)$$

where $c_1 = 2\pi hc = 3.7405 \times 10^{-16}$ W.m² and $c_2 = hc/k = 1.43879 \times 10^{-2}$ m.°K are the two radiation constants of Planck. The maximum of this distribution function occurs at:

$$\lambda_{\max} = \frac{1}{4.9656} c_2/T \quad (22)$$

In principle all three expressions (20), (21) and (22) can be used to determine the temperatures of a black radiator, but only the spectral concentration of the radiant emittance M_λ appears to be useful for thermometry. Absolute measurements however are not very accurate and therefore the values of $M_\lambda(\lambda, T)$ are compared to the value at the same λ but at some

standard temperature [e.g. the absolute temperature of the gold-point T_{Au}] which should be determined by other methods. One then obtains:

$$\frac{M_\lambda(\lambda, T)}{M_\lambda(\lambda, T_{Au})} = \frac{\exp(c_2/\lambda T_{Au}) - 1}{\exp(c_2/\lambda T) - 1} \quad (23)$$

This is actually the procedure followed for the definition of the International Practical Temperature Scale (see section 5). The International Practical Temperature Scale (1948) defines: $t_{Au} = 1063$ °C (corresponding to $T = 1336.15$ °K) as determined by gasthermometry. For details we refer to the literature [23]. See also Tab. 1 sect. 5.

b) *Intensity distribution in spectra and line broadening*: This method [24] which is useful for temperature determinations in hot gases, flames etc., is based on the MAXWELL-BOLTZMANN energy distribution law (6) for excited states corresponding to rotational, vibrational or electronic excitation. This law is applicable in these cases because the molecules of a dilute gas are essentially free. The number density of molecules in a particular excited state i with energy ϵ_i is given by

$$n_i \approx g_i e^{-\epsilon_i/kT} \quad (24)$$

where g_i is the statistical weight or quantum mechanical degeneracy of the state i and T is the thermodynamic temperature of the gas. Usually the temperature equilibrium which must exist, so as to allow us to use the MAXWELL-BOLTZMANN distribution law, is only local equilibrium but this is no objection to the applicability of (24). The intensity of a spectral line corresponding to the transition $i \rightarrow j$ is proportional to n_i and to the transition probability giving

$$I_{i \rightarrow j} \approx A_{i \rightarrow j} g_i e^{-\epsilon_i/kT} \quad (25)$$

Plotting $\ln(I_{i \rightarrow j}/A_{i \rightarrow j} g_i)$ for various spectral lines as function of the energy ϵ_i of the initial state thus should give a straight line, the slope of which determines the temperature T . The presence of a straight line is also an indication of the existence of local thermal equilibrium, although this is not necessarily true. It is obviously impossible in this article to make more than these brief remarks. Further discussion of this enormous field of spectroscopic temperature determinations must be left to specialist articles.

The determination of the line profiles is also an extremely important indication for the temperature of plasmas. The well known Doppler broadening due to the Maxwellian velocity distribution of the emitting particles gives rise to a Gaussian line broadening but usually the situation is much more complicated because of stark effects, natural broadening, impact broadening and other sources of line broadening. This complicates the situation very much and a theoretical analysis based on statistical mechanics or kinetic theory is needed to arrive at a temperature determination from such line profile measurements. For further information about temperature measurements in plasmas over 100000° K by spectroscopic methods we refer to several articles in "Temperature; Its Measurement and Control in Science and Industry" III (1962).

5. The International Practical Temperature Scale

This article was intended to present a brief summary of the principles on which the thermodynamic temperature is based: the principles of thermodynamics and of statistical mechanics and the various realiza-

tions of this thermodynamic temperature with gas thermometry in the "normal" temperature region, with the paramagnetic- and nuclear magnetic methods at low and very low temperatures, and finally with spectroscopic and radiation methods at high temperatures. One might call these methods "fundamental" because they are based on systems for which direct application of the principles of statistical mechanics is possible and which therefore guarantee that any temperature so defined is identical with the corresponding statistical mechanical and the thermodynamic temperature.

However these "fundamental" determinations, in particular for instance the gas thermometric methods, are rather laborious and not very practical. In order to establish a more convenient method for *practical temperature determinations* the Seventh General Conference on WEIGHTS and MEASURES in 1927 adopted a system for practical, convenient, accurate and reproducible temperature measurements. These are based on a number of fixed points and well defined expressions which establish a relation between temperature and the indications of certain physical instruments calibrated at these fixed points. This system for practical temperature determinations was named the *1927-International Temperature Scale*. It was intended to be as close as possible to the thermodynamic temperature scale for which it was considered to be a practical and convenient substitute.

The basic requirement for this International Temperature should be that it reproduces as accurately as possible the thermodynamic temperature. Some laboratories which have the experience and are equipped with the necessary instruments to make fundamental comparisons between the thermodynamic temperature scale and the international temperature scale are continuously doing research to improve the international temperature scale and to bring it up to date. This led to a first revision: the *1948-International Temperature Scale* and a second revision, mainly of the text but also with some significant changes, adopted by the Eleventh General Conference in 1960. It was then also decided to change the name into: *International Practical Temperature Scale* (to be quoted here as IPTS). The word "Practical" was included to avoid confusion, the adjective "International" might give the *wrong* impression that this IPTS forms part of the International System adopted by the General Conference; it is however the *thermodynamic temperature with the unit degree Kelvin* which is the basic quantity and unit for temperature in the International System; the International Practical Temperature Scale is only an internationally adopted *practical* temperature definition which may be used for convenience and which is as close as possible to the truly fundamental thermodynamic temperature.

It would be impossible also to give in this article a full discussion of the definition of the IPTS. There will be many occasions where articles in this journal will treat various aspects of it and new proposals for its revision. We therefore give only very briefly the present situation in the form of Tab. 1 which may be

Table 1

Temperature interval — Primary fixed points	Definition of International Practical Temperature
$t > 1063\text{ }^\circ\text{C}$ $t_{\text{Au}} = 1063\text{ }^\circ\text{C}$	<i>Radiation temperature definition</i> based on relative radiance: $\frac{L(t)}{L(t_{\text{Au}})} = \frac{\exp [c_2/\lambda (T_0 + t_{\text{Au}})] - 1}{\exp [c_2/\lambda (T_0 + t)] - 1}$ $c_2 = 0.01438\text{ m. }^\circ\text{K}^2$ $T_0 = 273.15\text{ }^\circ\text{K}$
$630.5\text{ }^\circ\text{C} < t < 1063\text{ }^\circ\text{C}$ $t_{\text{Au}} = 1063\text{ }^\circ\text{C}$ $t_{\text{Ag}} = 960.8\text{ }^\circ\text{C}$	<i>Thermocouple</i> ; electromotive force $E(t) = a + bt + ct^2$, calibration at: t_{Au} , t_{Ag} and $630.5\text{ }^\circ\text{C}$
$0\text{ }^\circ\text{C} < t < 630.5\text{ }^\circ\text{C}$ $t_{\text{S}} = 444.6\text{ }^\circ\text{C} \dagger$ $t_{100} = 100\text{ }^\circ\text{C}$ $t_{\text{tr}} = 0.01\text{ }^\circ\text{C}$	<i>Platinum thermometer</i> ; resistance $R(t) = R_0(1 + At + Bt^2)$, calibration at: t_{tr} , t_{100} , t_{S} . \dagger \dagger Recomm. 1960 to use: $t_{\text{zn}} = 419.505\text{ }^\circ\text{C}$ Condition: $R(t_{100})/R_0 \geq 1.3920$
$-182.97\text{ }^\circ\text{C} < t < 0\text{ }^\circ\text{C}$ $t_{\text{O}_2} = -182.97\text{ }^\circ\text{C}$	<i>Platinum thermometer</i> ; resistance $R(t) = R_0[1 + At + Bt^2 + C(t - 100)t^3]$, calibration of R_0 , A , B as above, determination of C using: t_{O_2}

the best way to give an impression of the construction of the International Practical Temperature Scale of 1948 as revised in 1960.

In 1964 the Consultative Committee on Thermometry worked out plans for modifications and extension of the International Practical Temperature Scale probably in 1967 or 1968. As these proposals will be discussed separately in Metrologia they need not be

Table 2

$0.5\text{ }^\circ\text{K} < T < 5.3\text{ }^\circ\text{K}$	<i>Liquid ^4He vapour pressure</i> based on table T versus p (Proc. Verb. Com. Cons. Therm. 1958, p T 192)
$0.2\text{ }^\circ\text{K} < T < 3.3\text{ }^\circ\text{K}$	<i>Liquid ^3He vapour pressure</i> based on table T versus p (Proc. Verb. Com. Cons. Therm. 1962, p T 188)

mentioned here in further detail. We only wish to give the principles of the ^4He and ^3He temperature scale recommended for general use in 1958 and 1962 respectively:

This will also be included in the future extension of the definition of the International Practical Temperature scale.

6. Final remarks

In the title of this article: Temperature as a basic physical quantity, the words "basic physical quantity" were added so as to stress the very special role which temperature plays, together with such other basic quantities as length, time, mass and electric current intensity in the whole assembly of all physical quantities in terms of which physical phenomena are described. These basic quantities are called "*basic*" in the sense that all the other quantities, such as velocity, force, energy, electric field strength, etc. can

be defined in terms of these basic quantities alone. Therefore these other quantities are usually called "derived" quantities.

From a purely theoretical point of view the question which quantities are labelled "basic" is largely a matter of taste, the requirement (I) being that the basic quantities are *independent*, i.e. that all other, derived quantities can be expressed in one and only one way in terms of the basic quantities. Often one adds the requirement (II) that, in such an expression in terms of the basic quantities, integral power exponents are necessary.

A well known example is the set of three basic quantities length, time and mass, which fulfils in the field of mechanics and electricity the requirement (I), but not the requirement (II): $\text{charge} = \text{mass}^{\frac{1}{2}} \times \text{length}^{\frac{3}{2}} / \text{time}$. Requirements (I) and (II) fix the number of basic quantities to three for mechanics alone, and to four when also the field of electricity and magnetism is included: the generally accepted choice for the basic quantities being length, time, mass and electric current intensity.

When thermodynamics is added as one of the disciplines, needed in particular for the description of all thermal phenomena, *two new quantities* are added: the *temperature* and the *entropy*. The fact that two new quantities have to be introduced in this case is just the difficulty leading to so many discussions and attempts at an "axiomatic" formulation of the set up of thermodynamics! These two new quantities are related only by *one* equation $dQ = T dS$ to the quantity heat Q , which is itself defined to be an energy by the first law of thermodynamics. Therefore one of the two quantities S or T (and the usual choice is the *thermodynamic temperature* T) has to be chosen as a basic quantity. The entropy S is then a derived quantity defined by $dS = dQ/T$, i.e. heat energy/temperature.

The definition of a basic quantity is always established by choosing arbitrarily for this quantity a particular situation or state or one particular sample, to which is attached by definition a particular exact numerical value for this quantity. This then defines the "unit" of this basic quantity. For instance the wavelength of the transition $2p_{10} - 5d_8$ in 86 Kr is defined to be (1/1650 763.73) meters exactly, which defines the meter as exactly 1650 763.73 times this particular wavelength. Similarly the thermodynamic temperature of the triple point of water is defined to be 273.16 degrees Kelvin exactly, which defines the degree Kelvin as exactly as (1/273.16) times the thermodynamic temperature of the triple point of water. The definition of the unit "degree Kelvin" for the thermodynamic temperature is thus exactly analogous to the definition of the other basic units.

Finally one might ask whether it would not be possible or even preferable to *eliminate* the thermodynamic temperature completely as an independent basic quantity. Various possibilities would exist

(1) (The temperature could be reduced to a pure number by defining the "temperature" of the triple point of water to be equal to the pure number 273.16 exactly (similar to defining the permittivity of vacuum to be equal to the pure number 1). The entropy S then obtains the same dimension as an energy and has to be expressed in the same unit: the joule. There would not

be a great change as far as the temperature is concerned because probably people would continue to speak of a "temperature of 500.15 degrees Kelvin" and a "temperature of 227 degrees Celsius" instead of an "absolute temperature of 500.15" and a "celsius temperature of 227" as would be logical in that case. The possible advantages in the temperature indication are then outbalanced by the disadvantages that, for instance, such very different quantities as energy and entropy would have the same dimension and unit! (This corresponds to the situation in electricity where capacity gets the same dimension and unit as length in the system based only on the three mechanical basic quantities length, time and mass.) Such a change would therefore give no advantages.

(2) The temperature could be reduced to an energy by defining the "temperature" of the triple point of water to be equal to 273.16 joules. The result would be that now the entropy becomes a pure number which is equal to the numerical value of the entropy expressed in joule/°K in the present system. The disadvantages would be great from the purely physical point of view because then such very different concepts as energy (or heat) and temperature would have the same dimension and the same unit, the joule. A major problem during the development of thermodynamics has been to make clear the distinction between the two concepts "heat" and "degree of heat" (temperature), which were confused for a long time. Giving these two different concepts the same unit would only add to the confusion.

(3) A third proposal which comes up every now and then is to make the molar gas constant $R = (8.3143 \pm 0.0012) \text{ J/mol}^{-1} \text{ } ^\circ\text{K}^{-1}$ by definition equal to a pure number e.g. 1. The "temperature" (T_k) would then be reduced to a molar energy with the unit joule/mole (or J/mol). This is a proposal which is entirely different from the proposals (1) and (2) because it means essentially that we would drop the thermodynamic definition of temperature and replace it by a kinetic definition.

In the proposals (1) and (2) the experimental methods of determining the temperature of the system remain the same. There remains one basic thermodynamic reference state, the triple point of water, and precision measurements of the ratio of a particular temperature relative to this triple point temperature allow for a high precision which is often better than 1 in $10^5 - 10^6$. However in proposal (3) the thermodynamic reference temperature, the triple point, is dropped completely and the determination of the temperature T_k would require the absolute measurement of the product $p V_m$ for a mole of an ideal gas, because the ideal gas law would read: $p V_m = T_k$. Such a change in the definition of temperature (and the same applies of course to any exact number replacing R) would therefore harm very much the precision of temperature determinations. Accurate absolute measurements of $p V_m$ are only possible with an accuracy of approximately 1 in 10^4 and the accuracy of temperature measurements would be reduced to only a few hundredth of a degree at room temperature. The thermodynamic temperature T would thus be replaced by a kinetic temperature $T_k = R T$, which could be measured with a much smaller accuracy than the thermodynamic temperature itself.

This example shows that another choice of the basic units, or reduction of its number by one, although it may seem possible or even attractive from the academic or symbolistic point of view, may have metrological consequences which are very serious and which necessitate the rejection of such proposals.

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Bureau des Longitudes, Paris 6^e/France

Astronomical Time

By

JEAN KOVALEVSKY

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With 7 Figures in the Text

Abstract

A definition of time-scales and criteria of uniformity of a time-scale are introduced in the first part of the paper. These considerations are applied to time-scales currently used in Astronomy: Sidereal and Universal Times. Each of them is defined, their equivalence is proved, and the precision with which each can be determined is discussed. The irregularities of the rotation of the Earth are the causes of the non-uniformity of these time-scales. A uniform gravitational time, Ephemeris Time, is then defined and the precision of its determination is discussed. All the three astronomical time-scales have a necessity of their own and cannot be interchanged. In order to reach a better understanding of the concept of time, it is necessary that all time-scales — including atomic time — should coexist and be compared with the highest possible precision.

I. Introduction

It is a remarkable feature that, among the three fundamental mechanical units, the unit of time plays a peculiar role: this notion presents difficulties that are not present in the definition of the unit of length or the unit of mass.

The reason of these difficulties lies in the fact that, while the physical concepts of length or mass can be reduced to certain scalar quantities, it appears that a similar reduction performed on the concept of time does indeed remove part of its properties.

These supplementary characteristics are not fundamental in some physical applications: therefore, it would be quite logical — and, actually, sufficient for most of the cases in Physics — to consider only a unit of time interval which is strictly a scalar quantity. But this is definitely not the case in Astronomy: in this Science, and especially in Celestial Mechanics, if the scalar properties of time are acknowledged and used, the notion of time-scale is just as fundamental. The unfortunate feature is that, as things stand by now, the necessary introduction of a uniform time-scale in Astronomy can only be made at the cost of a significant loss of precision in the measurements of time intervals (when compared with the use of atomic frequency standards for example).

But the necessity of having such a time-scale in Astronomy is such, that this loss of precision is a price that is not too high: astronomers are to keep a gravitational time-scale (like Ephemeris time) whatever other unit of time may be introduced. Actually, in some cases, astronomers have to keep using a time-scale — namely Universal Time — which is even incompatible with a constant unit of time!

It is the goal of the present review to endeavour to give evidence of the necessity in which astronomers are