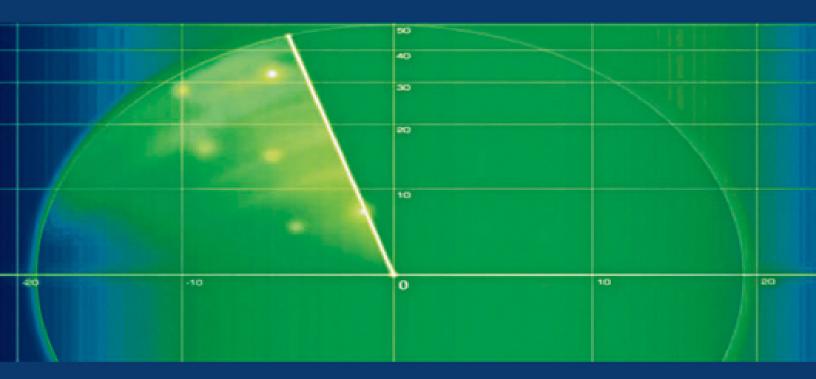
INSTRUMENTATION AND MEASUREMENT SERIES



Instrumentation and Metrology in Oceanography

Marc Le Menn





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Preface

The ocean is generally defined as "a vast stretch of salt water that covers the greatest part of the globe". However, the simplicity of this definition must not hide the complexity of this environment, which oceanography attempts to decrypt. More than just a stretch of salty water, it is a place with living rules, where study over takes the biology. Within the science of oceanography, there are fields of study focusing on geology and chemistry, but it is the problems posed by thermal, optical and dynamic properties that physical oceanographers seek to answer.

Numerous models and theories attempt to describe and predict these properties. To initiate and reinforce these, some measurements are necessary. The complexity of this environment and its hostility affect another field: instrumentation. In order to examine the complexity of this environment, specific technological developments are necessary. These developments fall under the field of oceanographic instrumentation.

This work mainly aims to describe the oceanographic instrumentation used to determine the physical properties of the ocean through *in situ* measurements. With the development of space satellite technology, new systems have appeared that have enabled us to discover these properties, creating a new field (that we will not discuss in this book): space oceanography. Space is a favored place from which we can observe the ocean, as it permits largescale study.

The instruments loaded on satellites use the properties of electromagnetic waves to measure the thermal, optical and dynamic characteristics of the ocean. Unfortunately, these waves are very rapidly absorbed or reflected by the oceanic environment, so if ocean-predicting models use "spatial" data, the collection of *in situ* observations remains an essential source of diagnostics to validate the models, and it is always necessary to develop complementary equipment that permits the study of deep water layers.

There are multiple fields of application for these studies. They concern the evolution of fundamental knowledge on the movement of water masses, the creation of thermal or density anomalies, and the coupling between the ocean and the atmosphere that lead to a better understanding of climate change. These also include the development of acoustic technologies that have multiple civil and military applications. The ocean is a favored environment for these technologies; however the propagation of acoustic waves is dependent on its physical characteristics, so the use of tools that permit emission and reception (sonar, echo sounders, Doppler current meters, etc.) must be optimized by measuring the properties of the environment if we want to achieve ultimate accuracies.

These accuracies cannot be achieved without the use of metrology. It is unusual to associate oceanography with metrology, but this is the other field that this book attempts Metrology is officially "the science to describe. of measurement and its applications", but it is, above all, the science that allows the referencing of measured data, and referencing is an essential part of oceanography when we ensure accuracy and replicability the want to of measurements. Oceanography is probably the area of physics where the requirements of the subject matter are greatest because the acquisition and interpretations of variables are often at the limits of our know-how.

This book, first and foremost therefore, is for instrumentalists and metrologists who want to know more

about measurements in oceanography. It is also for scientists who want to gather information on oceanographic instrumentation, and for all those for which this is an area of interest.

All of the chapters of this book are enriched with practical and theoretical details. Sections include recent relationships for the calculation of the physical properties of sea water, the measurement of certain physicochemical properties (carbonates, fluorimetry, etc.), suspended particulate matter, ways of positioning and probing in water, instrumented buoys, underwater platforms, etc. We also discuss the processes of calibration of these instruments, without which these measurements would not have all the legitimacy we attach to them.

> Marc Le Menn September 2012

Chapter 1

<u>What We Measure and</u> <u>What We Process</u>

<u>1.1. The quantities we want to</u> <u>know</u>

Measurements made in physical oceanography have two main aims: to improve our fundamental knowledge of the ocean and the functioning of our planet; and to optimize the use of acoustic tools, which also sometimes help us to gain knowledge of the ocean.

The improvement of fundamental knowledge is integrated with the more general topic of climate change. A global research program was launched in 1979 to try and model this evolution: the World Climate Research Program (WCRP). funded by the World Meteorological The WCRP is Organization (WMO) and UNESCO. To maximize the efforts of regard different countries with to oceanographic measurements, in 1982 the American National Science Foundation launched another program called the World Ocean Circulation Experiment (WOCE). In 1989 it created the WOCE Hydro-graphic Program Office, whose aim was to supervise quality coordinate. and ensure the of To ensure the quality of data measurements taken. collected, it was requested that "the standards to approach in terms of accuracy and reproducibility for the one-time survey, are to be the highest possible under current measuring techniques". With "repeat surveys, these standards must be approached sufficiently closely to achieve the appropriate regional goals".

There are several applications of this. The data collected will serve to determine the long-term evolution of ocean circulation. To be able to detect small changes over time, it is necessary to make measurements with low resolution and high reproducibility. The data must be comparable from one country to another and in a common format. Therefore, the measurements should be performed with great accuracy and be comparable to common references. Finally, it should be noted that at great depths the thermal stability of water masses is huge, so to detect small changes over time and space and in order that centers or institutions other than the one that carried out the measurements can verify such changes, the measurements must be made with high resolution, high reproducibility and high accuracy.

2003, the WOCE program was relayed by In an intergovernmental initiative called the Global Farth Observation System of Systems, which aimed to provide the means to overcome the lack of observations concerning key factors that influence the Earth's climate. In Europe, another initiative pursuing the same objectives also emerged called the Global Monitoring for Environment and Security (or GMES).

When using acoustic instruments, the specifications are less stringent. Oceanographic measurements performed using these specifications aim to determine the propagation speed or velocity of sound in water either locally or along an acoustic path. It is the temporal and spatial variability of physical characteristics of the environment and the lack of accuracy of velocity references that limit the accuracy of measurements, and that reduced the requirements on the measurement of influence quantities in comparison to those displayed by the WOCE program.

1.1.1. Velocity and density

Whether the measurements are performed to gain environmental knowledge aim acoustic or to use instruments, they have a common point: the measured quantities are the same. Indeed, oceanic circulation largely depends on the *density* **p** of water masses (the ratio between the mass of a sample and the volume it occupies). Similarly, velocity c is dependent on density. In adiabatic conditions, it is defined by,

 $[1.1]^{c=\sqrt{\frac{\partial p}{\partial \rho}}}$

where *p* corresponds to the pressure exerted by the acoustic wave, which results in rapid oscillations in density throughout the medium.

It is well-known that the density of a fluid depends on its temperature, pressure and composition. With variation in density, the velocity will also depend on these parameters. Temperature and pressure are therefore the primary variables to be measured.

The composition of sea water varies locally depending on the quantities of dissolved salts. These amounts change the *salinity*. Fochhammer introduced this concept for the first time in 1865. Salinity is a chemical parameter of sea water, and a characteristic of water masses, but its definition has continued to evolve since the creation of the concept, as it is a difficult parameter to measure in absolute terms.

The first accurate definition of the salinity of sea water dates from 1902 and was produced by Forch, Knudsen and Sörensen. It follows a protocol of measurement that they had developed showing that: "salinity is the quantity of solid material in grams contained in a kilogram of sea water, having converted the carbonates to oxides, bromide and iodide ions having been replaced by their equivalents in chloride, the organic materials having been oxidized."

This is the definition of absolute salinity, S_{a} , which is

expressed in $g.kg^{-1}$. From this definition, we see that it is not only dissolved salts that are measured but all dissolved matter, so the definition of absolute salinity, carried on to present day, is as follows:

"absolute salinity is the fraction of mass of dissolved materials contained in a sample of sea water, under reference conditions ($t = 25^{\circ}C$ and normal atmospheric pressure)."

Due to the difficulty of implementation, to date this definition has not been applied in routine measurements. To circumvent these difficulties, a *Practical Salinity Scale* was defined in 1978 (see <u>section 1.2.3</u>). This scale, which is called *PSS-78*, calculates a practical salinity *S* from the simultaneous measurement of temperature, pressure and electrical conductivity in a sample of sea water. The third common variable to be measured is therefore *electrical conductivity*. It is used to calculate the value of salinity that occurs in density and velocity calculations.

The PSS-78 is based on conductivity measurements — and thus on the speed at which ions move — and does not take into account all dissolved materials, hence biases exist between practical salinity S_p , which we can measure, and absolute salinity. These biases affect the calculation of density. To illustrate this point, let us take the simple example (cited in the TEOS-10 guide), where a small amount of pure water is exchanged with an equivalent mass of silicate compound that is mainly non-ionic. If this exchange takes place at constant temperature and pressure, the value of conductivity will also remain constant, while the absolute salinity and density will have increased. Conversely, if we replace a mass of silicates with the same mass of salt (NaCl), the absolute salinity and density will in principle remain unchanged, while the conductivity and therefore practical salinity will increase.

Until recently, the physical properties of sea water were calculated from the Equations of State 1980 or EOS-80, which were based on PSS-78. In 2009, these properties were redefined by a UNESCO working group called SCOR/IAPSO (Scientific WG 127 Committee Oceanic on Research/International Association for the Physical Sciences of the Ocean/Working Group 127). The group created the International Thermodynamic Equation of Sea water, known as TEOS-10. TEOS-10 is based on the Gibbs potential, which is a scalar function that represents the thermodynamic state of a system. For sea water, it is dependent on absolute salinity, temperature and pressure. This approach is similar to that defined for pure water in the 1970s by the International Association for the Properties of Water and Steams (IAPWS-95).

The Gibbs potential of sea water is denoted as $g(S_a, t, p)$. Here, g is in relation to the specific enthalpy h, which is a measure of the calorific content of a system, and entropy η that translates the amount of disorder or inaccessible nonmechanical energy:

 $[1.2] g = h - (273.15 + t)\eta$

 $g(S_a, t, p)$ is defined by:

[1.3] $g(S_a, t, p) = g^{w}(t, p) + g^{s}(S_a, t, p)$

where $g^{W}(t p)$ is the pure water part, which is determined by equations from IAPWS-95 (although it is advisable to program the codes given in the IAPWS-09 as they are faster) and $g^{S}(S_{a}, t p)$ is the saline part. The equations for calculating these quantities (and the coefficients of these equations) are provided in Annexes G and H of the TEOS-10 guide. For more information on the TEOS-10, refer to [IOC 10], which describes all of the basic thermodynamic properties that can be calculated from the Gibbs function and the derived variables of these properties.

Among the properties commonly calculated by oceanographers, we have the *specific volume V*, which is the inverse of density:

 $\begin{bmatrix} \underline{1.4} \end{bmatrix} V = \frac{1}{\rho} = V(S_A, t, p) = g_p = \frac{\partial g}{\partial p} \bigg|_{S_{\bullet}, T} \text{ in } \text{m}^3.\text{kg}^{-1}$

It is now defined as a derivative of the Gibbs potential with respect to pressure for a constant absolute salinity and *in situ* temperature *T*. Density then becomes:

$$[\underline{1.5}]^{\rho = \rho(S_A, t, p) = (g_p)^{-l} = \left(\frac{\partial g}{\partial p}|_{S_a, T}\right)^{-l} \text{ in kg.m}^3}$$

It is important to note that the maximum variation in sea water density, or in specific volume, is only 7% over the whole ocean surface. To improve the accuracy of numerical calculations of specific volumes made in engineering units, oceanographers use a derived quantity called the *specific volume anomaly* δ , which is defined by the relationship:

[1.6] $\delta = V(S_a, t, p) - V(S_{30}, 0, p)$

where V(S_{50} , 0, p) is the specific volume of a "standard" ocean, that is to say it would have a salinity of $S_{50} = 35.16504 \text{ g.kg}^{-1}$ and a temperature of 0°C. δ is expressed in units of $10^8 \text{ m}^3\text{kg}^{-1}$. The density anomaly or *density* excess $\gamma(S_a, t, p)$ is, in turn, defined by relationship [<u>1.7</u>], and is expressed in kgm ³.

$$[\underline{1.7}]^{\gamma(S_A,t,p)=\frac{1}{V(S_A,t,p)}-1000=g_p^{-1}(S_A,t,p)-1000}$$

where γ is the letter recommended by UNESCO to designate excess density. Many oceanographers, however, continued

to use the old notation, σ . To compare the values of density, they plot so-called "sigma-t" curves taking p = 0 in the calculation of $V(S_{\partial}, t, p)$ in order to normalize relatively to atmospheric pressure. Comparisons based on sigma-t are biased when calculated for deep layers, so they are performed by calculating the excess of potential density called σ_{∂} . θ designates the temperature of a sea water sample relative to pressure p = 0, or potential temperature.

[1.8] $\sigma_{\theta} = \gamma(S_A, \theta, 0) = \frac{1}{V(S_A, \theta, 0)} - 1000 \text{ in kgm}^3$

A slight increase in water temperature with increasing depth can be observed, which is due to compression. Water is a compressible fluid, so the volume it occupies decreases when subjected to increased pressure. This compression is accompanied by an increase in temperature. It is useful to calculate a variable that represents what the increase may be when compression is performed without heat exchange with the medium, i.e. adiabatically. This variable is called the *rate of adiabatic variation of temperature* or *adiabatic lapse rate*, $\Gamma(S, t, p)$. It is calculated from relationship [1.9] where *T* represents absolute temperature, T = t + 273.15 in Kelvin (K), and C_p^o is the specific heat of sea water at constant pressure for $S_a = 35.16504 \text{ gkg}^{-1}$ and $\theta = 25^{\circ}\text{C}$.

$$\Gamma(S_A, t, p) = \frac{\partial t}{\partial p} \bigg|_{S_a, \eta} = \frac{\partial V}{\partial \eta} \bigg|_{S_a, p} = \frac{(T+\theta)}{C_p^0} \frac{\partial V}{\partial \theta} \bigg|_{S_a, p}$$

with: $C_{p} = 3991.86795711963 \text{ Jkg-1K}^{-1}$.

In this expression, Θ designates the *conservative temperature*, which corresponds to potential enthalpy $h^{0}(S_{a}, \theta, 0)$ divided by C_{ρ}° . Potential enthalpy is the enthalpy that a plot of fluid would have if brought back to a reference pressure of 0 dbar in an isentropic manner (with constant and isohaline entropy or without the dissipation of mechanical energy). It allows evaluation of the "real"

thermal content of the ocean. Therefore, TEOS-10 enables us to calculate and to use the conservative temperature rather than the potential temperature, as it better represents the thermal content of sea water (by a factor of two).

 $\Gamma(S, t p)$ is expressed in °C Pa⁻¹. Knowing its value makes it possible to define the notion of potential temperature $\theta(S_a, t, p, pr)$ as the temperature that a water sample would have if taken from a depth of pressure p, brought up to the surface in an adiabatic manner without a change in salinity, which would then be placed under a reference pressure, p_r . It is calculated using the variable $\Gamma(S_a, t p)$ and the *in situ* measured temperature t_{in} :

 $[\underline{1.10}] \overset{\mathcal{H}(S_A,t,p,p_r) = t_{in} + \int_p^{p_r} \Gamma(S_A, \mathcal{H}(S_a,t,p,p_r),p')dp'$

The evaluation of $\theta(S_A, t_p, p_r)$ is carried out by a Newton-Raphson type iterative technique.

1.1.2. Pressure and depth

Pressure intervenes in the calculation of several oceanographic parameters, but it is not a representative quantity of the environment in the eyes of oceanographers: it is interesting to know depth so that measurements of other parameters can be positioned vertically. This quantity is not directly measurable; it is calculated through pressure measurements. Pressure is related to depth though the intermediary of the hydrostatic relationship:

 $[\underline{1.11}] p = p_0 + \rho gz$

where p_0 designates surface pressure, z the position on the vertical axis and g designates the acceleration due to gravity. In relationship [1.11], g depends on depth (the closer we get to the center of the Earth, the higher g becomes). This phenomenon is expressed by equation

[<u>1.12</u>], where g_0 is the acceleration of gravity at the surface of the ocean (which depends on latitude, φ) and γ_g is the average gradient of gravity.

 $\left[\frac{1.12}{g(z)}\right]g(z) = g_0(\varphi) + \gamma_z z$

As discussed in <u>section 1.1.1</u>, ρ also depends on pressure and we prefer to talk in terms of specific volume *V*. If the depth varies by *dz*, the pressure will vary by *dp* such that:

[1.13] $dp = \frac{1}{V(p)} g(z) dz$

Assuming hydrostatic equilibrium, relationship [1.12] linked to relationship [1.4] gives:

 $\left[\underline{1.14}\right] V(p) dp = (g_0(\varphi) + \gamma g) dz$

If we integrate equation [1.14], we get the depth *P* that we are looking for:

$$P = \frac{\varphi_0 - \int_0^p V(p)dp}{\left(g_0(\varphi) - \frac{1}{2}\gamma_g P\right)}$$

In practice, depth variable *P*, which is still present in the expression, is replaced with pressure variable *p*. Error is in the order of 5 cm for P = 10,000 m. φ_0 is the gravitational potential energy or *geopotential* at sea level. Its value is obtained by multiplying $g_0(\varphi)$ by the height of the free surface above the geoid. Integration of V(p) is performed by considering the successive variations in specific enthalpy *h* (defined by relationship [<u>1.2</u>]) between the layers of pressure p^i and p^{i+1} :

$$[1.16] \int_{0}^{p} V(p') dp' = \sum_{i=1}^{n-1} \left[\hat{h} \left(S_{\mathcal{A}}^{i}, \Theta^{i}, p^{i+1} \right) - \hat{h} \left(S_{\mathcal{A}}^{i}, \Theta^{i}, p^{i} \right) \right]$$

where Θ designates the conservative temperature defined in [1.9] and $\hat{h} = V$, knowing that it is possible to demonstrate that $\hat{h} = \delta h / \delta p = V$ for constant values of S_A and Θ .

The precise knowledge of depth requires not only pressure measurements, but also temperature and absolute salinity measurements. $g_0(\varphi)$ can be obtained if we know latitude φ , which comes from relationship [<u>1.17</u>] and includes a corrective term involving pressure p.

 $g_{d}(\varphi, p) = 9.7803185(1 + 5.278895 \times 10^{-3} sin^{2}(\varphi) + 2.3462 \times 10^{-5} sin^{4}(\varphi))$ $[\underline{1.17}]^{+} \frac{1}{2} \times 2.184 \times 10^{-6} p$

1.1.3. Speed and movement

Improving our basic knowledge of the ocean also requires us to measure the speed of oceanic current at different depths. This variable can be measured directly using purely mechanical means or purely acoustic means (see <u>section</u> <u>2.5</u>). Instruments used can be fixed vertically so the horizontal movement of the surrounding water can be measured. When acoustic means of measurement are used, corrections in velocity are sometimes necessary. These are carried out using temperature and conductivity sensors, but the bulk of the measurement is based on knowledge of frequency shift caused by the Doppler effect. This technique allows the measurement of speeds, either at a single point or over several levels of water.

We need to know the movement of water masses at depth or over long distances as well as the speed of marine currents. Such variations can be estimated by calculations based on the characterization of temperature and salinity of water masses. Movement is another variable that requires the measurement of temperature and salinity for an evaluation to be made. This technique is particularly useful when the ocean region being studied has a water intrusion with particular characteristics. Temperature-salinity diagrams can then be established. With these diagrams, it is possible to know the spatial displacement of a point of minimum or maximum salinity.

The variation in the position of water masses can also be assessed by measuring the movement of *trackers*. In fact, we can distinguish between what we call a *typical water*, which is a large volume of water of uniform temperature and salinity, and a *mass ofwater*, which corresponds to a large volume of water in which the properties vary within defined limits. The analysis of concentrations of certain chemical, biological or radioactive elements allows us to characterize and follow the spatial and sometimes temporal evolution of certain typical water and water masses. To do this, water samples are taken during oceanographic studies, and the samples are analyzed using laboratory chemical analysis techniques. These physicochemical techniques are not further described or addressed in this book as they lie within another field, but certain trackers have been the object of the development of specific instruments for in situ use. This is the case, for example, for dissolved oxygen and several other constituents. An overview is given in section 2.11.

Finally, we can use instruments to directly study the movement of water. These are floats or drifting buoys (see sections 3.2 and sections 3.3). These measurement processes comply with the fluid mechanics principles followed by Lagrange, which place the observer in the moving frame rather than the phenomenon being observed from a fixed point. To do this, Lagrangian buoys are "anchored" in the water mass that is being studied. For buoys on the water surface, the greatest difficulty lies in how they are anchored. The location is provided by ARGOS type satellite systems (see section 2.7). For buoys that are located underwater, the anchoring is done by varying their volume. Once dropped, these buoys descend to their immersion equilibrium within a few hours and move with the water mass in which they find themselves. Their location is provided by acoustic means that function over long distances (500 to 1,000 km) or by satellite. After a preprogrammed time, they rise to the surface, the data is

transmitted and their location is found. Nowadays, the majority of these buoys are also equipped with temperature, pressure, conductivity or physicochemical sensors (see section 3.3).

1.1.4. *Time and space*

In oceanography, the knowledge of variables that are measured or calculated is only partial if they are not correctly positioned in time and space. Bearing in mind the periods of evolution of natural phenomenon, temporal instrumental positioning is not a constraint for the developments except in cases where synchronization of several elements is required (see section 2.6). Due to satellite systems, positioning also is no longer a constraint. Excluding the ARGOS system or Iridium or Orbcom type communication systems used to follow drifting buoys, tools such as a *global positioning system* (GPS) can provide instant coordinates of a surface carrier anywhere in the world, as long as it is equipped with a receiver whose output can be gueried by embedded data acquisition systems. In the case of GPS, clock frequencies are transmitted to the mobile devices that require positioning. In the case of the ARGOS system, it is the mobile devices that emit а frequency of which the shift (Doppler effect), which is dependent on the distance separating it from the satellite, is measured to decipher the position (see section 2.7).

However, not all instruments are equipped with ARGOS emitters or GPS receivers. Many operate autonomously, especially those used in moorings. They are equipped with frequency-stabilized oscillators from which the data acquired can be dated. As these instruments are usually submerged for long periods of time, a stable clock is needed so that the dating of data is not subjected to temporal drift (see <u>section 2.6.2</u>).

<u>1.2. Linking of essential</u> <u>quantities in oceanography</u>

As explained in <u>section 1.1</u>, the need for the comparability of measurement results between different laboratories or even different countries, and over long periods of time, requires uniting quantities that we can measure to common references, and these must be made with great accuracy. Temperature is a basic variable of the International System of Units (SI). Its connection to the international metrological network is therefore direct. For this variable, we can obtain high-accuracy measurements because the field of ocean temperatures is restrained. It ranges from -2° C to $+35^{\circ}$ C. The specifications from the WOCE program are therefore high, as an accuracy of 2 mK needs to be approached with a repeatability value of 0.5 mK.

Pressure is an SI-derived unit, but the importance of this variable means that there are numerous types of calibration means and its connection is direct. Its unit is the Pascal (Pa). As 1 Pa is a small value, in oceanography we prefer to use one of its multiples, the bar (1 bar = 10^5 Pa), and sometimes even the dbar (1 dbar corresponds to approximately a 1 m water column). In the ocean, the range of this variable is large, going from 0 to 600 bar, but can be divided into sub-domains depending on the seabeds and the objectives of studies. The specifications of the WOCE program are less stringent for pressure than those for temperature; however the measurements must approach an accuracy of 3 dbar and a repeatability of 0.5 dbar.

Electrical conductivity is more problematic. On one hand, it is a derived unit that is not usually measured, but on the other hand it is merely a means by which to access knowledge of the salinity of water in oceanography. Its attachment to physical standards is indirectly achieved by prior knowledge of reference salinities. Its unit is the Siemens/meter (S m⁻¹), but we prefer to express it as mS cm⁻¹. It ranges from 2 mS/cm for brackish waters to 75 mS/cm for warmer and saltier waters. Here again, the specifications of the WOCE program are extreme, as the accuracy of conductivity measurements must approach 2 μ S/cm and their repeatability 0.5 μ S/cm.

Velocity is a quantity that is related to speed measurements, according to its unit. The connection of the propagation speed of sound to reference values, however, can only be made by an intermediary of complex polynomial formulas. The multiplicity of these relationships and their divergence for certain temperatures and pressures affect the accuracy of measurements that can be achieved, especially since none of them currently seem to be absolutely accurate.

Time is the variable for which joining is probably the easiest and the most immediate. This is due to the advent of *global navigation satellite systems.* If, for common applications, we consider a call to the speaking clock proven and sufficient to calibrate time-measuring instruments, clocks on board satellites allow the referencing and synchronization of receivers that can be separated by considerable distances with far greater accuracy. These points are discussed in <u>sections 1.2.5</u> and <u>2.6</u>.

Techniques for joining instruments measuring speed are outlined throughout <u>section 2.5</u>, first for rotor current meters and second for Doppler effect current meters considering aspects of the measurements of speeds, direction and correction for the inclination of instruments.

1.2.1. *Temperature*

Temperature is an intensive macroscopic quantity, meaning it is a variable that has the same value for all or part of a system at equilibrium. If we place a thermometer in an adiabatic setting, it will show its own temperature. This temperature is that of the surroundings, assuming there is thermal equilibrium between the thermometer and its surroundings.

We cannot add or subtract two temperatures. We can only classify the bodies from hottest to coldest depending on their temperatures. It is therefore not strictly a measurable variable and so it is treated as a stake-out quantity: we can only grade a physical phenomenon by temperature. This is how we constructed a temperature scale based on variations of other quantities selected to be references.

1.2.1.1. *The International Temperature Scale*

The first definition of a measurable temperature scale was proposed in 1852 by Sir William Thomson, alias Lord Kelvin, based on experimental work carried out by Carnot. This scale is therefore based on Carnot's principle applied to thermal motors:

- di-thermal, which means functioning with hot and cold sources;

- reversible motors, which means where the transformations consist of series of equilibrium states.

This principle says that:

"if a perfect fluid evolves reversibly between a hot source at temperature T_1 and a cold source at temperature T_2 , it receives a quantity of heat $Q_2 > 0$ from the hot source (counted positively) and yields a quantity of heat $Q_1 < 0$ to the cold source."

We show that this heat exchange does not depend on the nature of the thermal motor or on the agent of transformation (hot air, water vapor, water, alcohol, etc.). This principle allows the establishment of a relationship of proportionality between the amounts of heat exchanged and two functions dependent on T_1 and T_2 :

 $\begin{bmatrix} \underline{1.18} \end{bmatrix} \frac{Q_1}{Q_2} = -\frac{f(T_1)}{f(T_2)}$

Due to signing conventions, this ratio is always negative. To define f(T), we simply need to arbitrarily choose a continuous and monotonous function. If we choose $f(T) = \alpha . T$, it will be defined to within a constant. To determine α , it is sufficient for us to identify the value of the temperature of a remarkable and reproducible phenomenon.

To find this phenomenon, we lean towards the physical properties of the bodies that surround us, knowing that the state of a pure substance depends on three parameters: pressure P, temperature T and volume V. At constant pressure, if we add heat to a solid body, it changes state and begins to melt. The amount of heat Q that we must apply to a solid mass m in order for it to pass to the liquid state is called the latent melting heat L. It can be calculated by the relationship:

 $[1.19] Q = m \times L$

where L is a characteristic of the considered body. The temperature at which the change occurs is called the melting temperature. If constant pressure is maintained and a near-constant heat is applied, a pure substance will stay in equilibrium at its melting temperature, so long as there is solid to be melted (see Figure 1.1). This is a remarkable and reproducible phenomenon that can be used to define f(T).

There are temperature and pressure conditions that have been determined at which the three states — liquid, solid and gas — can be present. This is the case, for example, for distilled water at 0.01° C. This particular point on the phase diagram is called the triple point (see <u>Figure 1.2</u>). At this point, the three variables *P*, *V* and *T*, can only take one possible value that characterizes the substance. Triple points are therefore even more reliable than melting points when identifying temperatures. **Figure 1.1.** The principle offunction for melting fixed-point cells of pure substance, used to define the International Temperature Scale At constant pressure, the amount of melting obtained by introducing heat is remarkable and reproducible, providing an ideal measuring condition

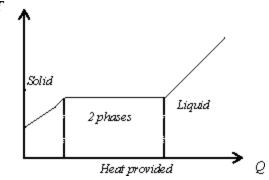
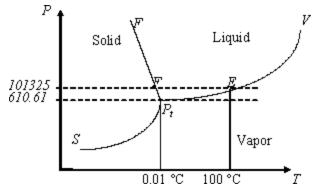


Figure 1.2. Phase diagram for distilled water. Curves F, V and S correspond to the equilibrium curves for melting, vaporization and sublimation, respectively. At the triple point, P_t , the three phases coexist



The temperature of the triple point of water was proposed as a reference value by Giauque. It was conventionally set at 273.16 K, knowing that the melting temperature of ice under normal atmospheric pressure is 273.15 K and the temperature at which water boils is 100°C above this value. From this, a unit could be associated to temperature. This unit is the Kelvin:

Kelvin is a 1/273.16 fraction of the thermodynamic temperature of the triple point of water.

Due to habit, the use of degrees Celsius remains authorized, but temperatures expressed as °C must include the symbol 't'. Here, we have:

 $[1.20] t(^{\circ}C) = T(K) - 273.15$

From this definition and relationship [1.18], it is possible to define the temperature T of any body by measuring the ratio of amounts of heat:

[1.21] T = - 273.16 × Q / Q_{ref}

Here Q_{ref} is the amount of heat exchanged to reach the triple point of water. From this definition, we can express it in terms of thermodynamic temperature instead of thermodynamic temperature scale, since it has an origin and relationship based on a ratio (instead of a reference cue). Thermodynamic temperature is therefore a measurable variable.

This principle has helped with the creation of the International Practical Temperature Scale, or IPTS, which is based on the measurement of temperature intervals and on a stake out from an origin. The values obtained using this method must be the closest possible to thermodynamic temperature values. The IPTS definition has therefore evolved over time to reflect technological and scientific developments. These evolutions are managed by the International Weights and Measures Committee. The first scale dates from 1927. It was revised in 1948, then in 1968, in 1976 (for the range 0.5 K to 30 K) and in 1990. With the revisions, the areas of use have been expanded and the accuracy of the scale has been improved.

In 1990, the term "Practical" disappeared and we now speak of the ITS-90. This scale is based on:

a) Temperature values assigned to a certain number of equilibrium states of high reproducibility. These are fixed points of definition. These fixed points are distributed between 13.81 K and 1,084.62°C (there are 18 fixed points

plus the choice of two points between 3 and 5 K). These are the phase transition points of metals or pure liquids. Two of points are in the ranges of oceanographic these temperatures: the triple point of water (Pt_{H2O}) for which the temperature is +0.01°C; and the melting point of gallium (Pf_{Ga}) at +29.7646°C. The reference probes having to measure negative temperatures must, strictly speaking, also be calibrated at the triple point of mercury (Pt_{Hq}), which is -38.8344°C. There are also two secondary fixed enter into the field of oceanographic points that temperatures: the triple point of phenoxybenzene at 26.8625°C and that of ethylene carbonate at 36.3135°C. These can also be used to check the calibration of temperature sensors, however they are less well-known than the ITS fixed points of definition and their use is not a requirement. (Note that metrologists have a habit of expressing themselves in Kelvin when they speak of low temperatures or temperatures below 0.01°C, and otherwise use degrees Celsius.)

b) Interpolation instruments. ITS-90 consists of four temperature ranges that partially overlap. Each range definition includes a reference instrument. The range that includes oceanographic temperatures goes from 13.8033 K to 961.78°C. In this interval, the instrument of reference is the platinum resistive thermometer. To be recognized as a reference, this instrument must meet a number of criteria. The main one concerns the purity of platinum. The purity is monitored by *PfGa* and *PtHg*. To evaluate this, we measure the ratios of resistance or reduced resistance W(t):

[1.22] $W(29.7646) = R_{29.7646} / R_{0.01}$ and $W(-38.8344) = R_{-38.8344} / R_{0.01}$

We must find:

[1.23] $W(29.7646) \ge 1.11807$ and $W(-38.8344) \ge 0.844235$

for the instrument to be considered a Standard Platinum Resistive Thermometer (SPRT).

c) To use these instruments, ITS-90 has additionally defined the interpolation relationships in each range. These relationships are used to calculate the difference between the measured ratio $W(T_{90})$ and the reference ratio $W_r(T_{90})$. In fact, given its size, the ITS range of interest to oceanography is divided into sub-ranges that may overlap. One of these ranges from -38.8344°C to + 29.7646°C. Its interpolation relationship is:

 $\begin{bmatrix} 1.24 \end{bmatrix} W(T_{90}) - W_{5}(T_{90}) = a[W(T_{90}) - 1] + b[W(T_{90}) - 1]^{2}$

where *a* and *b* are coefficients to be determined during the calibration of platinum resistive probes in the fixed points of this sub-range. The value of $W(T_{90}) - W_r(T_{90})$ is directly obtained during this calibration. When using the probe to measure an unknown temperature, the value of $W_r(T_{90})$ is extracted from equation [1.24] and is introduced into a polynomial relationship defined for a specified sub-range. In fact, ITS-90 defines one polynomial from 13.8033 K to 273.16 K,

.25]
$$T_{90} / 273.16 = B_0 + \sum_{i=1}^{15} B_i \left[\frac{W_r (T_{90})^{1/6} - 0.65}{0.35} \right]^i$$

[1

and a second polynomial [1.24] from 273.16 K to 964,78°C, where coefficients B_0 and B_i (i = 1 to 15), D_0 and D_i (i = 1 to 9) are provided in the ITS-90 reference publications.

[1.26]
$$T_{90} - 276.15 = D_0 + \sum_{i=1}^9 D_i \left[\frac{W_r (T_{90}) - 2.64}{1.64} \right]^i$$

As these polynomials are difficult to handle, the WOCE Hydrographic Program (WHP) defined a simplified relationship [1.27], which allows us to calculate a temperature t_{90} with accuracy greater than 0.1 mK in the area of oceanographic interest, which ranges from -2°C to +35°C.

 $\begin{bmatrix} 1.27 \end{bmatrix} t_{90} = 0.010015 + 250.7140(W_r - I) + 9.71421(W_r - I)^2$

Having improved the accuracy of the thermodynamic scale approach over the years, there are significant differences between the ITS and the IPTS. These differences and their correction relationships are given in the official International Bureau of Weights and Measures (Bureau International des *Poids et Mesures, BIPM.* See www.bipm.org) publications. Also, when processing data measured by a temperature sensor, it is important to know which temperature scale the sensor was related to, or to which temperature scale the data should be related. These corrections are particularly important in oceanography, as we seek high accuracy and may need to use data recorded decades ago. This is accentuated by the fact that temperature is used to calculate other quantities, such as salinity or velocity. In calculation relationships may have fact. the been established at a time before the ITS-90 was used. The instruments used to make temperature measurements, having been linked to the ITS-90, must be corrected before being introduced into these calculation relationships. To simplify this process, the WHP suggests а linking relationship between the IPTS-68 and ITS-90 as follows:

[1.28] $t_{90} = 0.99976 \times t_{68}$ or $t_{68} = 1.00024 \times t_{90}$

It ensures that the error introduced by use of these relationships is less than 0.5 mKintheareaof-2°C to + 35°C.

1.2.1.2. Uniting instruments to the ITS

SPRTs are composed of a platinum filament free of any constraints in order to avoid introducing biases from the support and the sensor temperature (see Figure 1.3). This means that instruments must be handled with care and their use is limited to the laboratory. Other technologies therefore had to be developed to help achieve *in situ* measurements with high resolution and high accuracy.